Non-Covalent Nanostructuration of Chromophoric Organic Materials

Settore scientifico - disciplinare : Chim/06

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Tomas
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<th>Meaning</th>
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<tr>
<td>1-D</td>
<td>Monodimensional</td>
</tr>
<tr>
<td>2-D</td>
<td>Bidimensional</td>
</tr>
<tr>
<td>3-D</td>
<td>Tridimensional</td>
</tr>
<tr>
<td>A</td>
<td>H-bond acceptor</td>
</tr>
<tr>
<td>Abs</td>
<td>Absorbance</td>
</tr>
<tr>
<td>Ac₂O</td>
<td>Acetic anhydride</td>
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<td>Acetonitrile</td>
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<td>Acetic acid</td>
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<td>ADA</td>
<td>Acceptor-Donor-Acceptor</td>
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<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
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<tr>
<td>a.u.</td>
<td>Arbitrary units</td>
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<td>Binol</td>
<td>1,1′-Bi-2-naphthol</td>
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<td>BMP32C10</td>
<td>Bis(m-phenylene)-32-crown-10 based cryptands</td>
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<td>BOC</td>
<td>tert-Butyloxycarbonyl</td>
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<td>1,3,5-Benzene trisamide</td>
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<tr>
<td>BuLi</td>
<td>n-Butyllithium</td>
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<tr>
<td>°C</td>
<td>Centigrade degree</td>
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<tr>
<td>C</td>
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<td>C-AFM</td>
<td>Conductive AFM</td>
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<td>C-C</td>
<td>Carbon - carbon</td>
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<td>CNT</td>
<td>Carbon nanotube</td>
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<td>CPK</td>
<td>Corey, Pauling, Koltun</td>
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<td>CTAB</td>
<td>Cetyltrimethylammonium bromide</td>
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<td>d</td>
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<td>H-bond donor</td>
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<td>Solute diffusivity</td>
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<td>Donor-Acceptor-Donor</td>
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<td>DAT</td>
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<td>Dimethylformamide</td>
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<td>Dimethylsulfoxide</td>
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<td>EtOAc</td>
<td>Ethyl acetate</td>
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<td>exc</td>
<td>Excitation</td>
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<tr>
<td>FET</td>
<td>Field effect transistor</td>
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<tr>
<td>FP-TRMC</td>
<td>Flash photolysis time resolved microwave conductivity</td>
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<td>FWHM</td>
<td>Full width at half maximum</td>
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<td>H-bonds</td>
<td>Hydrogen bonds</td>
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<td>HBC</td>
<td>Hexaperiheptabenzocoronenes</td>
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<td>h_m</td>
<td>Height minimum</td>
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### Abbreviations

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<td>$h_{\text{m}}$</td>
<td>Height maximum</td>
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<tr>
<td>HOPG</td>
<td>Highly oriented pyrolytic graphite</td>
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<td>HR-TEM</td>
<td>High-resolution TEM</td>
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<tr>
<td>IR</td>
<td>Infrared</td>
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<td>ISA</td>
<td>Ionic Self-Assembly</td>
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<tr>
<td>K</td>
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<tr>
<td>$K_a$</td>
<td>Association constant</td>
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<td>$K_e$</td>
<td>Elongation constant</td>
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<tr>
<td>$K_n$</td>
<td>Nucleation constant</td>
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<tr>
<td>LD</td>
<td>Linear dichroism</td>
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<td>LDA</td>
<td>Lithium diisopropylamine</td>
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<tr>
<td>M</td>
<td>Molar</td>
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<td>MALDI</td>
<td>Matrix-assisted laser desorption/ionization</td>
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<td>MCH</td>
<td>Methylcyclohexane</td>
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<td>Molecular Dynamics</td>
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<td>Molecular Mechanics 2</td>
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<td>MS</td>
<td>Mass spectrometry</td>
</tr>
<tr>
<td>MW</td>
<td>Microwave</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi-walled carbon nanotube</td>
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<tr>
<td>n</td>
<td>Solvent kinematic viscosity</td>
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<td>NDI</td>
<td>Naphthalene diimide</td>
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<td>$o$-DCB</td>
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<td>OLED</td>
<td>Organic light emitting devices</td>
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<td>OPE</td>
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<td>OPV</td>
<td>Oligophenylenevinilene</td>
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<td>ORTEP</td>
<td>Oak Ridge Thermal Ellipsoid Program</td>
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<td>$p/2$</td>
<td>Helical pitch</td>
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<td>PBI</td>
<td>Perylene bisimide</td>
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<td>PEG-b-PEI</td>
<td>Poly(ethylene glycol)-block-branched (ethyleneimine)</td>
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<td>Parametric Method 3</td>
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<td>PMI</td>
<td>Perylene monoimide</td>
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<td>ppm</td>
<td>Parts per million</td>
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<td>PTCAPS</td>
<td>3,4,9,10-Perylenetetracarboxylic acid potassium salt</td>
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<td>2,6-Bis(2-oxazolyl)pyridine</td>
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<td>Pyr</td>
<td>Pyridine</td>
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<tr>
<td>Quant.</td>
<td>Quantitative</td>
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<td>R</td>
<td>Radius</td>
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<td>r.t.</td>
<td>Room temperature</td>
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<td>SAS</td>
<td>Surfactant Assisted Self assembly</td>
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<td>Segment</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>SPM</td>
<td>Scanning Probe Microscopy</td>
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<tr>
<td>ssDNA</td>
<td>Single-stranded DNA</td>
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<td>STM</td>
<td>Scanning Tunnelling Microscopy</td>
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<td>SWCNT</td>
<td>Single-walled carbon nanotube</td>
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<td>T</td>
<td>Temperature</td>
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<td>TCB</td>
<td>1,2,4-Trichlorobenzene</td>
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<tr>
<td>TDB</td>
<td>Tridodecyloxybenzyl</td>
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<td>TEG</td>
<td>Triethyleneglycol</td>
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### Abbreviations

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<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TM-AFM</td>
<td>Tapping mode AFM</td>
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<tr>
<td>TMEDA</td>
<td>Tetramethylethylendiamine</td>
</tr>
<tr>
<td>TMS</td>
<td>Trimethylsilyl</td>
</tr>
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<td>TMSA</td>
<td>Trimethylsilyl acetylene</td>
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<tr>
<td>Tol</td>
<td>Toluene</td>
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<tr>
<td>UHV</td>
<td>Ultra high vacuum</td>
</tr>
<tr>
<td>Upy</td>
<td>Ureidopyrimidones</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultra Violet – Visible</td>
</tr>
<tr>
<td>vdW</td>
<td>van der Waals</td>
</tr>
<tr>
<td>VT</td>
<td>Variable temperature</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>Wavelength</td>
</tr>
<tr>
<td>( \tau )</td>
<td>Life time</td>
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ABSTRACT

In the last few decades materials possessing well-defined structural properties on the nanoscale and microscale have shown to be extremely promising for applications in several fields, such as microelectronics, biology, and solar cells fabrication. This is due to the fact that the manufacture of organic-based devices, for any kind of application, requires the development of reproducible protocols to engineer materials featuring precise structural properties. To improve control on the nanoscale level, both bottom-up and top-down approaches have been intensively exploited to date. Although nowadays the second is still predominant at applicative level, Moore’s law foresees its final limit in a few years. In this context strong hope is coming from the possibility to control, in a defined way, the assembly of opportunely functionalized molecules, called building blocks, through the exploitation of particular type of non-covalent interactions. For this purpose the key concepts proper of the supramolecular chemistry has been revealed to be extremely promising for the preparation of nano-aggregates provided with well defined structural and functional properties. In this context one of the factors that crucially affects the process of nanostructuration through non-covalent interactions is the geometrical and structural property of the single building blocks used. Indeed, the geometric structure of molecules can considerably influence their ability to self-organize into more complex objects and therefore by an accurate development of the structural characteristic of the single molecular module it will be possible to tune the structure and the properties of the final material.

Unfortunately in this context, even if great efforts have been undertaken by the scientific community to prepare well defined nanostructures through a supramolecular approach, the possibility to perfectly control the transmission of the geometrical informations from the molecular level to the final nanostructure still remains a partially unresolved task due to the high number of physical and chemical variables correlated to the self-assembly/self-organization process.

The aim of this thesis consists into the design and synthesis of a novel library of molecules, equipped with desired molecular functionalities, which by means of hydrogen bonding interactions can self-assemble and generate different types of nanostructured materials that can be studied at the geometrical and morphological level by means of the combined use of different microscopic techniques such as Transmission Electron Microscopy (TEM) or Atomic Force Microscopy (AFM). Intrinsically, our goal is to shed further light on the structural features of the molecular recognition process, leading to the formation of the final nanostructured material, giving the maximum importance to the investigation of the transfer of geometrical informations from the single building block to the final nanostructure.

In the first part of Chapter 1, the reader is introduced to the basic principle regarding the engineering of nanostructured materials through the different types of non-covalent interactions (hydrogen bonds, electrostatic, aromatic-aromatic and coordinative interactions) with a particular emphasis on the operative procedure developed in the last ten years. In the second part of the chapter instead, the
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attention is focused on the detailed description of the design and preparation of the nanostructuration process of the material through hydrogen bonds systems.

In Chapter 2, the first part of the experimental work of this thesis is introduced. In this context the synthesis of a molecular library of building blocks able to self-assembly via heterocomplementary H-bonds interactions and self-organize into different types of nanostructure if thermally stimulated, is reported. As for our precedent studies on the subject, the molecular modules used feature complementary terminal H-bonding sites, namely 2,6-di(acetylamino)pyridyl) and uracil moieties, which are connected to different aromatic units through linear ethynyl spacers. The peculiarity of the building blocks adopted for this study is centred on the fact that they possess as H-bonds recognition units uracil moieties protected with the tert-butyloxycarbonyl (BOC) group at the level of their imidic nitrogen. Due to the thermal instability of the BOC groups, the heating of the modules results into the cleavage of this protective group, inducing in this way the self-assembly process between the complementary building blocks (Figure 1).

Figure 1. Molecular structures of the Boc protected uracil based building blocks (91-93) and of their complementary bis(acylamino)pyridine derivative 84 used for the thermal induced self-assembly studies reported in Chapter 2.

The first part of the chapter guides the reader through the synthetic pathway adopted for the preparation and the spectroscopic characterization of the single building blocks, but also through the investigation of the different aspects of the thermal induced self-assembly process, such as the BOC deprotection phenomena and the molecular recognition process. In the second part of the chapter instead, great space will be given to the investigation of the microscopic characterization of the nanostructured morphologies by means of TEM and AFM. In order to have more detailed informations of the nanostructuration process not only the molecular geometry of the single building blocks was studied but also additional physical and chemical factors, such as the solvent composition or the temperature and concentration used, were taken in consideration to obtain the final nanostructure.

A further development of the previous work is reported in Chapter 3, in which the self-assembly and self-organization behaviour of axially chiral building blocks based on binaphthol core is studied (Figure 2). The principal task of this project regards the investigation of the transmission mechanism
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of chiral informations from the single building block to the resulting nano-object obtained by the self-assembly process.

Figure 2. Molecular structures of the axially chiral building blocks (R)-108 and (S)-108 based on the binaphthol structure, and of their complementary bis(acylamino)pyridine derivative 84 used for the chirality transfer studies in Chapter 2.

In the first part of this chapter the synthetic pathway toward the preparation of the single building blocks is discussed and their self-assembly mechanism in solution, is elucidated by means of different spectroscopic techniques, such as $^1$H-NMR, UV-Visible and Circular-Dichroism spectroscopy. The second part of the chapter is instead focused on the morphological aspects of the self-organized nanostructures deriving from the assembly of the chiral building blocks. In this context the morphology and the geometrical aspects of the resulting nanostructured materials were investigated by means of different microscopy techniques such as TEM and AFM. Moreover, a detailed evaluation of the morphological changes affecting the structure of the nanomaterial in relation with the solvent composition (i.e. polarity) is performed, in order to determine at the same time the best conditions necessary for the preparation of nanostructures provided with a controlled shape and to shed some light on the organization mechanism.

As last topic performed during this thesis, in Chapter 4 the supramolecular polymerization process was exploited in order to prepare nanostructured material provided with a certain degree of functionality. For this purpose a template approach was used in order to create hybrid material based on the self-assembly of organic supramolecular polymers onto an electroactive support.

Figure 3. Molecular structures of the di-porphyrin building blocks 112 and 113 based on the pyrene core and on their
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bidentate ligand 1,2-(4-(bispyridyl))-ethane \textbf{114} used for the preparation of highly chromophoric supramolecular polymers based on coordinative interactions reported in \textit{Chapter 4} (R: Mesityl groups).

In this work we decided to use as template nanomaterial Multi-Wall Carbon Nanotubes (MWCNTs), due to their outstanding electronical properties, and high aspect ratio character that makes them excellent candidate for any eventual application in nanoelectronic devices. Unfortunately the main drawback of this kind of nanomaterial is their low solubility in almost any organic solvent that decreases drastically their applicability. To avoid this drawback, we decided therefore to functionalize the pristine MWCNT following a supramolecular approach. For this purpose a series of di-porphyrin derivatives, able to form a supramolecular polymer through axial coordination, are synthesized (Figure 3). The ability of these compounds to produce polymers by coordination with the bidentate ligand 1,2-(4-(bispyridyl))-ethane was evaluated by means of different spectroscopic techniques, such as UV-Visible and Fluorescence spectroscopy, whereas the morphological aspects of the nanostructure resulting from their self-organization was studied by AFM images. Finally the obtained supramolecular polymers were used to prepare highly soluble MWCNTs, provided at the same time of a large number of antenna systems that can be of high importance for the preparation of nanoelectronic devices.

All the nanostructured systems described in this thesis provide a remarkable series of examples of the tremendous potential that the supramolecular approach possess for the fabrication of molecular devices of new generation, which are hardly achievable using the miniaturizing methods that are nowadays the most exploited.
Negli ultimi decenni, materiali caratterizzati da proprietà strutturali ben definite su scala nano e micrometrica, hanno dimostrato di essere promettenti candidati per applicazioni in diversi settori tecnologici quali la microelettronica, la biologia e nella preparazione di celle solari di nuova generazione. Ciò è dovuto al fatto che la fabbricazione di dispositivi basati su sistemi organici, per qualsiasi tipo di applicazione, richiede lo sviluppo di protocolli riproducibili al fine di poter sviluppare materiali caratterizzati da precise proprietà strutturali. Per migliorare il grado di controllo su nano-scala, sia approcci bottom-up che top-down sono stati intensamente studiati. Anche se attualmente il secondo approccio è ancora il predominante a livello applicativo, la legge di Moore prevede che il suo limite finale verrà raggiunto in pochi anni. La speranza di non dover far arrestare il progresso a causa dei limiti fisici con cui inevitabilmente l’approccio top-down si verrà a breve a scontrare, viene riposta nella possibilità di controllare su scala molecolare, in un modo definito, l’assemblaggio di molecole opportunamente funzionalizzate, chiamate “building blocks” o moduli molecolari, in modo da ottenere oggetti definiti e caratterizzati da specifiche proprietà. A questo scopo i concetti fondamentali propri della chimica supramolecolare si sono rivelati molto promettenti per la preparazione di nano-aggregati dotati di caratteristiche strutturali e funzionali ben definite. In questo contesto, uno dei fattori che influenzano in modo cruciale il processo di nano-strutturazione tramite interazioni non covalenti sono le proprietà geometriche e strutturali dei singoli building blocks utilizzati. Infatti la struttura geometrica delle molecole può influenzare notevolmente la loro capacità di auto-organizzarsi in oggetti più complessi e quindi da uno sviluppo accurato della caratteristica strutturale del singolo modulo molecolare sarà possibile sintonizzare la struttura e le proprietà del materiale finale. Purtroppo, benché grandi sforzi siano stati intrapresi dalla comunità scientifica per preparare nano- strutture ben definite attraverso un approccio supramolecolare, la possibilità di controllare perfettamente la trasmissione delle informazioni geometriche dal livello molecolare alla nano-struttura finale rimane ancora un compito parzialmente irrisolto a causa del numero elevato di variabili fisiche e chimiche correlate al processo di self-assembly/self-organization dei singoli building blocks.

Lo scopo di questa tesi consiste nella progettazione e nella sintesi di una libreria di molecole, dotate di opportuni gruppi funzionali, che per mezzo d’interazioni di legame idrogeno si possano auto-assemblare generando così differenti tipi di materiali nano-strutturati, i quali possano a loro volta essere studiati a livello geometrico e morfologico mediante l’uso combinato di diverse tecniche microscopiche come la microscopia elettronica a trasmissione (TEM) o la microscopia a forza atomica (AFM). Nello specifico, il nostro scopo è quello di chiarire ulteriormente le caratteristiche strutturali del processo di riconoscimento molecolare, che porta alla formazione del materiale nano-strutturato finale, dando la massima importanza all’indagine del trasferimento di informazioni geometriche dal singolo modulo molecolare alla finale nano-struttura. Nella prima parte del Capitolo I, il lettore viene introdotto ai principi fondamentali riguardanti la preparazione di materiali nano-strutturati attraverso
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diverse tipologie di interazioni non covalenti (legami idrogeno, interazioni elettrostatiche, aromatico-aromatico e di coordinazione), ponendo un accento particolare sugli sviluppi ottenuti in questo campo negli ultimi dieci anni. Nella seconda parte del capitolo invece, l'attenzione è rivolta alla descrizione dettagliata della progettazione ed esecuzione del processo di nano-strutturazione del materiale attraverso sistemi di legami idrogeno.
Nel Capitolo 2, viene introdotta la prima parte del lavoro sperimentale di questa tesi. In questo contesto, viene riportata la preparazione di una libreria di moduli molecolari capaci di auto-assemblarsi attraverso legami ad idrogeno e elettricamente complementari e di auto-organizzarsi in differenti tipi di strutture se stimolati termicamente. Come in precedenti lavori che abbiamo svolto sul medesimo argomento, i moduli molecolari utilizzati presentano gruppi capaci di indurre la formazione di legami idrogeno, in particolare le unità complementari 2,6-di(acetilammino)piridiniche e uraciliche, connesse a diversi gruppi aromatici tramite linker etilene. La peculiarità dei moduli molecolari scelti per questo lavoro è incentrata sul fatto che possiedono come unità di riconoscimento basate sui legami idrogeno dei gruppi uracilici protetti a livello degli azoti immidici con dei gruppi tert-butilloscarbonilici (gruppi Boc). Poiché i gruppi Boc sono termicamente instabili, scaldando i moduli si ottiene la deprotezione dei gruppi protettivi, inducendo in questo modo il processo di self-assembly tra moduli molecolari complementari (Figura 1).

Figura 1. Strutture molecolari dei building block (91-93) basati su unità uraciliche Boc protette e il loro complementare, il derivato bis(acilammino)piridinico 84, utilizzato per gli studi di self-assembly termicamente indotto riportato nel Capitolo 2.

Nella prima parte del capitolo viene riportata la via sintetica adottata per la preparazione e la caratterizzazione spettroscopica dei singoli moduli molecolari. Inoltre sono descritti i diversi aspetti del processo di self-assembly indotto termicamente, come il fenomeno della deprotezione del gruppo Boc e il processo di riconoscimento molecolare. Invece, nella seconda parte del capitolo vengono descritti in dettaglio le caratterizzazioni microscopiche della morfologia delle nano-strutture ottenute tramite TEM e AFM.
Allo scopo di avere informazioni più dettagliate sul processo di nano-strutturazione, non solo verrà studiata la geometria molecolare dei singoli moduli molecolari, ma verranno presi in considerazione addizionali fattori chimici e fisici influenzanti l’ottenimento delle nano-strutture finali, come la composizione del solvente o la temperatura e la concentrazione usati.
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Un altro sviluppo del lavoro precedente è riportato nel Capitolo 3, nel quale viene studiato il comportamento di auto-assemblaggio e auto-organizzazione di composti molecolari chirali a livello assiale, basati su molecole binaftoliche (Figura 2). Il principale scopo di questo studio si focalizza sull’indagine del meccanismo di trasmissione delle informazioni chirali dalla singola molecola al risultante nano-oggetto ottenuto dal processo di self-assembly.

Figura 2. Strutture molecolari dei building block chirali a livello assiale, (R)-108 e (S)-108 basati su una struttura binaftolica, e del loro derivato complementare bis(acilammino) piridinico 84 utilizzato negli studi di trasferimento di chiralità nel Capitolo 3.

Inizialmente viene presentata la via sintetica adottata per la preparazione dei singoli composti molecolari e il loro meccanismo di self-assembly in soluzione viene spiegato tramite varie tecniche spettroscopiche, come 1H-NMR, UV-Visibile e dicroismo circolare. La seconda parte del capitolo invece si concentra sulla caratterizzazione degli aspetti morfologici delle nanostrutture auto-assembleate derivanti dalle interazioni dei building block chirali. In questo contesto gli aspetti morfologici e geometrici del risultante materiale nanostrutturato verranno investigati tramite differenti tecniche microscopiche, quali il TEM e l’AFM. Inoltre è stata condotta una dettagliata valutazione dei cambiamenti morfologici che si riflettono sulla struttura del nanomateriale, come per esempio la polarità del solvente, in modo da poter determinare allo stesso tempo le migliori condizioni necessarie per la preparazione di nanostrutture dotate di una forma controllata e chiarirne il meccanismo del self-assembly.

Come ultimo argomento trattato in questa tesi, nel Capitolo 4, il processo di polimerizzazione supramolecolare è stato sfruttato per la preparazione di materiali nanostrutturati funzionali. A questo proposito un approccio templato è stato utilizzato per realizzare materiali ibridi basati sul self-assembly di polimeri organici supramolecolari su un supporto elettroattivo.
Figura 3. Strutture chimiche dei moduli molecolari a struttura diporfirinica 109 e 110 basati su un core pirenico e su un legando bidentato, 1,2-(4-bispiridil)-etano 111 usato per la preparazione di polimeri supramolecolari cromoforici basati su interazioni di coordinazione riportati al Capitolo 4 (R: gruppi mesitile).

In questo lavoro abbiamo deciso di utilizzare come nanomateriale templato i nanotubi di carbonio a parete multipla (MWCNTs), che grazie alle loro notevoli proprietà elettroniche e alle loro elevate caratteristiche monodimensionali si sono rivelati essere un ottimo candidato per un’eventuale applicazione in nanoelettronica nella preparazione di “devices”. Sfortunatamente il più grande svantaggio di questo nanomateriale è la bassa solubilità in quasi tutti i solventi organici, che diminuisce drasticamente una loro possibile applicazione. Per sormontare questo ostacolo abbiamo deciso quindi di funzionalizzare i nanotubi di partenza tramite un approccio supramolecolare. A tal proposito è stata sintetizzata una serie di derivati diporfirinici, capaci di formare polimeri supramolecolari attraverso coordinazione assiale (Figura 3). L’abilità di questi composti di organizzarsi in polimeri grazie alla coordinazione con il ligando bidentato 1,2-(4-(bispiridil))-etano è stata verificata tramite differenti tecniche spettroscopiche, quali l’UV-Visibile e la spettroscopia a fluorescenza, mentre gli aspetti morfologici delle nanostrutture risultanti dalla loro auto-organizzazione sono stati studiati tramite immagini AFM. Infine i polimeri supramolecolari ottenuti sono stati utilizzati per preparare MWCNTs altamente solubili, dotati allo stesso tempo di un grande numero di sistemi antenna che possono risultare di grande importanza per la preparazione di device nanoelettroniche.

Tutti i sistemi nanostrutturati descritti in questa tesi forniscono una considerevole serie di esempi dell’enorme potenziale che l’approccio supramolecolare possiede per la fabbricazione di device molecolari di nuova generazione, difficili da ottenere usando metodi di miniaturizzazione che sono oggigiorno i più sfruttati.
CHAPTER I

INTRODUCTION

1.1 The Challenge of Nanostructuration

Nowadays with the term “nanomaterials” the scientific community intend a class of functional materials characterized at least by one dimension below 100 nm. Such kind of objects can possess a wide variety of shapes, ranging from the more simple spherical shape, characteristic of nanoparticle and nanovesicle, to incredibly more complicated architecture such as helix or rosettes.\(^1\) The great interest revolving around this kind of systems is mainly centered on the fact that the properties of the material at the nanoscale level can be substantially different from its bulk correspondent.\(^2\) Indeed both electronical\(^3\), pharmaceutical\(^4\) and medicinal\(^5\) properties of several types of materials have proven to be significantly enhanced if an opportune process of nanostructuration was performed.\(^6\) In this context, the increased antimicrobial activity of silver nanoparticles\(^1b\) and the change in conductivity of different type of metal nanostructure\(^7\) in comparison with the pristine metals are among the most explicative examples. Basing on these considerations it is therefore reasonable to consider the study of the properties and preparation of such kind of materials a primary scientific discipline known as “nanoscience”. It is noteworthy to point out that, even if a general definition of nanomaterial is commonly accepted the elaboration of a general meaning for the term nanoscience is still far away from being recognized. As a general interpretation, however, nanoscience can be defined including also highest level of functional complexity related to the nano-objects, such as the study and the development of devices possessing dimension below 100 nm. The elaboration of such kind of definition highlight the possibility to opportunely design and produce, in a near future, functional devices characterized by highly defined geometrical and structural properties together with a strictly controlled functionality. This factor is nowadays of crucial importance since it can be considered the final point for the ongoing miniaturization of mostly all kind of electronic equipment’s. So far, the miniaturization of electronic components has been possible thanks to the constant development of new engineering techniques that permit the incorporation of an increasing number of electronic components inside the silicon boards.\(^8\) Unfortunately, accordingly with the Moore’s law the final limit of this “top-down” approaches will be shortly reached since the size of the components will be too low to be produced by physical methods\(^9\). In this context strong hope is deriving from the possibility to control, in a defined way, the assembly of opportunely functionalized molecules, called building blocks, exploiting non-covalent interactions. For these purpose the key concepts proper of the supramolecular chemistry has been revealed to be extremely promising for the preparation of nano-
aggregates provided with defined structural and functional properties.\cite{10} Although this type of “bottom up” approach is nowadays unexploited for the commercial production of devices in the real world, its potential advantages are remarkable, including: high convergence in the nanostructuration protocol, facile formation of the final nanostructures by simple mixing of the components, possibility to obtain defect free architecture due to the reversible nature of the interactions involved which can induce the most thermodynamically stable phase.\cite{11} Even if in the last decades great efforts have been undertaken by the scientific community to prepare organic nanostructures \textit{via} non-covalent interactions, the possibility to perfectly control the transmission of the geometrical informations from the molecular level to the final nanostructure still remain a difficult and partially unresolved task. In this introductory chapter we will therefore review the principal developments occurred in the last ten years in the field of supramolecular nanostructuration of organic materials, particularly emphasizing the relation between molecular and nanostructure geometry.

In the first section, a general overview about the basic principles inherent to the nanostructuration of organic materials \textit{via} non-covalent interactions will be presented whereas in the second part a more detailed view on the preparation of supramolecular nanostructures \textit{via} H-bonds will be discussed, focusing on the relationship between the nanostructure morphology and the molecular geometrical properties of their constituting components.
1.2 Methodological Approaches toward the Supramolecular Nanostructuration of Organic Materials

Due to the extremely rapid growth that the nanotechnology field has experimented in these last decades, several preparative approaches have been developed to organize single molecules into functional high-order architectures, such as colloidal, sol–gel polycondensation, template and non-covalent methods. Among all possibilities, the supramolecular approach revealed to be the one that produces the broadest variety of easily accessible and interesting molecular architectures.

In this context, the understanding of the self-assembly and self-organisation mechanism together with the direct visualization and morphological characterization of the final nanostructures by scanning probe (STM and AFM) and electronic microscopies (SEM and TEM) have attracted important consideration for the engineer and study of the resulting nanostructured material.

The geometrical properties of the final nanostructure and the order of its inner components is encoded in the shape and chemical properties of the molecular functionalities, but also in the strength and directionality of the secondary interactions used for the higher levels of integration. In this paragraph we will thus present a brief overview in which the different approaches exploitable for the preparation of nanostructured material can be summarize basing on the different interactions leading to the formation of the final nanomaterial, such as hydrogen bonds (H-bonds), coordinative, electrostatic and aromatic-aromatic interactions.

1.2.1 Hydrogen Bonds (H-Bonds)

Among all the different types of non-covalent interactions, H-bonds are the one that probably have been more exhaustively studied and therefore better understood. In general terms, H-bonds can be defined as a non–covalent attractive interactions between a positively charged hydrogen atom bonded to an electronegative atom (defined as H-bond donor, D-H) and a negatively charged atom possessing a lone pair of electrons (the H-bond acceptor, A). H-bonds can vary in strength from being very weak to being the strongest (and most directing) of the intermolecular interactions. H-bonds interactions are directional and complementary and can thus simplify engineering specific orientations and interactions between individual H-bond donor and acceptor moieties. So far, the exploitation of H-bonds as supramolecular tool for the production of nanostructured material has led to a wide range of nanostructures possessing different kinds of geometry and properties. The first clear example of H-bond directed self-assembly and organization is unequivocally considered the DNA double helix formation (Figure 1.1).
incorporation of artificial nucleobases into DNA stacks can lead to designer DNA double helices, of oligonucleotide strands for the construction of well-defined architectures by the ideal van der Waals distance, 

Aromatic interactions between the matched base pairs are organized and held at an ideal, though often adjustable, radius in order to highlight the formation of the π-π interactions.[21]

Tackling this process as a model for the development of complex supramolecular architectures, different groups in the last decades have exploited H-bonds interactions to induce the selective association of opportunely designed molecular modules. Among all, the groups of Meijer,[22] Ajayaghosh[23] and Yagai[24] are the one who most thoroughly investigated the possibility to produce in a controlled way nanostructured supramolecular materials through a careful design of the geometrical and stereochemical codes present in the single molecular modules. In this context, the first approaches toward the nanostructuration of organic materials via H-bonds leading to ordered arrays of functional materials exploit the use of molecular templates.[21] Indeed, even biomolecules such as DNA, have been used as oligomeric backbones to assemble aromatic chromophores into discrete, stacked helical structures.[25] For this task, single oligothymine strands provide a well-defined template with a specific H-bonding motif and, when matched with water-soluble aromatic guests (2-4) possessing complementary H-bonding motifs, UV-Vis and Circular Dichroism (CD) measurements indicated the formation of helical aggregates, morphologically characterized by Atomic Force Microscopy (AFM).[26]

Following an alternative approach, by exploiting a combination of H-bonds and π-π interactions, it was possible in the recent years to develop highly organized nanostructures to direct the controlled formation of the final assembly. Through the opportune design of molecules containing aromatic...
moieties (such as oligophenylenevinilene (OPV), oligophenyleneethinylene (OPE), perylene bisimides (PBI), etc.) and H-bonds recognition sites (such as triazines, acetimidopyridines, ureidopyrimidones, etc.), it was possible to develop an impressive range of hierarchically-organized supramolecular nanomaterials (Figure 1.3).\textsuperscript{[27]}

![Figure 1.3 Molecular structure (a) and optimized geometry (b) of an OPV derivative functionalized with a barbituric moiety able to self-assemble into nanoring on mica surface, as shown by AFM analysis (c). Schematic representation of the nanoring dimensions, all the values are reported in nanometres. Schematic depiction of the self-organization process of a dihydroxy OPV building block into helical nanofibers (e). Example of the supramolecular polymerization of a perylene diimide derivative through H-bonds assisted by π-π interactions.\textsuperscript{[27]}](Image)

If exploited in an opportune way, the presence of moieties that can originate secondary interactions (such as π-π interactions, van der Waals, or dipole-dipole interactions) can have a positive influence on the assembly process, not only inducing an increase of the association constant of the single molecules, but also resulting in a more efficient control on the geometrical properties of the final aggregates. A more exhaustive discussion of the mechanism adopted for the preparation of nanostructured material via H-bonds system will be introduced into the second part of this chapter.

### 1.2.2 Metal–Ligand Interactions

Like H-bonds, metal–ligand interactions are directional and well suited for the pre-programmed assembly of supramolecular architectures.\textsuperscript{[28]} Coordination (or dative) bonds vary significantly in strength and can approach the stability of covalent bonds. Therefore metal-ligand interactions provide a reversible and powerful tool for the design of supramolecular systems. One of the most interesting strategies, used for the preparation of nanostructured materials through coordinative interactions, is based on the metal mediated self-assembly between macrocyclic units containing a metal atom in their inner cavity.\textsuperscript{[29]} For this purpose porphyrins derivatives are nowadays among the most exploited systems, due to their peculiar structural and electronic properties.

Porphyrins are shape-persistent and conjugated macrocycles comprised of four pyrrolic subunits that are interconnected by methine bridges. These heterocycles can be used as proligands to coordinate various metals in their central cavities. The structural and electronic characteristics of their π-conjugated backbone, of the metal centre and of the functional groups appended to the periphery
modify and control the ability of metalloporphyrins to self-assemble into different supramolecular nanostructures through non-covalent interactions.\cite{30} In the last decades extensive efforts have been devoted to the development of multiporphyrin nanostructured materials due to their promising applications in molecular switching,\cite{31} electronic\cite{32} and photonic devices.\cite{33} Taking advantage of metal–ligand coordination interactions, chemists have produced mono-, bi and tri-dimensional metalloporphyrin based nanomaterials.\cite{28b} One of the first example of mono-dimensional multiporphyrin array based on metal ligand interactions was reported by Shinkai and co-workers who synthesized a porphyrin with eight pyridyl groups that self-assembles into a coordination polymer through Pd(II)-pyridine interactions with four cis-Pd(II) complexes (Figure 1.4a-b).\cite{34} As a consequence of the self-assembly process when a chloroform solution of polymer was dried and viewed under TEM, the formation of long nanofibers with a diameters of ca. 10 nm was observed (Figure 1.4c).

![Figure 1.4](image_url)

Figure 1.4 Molecular structures (a) of the octapyridyl derivative 5 and the Palladium complex 6. Molecular representation (b) of the supramolecular nanostructure formed by the metal mediated assembly between 5 and 6 and TEM image (c) of the porphyrin based nanofibers.\cite{54} PM3 optimized geometry (d) of the bipyridyl porphyrin derivative 7. UHV-STM image of the assembly obtained from the deposition of 7 on a Cu(111) surface, schematic representation with Hyperchem models (f) of the molecular structure of the porphyrin nanofibers on surface.\cite{19}

As a consequence of the coordinative nature of the interactions involved into the metal mediated self-assembly process, the morphology of the nanostructures obtained by this approach is strictly related to the composition of the chemical environment in which it takes place. For this reason many investigations have been performed so far, in order to relate the effect of the solvent used during the nanostructure preparation to the morphology and the geometrical characteristic of the final aggregates, showing how through the use of the same building blocks, it is possible to achieve different types of nanostructured materials (i.e passing from hollow nanoparticles to discrete nanorods) by the simple
variation of the physico-chemical parameters of the solvent involved.

The metal mediated self-assembly process was exploited not only in solution but also on surface\textsuperscript{[36]} for the production of mono and bi-dimensional supramolecular arrays based on coordinative interactions. In this context the collaborative work between our group and the one of Barth is a clear example of how porphyrins modules can be exploited to construct one-dimensional (1D) metal-coordinated polymers both on Cu(111) and Ag(111) surfaces.\textsuperscript{[35]} Indeed after the deposition of the A\textsubscript{2}B\textsubscript{3} porphyrin derivative 7, bearing two pyridyl groups at the opposite meso-positions, the formation of a linear arrays of porphyrins was observed as a consequence of the directing coordinative interactions between the pyridyl nitrogens and the metal atoms present on the surface.

A second approach widely employed for the preparation of nanomaterials based on coordinative interactions, consists into the formation of “linear coordination polymers”. Coordination polymers are reversible aggregates that can reversibly break and reconnect during their formations reactions, facilitating in this way the self-assembly process.\textsuperscript{[37]} The use of the concept of extended metal–ligand interactions to construct different nanostructures provides a way to diversify the properties of the assemblies through the modification of the peripheral functionalities of the organic ligands or by varying the choice of metal centres.

For instance, You and co-workers applied these concepts to obtain helical non-racemic polymers from imidazole substituted monomers.\textsuperscript{[38]} The coordination polymers obtained were derived from the self-assembly between Ag(I) ions and bent-shaped, achiral and ditopic imidazole derivatives 8 and 9 (Figure 1.5a). Such kind of polymers could gelatinize solvents including DMF, glycol, and mixtures of water and organic solvents. TEM images showed that the nanofibers obtained were composed by cylindrical aggregates with diameters of ca. 9 nm, lengths up to several microns with and helical pitch of ca. 8 nm (Figure 1.5b-d).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure15.png}
\caption{Molecular structure of the imidazole substituted monomers 8 and 9. Schematic representation (b) of the formation of the helical coordination polymer gelators formed from 8 or 9 in presence of Ag\textsuperscript{+} ions. TM-AFM image (c, d) at different magnifications of the resulting xerogel, on a mica surface and TEM image (e) of an isolated helical fibers of the same Xerogel.\textsuperscript{[38]}}
\end{figure}
Therefore nanostructures constructed from metal ions and organic bridging ligands into coordination polymers have been research targets of interest because they can be simple to synthesize, but offer plentiful opportunities for structural variation and potential access to useful properties.

1.2.3 Aromatic-Aromatic Interactions

Attractive interactions between aromatic systems have been extensively studied over the past 60 years.\cite{39} These interactions are mainly dominated by electrostatic forces, but are complicated by the various possible orientations of the aromatic moieties: edge-to face, stacked, and offset stacked.\cite{40} Additionally, the large molecular surfaces involved increases the importance of van der Waals interactions and desolvation. In aqueous solution, desolvation of the flat p-surface of aromatics leads to the aggregation and stacked structures (\textit{i.e.} the hydrophobic effect) and solubility of the aggregate is a major concern. At the present time aromatic interactions are commonly used to engineer and organize the structures of infinite assemblies in crystalline and liquid crystalline phases.\cite{41} In this context alkoxy-substituted triphenylenes were among the first discotic molecules shown to be liquid crystalline.\cite{42} Even if the aromatic core of triphenylenes is relatively small, polymerization of triphenylenes does occur in strongly apolar solvents such as hexadecane.\cite{43} Basing on these data, different type of highly \( \pi \)-conjugated scaffolds have been chemically modified in order to induce the formations of columnar aggregates.\cite{44} During these investigations numerous derivatives of molecules such as hexaperihexabenzocoronenes (HBC),\cite{45} porphyrins \cite{46} or phtalocyanine\cite{47} have shown to originate the formation of highly order columnar assemblies able to induce the formation of nanostructured materials that can be potentially exploited as nanoelectronics components. Indeed in many cases it has been found that due to the favourable interaction between \( \pi \) orbitals of the single molecules along the stacks the conductivity of this latter was incredibly increased in respect to the one of the single components. In this context Aida and co-workers reported the supramolecular polymerization of amphiphilic HBC molecules functionalized with alkylc and triethyleneglycolic (TEG) chains (Figure 1.6 a), both in THF and THF/water mixtures, where the HBC core was used to produce conductive graphene-like nanotubes.\cite{48}
The HBCs formed a stacked bilayer structure (Figure 1.6b, c) where the alkyl tails are interdigitated in the center of the bilayer and the ethylene glycol tails are located at the periphery, allowing the aggregate to be soluble in polar solvents like THF and water. In a subsequent work of Mullen, the introduction of perylene derivatives as aromatic substituent on the periphery of the HBC core have proved to be necessary not only for the formation of nanoribbons (Figure 1.6d-f), but also for the fine tuning of the electronic properties of the final assembly.\cite{Mullen1998} Indeed through the introduction of a perylene monomide (PMI) moiety, the formation of an electron donor/acceptor system between the electron rich coronene and the PMI subunits was formed. This dyad have tendency to self-assemble into ordered columnar arrangements. Moreover electrical measurements on the HBC-PMI derivative 11 films and nanoribbons (Figure 1.6f) exhibit ambipolar transport with a well balanced p- and n-type mobility as a consequence of the increased level of the single aromatic components induced by the self-assembly process.

1.2.4 Ionic Interactions
Electrostatic interactions between static molecular charges tend to be relatively strong as well as direction-dependent and they are often of central importance into the molecular recognition process. The strength of such interactions is strictly related to the dielectric constant of the solvent used during the self-assembly process, providing in this way an efficient control on the association constant of the single modules.\cite{Hill2010} Contrary to simple salt association, which results from the non-selectivity and long-range character of the coulombic interactions, into the Ionic Self-Assembly (ISA) process the secondary structural elements present into the single building blocks have to support the alignment
and the structural orders driven by the charge-charge coupling.\textsuperscript{531} In this context the first studies on the supramolecular aggregation of ionic amphiphilic molecules\textsuperscript{532} paved the way toward the constructions of the highly hierarchized functional nanostructures that are reported nowadays in literature. Indeed, the principles proper of the polyelectrolyte-surfactant complexation have rapidly expanded toward other self-organizing charged molecules. Mullen and Thünemann were the first to report on the columnar arrangement adopted from HBC anions derivatives, when supported by complexation with cationic polyelectrolytes.\textsuperscript{533} The same principles were used by the group of Antonietti several years later organizing functional dyes such as 3,4,9,10-perylenetetracarboxylic acid potassium salt 12 (PTCAPS) into long belt shaped micro-objects, via electrostatic interactions\textsuperscript{54} Indeed, through the use of the cationic hydrophilic block copolymer poly(ethyleneglycol)-block-branched (ethyleneimine) (PEG-b-PEI) as a polymeric additive, the crystallization of 12 was modified inducing the formation of belt-like structures.

Moreover, as a further consequence of the extended, wire-like $\pi-\pi$ interactions originated along the [020] axis of the belt, a remarkably high conductivity per single nanobelts was shown, proving the value of the ISA approach for the development of highly functional nanomaterials. A further development in the use of ionic compound for the nanostructuration of organic material is represented by the Surfactant Assisted Self assembly (SAS) technique, in which the self-assembly of an opportune building block is templated by the presence of an auxiliary surfactant that can control the geometrical properties of the final nanostructure. Following this approach, Liu and co-worker were able to produce a library of different nanostructures based on the self-assembly of zinc 5,10,15,20-tetra-(4-pyridyl)-21 H, 23 H-porphine (13) in presence of different amounts of cetyltrimethylammonium bromide (CTAB) in an acqueous solution (Figure 1.7e-f).\textsuperscript{555} Even if the mechanism of such phenomena is still under investigation, the author hypothesized that the ionic interactions deriving from the self-assembly of the
surfactant in the aqueous environment, can tune the π-π interactions responsible for the aggregation of the single compound 13 with a concentration dependant mechanism, providing in this way a new route for the elaboration of complex nanostructures before unachievable with the same building blocks.

1.3 H-Bond Nanostructured Organic Materials

For the engineering and development of functional supramolecular architectures, H-bonds are between the most useful non-covalent interactions due to their high selectivity, directionality and reversibility. These properties, if opportunely combined, can give the possibility to control the geometry and the morphology of the final supramolecular systems with molecular precision.\textsuperscript{[19, 56]} The strength of the supramolecular interaction deriving from H-bonds formation depend from a relevant number of factors such as the solvent used, the total number of H-Bonds involved and their spatial disposition into the recognition site. Despite the relative weakness of the isolated H-bond interactions, the conjugation of a precise structural design of the single molecular units, with a strict knowledge of the assembly mechanism, can result in the possibility to selectively prepare supramolecular systems characterized by highly controlled geometrical and structural features at the nanoscale.

In this paragraph the attention will be focused on the most significant development obtained in the field of H-bond based supramolecular materials in the last years. The construction of infinite and discrete nanostructured materials will be discussed giving a particular emphasis on the elucidation of the relationship between the structural characteristics of the single molecules and the geometrical and spatial features of the final nanostructures. The properties and the possible applications fields (OLED, FET, photovoltaic cells development and sensor) of all the resulting nanostructures will be then described in relation with the characteristics of the single isolated components. Moreover a general overview about the synthetic approaches developed to prepare the primary molecular modules will be presented. In order to categorize the different assemblies, a major division will be operated on their dimensionality: the first part of the paragraph will be focused on self-assembly/self-organization of molecular units for the nanostructuration of infinite systems (1-D assemblies and 2-D networks), whereas a second section will be centred on the discussion of the nanostructuration process aimed at the production of discrete systems such as nanoparticles, nanorings and toroids.

1.4 H-Bond Nanostructuration of Infinite Systems

Currently most of the supramolecular assembly of organic functional materials are constituted by polymeric arrays of molecules, defined as building blocks or molecular modules, held together by non-covalent interactions and able to associate in one or more dimension. In such kind of systems a strict control over the size and the dimension of the supramolecular entities is usually very limited and therefore for the resulting architectures can be grown in an infinite fashion along different dimensions, depending on the structural molecular features.
In these systems, H-bonds can both be employed as the only non-covalent interaction responsible for the nanostructuration process or can be associated to other types of interactions in order to modify the final morphology of the resulting architecture. In this section the attention will be focused mainly on the design and preparation of organic supramolecular nanostructures in which the H-bond interaction is occupying a key role in the nanostructuration process. Additional interactions will be described in connection to the geometrical control that they are imparting to the final nanostructure.

1.5 1-D H-bonded Nanostructured Materials

The preparation of homogenous nanoobjects based on H-bonds is one of the most interesting research area of nanotechnology, due to the potential applications that this structures can have in fields such as electronic, sensor production or for biomedical systems.\textsuperscript{[57]} The possibility to exploit single or multiple arrays of H-bond interactions for such purpose is very well known since the early 90s, thanks to the pioneering works of Lehn and co-workers, who synthesized the first supramolecular polymers based on self-assembly between multiple H-bonds recognition sites. In this work triple H-bonding interactions between uracil derivative 14 and bifunctional diaminopyridine module 15 induced the formation of a supramolecular polymers, which underwent self-organization into fibroid objects, displaying helicity as a consequence of the chirality of the single components (Figure 1.8a).\textsuperscript{[58]} This approach based on the molecular recognition process between diaminopyridine units and imidic systems was further exploited by Lehn to induce the assembly of different building blocks such as cyanuric derivative 16 and complementary molecule 17, inducing the formation of fibers observable through TEM analysis (Figure 1.8 b-d).\textsuperscript{[59]}

![Figure 1.8](image)

**Figure 1.8** Self-assembly process (a) between the diacetylaminopyridinic unit 15 and the uracil molecular module 14 developed by Lehn through the derivatization of a tartaric acid core,\textsuperscript{[56]} leading to the formation of a supramolecular polymer able to organize into helical fibroid material as a consequence of the chirality of the single building blocks. Molecular structures (b) of the supramolecular assembly between the cyanuric derivatives 16 and its complementary unit 17. Schematic representation (c) of two different multiple H-bonds arrays based on the imidic-diacetylaminopyridinic recognition motifs. TEM images (d-e) of the helical fibers obtained from the assembly of 16 and 17 (white segment represent the helical pitch distance).
As a consequence of this discovery, in the last twenty years, several approaches toward this goal have been pursued, dramatically increasing the palmares of 1-D supramolecular nanostructures available. In order to rationalize all these advancements, it is possible to classify the H-bonded mono-dimensional nanostructure on the base of the spatial orientation of the H-bond recognition units inside the supramolecular architectures. In this context two different classifications are possible:

- Nanostructures in which the H-bond systems are formed along the supramolecular chain (H-bonded main chains polymers)
- Systems in which the H-bond systems is formed perpendicularly to the supramolecular chain.

1.5.1 Nanostructuration of Organic Material through H-Bonded Mediated Supramolecular Polymerization

1.5.1a Basics of Supramolecular Polymerization

When the bonds that held together the monomeric units in a polymeric system are constituted by highly directional non-covalent interactions, supramolecular polymers are obtained. Although in the last decades a large number of approaches has been elaborated in order to create even more complicate polymeric architecture based on non-covalent interactions, it was only after the careful design of multiple H-bonds supramolecular polymers that it was possible to obtain systems showing true polymeric materials properties, both in solution and at the solid state. The great hope revolving around such kind of materials is mainly due to the possibility to combine in an easy and facile way many of the attractive properties of conventional polymers with the ones relating to the reversibility of the non-covalent bonds between monomeric units. Indeed, many physico-chemical properties of this polymeric material, such as degree of polymerization, and its chain conformation, can be opportunely tuned modifying the strength of the non-covalent interactions that can be adjusted in a reversible way, originating in this manner a material able to respond to the external stimuli in a way impossible for conventional polymers. As a general principle, it is possible to form all the known structures of polymers, such as linear homo- and copolymers, branched structures and cross linked networks, using a directional complementary couple (A-B) or a self complementary unit (A-A). If non-covalent association of bifunctional monomers forms the polymer, the degree of polymerization will be determined by the association constant of the terminal groups and by the concentration of the solution. To produce high molecular weight macromolecules a strong prerequisite is the possibility to use monomers characterized by high association constants ($K_a$).

A further factor that can increase the stability of the resulting supramolecular polymers can be considered the presence of aromatic portions, which give a planar shape to the single monomeric units, and therefore the possibility to self-assemble and organize along both sides of the molecular plane. Such kind of interactions (mostly $\pi-\pi$ interactions) not only results in an increase of the association constant of the single monomers (and therefore also of the polymerization degree) but also in the
formation of much stiff and rod-like polymer morphologies. Differently from the standard polymerization reactions, the extent of supramolecular polymerization reaction is directly coupled to thermodynamic forces such as concentration, temperature, and pressure due to the reversible nature of the interactions involved. The major mechanisms, through which supramolecular polymerization occurs are the isodesmic[60] and/or the cooperative mechanism.[61] The first mechanism is characterized by the reversible formation of every single non–covalent bond, thus the process is strictly identical from a thermodynamic point of view and for this reason is characterized by a single association constant for each reversible step of the self-assembly process. On the other hand, the cooperative mechanism occurs in two distinct stages: a first stage known as “nucleation” step, represented by a linear isodesmic supramolecular polymerization characterized by an association constant $K_n$ related to the association of each monomer to the so-called “Polymerization Nucleus” and a second step, known as “elongation phase”, in which the addition of the monomers to the “Supramolecular Nucleus” continues, but with an association constant $K_e$ (elongation constant) higher than the previous one. For a more detailed insight into the principles of the supramolecular polymerization process the reader is referred to the review and works of Meijer and De Greef on the subject.[22, 26a, 56a, 62]

1.5.1b H-Bonded Supramolecular Main-Chain Polymers

To this class belong all the nanostructures in which the H-bond recognition systems are formed along the supramolecular chain and the H-bond itself is the main responsible for the formation of the 1-D nanostructure. The formation of the final nanostructure is induced only by H-bonds interactions or can be assisted by secondary interactions able to increase the association strength between the single modules, such as van der Waals or π-π interaction. One of the most important steps towards the preparation of main-chain H-bonded supramolecular polymers is the synthesis reported by the groups of Meijer and Sijbesma in 1998, in which ureidopyrimidones (Upy) derivatives dimerize through the formation of a supramolecular complex based on four H-bonds, characterized by a dimerization constant exceeding $10^6$ M$^{-1}$ (Figure 1.9b).[63] The high dimerization constant characterizing this family of H-bond molecular receptors can be explained taking into account the formation of intramolecular H-bonds between the ureidic carbonyl and the N-H of the pyrimidine fragments, that is able to stabilize the DDAA configuration. This discovering paved the way for the subsequent development of many different type of supramolecular homo and co-polymer based on multiple H-bonds interactions, due to the easy synthesis and high association constant. Recently, the UPy recognition unit has been used for the development of highly luminescent supramolecular polymers by the groups of Meijer and Schenning.[64] In this work, three $p$-conjugated supramolecular building blocks 18-20 (blue, red and green emitting respectively) functionalized at their termini with UPy moieties were synthesized (Figure 1.9a). The self-assembly process between these monomers resulted in the formation of a mixed supramolecular co-polymer, provided with three different kinds of chromophores, which at a certain mixing ratio led to the emission of white light (Figure1.9c, d). The same kind of white
emission was not achievable using a mixture of the bare unfunctionalized chromophores, highlighting in this way the key importance of the organization induced by the H-bond mediated. Simultaneous addition of aliquots of 19 and 20 into a solution of 18 induced the formation of the proposed supramolecular co-polymer, which at the $3/4/5$ ratio: 33:8:59 afforded white photoluminescence (Figure 1.9d). Moreover, a spin coated ODCB solution (4.5-9 x $10^{-3}$ M) of the supramolecular polymer (ratio of $3/4/5 = 10:6:84$) gave rise to a white photoluminescent film, showing the effective applicability of such system toward the preparation of luminescent devices of new generation.

Figure 1.9 Molecular structures (a) of the UPy derivatives 18, 19 and 20, blue, red and green emitting respectively. Structural representation (b) of the quadruple H-bonds system established during the dimerization of UPy derivatives. Schematic representation of the white-light emissive process of the supramolecular polymer formed by 18, 19 and 20. Photoluminescence titration experiment (d) in CHCl$_3$ (blue line: pure module 18; green line 18 whit different amounts of 19; red lines: 18 with different amounts of 19 and 20), the inset show the spectra relative to a ratio (18/19/20) of 59:33:8 (c18=1.6 x 10-6 M, $\lambda_{exc} = 364$ nm). Solution of the three different chromophores (19, 20 and 18 respectively) and a mixture of the three in CHCl$_3$ ($\lambda_{exc} = 365$ nm).

Recently the same recognition system employed by Lehn to prepare linear supramolecular assemblies in solution has been also thoroughly investigated on surface in a joint collaborative network by our group by means of UHV-STM. After the co-deposition of building blocks 21 and 22 on Ag(111) the formation of a periodic wire like assembly [21-22] occurs (Figure 1.10b-f) as a direct consequence of the instauration of multiple H-bonds between the diacetylaminoypyridinic moieties of 21 and the uracil recognition sites of 22. In addition, on the same work, it was shown that the length and the morphology of the resulting linear assemblies could be tuned by the addition of a third component, the anthracenic derivative 23, that could act as a supramolecular stopper, terminating in this way the elongation of the single supramolecular chains on surface.
Another brilliant example of supramolecular structure in which the H-bonding system was formed along the polymerization axes, was developed by Pei, Wang and co-workers who synthesized aromatic hexa-acid 24, able to self assemble into uniform nanowires with a very high solid quantum efficiency (22 %) (Figure 1.11).

In this case, the exploitation of a rigid tridimensional skeleton as building block core, totally increases the emissive properties of the resulting nanostructure into the first known example of a luminescent supramolecular nanowire based on multiple H-bond interactions.

Another category of molecules able to induce the formation of supramolecular main-chain polymers is constituted by the simple N–unsubstituted perylene bisimide (PBI). The supramolecular polymerization of such compounds in apolar solvents is mainly driven by the formation of H-bonds
pair upon antiparallel arrangements of their imidic termini and the collateral aggregation of the resulting chains. Würthner and co-workers, recently synthesize a series of highly fluorescent tetraaryloxy-substituted PBI derivatives 25-29 (Figure 1.12a), equipped with different peripheral chains, in order to extensively investigate the homo-molecular recognition process between PBI molecular modules substituted with different bulky groups at the bay positions.\(^{[67]}\)

![Chemical structures and AFM images](image)

**Figure 1.12** Chemical structures (a) of PBI derivatives 25-29. TM-AFM images (b, c) at different magnifications of the self-assembled nanofibers obtained by drop casting a MCH solution of 28 on a silicon surface. Schematic representation (d) of the homomolecular self-assembly between the PBI units. Molecular model (e) obtained with AMBER force field for the supramolecular structure of perylene bisimide 25 aggregates. The half of an helical pitch µ/2 was calculated as 6 nm.\(^{[67]}\)

By combining different spectroscopic (UV-Vis, CD and LD spectroscopy), and microscopic (AFM, STM) techniques it was possible to reveal that the self-assembly between PBIs units was occurring through the formation of extended double string cables, which consist of two H-bonded supramolecular polymeric chains of densely packed and strongly excitonically-coupled PBI chromophores, able to provide highly fluorescent J-aggregates (Figure 1.12c). The aggregation stability of the nanostructure and the photoemissive properties of the J-aggregates have proven to be in strict relation with the structure of the peripheral alkoxy substituent. Furthermore, concentration-dependent UV-Vis absorption studies proved the presence of a cooperative nucleation-elongation mechanism responsible for the aggregation of the assemblies in which the PBI core was functionalized with chiral alkoxy-moieties, providing a nucleation equilibrium constant of \(K_n = 13 \pm 11\) L mol\(^{-1}\), and an elongation constant of \(K_e = 2.3 \pm 0.1 \times 10^6\) L mol\(^{-1}\) in methylcyclohexane (MCH).

Another important class of compounds able to unidimensionally self-assemble into supramolecular nanostructure are the 1,3,5-benzene trisamide (BTA). This aromatic module is very well-known in literature thanks to its ability to induce the formation of 1-D supramolecular polymers both in solution and at the solid state, as a result of the three-fold \(α\)-helix type arrangement of its intermolecular H-bonds.\(^{[68]}\) On the basis of UV-Vis and CD spectroscopy, several alkylated BTA derivatives have proved to self-assemble by means of highly cooperative processes. In this context, the highest degree of
cooperativity was shown by chiral molecular derivatives that were also able to induce chiral amplifications by means of “sergeant-and-soldier” effect.\(^{[69]}\) As a consequence of the different functionalizations at the level of the amidic functionalities, different types of supramolecular systems can be formed, such as nanorods,\(^{[70]}\) nanofibers\(^{[71]}\) or liquid crystals.\(^{[72]}\) In a recent work, the group of Nolte was able to synthesized the tri-porphyrinoid derivative of BTA 31, that was able to self-assemble in CHX already at micromolar concentrations into long, chiral supramolecular polymers, which precipitated as fibers when the solution was drop casted on mica surface.\(^{[73]}\)

In contrast, in CHCl\(_3\) BTA derivative 31 resulted to be molecularly dissolved up to concentration of 0.02 mM and after drop casting on mica surface no macroscopic precipitation of fibroid material was observed. However, when the CHCl\(_3\) solution was subjected to a spinoidal dewetting, equidistant pattern of 1-D columnar assembly with a diameter comparable with the one of the single molecule were formed (Figure 1.13c-e).

Exploiting the same recognition motif, Marcelis and co-worker, exploiting BTA derivative 30, were able to organize triphenylene groups into columnar nanostructures forming plastic hexagonal discotic phases possessing the highest charge carrier mobility (0.12 cm\(^2\) V\(^{-1}\) s\(^{-1}\) at 180 °C) known ever amongst triphenylenes-based liquid crystalline systems.\(^{[74]}\) The tris-amide functionality has been also very recently exploited by Garcia and Sanchez to study the transfer of chirality in different columnar nanostructures obtained with OPE derivatives.\(^{[75]}\)
Figure 1.14 Molecular structures (a) of the two series of OPE building blocks synthesized by Sanchez and co-workers. TM-AFM images of the linear nanostructures (b,c) obtained by deposition of a toluene solution of 1a and 2c on mica surface. SEM image of an organogel structure formed by 1a alone (d). (Inset) Picture of the gel–sol transition of the organogel formed by 1a in toluene.

For this purpose two series of OPE derivatives 32-37 and 38-43 bearing different solubilizing chains were synthesized (Figure 1.14a). The first composed by OPE trisamides with a variable number of chiral side chains that self-assemble following a cooperative mechanism, and a second constituted by OPEs with a variable number of ether and amide functional groups. CD spectroscopy of the self-assembled nanostructures originating from the first series showed that the presence of only one stereogenic center in the peripheral chains was sufficient to achieve helical organization with a preferred handedness, whereas in the case of compounds 38-43, no helical organization was observed. More interestingly, by mixing achiral trisamide 32 with chiral but non-helical bisamide 40 generated helical nanostructures with a preferred handedness in a cooperative fashion, in a process involving the transfer of helicity from 32 to 40 and the amplification of chirality from 40 to 32, showing a very rare example in which the molecular chirality is obtained from the formation of host–guest complexes between structurally-analogous species that, alone, are CD-silent.

Another elaborated example of non-covalent nanostructuration based on H-bonds, took advantage of the crown ether based molecular recognition. The ability of crown ether to originate H-bonds interactions with ammonium cation forming pseudo-rotaxane structure, have been exploited frequently in literature with the aim to construct supramolecular architecture possessing different geometries and functions. In this context, in a very recent work, the group of Huang have prepared molecular module 44 containing a dibenzo-[24]crown-8 (DB24C8) moiety and a dibenzylammonium (DBA) cation separated by a fifteen terms flexible alkylic chain (Figure 1.15a). Such module was able to self-assemble into linear supramolecular polymers in apolar solvents, that were able to further self-organize into different kind of nanomaterials such as rod-like nanofibers or gel (Figure 1.13b, c) as a function of the used concentration. Moreover, the supramolecular polymer showing reversible gel–sol phase transitions upon heating and cooling or addition of base and acid (Figure 1.15c), was
successfully employed for the selective release of guest molecules such as Rhodamine B.

Figure 1.15 Molecular structure (a) of the pseudorotaxane building block 44 synthesized by Huang and co-workers. SEM image (b) of a linear rod-like nanofibers obtained from the self-assembly/self organization of 44. A polymeric film (c) prepared from [44]$_n$ (left) and the schematic representation of the reversible sol-gel transition of 44 at different pH and at different temperatures. Schematic representation of the homomolecular self-assembly process between the single units of 44 leading to the formation of the supramolecular polymer [44]$_n$.

Exploiting the same strategy, Gibson and co-workers have also developed the first type of AA-BB supramolecular polymer based on bis(m-phenylene)-32-crown-10 based cryptands (BMP32C10) and paraquat derivatives. The self-organization of such supramolecular polymers leads to the formation of linear nanofibers observable by SEM.$^{[78]}$

1.5.1c H-Bond Systems Perpendicular to the Supramolecular Chain
The formation of nanostructures in which the H-bonding units is aligned along the direction of the supramolecular polymer is not the only way in which 1-D nanostructure can be originated. Indeed through an accurate design of the single building block geometry, it is possible to insert arrays of H-bonds donor and acceptor functionalities that can induce the formation of highly stable π conjugated supramolecular structures able to further self-assemble in a highly directional fashion, thanks to the increase in strength of the π-π interactions. As a consequence of this process, highly hierarchized supramolecular materials are formed by a recognition process mediated by the concomitant action of H-bonds and π-interactions, which grow orthogonally to the H-bond direction.

Among all the functional systems able to polymerize through this mechanism, p-phenylenevinylene revealed to be the most exploited. In an extensive work of Meijer and Schenning, p-phenylenevinylene derivative 45 functionalized at one peripheral positions with an ureidotriazine (Figure 1.16a) was prepared and its ability to dimerize via multiple H-bonds formation and subsequently to polymerize via π-π interactions was extensively studied.$^{[79]}$ Such process produced the formations of helical nanofibers with an approximate length of 100 nm that could show a preferred handness, if opportunely functionalized with chiral lateral chains.$^{[80]}$ The morphology of the supramolecular OPV nanofibers
was investigated on surface by means of Atomic Force Microscopy. Unfortunately the electrical conductivity of the resulting nanofibres, as deposited on Au-Pd electrodes, has proved to be considerably low due to the presence of defects within the fibers or to an intrinsically-poor conductance of the stack.\[^{81}\]

![Figure 1.16 Molecular structure (a) of the ureidotriazine functionalized OPV 45. Schematic representation (b) of the self-assembly/organization process leading to the formation of the helical nanofibers. TM-AFM image (c) of the nanofibers as obtained after spin coating on graphite (inset: lateral profile as obtained form the red line reported on the main image)\[^{79a}\]. Molecular structures of the thiénylvinylene derivatives 46 and 47. TEM image (d) of fibers created by the self-assembly of 46. C-AFM measurements (e, f) of 46 and 47 xerogels from decane solution drop casted on HOPG (c = 1 × 10^-4 M). I-V curves of undoped (a) and doped (b) xerogels of 46 (1) and 47 (2).\[^{82}\]

The self-organization of thiénylvinylene moieties H-bond based supramolecular nanofibers featuring organic gel (Figure 1.16d) has been also studied by the group of Ajayaghosh.\[^{82}\] The ability of the nanofibers to give charge transfer phenomena was studied by means of electrodeless flash photolysis time resolved microwave conductivity (FP-TRMC) revealing higher values of $\Sigma \mu_{max}$ (6.0 × 10-2 cm² V-1 s-1) for the fibers obtained in decane solutions in comparison with the ones obtained in CHCl₃, as a consequence of the H-bonded monodimensional assembly formation (Figure 1.16f, g).

Through the same kind of approach, it is possible to organize into 1-D nanostructures also molecules that do not possess a flat aromatic surface, for example due to presence of chiral elements into the aromatic core. In this context, exemplar is the work of Takeuchi and co-worker, in which the organization of the phthalazidazole-helicene 48 into trimeric disks led to the formation of fibrous assemblies in nonpolar solvents such as chloroform and toluene (Figure1.17).\[^{83}\] Moreover, as a consequence of the structure of the building blocks, both assemblies deriving from (M)-48 and (P)-48 showed elevated values of Circularly Polarized Luminescence ($\varpi_{circ}= 0.035$ at the peak maxima) that can be considered as the highest value ever reported amongst organic molecules without a hosting matrix.
Self-complementarity between modules having multiple H-bonded based recognition sites is therefore an excellent instrument to pre-organize a discrete number of supramolecular oligomers (such as hetero-molecular systems in which, by the combination of different type of building blocks, it will be possible to increase the complexity of the initial oligomeric structure), into larger structures able to polymerize in different supramolecular nanostructures such as helix, wires or tubes. As shown recently by Yagai and co-workers for the case of melamine-functionalized OPV molecules 49 and 50 (Figure 1.18a), passing from a self-complementary to a co-assembled supramolecular system, it was possible to tune in a drastic way the morphology and the complexity of the resulting nanostructures. After the deposition of 50 on HOPG the formation of fibers with a diameter of 8 nm was observed by means of AFM analysis (Figure 1.18c). On the other hand, the deposition under the same experimental conditions of molecule 49, resulted in the formation of ill-defined nanostructure as a consequence of the lacking of the assisential H-bond interactions originated from the amidic functionalites of 50. Nonetheless, the combination of 49 with cyanuric acid (CA) induced the formation of ring shaped nanostructures (Figure 1.18d), efficiently reconverted into fibrilar nanoobjects by increasing the concentration of the modules. This transition is mainly originating from the formation of a different kind of supramolecular oligomer in solution, between the melamine functions of 49 and the imidic residues of CA (Figure 1.18d,e), forming a supramolecular heterotetramer that, depending on the concentration, can originate both rings and fibers.
In a further development, the same recognition units composed by melamine and CA was employed to investigate the option to organize functional chromophores such as PBI derivatives into helical nanostructures. The preparation of discotic supramolecular complexes by mixing melamine’s derivative 51 equipped with two PBI chromophores and CA (Figure 1.19a-c), was confirmed by UV-Vis and Fluorescence titration, leading to the formation of a 3:1 complex in MCH between molecules 51 and CA, respectively. Microscopic investigations (TEM and AFM) revealed that the complex hierarchically organized into fibrous columnar assemblies, which resulted into the formations of gels.

Induced by an evaporation-induced organization into columnar assemblies, wide area TEM analysis has shown the presence of different types of fibrous entities (Figure 1.19c) classified as thin fibrils, thin fibers and thick fibers. CD investigation showed that in the helicaloidal structuration of the
columnar stacks is determined by the direction of the rotational displacement of the H-bonded core, which is commanded by the intercomplex asymmetric interaction between the internal chiral chains of the primary discotic entity. In addition, the obtained columnar aggregates have shown a remarkable retention of chirality upon dilution and on time, maintaining their CD activity up to two weeks after their preparation.

![Molecular structure of the H-bond based trimer formed by the self-assembly of PBI 53 and two units of melamine functionalized OPV derivative 52. CPK representations (b) of the optimized OPV derivative 53 (left) and of its disposition along the nanofibres (right). TM-AFM images (c) of the fibers obtained upon spin coating of a MCH solution of molecule 52 and 53 in 2:1 ratio.](image)

The \( \pi-\pi \) stacking interactions that usually originate from the organization of the molecular modules in which the H-bonding system is orthogonally oriented to an aromatic moiety, can be efficiently exploited in order to produce ordered 1D-nanostructures characterized by high electrical conductivity. For this purpose, the molecular recognition process between diaminotriazine and PBI in order to produce \( p-n-p \) junction have been thoroughly studied by different groups.\(^{[86]}\) In the works of Meijer, PBI derivative 53 was exploited in order to form a H-bond based trimer in which the two molecules of OPV derivative 52 where associated at both termini of the PBI modules (Figure 1.20a).\(^{[87]}\) After the trimerization process, due to the increase of the \( \pi \)-conjugated surface of the supramolecular complex, the formation helical columnar stacks, with a diameter of approximately 7 nm, occurred. The resulting nanofibers have proven to serve as an efficient “supramolecular wire” for the antiparallel transport of both electrons and holes. The occurrence of an electron transfer phenomena within the columnar structure, from the electron donor OPV to the electron acceptor (PBI), was outlined by time resolved TA spectroscopy, proving in this way the functionality of the supramolecular system.
1.6 2-D H-Bonded Networks

The investigation of the electronic and geometrical properties of molecular materials bi-dimensionally arranged on surface can be extremely important in a next future for its potential application in the field of fabrication of nanoelectronic devices. In this context the continuous development of the Scanning Probe Microscopy (SPM) in the last decades have allowed the observation and the characterization at the molecular resolution of the geometrical properties 2-D networks. In particular, among all the SPM techniques, the Scanning Tunnelling Microscopy (STM) have become the chosen technique for characterizing the formation of mono and multi molecular layer on different types of conductive surfaces. In these systems, the process of formation of the first monolayer and its stability are generally ruled by the molecule substrate interactions defining in this way also the orientation of the molecular domain. However, intermolecular forces are also fundamental parameters in such systems due to the fact that the adsorbed molecules in general posses sufficient mobility to redistribute on the surface in order to form the most thermodynamically stable phase. In this context, intermolecular non-covalent interactions acting between molecules in a parallel direction respect to the substrate can decide the structural features of the final 2-D assembly. Among all the possible strategies, the incorporations of H-bonds motifs in conjugated molecules to inducing a controlled self-assembly process on surface is one of the most successful approaches due to the high directionality and reversibility of this type of interactions, which give the possibility to pre-design the geometrical and structural features of the resulting network. So far a conspicuous number of example describing the preparation of mono and bi-component 2D networks through the formation of H-bonding interactions have been published. One of the first examples of bi-component porous networks characterized by the presence of empty hexagonal pores was reported in 2003 by the groups of Beton, Champness and co-workers. They described the formation of hexagonal arrays by the co-deposition of the PBI derivative 54 and melamine 55 on a Ag(111) terminated silicon surface under UHV conditions.

![Figure 1.21](image)

**Figure 1.21** Schematic representation of the self-assembly process between PTCDI–melamine inducing the formation of the honeycomb network on surface. a) Chemical structure of PTCDI 54 and melamine 55. b) STM image of a PTCDI–melamine network at different magnifications. The inset of figure b) is an high resolution view of the Ag/Si (111) $\sqrt{3}\times\sqrt{3}$R30$^\circ$ substrate surface.

As revealed by STM images (Figure 1.21b, c), the two molecular modules organize in such way that hexagonal domains are formed. In this system melamine and PTCDI modules were arranged to form
the vertices and the straight edges of the hexagonal domains, respectively (Figure 1.21c), as a consequence of the self-assembly process induced by the instauration of triple H-bonds system between the recognition moieties of the molecular components.

The self-assembly of organic molecules on surface guided by H-bonds interactions, most often involves the use of planar compounds equipped with rigid chemical functionalities to direct the self-assembly in order to produce a two-dimensional system. However in a recent work of Linderoth and Besenbacher, the first example of an extended 2-D architecture formed by H-bond recognition between molecules that exhibit a pronounced three-dimensional structure has been reported.[92] After the deposition of the diaminotriazine functionalized (hexaphenyl)benzene derivative 56 on a Au(111) surface, the formation of both linear (1-D) and long range ordered 2-D supramolecular networks were observed by UHV-STM. The different arrangements derive from the combination of N-H···N bonds between the diaminotriazine (DAT) functional moieties of the single molecules.

![Figure 1.22](image)

Figure 1.22 Chemical structure of the molecular lander 56 (a) and its respective space-filling model (b) (white: hydrogen, blue: nitrogen and cyan: carbon). STM images of three of the different bidimensional architecture obtained by the deposition of 56 on Au(111) (b-d). The representative molecular disposition in the supramolecular network is reported below each images (f-h) and the yellow circle are highlighting the different interactions between the DAT units of different molecules (marked as A, A', B and B').

The most common approach for the preparation of 2-D systems with a controlled geometry consist into the deposition of molecular modules having a pre-defined recognition site able to induce the formation of the self-assembly process. Using a different approach, the groups of Stöhr and Gade exploited a molecular system in which the molecular recognition sites could be activated directly in situ enabling hydrogen-bonding interactions, which lead to the formation of highly stable molecular networks under UHV conditions.[93] The authors reported that by thermal dehydrogenation of 4,9-diaminoperylene-quinone-3,10-diimine (DPDI) 57 on a Cu(111) surface (Figure 1.23a) the formation of a supramolecular network based on H-bond donor and acceptor was observed by UHV-STM analysis (Figure 1.23b). The resulting periodic honeycomb structure has revealed to be thermally very stable (up to > 300 °C) as a consequence of an irreversible chemical transformation and of the
combination of intramolecular H-bonds and strong π-bonding between the organic molecules and the surface metal atoms.

Exploiting the same approach, our group has investigated the controlled formation of a two-component porous network at the solid–liquid formed using melamine 58 and the bis-uracil module 59 in 1,2,4-trichlorobenzene (TCB) on highly oriented pyrolytic graphite (HOPG) surfaces (Figure 1.24a). The structural characteristic of melamine, i.e its ability to form three H-bond systems oriented at 120° each one, directs the assembly of the network forming the resulting honeycomb structure. The porous network was formed only with low concentration solutions (∼ 2.0 μM) since at higher concentration (∼ 20 μM) only tightly packed monolayers of 58 were formed due to the competitive physisorption of the two molecules.

By working at the sub-monolayer coverage (∼ 2.0 μM), it was possible also to investigate the formation of discrete polygonal assemblies featuring porous domain at the solid-liquid interface. In order to engineer these assemblies, two different molecular modules were exploited: the tetrakis[ethynilpyrene] derivative 60 and the diacetylamino pyridine derivative 61 bearing complementary triple H-bonds recognition sites (Figure 1.24b-g). The discrete H-bonded assemblies were nucleated in solution and studied at very low-concentrated solutions (< 10 μm). STM analysis showed the formation of hybrid-polygonal assemblies between 60 and 61, resulting in the formation of different type of self assembled cyclic oligomers characterized by rhomboidal and rectangular shape, formed as a consequence of the pre-programmed disposition of the H-bonds recognition moieties into the starting building blocks. Tacking into account the differences into the absorption energy of the single components and the tendency of this latter to minimize the occupied areas, the control of the deposition of two different molecules on a surface can be considered a very difficult task. This approach, preventing the competitive adsorption between the modules, can be considered a valuable route to the future engineering of multi-components nanostructures on surface.

**Figure 1.23.** a) Schematic representation of the hexagonal assembly of DPD1 57; b) STM image of the self-assembled architecture formed by 57 after thermal activation on a Cu(111) surface under UHV conditions. [93a]

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A further approach for the preparation of two-dimensional networks on surfaces take in account the exploitation of a biomimetic approach. In this context, He and co-worker have used DNA to engineer an infinite 2D porous networkable to induce the formation of highly extended nanostructured arrays with a length that can arrive up to 1 mm (Figure 1.25). The fundamental unit used for the preparation of the supramolecular network, was characterized by a three point star shape and was produced by the selective association of seven DNA single strands. In this case, palindromic sequences were used to ensure that the H-bonds interaction in all the direction would have the same strength. After the mixing of the DNA strands, in the appropriate proportions in a tris-acetic-EDTA-Mg²⁺, the material was consequently deposited onto mica surface and AFM analysis of the surface showed the formation of extended, highly ordered, hexagonal 2D crystalline array characterized by pores diameters of 29 ± 0.1 nm.

The functions of the surface-supported supramolecular network produced by H-Bond recognition, has proved in these years to be not only correlate to the ability of these latter to act as a host-guest system for the ordered entrapment of molecules on surface. In a recent work of Borguet and co-worker, by STM investigation of the tetracarboxylporphyrin 62 on Au (111) in an acidic medium (HClO₄ 0.01 M), the formation of three different types of ordered 2-D arrays was observed as a consequence of the
instauration of multiple intermolecular H-bond interactions between the carboxylic moieties. In this ordered systems, single molecules can be slowly reduced by tuning the potential of the underlying electrode, showing that the more negative the potential was, the faster the reduction reaction occurred (Figure 1.26b-e).

**Figure 1.26** Molecular structure (a) of the tetracarboxylporphyrin derivative 62. STM images (b-e) relatives to the slow reduction dynamic of 62 after that the potential was stepped from 0.12 to 0.1V (c=0.01M HClO₄), revealed by the increase of the number of bright spots from b to c (50, 80 100 and 150 respectively).

These results, along with the possibility to organize the single electroactive molecules in a very efficient way, shed new light on the possibility to exploit the new generations of 2-D supramolecular networks for the productions of high performances solar cells or nanoelectronic devices.

### 1.7 H-Bond Discrete Nanostructures

One of the principal target in the field of supramolecular nanostructuration of organic materials, consist in the possibility, through a strict control over the self-assembly process, to govern the relation between the size of the supramolecular object and the structural and geometrical information’s present in the single building blocks. In this context great importance is related to the possibility to control the number of the molecules that are associating in order to induce the formation of nanostructures characterized by an extremely precise dimension, and at the same time a relatively high monodispersity. In this paragraph the recent developments in the preparation of discrete nanostructure based on H-bonds interactions are reviewed. In the first section the formation of discrete assembly through a templated approach will be discussed, whereas in the second section the formation of discrete entity by a self-assembly/self-organization process of low molecular weight building blocks will be reviewed.

#### 1.7.1 H-bond Templated Nanostructures

One of the most intuitive and at the same time effective approaches used for the preparation of supramolecular material featured with a controlled dimension, consist in the use of a template molecule, able to organize in precise fashion a finite number of building blocks, through the use of non-covalent interactions. Due to the high directionality and complementarity of the H-bonds systems, this interaction is among the most useful to exploit for this task. For this task in general rigid linear molecules have been used in order to template in a monodisperse manner stacked 1-D nanostructures. In this context the group of Matile, exploiting a combination of H-bonds and aromatic...
electron donor-acceptor interactions, was able to construct a supramolecular tubular nanostructure that could be exploited as synthetic ion channel, able to be opened in response to chemical stimulation.\cite{100}

![Figure 1.27](image)

**Figure 1.27** Schematic representation (a) of the oligomeric template 63 used for the preparation of the artificial pores synthetized by Matile and co-workers. Schematic representation (b) of the H-bonds interactions (left) and aromatic donor-acceptor interactions (right) occurring along the pore structure. Schematic depiction of the pore structure (c), red tiles represent the DAN units whereas the green one represent the NDI fragments. Axial (d) and top view (e) of the geometry optimized model of the supramolecular pore (DANS units are represented in red).\cite{100}

The rigid supramolecular template 63 were synthetized attaching to a rigid \( p \)-octyphenyl rod molecule, eight naphthalene diimide (NDI) derivatives functionalized with amidic functions, that acting through self-recognition mediated by a complex combination of H-bonds and \( \pi-\pi \) interactions induces the formation of a closed \( p \)-helix channel. The addition of an electron rich DAN derivative (figure 1.27 b left) resulted in its intercalation between the aromatic planes defined by the NDI subunits, with a consequent structural change in the supramolecular architecture of the nanostructure corresponding to the formation of an open channel. This structural modification, leading to an external control of the opening of the supramolecular pore, was attributed to the formation of a charge transfer process between the NDI and the DAN units, able to induce the parallel disposition of their aromatic systems ad therefore the opening of the channel.

The template approach based on H-bonds interactions has been also successfully exploited for the preparation of more complex discrete architectures such as the preparation of ladder-like or helix supramolecular nanostructures. In one of the first works, the group of Sada has reported the formation of a well defined ladder-like complex based on the H-bonds interactions between an oligomer having secondary dialkylammonium cations (constituting the rails of the ladder) and a porphyrin di-functionalized with 2,6-Bis(2-oxazolyl)pyridine (PYBOX) moieties at the 5 and 15 \( meso \) positions (constituting the bars between the rails).\cite{100} As a further development of this work, through the introduction of chiral PYBOX moieties on the porphyrin core, the synthesis of bis-PBOX derivative 64 was performed (Figure 1.28a).\cite{102} After mixing chiral unit 64 with the polycationic oligomer 65,
the formation of helical nanostructure on HOPG surface was observed by AFM microscopy (figure 1.28b).

![Figure 1.28](image)

**Figure 1.28** Molecular structures (a) of porphyrin derivative 64 (left) and of the polycationic oligomer 65 (right). TM-AFM image (b, left) of the helical nanostructures formed by the H-bonds mediated assembly between 64 and 65, and its schematic representation (right) black lines marks are used to highlight the step distance in the helix. Representative depiction (c) of the templated self-assembly process between 14 and the oligomeric derivative 15. d) CD (top) and UV-Vis titration spectra of molecule 64 with modules 65. 

CD and UV-Vis analysis of the mixture of 64 and 65 gave a further confirmation of the helical structure of the templated assembly in solution. Indeed during titration experiments the positive Cotton observed by CD in the Soret band of 64 was completely reverted showing a decrease in the intensity (figure 1.28d). Such result confirmed the formation of an helical arrangements as a probable consequence of the twisted π-π stacked interactions between the single units of 64, due to the presence of the isopropyl groups on the oxazolyl rings. Another valid approach recently used for the preparation of H-bonds templated nanostructures take advantage from the biomimetic exploitation of oligomeric nucleic acids as linear organic templates. This approach was demonstrated for the first time by Iwaura et al. that was able to co-assemble thymidine functionalized OPV molecule, using a complementary oligo-adenylic eicosamer in aqueous solution. AFM analysis, in combination with CD and UV-Vis investigations showed the formation of helical stacked structures. Basing on these results, in a series of more recent works, the preparation of helical stacks formed of chromophoric conjugate molecules was attempted. The groups of Meijer and Schenning demonstrate that a single strand of DNA is able to template a supramolecular strand of chromophores yielding a new type of DNA hybrid (Figure 1.29a, b). In this type of hybrid constructs, an oligothymine unit was used to template via multiple H-bonds interactions the stack of different chromophores such as the naphthalene 65 or the OPV 66 derivatives, bearing a DAT units each as molecular recognition site. The formation and the stability of the supramolecular constructs was monitored by variable temperature CD and UV-Vis spectroscopy showing that the binding of the chromophores to the ssDNA is completely reversible and...
the formation of the helical stack follow a nucleation-growth mechanism.\textsuperscript{[105]}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.29.png}
\caption{Molecular structures (a) of the naphthalene derivative 66 and of the OPV derivative 67 used by Meijer and Schenning for the preparation of the H-bond templated chromophoric stacks.\textsuperscript{[104]} Schematic representation of the assembly process between the oligothymine single strand and the DAT functionalized chromophores inducing the formation of the helical stacks. Molecular structure (c) of the adenosine derivative 68 and of its N-3 protonated species (c) responsible for the pH dependent chirality inversion of the helical stack. Schematic representation (e) of the pH dependent hardness inversion of the helical chromophores stack.\textsuperscript{[106]}}
\end{figure}

As a further development of this work, in 2009 the group of Schenning developed a new type of chromophore able to respond to pH variation. Diamino-purine derivative 68 (Figure 1.29c) was synthesized and its ability to reversibly associate with an oligothymine template was investigated in solution by means of CD and UV-Vis spectroscopy.\textsuperscript{[106]} Also in this case, both techniques confirmed the reversible association process forming right-handed supramolecular helices between the oligothymine strand and achiral guest 68. Remarkably, by changing the pH from 8 to 2, the CD spectra showed a complete inversion of the Cotton effect proper of the right handed helix, highlighting in this way the passage from a right handed to a left handed helix. The pH dependent chirality inversion was hypothesizing to be related to the protonation of the N-3 position of the diamino-purine moieties of 68. This phenomenon can be responsible for the change of conformation of the polyethilenoxy chains present on the purine fragment that, due to electrostatic interactions, can induce a conformational rearrangement of 68 (Figure 1.29d) responsible for the stabilization of the left-handed helix.

\subsection*{1.7.2 H-Bonded Nanostructures of Low Weight Molecular Modules}

The self-assembly process of low molecular weight building blocks into discrete supramolecular entities is considered nowadays one of the most interesting field of nanotechnology. The variety of supramolecular nanostructures achieved through this approach is growing extremely fast in the last years as the different method employed for their preparation. Focusing on the use of H-bonds as principal non-covalent interactions for the preparation of discrete nanostructure deserves particular attention was the one of H-bonded supramolecular nanoparticle and nanovesicles. In this context, the work performed by Reinhoult on melamine functionalized calix[4]arene represent one of the first key
example of formation of discrete nano-objects through H-bonds interactions. Upon mixing three equivalents of calix[4]arene derivative 69 with six equivalent of merocyanine dye 70, the formation of an assembly comprised of two coplanar chiral rosettes was obtained (Figure 1.30a). The assembly of the whole structure is induced by the highly cooperative action of thirty-six H-bonds formed between the melamine and the barbiturite moieties. Another strategy for the preparation of supramolecular systems featuring spherical geometries consist into the exploitation of molecular modules capable to assemble by a delicate combination of H-bonds and π-π interactions. In the last years, the group of Ajayaghosh has used this principle to direct the self-assembly of OPE derivatives into the formation of spherical nanoparticles. For this task, two OPE derivatives 71 and 72, bearing at their termini hydroxy and methyl groups respectively, were synthesized (Figure 1.30b).

-Vis spectra of a solution of 71 in CHCl₃ showed a strong π-π* absorption band at 377 nm, that led to red-shifted bands at 385 and 419 nm, whereas no considerable differences were noticeable in the case of derivative 72. These changes in the absorption spectra of compound 71 are attribute to the formation of J-type aggregates due to the formation of intermolecular H-bonds. TM-AFM and HR-TEM investigations of a decane solution (1x 10⁻⁶ M) of derivative 71, showed the formation of highly mono-dispersed nanoparticles provided with spherical geometry and a vesicular structure (Figure 1.30c-f).

![Figure 1.30](image_url)

**Figure 1.30** Self-assembly process (a) between calix[4]arene derivative 69, and the merocyanine 70, producing a supramolecular discrete nonameric complex. Molecular structures (b) of the OPE derivatives 71 and 72 and TM-AFM image (c) and HR-TEM image (inset) of the spherical nanoparticles obtained by the H-bond mediated self-assembly of 71. Schematic representation (f) of the interconversion mechanism between nanoparticles and gel structure. SEM images of the gel produced by OPE derivative 71 in decane. Photograph of the gel in decane (f) under UV illumination (365 nm).

Most remarkably, AFM images at higher concentration (1 x 10⁻⁵ M) showed higher tendency of this vesicles to agglomerate and fuse, until the formation of a self-supporting gel with a strong blue fluorescence (λ_max=443 nm) is obtained at 3.4 x 10⁻³ M, due to the transformation of the spherical
nanostructure into micrometer size fibers. In a further development of the same work, he introduction
of a chiral centre into the lateral chains of the OPE core led to the selective transformation of the
particle obtained by OPE derivative 71 into helical fibers, through a sergeant-soldier type mechanism.
In a collaborative work with the group of Dr. N. Armaroli, our group has recently developed a novel
approach for the preparation of both hollow and filled spherical nanostructure, through the
combination of both H-bonds, aromatic-aromatic and solvophobic interactions.[109] Under temperature
and solvent polarity control, supramolecular adducts between two p-conjugated units, bearing
complementary H-bonding groups can be obtained in solution and further organize into hollow
spherical nanoobjects provided with a vesicular structure. In this work the possibility to change the
size distribution and shape by changing the stoichiometric ratio of the molecular components was
proved to be a consequence of the solvophobic/solvophilic interaction established between the
supramolecular species (Figure 1.31). For this task building blocks 73 is and 74 bearing
complementary H-bonds recognition moieties were synthesized. Molecule 73 consisted of a p-
disubstituted central benzene ring bearing at both sides two 2,6-bis(acetylamino)-pyridyl moieties,
whereas molecule 73 possessed only one H-bonds recognition site consisting of an uracil moiety. These
molecular units are known to undergo a self-assembly process trough the formation of triple H-
bonding systems with high association constant in apolar solvents (between 10³ and 10⁵ M⁻¹).\[110\]

![Figure 1.31 Schematic representation (a) of the self-organization process between molecular modules 73 and 74 resulting in the formation of H-bond based vesicular nanostructures. TEM (b) and TM-AFM (c) images of a drop casted solution of molecules 73 and 74 in 1:2 ratio (insets: detail on the single nanoparticle).](image)

Due to the highly chromophoric features of both compounds, their self-assembly process in solution
was monitored by Uv-Vis and Fluorescence spectroscopy in a strongly apolar solvent such as CHX.
Uv-Vis spectrum of the ternary mixture [73×(74)₂] presented the formation of a red-shifted new band,
that was not present in the spectra of the preliminary and isolated compounds, that is attributable to the
presence of π-π interactions most likely induced by the preliminary formation of an H-bond based
hetero-trimers between one unit of 73 and two unit of 74. TEM and TM-AFM investigations,
highlighted the ability of both isolated molecules 73 and 74 to self-assemble into spherical micro and
nano-objects with diameters ranging from 10 nm to over 1 mm. Remarkably, TEM and AFM analysis
of drop casted solutions of a 1:2 mixture of 73 and 74 respectively, showed the presence of
supramolecular vesicles provided with an highly uniform distribution size (diameter ranging from 80
to 180 nm). Such results confirm that the self-assembly between 73 and 74 increase the solute-solvent
interactions as a consequence of the change of the solvophobic 2,6-di(acetylamino)-pyridyl moieties
into the more solvophilic anthracenyl fragment favouring in this way the thermodynamical formation of the spherical supramolecular vesicles.

Another important challenge in the development of discrete nanostructures is considered the preparation of nano-objects characterized by a circular shape such as rings or toroids. In this context Ajayaghosh and co-workers have recently reported the hierarchized assembly of melamine functionalized OPE derivatives in presence of cyanuric acids (CA) derivatives, resulting in the formations of luminescent toroids nanostructures.[111] The bi-component system formed by OPE functionalized derivative 75 and CA derivative 76, is able to self-assemble into discrete H-bonds based rosette, from which through π-π stacking interaction the final toroid structure is evolved (figure 1.32a).

**Figure 1.32** Schematic representation (a) of the self-assembly process between melamine-linked OPE 75 and cyanurate 76, inducing the formation of toroid nano-objects. TM-AFM image (b) of an equimolar mixture of 75 and 76 as spin coated from decane solution on HOPG (Inset: image obtained by low-force tapping mode).[111]

Absorption measurements showed that the major driving force leading to the rosette association was the formation of H-type aggregates induced by the OPE fragments of 75. Moreover molecular modelling simulations have highlighted that the aromatic planes defined by the OPE moieties were rotated of 45°C in respect to the H-bond plane, confirming that an extended association of rosettes in such tilted conformation could lead to the formation of columnar assemblies provided with a certain degree of curvature, resulting therefore also into the formation of toroidal objects. In a very recent paper the preparation of H-bonded based toroidal nanostructures was achieved by the group of Yagai, through the self-complementary assembly between OPV derivatives opportunely functionalized with barbiturate moieties at one of their termini.[112] Compound 76-78 consisted of a barbituric acid H-bonding head-group, of an OPV π-conjugated segment and of a wedge-shaped tridodecyloxybenzyl (TDB) moiety (Figure 1.33a). UV-Vis spectra of a MCH solution of this class of compounds showed a strong hypochromic effect in comparison to the one in THF as a consequence of an associative phenomenon. Also in this case the authors hypothesize that the formation of the ring structures was caused by the specific curvature encoded within the π-π stacked columnar nanostructures of the supramolecular macrocycle formed through H-bonds in diluted conditions.
Figure 1.33 Molecular structures (a) of the barbituric derivatives 76-78 used by Yagai and co-workers to induce the formation of discrete supramolecular nanorings. TM-AFM images of a spin coated solution of 78 on HOPG surface revealing the formation of interlocked nanoring structures resembling the formation of catenanes.[112]

Most notably, close AFM investigations of spin-coated solutions (1x10^4 M) of 76 and 78 in MCH on HOPG showed the formation of interlocked structures made of two nanorings, whereas for the derivative 76 any interlocked structures were observed. This can be rationalized taking into consideration the different type of supramolecular macrocycles formed by the different OPV building blocks. In the case of OPV derivative 76, the ring structures resulting from the π-π interaction of the supramolecular macrocycles were too small (average diameter of 25 nm) to allow an effective interlocking of the single nanoring and the resulting nanostructures were therefore constituted only by isolated circular units.

A further strategy, recently used for the preparation of discrete nanostructures composed by an extremely restricted numbers of supramolecular building blocks, consists into the exploitation of surface based methods. Indeed the size control of H-bonded assemblies and the relative positioning of a small number of supramolecular building blocks can be achieved more easily if the self-assembly process is restricted in only two dimensions. One of the systems that are most studied so far is the one regarding the self-association of the diaminotriazine OPV derivatives 79-81 (Figure 1.34a).[113]

Figure 1.34 Molecular structures (a) of the OPV derivatives 79-81. Mirror type domains (a-h) obtained at the solid liquid interface from the deposition of 79 and 80 respectively.[113] Molecular structures (d) of the NBI derivative 82 and of the melamine functionalized OPV building block 83 and the schematic representation of their self assembly process on surface (e). STM image of the-assembled discrete nanostructure (f), the green circle highlight the formation of the H-bonded rosette.[113]
All the derivatives self-organize at the 1-phenyloctane/HOPG interface into chiral hexameric rosettes as a result of the formation of H-bond pairs between the diaminotriazine moieties (Figure 1.34b, c). Enantiomerically pure molecules 79 and 80 lead to the exclusive formation of one of the two possible mirror-type arrangements whereas for the case of the achiral derivative 81 appeared in the formation of equal amount of mirror-image domains.

Using this approach it is also possible to induce the formation of monolayers constituted by the hetero-association of a mixture of different building blocks. In this context, H-bonded rosettes between OPV derivative 82 and N-unsubstituted NBI derivatives 83 have been visualized at the HOPG-solvent interface by STM measurements.\textsuperscript{[113b]}} Despite the disordered nature of the assembly originated (Figure 1.34f), the formation of the heterocomplex at the solid liquid interface was demonstrated using a bias depending imaging technique able to discriminate between the electronic properties of the single components.

1.8 Bibliography


CHAPTER I


CHAPTER II

THERMAL NANOSTRUCTURATION
OF H-BONDED SUPRAMOLECULAR POLYMERS

2.1 Introduction
Among the various bottom-up approaches, the exploitation of non-covalent interactions, capable to induce the selective and controlled association of molecular components leading to aggregates of defined structural properties, has turned out to be extremely promising. In this field, the key concepts of molecular recognition through non-covalent interactions (i.e. supramolecular chemistry) have been very effective tools for the preparation of nanostructured organic materials displaying controlled geometry and shape.\textsuperscript{[1]} The exploitation of highly directional non-covalent interactions, such as multiple H-bonds, has been employed to induce the formation of supramolecular polymers, macromolecular structures in which single monomers are held together through reversible non-covalent interactions.\textsuperscript{[2]} In this context the exploitation of molecular recognition sites based on complementary multiple H-bonding systems are versatile tools to organize and tune the shape of materials at the nanoscale level.\textsuperscript{[3]} Our work on self-assembled and self-organized microstructures started with the preparation of vesicular nanostructures under temperature and solvent polarity control\textsuperscript{[4]} (i.e. through solvophobic/solvophilic interactions that are established in binary or ternary supramolecular adducts) by means of supramolecular ensembles formed through the recognition of complementary\textsuperscript{[5]} monouracil and bis-2,6-di(acetylamino)pyridyl H-bonding moieties. The choice of using this kind of molecular dyad as recognition systems is based on the high complementarity and directionality of the resulting interactions that is originating from the formation of a triple DAD-ADA, H-bond system (Figure 2.1).\textsuperscript{[6]} Moreover, its medium binding strength in organic solvents ($K_a \sim 10^3$ M$^{-1}$ in CHCl$_3$) allows to maintain a certain degree of reversibility and dynamicity during the self-assembly process, inducing in this way the formation of the most thermodynamically stable system.

![Figure 2.1 Schematic representation (a) of the H-bond based complex between 1\textsuperscript{H}-hexyluracil and bis-2,6-di(acetylamino)pyridine.\textsuperscript{[9]} Schematic representation (b) of the self-assembly/self-organization process between monouracil derivative 90 and diacetylimidopyridine unit 84 leading to the formation of H-bond based vesicular nanostructures.\textsuperscript{[9]}](image-url)
Along these lines, we also prepared a library of several chromophoric acetylenic scaffolds peripherally equipped with 2,6-di(acetylamino)pyridine or uracil-type terminal fragments that, by taking advantage of self-assembly and self-organization, led to the formation of nanostructures of different shapes and sizes in solution such as nanoparticles, nanovesicles, nanofibers, and nanorods, also with helicoidal variants (Figure 2.2).7

Unfortunately, as a consequence of the high number of molecular recognition sites, molecules 84-89 are characterized by a low solubility in most of the common organic solvents (especially due to the instauration of homomolecular H-bonds between the single isolated units that induced the formation of low soluble high-molecular weight supramolecular polymers) and therefore difficult to manipulate. In order to obtain a further control on the self-assembly/self-organization process and to avoid collateral aggregation phenomena due the homomolecular H-bonds, we have decided to exploit a thermally activated cleavage reaction to induce the self-assembly process. For this purpose, we developed a new library of uracil derivatives bearing a tert-butyloxyxcarbonyl (BOC) protecting group at the imidic nitrogen of the uracil recognition site (Figure 2.3).

The choice of such protective group is mainly centred on its ability to be selectively removed upon mild thermal conditions, therefore without using any additional reagent that can hamper the H-
bonding mediated self-assembly process. Moreover, preventing the formation of the homomolecular recognition process and due to the presence of the \textit{tert}-butyl chains, such group is considered an ideal function to increase the solubility of the single modules and therefore of their processability. Each molecular module possesses different geometrical features and a different number of recognition sites (two, three and four, respectively), that in the presence of the complementary module 84 under thermal activation undergo supramolecular polymerization, originating novel nanostructured morphologies featuring different geometrical and structural topographies (Figure 2.4).

![Diagram](image)

**Figure 2.4** Schematic representation, using PM3 optimized molecular structures, of the thermal induced self-assembly process between the BOC protected molecular modules and the diacetilaminopyridine unit 84, leading to different kinds of supramolecular assemblies (lateral chains of module 84 are not displayed for clarity).

Additionally, from the thermal-induced self-assembly of linear molecule 91 with complementary di(acetylamino)pyridine derivative 84, the formation of linear extended nanostructure was expected as a consequence of the molecular geometrical constraint, presenting their respective recognition moieties at 180° from each other. In the case of the assemblies [92\textcdot 84]_n and [93\textcdot 84]_n, due to the bi-dimensional features characterizing the uracil derivatives, the formation of two different types of 2-D supramolecular arrays was expected.

At the mechanistic level, the self-assembly mechanism between these modules was induced by thermal stimulation of a binary equimolar mixture containing molecular modules 91, 92 or 93 with their complementary unit 84. When the temperature of the resulting mixture was raising to a sufficient level, the pyrolysis of the BOC protective group occurred inducing the restoration of the ADA recognition properties of the uracil function.

In our project, the self-assembly process between the BOC protected uracils modules 91-93 and the
complementary unit 84 and therefore the final morphology of the resulting supramolecular nanostructures were strictly related to the thermal deprotection of the imidic systems of the uracil fragment. Since the data present in literature about this approach were somehow restricted, in this work it is reported the characterization of the thermal deprotection reaction by combining different analytical techniques, such as TGA, $^1$H-NMR, UV-Vis and fluorescence spectroscopy.
CHAPTER II
Thermal nanostructuration of H-bonded supramolecular polymers

2.2 Synthesis and Characterisation of the BOC-Protected Modules

In this section the rational behind the design of the single molecular modules along with the synthetic pathways adopted for their preparation have been reported. In the first section the synthetic pathway toward the preparation of novel BOC-protected molecular modules 91-93 is reported in detail, whereas in the second section a brief overview about the synthetic route leading to the preparation of the known di(acetylamino)pyridine derivative 84 is described.

2.2.1 Synthesis of the BOC-Protected ADA Molecular Modules

The structure of molecular modules 91-93 is mainly composed of two different parts: the BOC protected uracil moiety, responsible for the thermally induced self-assembly process, and a multi-substituted rigid aromatic core, determining the geometry of the molecular module, supposed to direct the morphology of the resulting nanostructure. The retrosynthetic approach used for their preparation is shown in Figure 2.5. The synthetic pathway is mainly based on the exploitation of the Sonogashira\textsuperscript{\textregistered} cross-coupling reaction between the BOC protected iodouracil derivative 96, that represent the recognition unit of the single molecular modules, and three differently-substituted aromatic cores 98, 100 and 103.

Figure 2.5 Illustrative retrosynthetic pathway used for the preparation of molecule 91 from the respective iodinated uracil derivative 96 and diethynlated aromatic precursor 98 through a two-steps Sonogashira cross-coupling reaction.

We have decided to use ethynyl linkers to couple the H-bonding recognition units to the aromatic cores to impart a linear geometry and at the same time a certain degree of flexibility able to facilitate the molecular recognition process between the single molecular modules. To perform the coupling between the two moieties, it was necessary to modify the uracil fragment by introducing an iodine atom, which would allow the exploitation of the Sonogashira type C-C cross coupling reactions (Figure 2.5). Notably, in order to endow some solubility to the final molecules, we also introduced a hexyl chain at the uracil N1 position. BOC protected 1-hexyl-6-iodo uracil 96 was prepared using a four steps protocol, starting from the commercially available uracil, that is reported in Scheme 2.1.
1-Hexyluracil 94 (44%) was obtained by alkylation at N1 position of the uracil scaffold by treatment with 1-bromohexane in the presence of K₂CO₃ and DMSO. Alkylation of uracil at N1 position is not preferential and as a result of this reaction also the di-alkylate product (at positions N1 and N3) is obtained (35%). Molecule 94 was then treated with LDA in THF at -78 °C to give C6 lithiated intermediate, which reacted with I₂ to afford iodinate synthon 95 in 60% yield. Finally the treatment of derivative 95 with BOC₃O in a mixture of pyridine and AcCN at 60 °C overnight, afforded BOC-protected iodouracil derivative 96 in 40% yield. In parallel, bis- and tris-ethynylated benzene cores 98 and 100 were synthesized starting from halogenated precursors, as reported in Scheme 2.2.

1,4-Di(ethynyl)benzene 98 and 1,3,5-tri(ethynyl)benzene 100 were successfully obtained by reaction of TMSA under classic Sonogashira conditions ([Pd(PPh₃)₄] and CuI as catalysts, NEt₃ as base and THF as solvent) with the iodinated and brominated (respectively) aromatic precursors (Scheme 2.2). Both protected intermediates 97 and 99 were efficiently deprotected by treatment with a solution of KOH (1M) in a mixture of THF/MeOH (2:1).

Differently from the previous cases, the preparation of the pyrene based core started from the unfunctionalized pyrene. Tetramethylated precursor 101 was synthesized by refluxing commercially available pyrene in nitrobenzene in the presence of Br₂. After 15 minutes a green precipitate was formed and the heterogeneous phase was allowed to react for other 4 hours. After the addition of EtOH, the tetrabrominated product 101 was isolated by suction filtration as a pale green solid.
Unfortunately, 1,3,6,8-tetabromopyrene 101 resulted to be insoluble in all common organic solvents and could only be characterised by IR and EI-MS. When molecule 101 reacted under Sonogashira conditions with TMSA in the presence of \([\text{Pd}(\text{PPh}_3)_2\text{Cl}]\), CuI and PPh_3, it yielded TMS-protected tetraethylxynyl derivative 102 (88%) as a highly soluble crystalline orange solid. In this case due to the presence of the solubilizing TMS groups, it was possible to exhaustively elucidate the structure of 102 through the common analytical techniques such as IR, NMR and EI-MS. The subsequent cleavage of the TMS protecting groups by dispersion of 102 in MeOH/THF (2:1) in the presence of 1M aqueous solution of KOH afforded tetra(ethynyl)pyrene 103 as a yellow solid, presenting a very low solubility in the conventional organic solvent. The targeted modules bearing the BOC-protected uracil sites was prepared by Sonogashira reaction of the BOC protected 1-hexyl-6-iodouracil 96 with the corresponding ethynylated benzoid derivatives, 1,4-bis-(ethynyl)benzene 98, 1,3,5-tris(ethynyl)benzene 100 and 1,3,6,8-tetra(ethynyl)pyrene 103 to yield modules 91, 92 and 93 respectively (Scheme 2.4).

Di-, tris- and tetra-uracil bearing modules 91, 92 and 93 showed a remarkably high solubility in many organic solvents, if compared with the previously synthesized analogues not bearing the BOC group.
As a matter fact, in the case of bis-uracil module 91 it was possible to isolate the final compound through CC (SiO$_2$; EtOAc/CHX 1:1), whereas in the case of molecules 92 and 93 a precipitate was formed during the reaction (indicating the successful formation of the targeted compounds) as a probable consequence of the formation of extended π-π interactions favoured by the polar solvent such as NEt$_3$. Therefore in these cases the crude mixtures were directly concentrated under reduced pressure and the purification was carried out by repeated precipitation cycles from CHCl$_3$ upon increasing additions of MeOH. In any case, due to the high solubility of these modules in mildly polar solvents such as CHCl$_3$ or THF, it was possible to characterize both modules 92 and 93 with the normal spectroscopic techniques, such as $^1$H-NMR, $^{13}$C-NMR, IR and ESI-MS.

2.2.2 Synthesis of the DAD Molecular Modules

As for the preparation of molecular angular modules 91-93 and linear unit 84, it was decided to use the Sonogashira cross-coupling reaction to link the aromatic core to the molecular receptor subunits. For this reason the first stages of the synthetic pathway leading to the preparation of molecular module 84 were focusing on the synthesis of two intermediates, 106 and 107 (Figure 2.6).

Diiodinated intermediate 107 was synthesized accordingly to the literature procedure developed by Swager and co-worker.$^9$ Concerning pyridine derivative 106 was instead prepared starting from the commercially available 4-bromo derivative. Treatment of such compound with Ac$_2$O in the presence of pyridine in CH$_2$Cl$_2$ at 0 °C for 1 hour, afforded the halogenated di(acetylamino)pyridine derivative 104 that was subsequently submitted to a Sonogashira cross-coupling with TMSA in the presence of [Pd(PPh$_3$)$_3$], CuI, as catalysts, and THF, DMF and Et$_3$N as solvents, leading to TMS-protected acetylenic derivative 105 in 60% yield. Subsequent deprotection from the TMS group was performed through basic treatment of a THF/MeOH (2:1) solution of 105 with 1M solution of KOH, yielding terminal acetylene derivative 106 in quantitative yield (Schema 2.5).
2.3 Characterization of the Thermal Deprotection Process

To characterize the thermally-induced BOC-deprotection reaction, thermogravimetric analysis (TGA) of BOC protected modules 91-93 was firstly carried out (Figure 2.7). TGA is a technique in which the mass of a substance is monitored as a function of temperature as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere. TGA measurements are used primarily to determine the decomposition of materials and to predict their thermal stability at temperatures up to 1000 °C. This technique can characterize materials that exhibit weight loss due to decomposition, oxidation, or dehydration processes and it is especially useful for the study of polymeric materials, including thermoplastics, elastomers and composites. The TGA instrumental equipment consists of a sample pan that is supported by a precision balance. That pan resides in a furnace and is heated or cooled during the experiment. The mass of the sample is monitored during the experiment while a purging gas controls the sample environment. The gas may be an inert (such as Nitrogen or Argon) or a reactive gas (such as Oxygen or Air) and it is constantly flowing through the furnace and therefore over the sample exiting through an exhaust.
In a typical experiment, a known amount of compound was exposed, under inert N$_2$ flow, to a variation of temperature ranging from 50 to 300 °C. In the case of molecular modules 91 and 92 the total weight loss observed was in good agreement (28.39 and 28.43 % respectively) with the theoretical value for the loss of all BOC groups (28.40 and 28.50 % respectively). Only in the case of the pyrenic derivative 93 a small difference between the calculated (27.10 %) and the experimental (24.90 %) weight loss percentage was detected. This difference is explainable taking in consideration the low stability of the pyrene core at temperatures over 250 °C which seems to undergo further weight loss affecting the final measurement. From the weight loss of molecules 91-93, it was possible to elaborate the first derivative curve presenting a maximum peak at 144, 139 and 131 °C respectively (Figure 2.7c); these values can be considered to be the average temperatures at which the pyrolysis of the BOC groups occurs at the highest speed and can be therefore exploited as the operative temperatures to induce the thermal cleavage with the maximum efficiency.

To further confirm the selective thermal deprotection and the integrity of the deprotected synthons after the thermal measurements, the organic residues were characterized by $^1$H-NMR spectroscopy in DMSO (Figure 2.8). The $^1$H-NMR spectra of compounds 91-93 showed the total disappearance of the BOC proton resonances centred at 1.60 ppm and the onset of a broad resonance at 11.5 ppm, which is unambiguously attributed to the imidic protons of the free uracil moieties. The other signals were maintained, confirming that the molecular skeleton of both molecule 97 and 98 was preserved and that only BOC groups were efficiently removed after thermal treatment.
Figure 2.8 1H-NMR spectra obtained for the derivative 91 before (top) and after (bottom) having been submitted to the TGA measurements, in CDCl₃ and DMSO-d₆, respectively. It is evident the disappearance of the BOC singularity at 1.8 ppm and the appearance of a broad signal at 11.5 ppm imputable to the imidic hydrogen of the uracil moiety.

Unfortunately in the case of compound 93, the residue obtained from the TGA analysis was not characterizable through the normal 1H-NMR techniques as a consequence of its extremely low-solubility deriving from the formation of extended H-bonds. Therefore, in order to obtain more detailed information about the effective temperature range over which the self-assembly can occur without destroying the deprotected pyrenyl module, TGA analysis of deprotected molecule 93a was also performed over the same interval of temperature (Figure 2.9).

Figure 2.9 Molecular structure (a) of deprotected pyrene derivative 93a. Combined T-dependent weight-loss profile (b) for molecules 93 (black curve) and 93a (red curve). (c) Combined derivatives of the weight-loss curves for molecules 93 and 93a (black and red curves, respectively) showing a maximum peak centred at 130.8 °C and no meaningful variations for 93a.

The comparison between the thermal behaviour of molecules 93 and 93a remarkably shows the presence of a weight loss of 24.90 % imputable only at the presence of the BOC protective group. The
thermogravimetric profile of 93a showed firstly a “plateau” region (from 50 to 180 °C) in which the module can be considered to be thermally stable because of the absence of any significant change in its weight (weight loss < 0.5%, comparable with the difference noticed with modules 91 and 92). In the second part of the curve (from 180 until 300 °C), the weight loss increases until reaching a maximum of 6%. By combining the two weight-loss profiles of molecules 93 and 93a, it can be concluded that the molecular framework is thermally stable until 180 °C.

2.4 Self-Assembly and Self-Organization of the BOC Protected Ethynylbenzene Molecular Modules

In order to characterize the self-organization process of the H-bond based supramolecular polymers induced by the thermally triggered BOC deprotection process, TM-AFM investigations were performed combining angular modules 91 or 92 with linear unit 84, followed by a thermal treatment at about 140 °C. At the operative level, a mixture of CH2Cl2 with high-boiling solvents (such as o-Xylene, b.p. = 145 °C) was used as media to perform the thermal polymerization.

Due to the lowest degree of molecular complexity, the first assembly to be studied is the one between the two complementary linear units 91 and 84 (Scheme 2.6). In this context, the thermal stimulation of a solution containing the two modules should induce the pyrolysis of the BOC group, inducing the formation of the H-bonding active module 91a, able to undergo self-assembly with complementary unit 84, inducing in this way the formation of a highly π-conjugated linear supramolecular copolymer.

![Scheme 2.6](image)

Scheme 2.6 Schematic representation of the self-assembly process between molecular modules 91 and 84, induced by the thermal removal of the BOC protecting group. Due to the linear structure of the two complementary units the formation of the linear supramolecular copolymer [91a·84]n is expected.

In a typical experiment, a 1:1 mixtures of molecules 91 and 84 were prepared in a CH2Cl2/o-Xylene (9:1) solution, drop casted on a freshly cleaved mica surface, and heated at 145 °C under Ar atmosphere for 15 min. As intuitively expected from their molecular shape and their reciprocal positioning of the recognition sites, the combination of 91 and 84 led to the formation of linear structures resembling rods or blocks with nanoscopic dimensions (Figure 2.10a, b, d, e).
The observed rectangular objects exhibited a flat surface with a linear shape and well-defined borders. The average dimensions of the objects ranged from 50 to 500 nm in length, from 40 to 200 nm in width, and from 1 to 9 nm in height. In all the obtained AFM images, it was possible to observe the formation of a multi-layered system (Figure 2.10f) in which the nanostructures were distributed on the mica surface in different planar objects one on the top of the other. From the profile analysis of the sample obtained (Figure 2.10c) the average height of each one of this layer was calculated to be of 2.2 nm with maximum variations from this value of ca. 2.0.

By comparison with the structures obtained by direct mixing of modules 91a and 84 (Figure 2.11), increased homogeneity of the nanostructures is evidenced. Indeed, in the case of the direct mixing of molecules 91a and 84 in CHX at a 1:1 molar ratio, a precipitate was immediately detected, indicating the formation of an insoluble supramolecular polymeric aggregate, which cannot be dissolved at temperatures as high as 353 K. Therefore, to avoid the formation of intractable materials, the nanostructuration studies were carried out in toluene, which also exhibits low polarity but it more akin to dissolve organic conjugated aromatic systems.

AFM images of the nanostructures deposited from a toluene suspension on mica and recorded at different areas of the sample indicated the presence of wires-like morphologies of length above 400 nm and width ~30 nm (Figure 2.11). Even if, also in this case, linear nanostructures were originated from the assembly process, their morphology seemed to be strictly affected from secondary aggregation phenomena that resulted in an increase of the bundling of the single nanofibers.
We tentatively explained it by considering that the thermally induced self-assembly of 91a and 84 occurs directly on the surface and thus in a confined environment, which having fewer degrees of freedom reduces the number of possible secondary aggregation phenomena. Moreover, the aliphatic lateral chains present on both complementary modules can foster aggregation of the supramolecular system in solution by means of secondary solvophobic interactions. At the solid/liquid interface not only this effect may be reduced, but the interaction between the single molecules and the surface can increase the order of the system and thus favour the formation of flat, well-defined nanostructures. Remarkably, surface-modulation of the self-organization process is strongly dependent on the concentration of the deposited molecular modules. At higher concentration, at which the interaction with the surface is less extensive and thus the intermolecular interactions dominate, no ordered nanostructures were observed (Figure 2.12a-d). Indeed, upon increasing the concentration of the modules (from 0.14 mM to 1.14 mM) the formation of a completely amorphous organic structure was observable by AFM analysis. In this case, through the profile analysis of the resulting surface, it was impossible to evaluate the formation of any planar or regular structure resembling the multi-layer systems obtained using the BOC protected modules 91 (Figure 2.12c).

The same operative procedure was used for the characterization of the nanostructured material deriving from the self-assembly process between the BOC protected module 92 and the linear complementary unit 84. Due to the three-folded structure of building block 92, that bears three BOC protected uracilic systems with an angle of 120°, the association process with molecular module 84 was expected to induce the formation of extended bidimensional planar nanostructures (Scheme 2.7)
Scheme 2.7 Schematic representation of the self-assembly process between molecular modules 92 and 84 inducing the formation of the active compound 92a by thermal removal of the three BOC protecting groups leading to the formation of the 2-D supramolecular copolymer [92a•84].

TM-AFM investigations of the binary mixture of molecules 92 and 84 (0.12 mM) in a mixture of CH₂Cl₂ and o-Xylene (9:1), followed by thermal treatment on mica surface, unexpectedly showed the formation of nano-objects with circular shapes, resembling that of a ring or a crown (Figure 2.13 a-c). The average dimensions of the objects estimated through AFM analysis ranged from 680 to 860 nm and 290 to 390 nm in outer and inner diameter, respectively, and from 1 to 4 nm in height. The presence of these circular nanostructures has been observed on all the samples submitted to the thermal treatment process, showing a homogeneous distribution all over the surface, with a remarkably low presence of secondary aggregated material. At higher concentrations (1.2 mM), the presence of such circular-shaped nanostructures was still noteworthy, even if a morphological change in the final nanostructure occurred (Figure 2.13d,e). Indeed, a layer of flat and planar organic material seemed to have originated from the previously cited ring structures, finally covering the entire mica surface (Figure 2.13). The unique geometrical features of these assembled objects can be tentatively attributed to a biphasic nature of the self-assembly/self-organization processes, which could originate from a nucleation step, taking place during the thermal polymerization process and responsible for the formation of the ring shaped nanostructures. As a consequence of the three-folded geometry of module 92, assembly [92a•84]ₙ could give birth to a flat nanostructured system at higher concentrations, possibly covering the entire surface.
This example suggested how a univocal correlation between the molecular structure of the organic module and the architecture of the nano-objects is difficult to be achieved. Thus, the elucidation of the mechanisms of formation of the observed nanostructures would need an inquiry into the link between molecular short-range and macromolecular long-range scales. In principle, a promising framework for this approach would be supplied by the theories of self-assembling patterns and interfaces, successfully exploited and improved over the years to understand the complex energetic and geometric issues of self-organized dispersions such as micelles, vesicles, and microemulsions.\[15\]

### 2.5 TM-AFM Investigations on the Isolated Compounds

Due to the complexity of the self-assembly/self-organization mechanism (occurring at the solid-liquid interface and involving elevated temperatures) and in order to prove that the nanostructures obtained from the previously mentioned procedure are effectively correlated to the formation of a bi-components supramolecular systems produced by the thermal cleavage of the BOC protecting group, a series of detailed microscopic investigations were performed on the single compounds and on the thermally untreated mixtures. As expected, deposition on Mica surface of both single modules $91$ and $92$ led to the formation of amorphous material, as a consequence of the lack of self-complementary H-bonding interactions. As a consequence of the lack of directional interactions such as H-bonds, it is logic to hypothesize that the most effective driving process inducing the aggregation of the material on the mica surface is the evaporation process and the intermolecular forces between the solvent molecules and the solutes. Similar results were obtained from the deposition at room temperature of mixture $[91-84]_n$ and $[92-84]_n$. Also in this case, the formation of completely amorphous material occurred, underlying the importance of the presence of the H-bonding molecular recognition units for the nanostructuration process (Figure 2.14).
2.6 Self-Assembly and Self-Organization of the BOC-Protected Pyrenyl Molecular Modules

As in the case of the self-assembly process between molecular modules 92 and 84, thermal induced deprotection of the four BOC groups of molecule 93 should induce the formation of an extended 2-D supramolecular system held together by H-bonds interactions (Scheme 2.8).

Scheme 2.8 Schematic representation of the self-assembly process between molecular modules 93 and 84, induced by the formation of the active compound 93a by thermal removal of the four BOC protecting groups leading to the formation of the 2-D supramolecular copolymer [93a•84].
To study the molecular behaviour during the thermally activated self-assembly process between the pyrene derivative 93 and its linear complementary unit 84, UV-Vis absorption and emission measurements in solution were carried out as a function of temperature, in order to take advantage from the strong chromophoric features of both molecules. For this purpose o-DCB was chosen as experimental solvent, due to its high boiling point (180 °C) that gave us the possibility to explore a wide range of temperature and at the same time to provide an apolar environment able to favour the formation of multiple H-bonds systems in solution. The absorption and emission spectra of molecules 93 and 84 in o-DCB are presented in Figure 2.15 (a,b). Molecule 93 exhibited structured absorption and emission features related to the presence of the central pyrenyl core comparable to the one reported in literature.\(^{[16]}\) Quite similar absorption and emission profiles are reported for molecule 93a indicating that the presence of the BOC groups does not alter, as expected, the photo-physical properties of the final molecule.

![Figure 2.15](image)

**Figure 2.15** (a) Absorption and (b) emission spectra of molecules 93 and 84 in o-DCB; (c) absorption and (d) emission spectral changes of a 17 μM solution of pyrene 93 in o-DCB, held at 423 K for different time periods (see the graph) and cooled to 293 K, upon addition of an equimolar solution of 84. Upon addition of 0.2 mL of DMSO, a complete restoration of the algebraic sum of the absorption and emission spectra of an equimolar mixture of 93 and 84 was observed. Variable-temperature (inset of d) absorption spectra of the [93a•84]\(_n\) assembly starting from 313 K (red line) until 403 K (black line).

Molecule 84 exhibited absorption and emission features with maxima at 383 nm (λ = 39 000 M\(^{-1}\) cm\(^{-1}\)) and 433 nm, respectively. The stability of molecule 93 was investigated by variable-temperature VT-UV-Vis absorption spectroscopy by varying the temperature of the solution from 20 to 150 °C. A
small blue shift was observed (5 nm) in the absorption spectra from 480 to 475 nm. These spectral changes are completely reversible upon cooling the sample, indicating that tetratopic module 93 was stable to decomposition at the temperature needed for the thermal cleavage of the BOC group, in agreement with what it was observed with the thermogravimetric measurements. The absorption and emission spectra of the solution containing a 1:1 molar ratio of molecules 93 and 84 prepared without any temperature treatment was an algebraic sum of their components indicating the absence of intermolecular interactions. Interestingly, upon addition of an equimolar solution of linear module 84 to a preheated (150 °C for different time intervals and then cooled to 20 °C) 17 μM solution of tetratopic pyrene 93, a progressive decrease in the absorption feature at 480 nm and the concomitant onset of a new band at 505 nm (Figure 2.15a) were observed. The emission spectra recorded under identical conditions exhibited a decrease in fluorescence intensity (Figure 2.15b). These observations, along with the formation of a new red-shifted absorption band and the quenching of the pyrene-centered fluorescence, were attributed to the formation of H-bonded supramolecular assemblies initiated by the thermal cleavage of the BOC protecting group.\textsuperscript{[4, 16]} This was further proven by the addition of 0.2 mL of DMSO, in which we observed a complete restoration of absorption and emission spectral profiles, showing the disruption of the triple-hydrogen-bonding interactions and, subsequently, of the supramolecular assemblies.

![Figure 2.16](image_url)

**Figure 2.16** (a) Absorption and (b) emission spectra of a 1:1 mixture of molecules 93 and 84 in o-DCB. Red line showed the algebraic sum of the absorption/emission spectra whereas the blue one was the experimentally obtained spectra.

Similar results were obtained when the absorption spectra of [93a-84]ₙ were recorded as a function of temperature (inset of Figure 2.15d). Upon increasing the temperature from 313 to 403 K, a continuous decrease in absorption intensity above 500 nm with the concomitant formation of blue-shifted absorption, with maxima at around 472 and 447 nm, was clearly observed. As shown in the inset of Figure 2.15d, the absorption spectrum at 403 K (black curve) resembles that of the algebraic sum of the individual components or that obtained after the addition of DMSO, thus confirming the breaking of the supramolecular assembly at high temperature. To characterize the ability of the molecular
modules to hierarchically self-organize into more complex objects, TM-AFM imaging was performed. The morphologic and geometric characterization of the macroscopic \([93a \bullet 84]\)_a assemblies was performed by drop casting a solution of molecules \(93\) and \(84\) (1:1) (20 μL of a 0.12 mM solution in a 9:1 mixture of DCM/o-xylene) onto mica surfaces heated to different temperature (Figure 2.18) As clearly seen in Figure 2.17, the microscopic imaging showed the formation of highly regular discrete nanostructures, the morphology of which resembles that of a crater. Such hierarchical nanostructures possess highly reproducible structural characteristics that are strictly dependent on the applied temperature (Figures 2.17 and 2.18).

![Figure 2.17](image)

**Figure 2.17** (a-c) TM-AFM topography of the crater-like self-organized morphologies as obtained from the assembly of molecules \([93a \bullet 84]\)_a in solution on mica surfaces at 145 °C and (d) their 3D representation. (e) Cross-sectional profiles of three different nanocraters (See those marked in Figure b). (f) Schematic representation of the nanostructure profile displaying some of their distinguished geometrical parameters such as the total height \(h_s\), the depth of the central opening \(h_n\), and the outer radius \(R\).

The formation of nanocrater structures was observed from 120 to 145 °C, a range of \(T\) that perfectly fitted with the cleavage temperature of the BOC group as estimated from the TGA analysis under non-destructive conditions. The total absence of nanostructures at temperatures lower than 120 °C suggested that, together with the TGA and the acquired UV-Vis data, some temperatures near or below this value give the actual lowest thermal limit at which the deprotection reaction takes place; therefore, the self-assembly/self-organization process can occur at the solid-liquid interface of our system. However, the impossibility of finding other nanostructured objects at 195 °C can be attributed either to the instability of the single modules at that temperature or to an inherent instability of the
supramolecular nanostructures.

Figure 2.18 TM-AFM images showing the morphologies evolution of the nanocraters derived from the assemblies [93a• 84], at various T: (a) 120, (b) 131, (c) 136, and (d) 145 °C. (e) Panoramic view of the nanocraters at 145 °C. (f) Three-dimensional graphical representation of the height distribution percentages of the nano-assemblies at different T.

Although we cannot exclude the first reason, the second cause seemed to be more probable as the TGA analysis showed a high thermal stability of modules 93a and 84.

The discoid crater-like shape exhibited by the hierarchical nanoaggregates can be derived from a delicate balance between the H-bonded molecular recognition events, the self-organization between the self-assembled polymers, and a few physical variables occurring during solvent evaporation under the specific temperature at the interface with the solid mica substrate. In fact, if we consider the molecular self-assembly alone, it should, in principle, lead to the formation of a 2-D polymeric structure, being the organization of which dependent on secondary intermolecular or molecule-surface interactions. However, the local change in the solution properties during such process can template the morphological aspects of the final structures. In particular, the variation of the geometric and spatial features of the morphologies as monitored at different T by means of Atomic Force Microscopy (AFM), it has been interpreted by a non-equilibrium diffusion model for two chemical species in solution. The formation of nanostructures turned out to be affected by the solid substrate (molecular interactions at a solid-liquid interface), by the matter-momentum transport in solution (solute diffusivity $D_0$ and solvent kinematic viscosity $n$), and the thermal-dependent cleavage reaction of the BOC functions (T-dependent differential weight loss, $q = q (T)$) in a T interval extrapolated to ~ 60 K. For further details on the theoretical simulations see [18].
CHAPTER II
Thermal nanostructuration of H-bonded supramolecular polymers

2.7 Bibliography


CHAPTER III

SELF-ORGANIZATION OF BINAPHTHOLS INTO CHIRAL FIBRES THROUGH H-BONDS

3.1 Introduction

As a further development towards the preparation of nanostructured supramolecular architecture via H-bonds interactions, we have decided to increase the degree of complexity of the geometrical informations contained into our self-assembling building blocks. For this purpose we have developed a new generation of building blocks, with enhanced 3-D features that at the same time bears an element of asymmetry on their central aromatic core. In order to reach this target, it was chosen to adopt as geometric core, the 1,1′-bi-2-naphthol (BINOL) moiety (Figure 3.1).[1] Indeed, in this compound due to the presence of two hydroxyl groups on the 2 and 2′ position of the binaphthalene system, the rotation around the 1,1′ bond is completely hampered, inducing the formation of two atropoisomeric forms known as R and S-Binol both provided with axial chirality.[2] Due to these factors, the structure of Binol results to be quite peculiar, presenting an angle of 90° between its two naphthalene planes, which have been revealed through X-ray crystallographic analysis.[3] Furthermore, in the last decades, the importance of such compound has raised tremendously due to its emerging applications in many technological fields.[4] It is indeed very well known the ability of Binol to act as chiral ligand[5] that can be used in fields like enantioselective catalysis,[6] or for the preparation of chiral luminescent complexes.[7]

![Molecular structure of (R)-1,1′-bi-2-naphthol (Binol) (a) with the corresponding IUPAC numeration. ORTEP visualization (b) of the crystal structure of the Binol molecule showing the 90 °C angle between the two naphthalene planes (carbon: grey, hydrogen: white, oxygen: red).[3] Molecular structure (c) of the uracil functionalized derivative (R)-108 used for the preparation of the chiral nanostructure.](image)

With the aim to exploit the structural characteristics of the Binol fragment in order to impart chirality at the nano and microscopic level, in this work we have prepared a series of enantiomerically-pure uracil-derived binaphthol ((R)-108 and (S)-108) that, in the presence of the bis-2,6-di(acetylamino)pyridine derivative 84, underwent non-covalent polymerization inducing...
the formation of supramolecular chiral copolymers $[(R)-108\cdot84]^n$ and $[(S)-108\cdot84]^n$, respectively (Figure 3.2). These new polymeric chiral entities revealed to self-organize into different kind of nanostructures, transferring the molecular stereogenic informations to the microscopic level.

![Image](image_url)

**Figure 3.2** Lateral (a) and top (b) view of the PM3 optimized geometrical structure of binaphthol derivative $(R)-108$, as implemented within Spartan. Schematic representation (c) of the self-assembly process between molecular modules $(X)-108$ and $84$ leading to supramolecular polymer $[(X)-108\cdot84]^n$ (X: R or S).

Indeed, under temperature and solvent control we have successfully demonstrated that the self-organization of the H-bond based supramolecular polymers $[(R)-108\cdot84]^n$ and $[(S)-108\cdot84]^n$ can induce the formation of both chiral fibroid material or alternatively the production of spherical nano-objects depending on the experimental conditions. Moreover the transition process between the two types of self-organized material has been thoroughly investigated at the morphological level by means of different microscopic techniques such as TEM and AFM. In this context the possibility to transfer the chirality from the single building block to the final nanostructure can be very useful in a very next future for the preparation of new generations chiral functional materials able to switch from homogeneous to heterogeneous systems, in response to external stimuli, such as a change of solvent or temperature.

### 3.2 Synthesis of the Uracil Functionalized Binol Building Blocks

Both chiral modules $(R)-108$ and $(S)-108$ were prepared following a four-steps synthetic protocol starting from the enantiomerically pure R and S binaphthols, respectively (Scheme 3.1). After the alkylation of the commercially available $(R)$ and $(S)$ binaphthols by treatment with K$_2$CO$_3$ and Mel in DMF at 80 °C, dimethylated derivatives $(X)-109$ were obtained in quantitative yield and purified by simple precipitation of the crude mixture with water, followed by suction filtration of the resulting dispersion.$^[8]$ Methylation of the pristine Binol substrate resulted in the formation of a highly fluorescent compound (feature that will be characteristic of all the derivatives synthesized from this point on) that was characterized by melting point, $^1$H-NMR, $^{13}$C-NMR, IR and ESI-MS. Subsequently, modules $(X)-109$ were submitted to an ortho-lithiation reaction by treatment with BuLi in presence of TMEDA at room temperature, to originate the C(3,3’) dilithiated derivatives. Quenching of the reaction with a THF solution containing 3.0 equivalents
CHAPTER III  
Self-organization of binaphthols into chiral fibres through H-bonds

of iodine at -78 °C afforded diiododerivatives (S)-110 and (R)-110 in 35 and 45% yield, respectively.\cite{9} Pd-catalyzed Sonogashira cross-coupling between derivatives 110 and TMSA in presence of [Pd(PPh$_3$)$_2$Cl$_2$] and CuI at 110 °C, followed by in situ deprotection with K$_2$CO$_3$, afforded diethynylated compounds (S)-111 and (R)-111 in 75 and 65% yield, respectively.\cite{10} Finally, Sonogashira-type cross-coupling reaction between (X)-111 and iodouracil derivatives 95 in the presence of [Pd(PPh$_3$)$_4$] and CuI yielded modules (R)-108 and (S)-108 in 55 and 65% yield, respectively.

Scheme 3.1. Synthetic pathway adopted for the preparation of (R)-104 and (S)-104. (a) MeI, K$_2$CO$_3$, DMF, 80 °C; b) BuLi, TMEDA, I$_2$, Et$_2$O, -78 °C; c) 1. [Pd(PPh$_3$)$_2$Cl$_2$], CuI, TMSA, Tol, NEt$_3$, 110 °C; 2. K$_2$CO$_3$, THF/MeOH; (e) [Pd(PPh$_3$)$_4$], CuI, 95, THF, NEt$_3$, r.t.

In both cases, the metal-catalyzed cross coupling reaction between uracil derivative 95 and the respective binaphthol synthons afforded a mixture of mono and di-substituted derivatives that were also isolated by means of a series of repetitive CC (starting from CHX/EtOAc 7:3 up to CHX/EtOAc 3:7). Complete isolation of pure binaphthol derivatives (R)-108 and (S)-108 was obtained by sequential reprecipitation of the compounds from a CHCl$_3$ solution upon increasing amount of CHX. Precipitation of these classes of ditopic compound in apolar solvents such as CHX is facilitated by their tendency to originate homomolecular H-bonded polymeric architectures of high molecular weight displaying with very low solubility. Complementary linear module 84 and uracilic derivatives 95 were synthesized and purified following the synthetic protocols reported in Chapter II.\cite{11}

3.3 Spectroscopic Characterization of the Self-Assembly Process

To shed light on the effective occurrence of the H-bond based molecular recognition process, variable temperature VT-$^1$H-NMR analysis were performed on a mixture of (R)-108 and 84 (Figure 3.3) in a nonpolar solvent.\cite{12} In this context qualitative evidence for the supramolecular
polymer $[(R)-108\cdot84]_n$ formation were noticed upon mixing stoichiometric amounts of binaphthol derivative $(R)-108$ and its complementary linear unit 84 in tetrachloroethane-$d_6$ at 5 mM concentration with respect to each molecular component. When a solution of such a mixture in tetrachloroethane-$d_6$ is heated from 20 °C to 80 °C, the $^1$H-NMR spectra showed a shift at higher fields of the NH proton resonances involved in the multiple H-bonding recognition (from 10.5 to 9.0 ppm and from 8.0 to 7.6 ppm, respectively), clearly indicating the progressive disruption of the H-bonds, and thus of the assemblies. Indeed, at low temperature the H-bonding mediated association was much stronger and resulted in a more highly associated polymeric material, and further aggregation into supercoiled fibers may set in (Figure 3.3). Moreover the complete reversibility of the process in this range of temperature gave us also an indirect proof about the stability of the single modules in such conditions.

![Figure 3.3](image)

**Figure 3.3** Schematic representation (a) of the H-bond system disruption induced by the increase of temperature from 20 to 80 °C (numbers between brackets are referred to the chemical shift values, in ppm of the single nuclei). VT-$^1$H-NMR spectra of a 1:1 mixture of $(R)-108$ and 84 in tetrachloroethane-$d_6$, showing a progressive disruption of the assemblies $[(R)-108\cdot84]_n$ (reported on the top). Imidic protons of $(R)-108$ are marked with letter $a$, while the amideic ones of 84 are marked with letter $b$.

Further support for the H-bond mediated formation of nanostructures was provided by a series of spectrophotometric (UV-Vis and fluorescence) studies upon monitoring of the chromophoric behavior of polymer $[(R)-108\cdot84]_n$ in relation to a temperature variation. The electronic absorption and emission spectra of $(R)-108$, 84 and of its supramolecular adduct $[(R)-108\cdot84]_n$ obtained upon mixing the two components in a 1:1 ratio (3.5 µM each) in a CHX/THF solution, (5% v/v) are shown in Figure 3.4a. The absorption spectrum of $(R)-108$ is entirely placed in the UV region and is weaker and narrower compared to that of 84.
Both molecules exhibited fluorescence, and the related quantum yield of (R)-108 ($\Phi_n = 0.12$) was smaller than that of 84 ($\Phi_n = 0.18$). The absorption and emission features of 84 in the CHX/THF mixture were red-shifted compared to more polar solvents such as MeOH and THF.\[^{13}\] These findings confirmed the solvophobic-driven self-aggregation of 84 most likely through J-type as previously observed by us.\[^{11, 13}\] Although the UV-Vis spectrum of [(R)-108•84]$_n$ was dominated by the characteristic features of 84, some notable differences were present in comparison with the algebraic sum of the two isolated components. A smaller intensity ratio between the peaks at 340 and 415 nm, along with an enhanced absorption tail after 450 nm, were observed. Furthermore, the emission of [(R)-108•84]$_n$ showed a weak shoulder at the longer wavelengths and, compared to 84, a lower quantum yield ($\Phi_n = 0.12$) and a higher full width at half maximum (FWHM), i.e. 80 nm (84: 62 nm, Figure 3.4a inset). In this case, differently from previous reports,\[^{11, 13}\] the supramolecular interaction between (R)-108 and 84 does not resulted in distinctly new absorption and fluorescence bands in the low energy spectral region. Despite the presence of a self-organized fiber-like and particle-like arrangement as displayed by the microscopy imaging technique, the quasi-perpendicular orientation adopted by the naphthyl rings drastically reduces the interpolymeric $\pi-\pi$ interactions between single self-assembled [(R)-108•84]$_n$ chains, thus leading to a looser aggregation. However, the small changes observed in the absorption and emission spectra of [(R)-104•84]$_n$ along with their lifetime values (3.4 ns for (R)-108; $\tau_1 = 1.5$ ns; $\tau_2 = 3.7$ ns for 84; $\tau_1 = 1.2$ ns; $\tau_2 = 4.2$ ns for [(R)-108•84]$_n$) are ascribed to the presence of the H-bonded self-
organized structures in CHX/THF (Figure 3.5).

By cooling down the sample \([{(R)}-108\cdot84]_n\) to 278 K, the absorption bands move to red and decrease in intensity (Figure 3.5a) whilst the emission features remained virtually the same apart from minimal peak intensity variation (Figure 3.5 b). This was ascribed to a kinetically-favored self-aggregation of 84 in apolar solvents, CHX/THF (5% v/v), which occurs faster than intermolecular interaction between \((R)-108\) and 84 preventing the heteromolecular self-assembly. The self-organization process between \((R)-108\) and 84 in the CHX/THF mixture was further confirmed by VT-UV-Vis and fluorescence measurements. On increasing the temperature to 353 K, the absorption spectrum of \([{(R)}-108\cdot84]_n\) showed an isosbestic point at 393 nm, a gradual hypsochromic shift and an increased peak intensity ratio between the bands centered at 340 and 415 nm (Figure 3.4b). In particular, the absorption tail in the lowest-energy spectrum completely vanished. Likewise, the emission at high temperature showed blue shifted maximum with substantially reduced FWHM (52 nm) and the disappearance of the extended shoulder at longer wavelengths (Figure 3.4c). These observations indicate the presence of isolated units of 84 in the sample. In order to corroborate the presence of H-bonding interactions between \((R)-108\) and 84, an H-bond disrupting polar solvent such as DMSO (5% v/v) was added to a solution of \([{(R)}-108\cdot84]_n\). Due to the H-bond breaking induced by DMSO, the absorption spectrum of \([{(R)}-108\cdot84]_n\) showed blue shifted bands with discernible signatures of individual molecular units \((R)-108\) and 84 (Figure 3.4d). Similarly, the fluorescence spectrum moved to higher energy (as observed at 353 K) exhibiting much higher intensity (Figure 3.4d inset). Owing to the high quantum yield of monomer unit 84 (\(\Phi_{nl} = \sim 1.0\)), the emission peak of the latter masked the signal from the weakly emissive \((R)-108\) (\(\Phi_{nl} = 0.12\)) in this solvent mixture. To investigate the chirality expression on the self-organized assemblies originated from the combination of \((R)-108\) and \((S)-108\) with the linear ditopic unit 84, CD experiments were also carried out both on the single components and on the relative assemblies (Figure 3.6).
The CD spectra of the binaphthol derivatives are characterized by a maximum at 260 nm and an overall CD effect, which take place in the region between 220 and 390 nm (Figure 3.6b). When linear module 84 is added to a CHX-THF solution of (R)-108 or (S)-108, a new band appeared in the region of 400-480 nm (Figure 3.6a-c-d), a spectral portion in which none of the single components are CD active. This new band can be attributed to the formation of a new chiral entity defined by a high level of order between its molecular components, in which the molecular chirality is effectively transferred to the supramolecular complex. The variation of the CD effects as a function of temperature was recorded for both [(R)-108•84]_a and [(S)-108•84]_a assemblies displaying similar trends. Notably, the behavior of the new band at 430 nm resulted in strict accordance with the data reported in the temperature-dependent UV-Vis measurements (Figure 3.4b and 3.5a). Also in this case the VT experiments from 10 to 80 °C induced a progressive reduction of the CD effect (attaining zero at approximately 50 °C) displaying the non-covalent nature of the intermolecular interactions (i.e H-bonds and π-π stacking).
3.4 Microscopic Characterization of the Self-Assembled Nanostructures

A further confirmation of the presence of supramolecular nanostructured systems in solution, was obtained through microscopic analysis of drop-casted solution containing \([(R)-108\cdot84]_a\) or \([(S)-108\cdot84]_a\) onto mica surface. In order to obtain a good solubility of the modules and at the same time to induce the formation of the H-bonds systems between the complementary building blocks a mixture composed by THF and CHX was used to prepare the solution containing the supramolecular polymers. Indeed, due to the presence in both molecular modules of highly polar moieties such as the uracil and the diacetilaminopyridine fragments, the solubility of these compounds in strongly apolar solvents was remarkably low. For these reasons in a typical experiment an equimolar quantity of molecular modules \((R)-108\) or \((S)-108\) and \(84\) were firstly dissolved into a minor amount of THF (solvent able to completely solubilize both compounds) and then diluted to the necessary volume with CHX. Aim at favoring the formation of the most thermodynamically stable architectures, the resulting mixture was cyclically heated several time and finally drop-casted onto mica surface or onto carbon coated grid for the microscopic visualization. In order to investigate the best solvent compositions for the preparation of the chiral H-bonded materials, different ratios of CHX and THF were investigated (80:20, 90:10 and 95:5 v/v, respectively). In the first case (CHX-THF 80:20 v/v), the formation of round shaped nanostructures was observed through the combined use of TEM and TM-AFM analysis (Figure 3.7).

![Figure 3.7](image)

**Figure 3.7** Topographic TM-AFM (a-b) and TEM (g-h) images of the chiral nanovesicles obtained from a 1:1 solution of \([(R)-108\cdot84]_a\). 2-D (c) and 3-D (f) representation of different phase images, highlighting the presence of two regions on the spherical nanostructure. Representative profiles (d,e) obtained from subfigure b and c respectively (red lines). (h) TEM details of the nanovesicles wall. Three-dimensional graphical representation (i) of the height distribution percentages of the nano-assemblies at different solvent ratio (red: 80:20, orange: 90:10 and yellow: 95:5 of CHX-THF in v/v) was obtained through AFM investigation.
Through detailed TM-AFM analysis, spherical nano-objects, characterized by height values ranging from 1 to 20 nm with an average centered on 12 nm, were obtained from a 80:20 solution of CHX:THF (Figure 3.7). With the aim to shed further light on the structure of such morphologies, AFM phase imaging measurements were performed on the drop casted material. Phase imaging is a powerful extension of TM-AFM,\cite{14} enabling the characterization of nanometer-scale properties such as changes in the composition, adhesion, friction, viscoelasticity, often not revealed by classical SPM measurements.\cite{15} In phase imaging, the phase lag of the cantilever oscillation, relative to the signal sent to the cantilever’s piezo driver, is simultaneously monitored by the AFM controller.\cite{16} The phase lag is very sensitive to variations in physical properties such as materials’ adhesion and elasticity.\cite{17} Notably in our case, phase imaging of the single spherical morphologies revealed the presence of two different regions (Figure 3.7c-f), each characterized by a different contrast as a consequence of the different mechanical properties. Indeed, the presence of a darker zone in the center of the nanospheres (notably the contrast is inverted in comparison with the topographic image, Figure 3.7b-c) could be in principle attributed to an increase of elasticity of the material probably originating from hollow zones or a different local density.\cite{18} This data in combination with the visualization by TEM analysis of a brighter region, resembling a membrane-like structure (Figure 3.7 g-h), covering the entire surface of the nanospheres, led us to hypothesize the formation of a H-bonded organic nanoparticle. Moreover, a statistical analysis of the morphologies’ diameter values as obtained by AFM analysis as a function of the solvent mixture, clearly showed a rise of the nanosphere diameter upon decreasing concentration of THF (from 12 to 21 nm). Remarkably, TM-AFM analysis of [(R)-108•84]$_n$, as drop-casted from a CHX solutions containing only a 5% v/v of THF displayed the formation of a novel fiber-like morphologies. The fibrous materials displayed diameters ranging from 5 to 10 nm and average lengths between 800 and 3000 nm. The same morphologies were also obtained upon deposition of the enantiomeric supramolecular systems [(S)-108•84]$_n$. 

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Figure 3.8 Topographic TM-AFM (a,c,d) and TEM (e,f) images of nanofibers as obtained from drop casting a solution of \([(R)-108\cdot84]\)_n on mica surface and on a carbon coated grid, respectively. AFM comparison between the morphologies of the nanofibers obtained from (b) \([(S)-108\cdot84]\)_n and (c) \([(R)-108\cdot84]\)_n. (g) Details of an helicoidal arrangement of a fiber composed of \([(R)-108\cdot84]\)_n.

Similar fibers lengths and diameters have been observed for both H-bonded polymers, \([(R)-108\cdot84]\)_n and \([(S)-108\cdot84]\)_n. As previously mentioned (Paragraph 3.3), CD investigations of a diluted solutions containing \([(R)-108\cdot84]\)_n and \([(S)-108\cdot84]\)_n under the same solvent conditions showed the formation of a new band, centered at 430 nm but presenting opposite signs. This observation, together with the formation of fibroid morphologies can be considered as a clear proof of the transfer of stereogenic informations from the single chiral molecular module to the final nanostructured nano-objects, through the formation of self-organized fibrous morphologies in which the different single polymeric structures are held together by the combination of van der Waals and \(\pi-\pi\) stacking type non-covalent interactions. Notably, both TM-AFM and TEM images clearly display that most of the imaged nanofibers present a remarkable inclination to self-wrap, forming coiled architectures (Figure 3.8f-g). Considering the presence of CHX as main solvent, it is reasonable to hypothesize that the aliphatic C_{12}H_{25} and C_{6}H_{13} appends, present in the linear module and in the binaphthols units, are hexohedrally exposed on the external surface of the fibers, thus forming an extended hydrophobic surface subsequently favoring van der Waals inter-fiber interactions.

In light of these new data, we have decided to perform a more detailed microscopic investigation on the solvent effect on an intermediate CHX solution containing the supramolecular polymer \([(R)-108\cdot84]\)_n with 10% in v/v of THF, with the aim to elucidate in a more exhaustive way the interconversion mechanism between nanovesicles and nanofibers. Interestingly, by TEM and TM-AFM investigation, hybrid morphologies have been observed on the surfaces. In particular, even
though the spherical morphologies are predominant under these conditions, fibrous materials have been also observed (Figure 3.9 a-e). Interestingly, the material is characterized by the presence of spherical morphologies peripherally decorated by fibrous ramifications, with diameters between 5 and 50 nm and length up to several micrometers, that arise as thin nanostructures from the central spherical structure.

![Images](a) 500 nm (b) 500 nm (c) 50 nm (d) 350 nm (e) 75 nm (f) Lateral profile of one of the fibers as obtained through AFM analysis, showing the irregularity of the surface.

**Figure 3.9** Topographic TEM (a-c) and TM-AFM (d, e) images of the nanofibers as obtained by drop-casting of a solution of [(R)-104•84]n. (f) Lateral profile of one of the fibers as obtained through AFM analysis, showing the irregularity of the surface.

With respect to the fibrous morphologies as obtained from solution of CHX containing 5% v/v of THF, the morphology of such ramifications displayed some substantial structural differences, as they appeared as bamboo-like structure. Through an accurate analysis of the fibers profile by AFM measurements (Figure 3.9e-f), it was possible to notice that the ramification were not homogeneous, as the one prepared with he previous method, but presented a greater number of defects (Figure 3.9f) that could be imputable to the increase of polarity of the solvents leading to the formation of supramolecular material characterized by a less degree of stiffness and stability. Notably, also the geometrical and structural features of the fibers were affected from the change in the solvent composition, showing a decrease in their level of monodispersability, with the formation of a second class of spherical nanostructure with an average diameter of 30 nm.

In conclusion, we have shown that exploiting complementary multiple H-bonding interactions as established between enantiomerically pure uracil-derived binaphthols and di(acetylamino)pyridinic linear modules, it was possible to prepare different kinds of nanostructured materials under solvent and temperature control. In particular, different morphological structures such as nanofibers or nanospheres have been observed. Moreover, through a detailed microscopic investigation of the self-organization process as undertaken in different solvent mixtures, it was possible to isolate a hybrid material, in which both spherical and
linear morphologies were present. Further developments of this work will be aimed at the understanding of the molecular organization of the single modules within the different nanomorphologies and the study of the general principles ruling the relation between molecular structures and morphological properties of the resulting nanostructures. To perform this task, molecular modeling simulations based on MM and MD simulations are under development in collaboration with the group of Dr. M. Surin at the University of Mons (Belgium). These materials hold great promises for the design and preparation of new luminescent or catalytically-active substrate for stereoselective synthesis, in which the solvent and temperature effects can induce a switching of the functional material phase, i.e. from a homogeneous to a heterogeneous system.

3.5 Bibliography

CHAPTER IV

CONSTRUCTION OF PORPHYRIN-MWCNT SUPRAMOLECULAR MATERIALS THROUGH COORDINATIVE POLYMERIZATION

4.1 Introduction

In order to further evolve our work on the self-assembly and self-organization of chromophoric molecules into supramolecular nanostructured materials, we decided to develop a new class of hybrid systems composed by a carbon nanostructure acting as template, and a supramolecular polymer constituted of an ordered arrangement of chromophoric building blocks. The high interest revolved around the preparation of such type of composite materials is not only due to the peculiar properties of the resulting nanostructures, but also to the ease of preparation that, taking advantages from the high convergence and modularity of the supramolecular approach, gives the opportunity to obtain the hybrid materials in a relatively low amount of time, and at considerably low costs.

In our case we chose to adopt as template system multi-walled carbon nanotubes (MWCNT). Carbon nanotubes (CNTs) are hollow carbon nanostructures that can be viewed as a rolled-up graphene sheet. They have been discovered in the ‘50-’60 and reported as carbon filament, but only in 1991 Iijima described them at the atomic level. CNTs can be classified mainly in two groups: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), depending if they are constituted by one single layer of graphene or by multiple concentrical graphene sheets coaxially arranged around a central hollow core.

Since their discovery, CNTs have raised a great deal of interest due to their potential applications in a wide range of different applications such as for example field-emission devices preparation, molecular electronics and microelectronics, or sensor productions. Unfortunately, the principal drawback affecting the exploitation of CNTs at any level consists in their low solubility in mostly all the known solvents. Therefore, to render CNTs processable and allow their widespread use in real applications, chemical functionalization has been widely exploited in order to enable the integration of CNTs into multicomponent organic materials.

In this context, two main approaches have been undertaken so far to increase the solubility of CNTs, namely the covalent and non-covalent approach (i.e. supramolecular). While the latter approach does not lead to structural modification of the carbon framework, preserving its key electronic and structural properties, covalent derivatization often leads to substantial structural and physical alterations as a consequence of the rupture of π-conjugation.

Concerning the supramolecular functionalization of CNTs, both polymeric systems and single molecules have been exploited efficiently. In the first class, the most remarkable examples are
constituted by highly conjugated polyaromatic polymeric architectures and DNA sequences that can provide systems able to non-covalently “wrap” the CNTs surface exploiting van der Waals and π-π interactions.\(^\text{[10]}\) It is interesting to point out that in some works reported in literature, the presence of conjugated molecules onto the CNTs surface can lead to an improvement of their electronic properties, such as for example conductivity and charge mobility.\(^\text{[11]}\) Recently also supramolecular polymers have attracted the attention of the scientific community as a potential category of organic based architecture able to induce the selective and reversible functionalization of different kinds of CNTs.

In 2005 the group of Stoddart reported on the use of a supramolecular polymer based on two building blocks, a Zn\(^{II}\) metalloporphyrin complex and a cis-protected Pd\(^{II}\) complex to induce the solubilization of SWCNTs obtaining in this way a composite material soluble in aqueous solution.\(^\text{[12]}\)

In a very recent paper, our group described the non-covalent functionalization of MWCNTs in apolar solvents through the formation of H-bond based supramolecular polymers.\(^\text{[13]}\) To this end, a library of phenylacetylene molecular scaffolds equipped with complementary uracil and 2,6-(diacetylamino)pyridine recognition units has been employed for the solubilization of pristine MWCNTs in apolar solvents such as CHCl\(_3\), CHCl\(_2\) and Toluene. A new protocol for CNTs purification and solubilization has hence been developed, based on the execution of several cycles of filtration and centrifugation of the composite supramolecular material, aimed to the isolation of the most soluble CNTs obtained. In order to exploit this new procedure for the preparation of functional hybrid materials, we have decided to prepare a series of di-porphyrin derivatives that, if opportunely mixed with a linear ditopic ligand such as 1,2-(4-bispyridyl)ethane can originate different types of supramolecular polymers based on multiple coordinative interactions, under solvent and temperature control. The final goal of this work regards the exploitation of these coordination-based polymers to obtain two objectives at the same time: the solubilization of MWCNTs due to the adhesion of the polymers onto the carbonaceous structure, and contemporarily the tuning of their electronic properties thanks to the interaction with the porphyrinic antenna, yielding an interesting hybrid for applications in the field of nano-electronic.

The two porphyrin based molecular modules that were designed for this task are reported in Figure 4.1.
Their structure was mainly based on two different moieties: two peripheral Zinc-porphyrins subunits and a central aromatic core, defining the geometry of the single building blocks, bridged together by linear ethinyl linkers. The aromatic cores adopted for the preparation of module 112 and 113 were two different regioisomers of pyrene either functionalized in the 1,6 or 1,8 positions. Specifically, those two were chosen in order to investigate the effects of the peculiar molecular geometry of the two positional isomers on the features of ultimate supramolecular assembly, specifically its capability to adhere and establish an effective electronic communication with the CNTs. The choice to use this kind of aromatic core was mainly due to its very well known ability to interact with the CNTs’ sidewall principally via π-π interactions, providing in this way a perfect non-covalent binding site for the anchoring of the building blocks (and therefore also of the final supramolecular polymer) to the carbonaceous template. The Zinc-porphyrin units were instead functionalized with three different mesityl groups at the meso positions. The presence of such aromatic groups was intended to inhibit intra-porphyrin stacking interactions, which could have sorted a negative effect on the complexation reaction leading to secondary aggregation phenomena that would have decreased in principle the order of the system. For such reason, mesityl groups were chosen as substituents for the meso position, as they present the well known tendency to dispose orthogonally to the plane of the porphyrin moiety, as a consequence of the presence of the two methyl groups in the 1 and 5 positions, that drastically hinders the rotation across the C-C bonds that link the porphyrin macrocycle to the mesityl fragment. These structural features induced the formation of completely shielded porphyrins that were not able to interact one with each other by means of the normal π-π interactions.

In the first part of the chapter the synthetic pathway leading to the preparation of 112 and 113 is discussed and the investigation of the self-assembly process in solution is reported. In order to characterize the axial complexation between the bidentate linker 114 and the two porphyrin derivatives 112 and 113 we decided to exploit the highly chromophoric characteristics of the latter by following their self-assembly process in solution with the help of UV-Vis and fluorescence spectroscopy. The morphological aspects of the polymers obtained were instead evaluated by means of TM-AFM
analysis in order to characterize the formation of any nanostructured material originating from the coordination based self-assembly process. Finally the resulting nanostructured polymers were used for the solubilization and consequent supramolecular functionalization of MWCNTs. The morphology and the structural characteristics of the resulting materials were investigated by means of TM and phase imaging AFM spectroscopy, whereas the dispersibility of the hybrid supramolecular material was evaluated by means of transmission electron microscopy.

4.2 Synthesis of the Porphyrin Based Molecular Modules

The synthetic pathway adopted for the preparation of the molecular modules involved in this study is reported in scheme 4.1. As a first step, the synthesis of the pyrenyl core was undertaken in order to produce the two 1,6 and 1,8 regioisomeric di-ethinylated derivatives suitable for the conjugation reaction with the opportune porphyrinic moieties.

![Scheme 4.1](image)

Scheme 4.1 Synthetic pathway adopted toward the preparation of the pyrene moieties employed for the synthesis of the multi-porphyrin modules. a) Br₂, CCl₄, r.t. 4h, 35%; b) I₂, KIO₄, AcOH, 25%; c) TMSA, [Pd(PPh₃)₄], CuI, Tol, Et₃N, 120 °C, 1h, MW; d) KOH, MeOH, THF, 65-75 %; e) TMSA, [Pd(PPh₃)₄], CuI, Tol, Et₃N, 120 °C, 14 min., MW.

The first step toward the preparation of different aromatic cores was based in each case onto the separation of the products obtained by statistical halogenation of the commercially available pyrene. It was found, indeed, that when the halogenation reaction was performed with simple bromine as halogenating agent in CCl₄ as solvent at room temperature, the more abundant product resulted the 1,6-dibromopyrene. Interestingly, if this reaction was performed with iodine in presence of KIO₄ at 120 °C with MW irradiation, the 1,8 di-substituted product was instead obtained. With such procedures starting from the pristine pyrene, it hence resulted possible to obtain both compounds 115 and 118 in an extremely high purity, with a yield of 35 and 25 %, respectively.

Both molecules 115 and 118 were subsequently submitted to Pd(II) catalyzed “Sonogashira Cross-Coupling” with TMSA. In this context for the derivatives 115 and 118 the coupling with TMSA in presence of [Pd(PPh₃)₄] and CuI as catalyst at 120 °C (for 1h and 14 min. respectively) yielded the respective trimethylsilylethinyl derivatives, that were successfully deprotected by treatment with KOH in a MeOH/THF solution to provide the diethynilated regioisomers 117 and 120 in 65 and 75 % yield,
respectively. The synthesis of the porphyrin moiety 121 was instead attempted by the classical acid mediated condensation of freshly distilled pyrrole in presence of BF₃·Et₂O and DDQ with a 3:1 mixture of mesyaldehyde and p-iodobenzaldehyde aimed to obtain the statistical mixture of differently meso-substituted porphyrins (Scheme 4.2).

![Scheme 4.2](image)

Scheme 4.2 Synthetic pathway adopted toward the preparation of porphyrin moieties employed for the synthesis of the di-porphyrinic modules. a) BF₃·Et₂O, DDQ, Et₃N, CH₂Cl₂, 2h; b) Zn(AcO)₂, CH₂Cl₂, MeOH, 4h, 7%.

Unfortunately, due to the low difference in polarity of the iodo-substituent in respect with the mesityl one, any attempt to purify by CC the mixture of porphyrins resulted from the acid mediated condensation did not achieve the isolation of the pure A₃B derivative (A:mesityl, B: 4-iodobenzene). Exhaustive metallation of the statistical mixture of the different porphyrins obtained by treatment with a saturated solution of Zn(AcO)₂ in MeOH/CH₂Cl₂ (Scheme 4.2) instead resulted in the formation of a mixture of porphyrins with an enhanced difference in polarity that was successfully purified by CC, followed by different precipitation cycles in MeOH.

Finally, as shown in Scheme 4.3, the complete di-porphyrinic modules 112 and 113 were obtained by “Sonogashira Cross coupling” of molecule 121 with the pyrenyl scaffolds 117 and 120 in presence of [Pd(PPh₃)₄] and Cul in the mixed solvent THF/Et₃N (1:1) producing the envisaged chromophoric modules 112 and 113.

![Scheme 4.3](image)

Scheme 4.3 Synthetic pathways adopted for the synthesis of the bisporphyrin modules 109 and 110 starting from the iodoporphyrin derivative 118. a) 117, [Pd(PPh₃)₄], Cul, THF, Et₃N, overnight, 60%; b) 120, [Pd(PPh₃)₄], Cul, THF, Et₃N, overnight, 55%.
Both modules 112 and 113 presented sufficient solubility to allow their purification first by standard CC techniques, followed by several cycles of precipitation from MeOH followed by re-crystallization in CH₂Cl₂/CHX by vapour exchange technique. However, in both cases the solubility of the resulting modules was sufficient for the characterization of the modules by means of ¹H-NMR, IR and MALDI-MS.

4.3 Spectroscopic Characterization of the Complexation Process

The coordination event between the zinc metal atom contained into the porphyrinic macrocycles and the nitrogen of the pyridinic linker 114, basic yet fundamental act leading to the formation of the supramolecular polymers, was investigated through UV-Vis and fluorescence spectrosopies. Specifically, titration of the diporphyrin modules 112 and 113 with increasing amounts of linker 114 were carried out in order to monitor the formation of the supramolecular species (Figure 4.2).

For both modules, remarkable variations in the absorption profiles were evaluated during the UV-Visible titration, as a consequence of the cumulative addition of linker 114. In case of compound 112 a bathochromic shift of both the B and Q bands (from 418 to 428 nm and from 552 to 566 nm, respectively) was detected, together with a notable hypochromicity and with the formation of two isosbestic points at 423 and 557 nm. These results were in agreement with previously reported examples of coordination phenomena between a nitrogen and a zinc present in a porphyrinic system.¹⁴ Extremely similar results were obtained for the UV-Vis titration of compound 113. Indeed,
also in this case the bathochromic shift of both B and Q bands was detected (from 419 to 427 nm and from 555 to 571 nm, respectively) as well as the presence of two isosbestic points at 422 and 560 nm. Comparable results were also obtained from fluorescence titration experiments: after addition of several aliquots of linker 114, both the fluorescence profiles of 112 and 113 expressed a bathochromic shift with the formation of three clear isoemissive points at 600, 620 and 650 nm, for module 112, and at 602, 627 and 659 nm, for module 113, thus confirming the effectiveness of the coordination process. It is also noteworthy to point out that the maximum shifts of both Q and B bands observed during the spectroscopic titration experiments, were reached when one equivalent of compound 114 was added to the relative porphyrin modules, suggesting in both cases the formation of a supramolecular species in which the two compounds were present in a 1:1 ratio.

In order to characterize more in detail the complexation process and its reversibility, also variable temperature (VT) UV-Vis spectroscopy experiments were carried out (Figure 4.3)

![Figure 4.3 VT-UV-Vis spectra of the 1:1 mixture of molecule 114 with di-porphyrin modules 112 (a, b) and 113 (c, d). Full reversibility of the complexation process is evident in both cases due to the restoration of the single profiles in both heating (a, c) and cooling (b, d) cycles. All spectra are normalized to the same intensity for clarity of comparison.](image)

In a typical experiment a 1:1 mixture of the molecular modules 112 or 113 with the ditopic linker 114 was subjected to a variation of temperature ranging from 20 to 80 °C (Figure 4.3 a and c). During the process a complete restoration of the spectral features relative to the uncomplexed porphyrin modules were observed, pointing out the complete destruction of the supramolecular assembly based on the N-Zn coordination bond. Remarkably, upon cooling back the systems from 80 to 20 °C, a complete reversion of the situation was observed for both systems (Figure 4.3 b and d) proving the full
Construction of porphyrin-MWCNT supramolecular materials through coordinative polymerization

reversibility of the coordination process, and therefore the effectiveness of the whole supramolecular approach. Taking into account the experimental data obtained during the complexation study in solution of 112 and 113, different kinds of supramolecular arrays were plausible (Figure 4.4).

![Different supramolecular arrays originated by the coordinative interactions between the bidentate linker 114 and the diporphyrinoid modules 112 and 113. (in green and blue respectively). Mesityl groups are omitted for clarity.](image)

**Figure 4.4** Different supramolecular arrays originated by the coordinative interactions between the bidentate linker 114 and the diporphyrinoid modules 112 and 113, (in green and blue respectively). Mesityl groups are omitted for clarity.

Even if an exhaustive elucidation of the structural features characterizing the coordination polymers based on the self-assembly between 112 and 113 with the linear linker 114 is far aside from the primary tasks of this project, some preliminary hypothesis based on the experiment data obtained so far can be proposed. In this context both modules 112 and 113 can originate in solution supramolecular polymers, due to the ditopic natures of their coordinative recognition sites. In the case of the assembly [112•114]n, a polymeric chain with the pyrene units disposed into a “zig-zag” fashion could be in principle obtained as a consequence of the divergent disposition of the porphyrin units. For the assembly between 112 and 114, two main conformations can be present in solution, due to the co-axial disposition of its porphyrin moieties: an heterotetrameric complex [112•114]2, in which two bispyridinic linkers are complexing other two units of 114 in a rigid square like fashion, and an open linear polymeric system characterized by a high degree of flexibility.
4.4 TM-AFM Investigation of the Coordination-Based Polymers

In order to characterize at the microscopic level the structural features of the nanomaterial originating from the supramolecular assemblies obtained so far, TM-AFM measurements were performed (Figure 4.5 and 4.6). In this context the nanostructures obtained after the deposition of the assemblies [112•114]n and [113•114]n were found to be substantially different in terms of geometrical features.

![Figure 4.5](image1)

**Figure 4.5** TM-AFM images obtained from the deposition of the supramolecular arrays originated by the coordinative interactions between the bidentate linker 114 and the di-porphyrinic module 112 (a, c). Profile analysis (d) relative to the section lines reported in subfigure b. 3-D representation of the topographic TM-AFM images of subfigure a (e).

In the case of [113•114]n after deposition of a CHX solution containing the supramolecular complex onto a mica surface by drop casting technique, it was possible to observe the formation of a porous nanostructured array covering homogeneously all the sample surface. Notably the supramolecular 2-D nanostructure obtained was characterized by constant height of approximately 3 nm and homogeneous distribution of the pore diameters ranging from 25 to 350 nm.

![Figure 4.6](image2)

**Figure 4.6** TM-AFM images obtained from the deposition of the supramolecular arrays originated by the coordinative interactions between the bidentate linker 114 and the di-porphyrinic module 113 (a, b). Profile analysis relative to the section line reported in subfigure b (c). 3-D representation of the topographic TM-AFM images of subfigure b (d).

On the other hand, from the deposition by drop casting of a CHX solution of [113•114]n, the presence of spherical nanoparticles covering the entire surface was observed. TM-AFM analysis of the supramolecular nanoparticles obtained showed a very homogeneous diameter distribution for such objects, ranging from 150 to 250 nm, and the presence of melted nanoparticles deriving most probably from the evaporation process.
4.5 Preparation of the MWCNT-Porphyrin Hybrid Materials

The procedure adopted for the reversible supramolecular functionalization of pristine MWCNTs with the coordination-based polymers previously discussed, is depicted in Figure 4.7. In all the cases the behaviour in solution of the hybrid MWCNTs-[X•114]_n (with X = 112 or 113) was monitored both by visual inspection and by using UV-Vis spectroscopy.

Figure 4.7 Schematic representation of the supramolecular functionalization protocol for the reversible solubilization of MWCNTs with the coordination based supramolecular polymers [X•114], with X = 112 or 113. Vials pictures are relative to the functionalization process undertaken with module 113; solutions obtained with 112 are comparable with those reported in this figure.

In a classical experiment, a sample of MWCNTs-[X•114]_n was prepared by addition of (5 mL) an equimolar solution of the complementary modules ([112•114]_n or [113•114]_n, 3.0 mM each) to a pre-sonicated (10 min) dispersion of pristine MWCNTs (10 mg) in the mixed solvent CHCl₃-CHX (1:1 ratio, 100 mL), and allowing the whole to stir for 16 h at room temperature. As a consequence of this procedure a very stable black solution (Figure 4.7 Step 2) was obtained. As a counterproof, the attempt of producing a dispersion of MWCNTs with only X was also performed (Figure 4.7 Step 1). As a result, a very less stable dispersion was obtained, which after ca. 1h produced the formation of a black massive precipitation with complete discoloration of the solution, thereby indicting the effective adsorption of the porphyrinic modules 112 and 113 on the MWNTs surface and yet their incapability to maintain the CNTs in suspension in absence of the supramolecular structure. The stable suspension obtained in presence of both X and 114 was further purified by centrifugation at 15 krpm for 30 min (Figure 4.7, Step 3) to remove the aggregated MWCNTs, and the supernatant solution was filtered through a Teflon Millipore® (0.10 μm) filter and thoroughly washed with a 1:1 CHCl₃/CHX mixture to remove the excess of free molecules. The resulting black powder namely, MWCNTs-[X•114]_n hybrid,
was dried overnight under vacuum. Dissolution of MWCNTs-[X•114]_n (Figure 4.7) in CHCl_3 finally led to a very stable grey solution (after several weeks, no precipitation was observed). These purified MWCNTs-[X•114]_n hybrid solutions were further characterized using various microscopic and spectroscopic techniques (vide infra). As a consequence of this experiment, we assume that the solubility of MWCNTs is induced by the in situ formation of the two different coordination polymers [109•114]_n and [110•114]_n able to wrap around the MWCNTs sidewall inducing in this way their solubilization. This proposed mechanism was further confirmed in an indirect way by adding 20 μL of TFA to the mixture of MWCNTs and [X•114]_n. As a consequence of this addition, complete precipitation of the CNT materials occurred, most probably induced by the protonation of the pyridine nitrogen of 114 leading to the disruption of the self-assembled polymers responsible for the solubilisation process.

The presence of supramolecular polymers [X•114]_n on the surface of MWCNTs was further quantified through TGA investigations (Figure 4.8).

![Molecular structures](image)

**Figure 4.8** Molecular structures (a) of the modules investigated by TGA analysis, TGA plots of the coordination polymers (b) and of the different CNT based materials (d). Resuming table (c) containing the different values extrapolated from the TGA investigations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight loss at 550 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>[112•114]_n</td>
<td>62.0 %</td>
</tr>
<tr>
<td>[113•114]_n</td>
<td>50.3 %</td>
</tr>
<tr>
<td>[112•114]-MWCNT</td>
<td>9.1 %</td>
</tr>
<tr>
<td>[113•114]-MWCNT</td>
<td>6.5 %</td>
</tr>
</tbody>
</table>

The first set of experiments was aiming to the achievement of the characterization of the thermal stability of the coordinative polymers obtained. In this context, TGA investigations showed that the polymer who was subjected to the highest weight loss after the thermal treatment (550°C) was [109•114]_n, that lost up to 62.0 % in weight (in comparison with the 50.3 % of [113•114]_n). However at lower temperatures (up to 120 °C) the TGA plots showed that both the polymers possess a remarkably high thermal stability with practically no weight loss (< 1.0 %) as corroborated by the data.
previously obtained from the VT-UV-Vis analysis (paragraph 4.3). Notably the same trend was noticed also when the TGA analysis of the hybrid CNT-polymers hybrids was performed. In this context it was possible to calculate a higher degree of functionalization for the MWCNTs-[112•114]_n (weight loss: 9.1 %, Figure 4.8c) in respect to the one obtained from MWCNTs-[113•114]_n (weight loss: 6.5 %, Figure 4.8c).

To increase the characterization level of the supramolecular composite material obtained by the conjugation of coordinative polymers and MWCNTs, TM-AFM investigations were carried out (Figure 4.9).

![Figure 4.9](image)

**Figure 4.9** Topography TM-AFM images obtained from the analysis of MWCNTs-[112•114]_n (a), MWCNTs-[113•114]_n (g) and pristine MWCNTs (d). Phase images obtained for MWCNTs-[112•114]_n (b), MWCNTs-[113•114]_n (h) and pristine MWCNT (e). Functionalization mapping obtained from the addition of the height image to the topographic one, for MWCNTs-[112•114]_n (c) and for MWCNTs-[113•114]_n (i). 3D-Image of the MWCNTs-[112•114]_n showing the periodic lumps (f).

For this purpose both the topography and the phase imaging analysis were performed on the resulting material. For this purpose, in a typical experiment a CHCl₃ solution of the MWCNTs-[X•114]_n composite material was drop casted onto a freshly cleaved mica surface (Figure 4.9 a-c and g-e) and compared to a dispersion of un-functionalized MWNTs. The topographic analysis conducted to
evaluate the morphological properties of MWCNTs-[X•114]n, showed in both cases the presence of very well dispersed MWCNTs as a probable consequence of their high dispersibility into the starting organic solvent (CHCl₃).

A closer analysis of these samples clearly showed the presence of periodic structures having alternating lumps on MWCNTs (Figure 4.9 a,g) that were not present in the case of the pristine MWCNTs (Figure 4.9 d,e). The distance between two adjacent heights was found by profile analysis to ranges from 20 to 50 nm. These periodic structures were attributed to the supramolecular coordination based polymeric nanowires that wrap around MWCNTs thus imparting their solubility. The final confirmation of the presence of soft organic material onto the CNT surface was given by phase imaging of the composite MWCNTs-[X•114]n hybrid systems (Figure 4.9 b,h). Indeed, in both cases the phase analysis revealed the presence of areas of the sample characterized by different contrast as a consequence of the presence of parts of the CNTs’ surface characterized by different mechanical and viscoelastic properties. These changes are ascribable to the adsorption onto the CNTs surface of organic material possessing different physical properties in respect to the graphitic CNTs backbone. By summing the phase imaging to the topography, we were able to produce a topographic functionalization map indicating the areas in which the local density of the polymer was higher along the CNTs backbone (Figure 4.9 c, i). In the case of MWCNTs-[112•114]n the disposition of the polymers seemed to be more localized in small areas, ranging from 50 to 100 nm, along the MWCNTs structure, whereas for the MWCNTs-[113•114]n system the distribution of the polymer seemed to be more uniform along the material.

UV-Vis analysis of the MWCNTs-[X•114]n composite materials was also performed in order to characterize at the qualitative level the presence of the porphyrinic antenna systems on the CNTs surface.

![Figure 4.10](image-url) Superimposed UV-Vis spectra of the composite materials composed by MWCNTs-[112•114]n and MWCNTs-[112]n (a), and of MWCNTs-[112•114]n and MWCNTs-[112]n (b).

Our previous investigations have shown that molecules 112 and 113 exhibit intense absorptions in the UV-Visible region and are good luminophores in solution (CHX) as well as their polymeric derivatives. UV-Vis investigation were therefore carried out on both the assembly constituted by MWCNTs-[X•114]n and MWCNTs-[X]n in order to verify the effectiveness of the complexation.
reactions (Figure 4.10). UV-Vis spectra of the single components hybrid materials composed by MWCNTs-[X]n showed in a remarkable way the presence of Soret bands, relative to the porphyrin structures with maxima at approximately 420 nm (comparable with the value obtained from the previously studied uncomplexed systems). At the same time the exponential absorption features characteristic of the MWCNTs resulted to be very low in comparison with the systems composed by MWCNTs-[X•114]n, this can be ascribed to the lower solubility that MWCNTs-[X]n systems possess in comparison with the polymeric one, inducing in this way the presence of a lower fraction of dispersed CNTs in solution. Most notably in the case of MWCNTs-[X•114]n, the Soret band peaks resulted to be shifted in comparison with the MWCNTs-[X]n, as a consequence of the occurrence of the supramolecular polymerization process also in the presence of MWCNTs as templating material. Conceptually, the research described in this work introduces the idea of using coordination based polymers to induce a reversible supramolecular functionalization of MWCNTs, exploiting the dynamic axial coordination process between different di-porphyrin derivatives and a complementary bidentate linear units. Characterization of the MWCNTs-[X•114]n hybrid materials was provided by the combination of different complementary techniques such as spectroscopic (absorption and emission), thermogravimetric (TGA) and microscopic (AFM). As a further step toward the optimization of this work, the material obtained so far will be inserted into new generation functional devices, such as field effect transistor (FET), in order to investigate its charge transfer ability under light and dark conditions and to prepare new functional materials based on the dynamic coordination approach method.

4.6 Bibliography


CHAPTER V

EXPERIMENTAL PART

5.1 Instrumentation

Thin layer chromatography (TLC) were conducted on pre-coated glass plates with 0.25 mm Macherey-Nagel silica gel with fluorescent indicator UV254.

Column chromatography (CC) were carried out with Merck silica gel 60 (particle size 40-63 mm).

Melting Points (m.p.) were measured on a Büchi SMP-20.

Nuclear magnetic resonance (NMR) 200 MHz \(^{1}\)H-NMR and 50 MHz \(^{13}\)C-NMR spectra were obtained on a Varian Gemini 200 spectrometer. 400 MHz \(^{1}\)H-NMR spectra were obtained on a Jeol JNM-EX400. Chemical shifts are reported in ppm using the solvent residual signal as an internal reference (CDCl\(_{3}\): \(\delta\)\(_{H}\) = 7.26 ppm, \(\delta\)\(_{C}\) = 77.16 ppm, CD\(_{3}\)OD: \(\delta\)\(_{H}\) = 3.31 ppm, \(\delta\)\(_{C}\) = 49.00 ppm, Me\(_{2}\)SO-\(d_{6}\): \(\delta\)\(_{H}\) = 2.50 ppm, \(\delta\)\(_{C}\) = 39.52 ppm, C\(_{6}\)D\(_{5}\)N: \(\delta\)\(_{H}\) = 7.19, 7.55, 8.71 ppm, \(\delta\)\(_{C}\) = 123.5, 135.5, 149.5 ppm). Coupling constants (\(J\)) are given in Hz. The resonance multiplicity is described as \(s\) (singlet), \(d\) (doublet), \(t\) (triplet), \(q\) (quartet), \(dd\) (doublet of doublets), \(m\) (multiplet), \(br\) (broad signal).

Infrared spectra (IR) in KBr were recorded on a Perkin Elmer 2000 spectrometer by Paolo de Baseggio.

Mass spectrometry measurements (MS) Electrospray Ionization (ESI) performed on a Perkin-Elmer API1 at 5600 eV and Electron Impact (EI) performed on a Ion trap GCQ Finnigan Thermoquest at 70 eV were recorded at Università degli Studi di Trieste by Dr. Fabio Hollan.

Optical rotations and CD measurements. Optical rotations were measured on a polarimeter with a sodium lamp (\(l = 589\) nm) and are reported as follows: \([\alpha]^{25}_{D}\) (c = g (100 mL)-1, solvent). CD spectroscopy was performed using a Jasco J-815 spectropolarimeter.

5.2 Materials and General Methods

Chemicals were purchased from, Aldrich, Fluka and Riedel and used as received. Solvents were purchased from JTBaker and Aldrich, and deuterated solvents from Cambridge Isotope Laboratories.

General solvents such as CH\(_{2}\)Cl\(_{2}\), EtN\(_{3}\), Toluene, THF and were distilled from CaH\(_{2}\), Na and Na/benzophenone, respectively. Other solvents used were of synthetic grade.

Low temperature baths were prepared using different solvent mixtures depending on the desired temperature: - 78 °C: acetone/liquid N\(_{2}\); -10 °C: ice/NaCl; 0 °C: ice/H\(_{2}\)O.
When anhydrous conditions were required, reaction flasks were dried with a heating gun (300-500 °C), placed under vacuum (aprox. 1 mmHg) using a Schlenk line and purged with N₂ or Ar. To adjust the reaction flask’s necks silicon stoppers were used, and ballons filled with Ar where used to keep the inert atmosphere. The addition of reagents was done by means of plastic or crystal syringes.

For all the Sonogashira reactions it was necessary to work with an oxygen free atmosphere, to achieve so, the “Freeze-Pump-Thaw” technique was used. Such technique involves freezing (using liquid N₂) the reaction material under high vacuum in a reaction flask that is connected to the vacuum line under Ar atmosphere. The frozen sample is then thawed until it liquefies and is kept in this form for some time (ca. 10-15 min) without interrupting the vacuum.

5.3 Specific Instrumentation and Techniques

5.3.1 Spectrometric Characterisation

The solutions for spectroscopic studies were prepared by injecting microlitre amounts (10/20 µL) of 1 mM solutions in THF of each compound into 3 mL of cyclohexane. Electronic absorption and emission measurements were carried out, respectively, on a Lambda 950 UV/VIS/NIR spectrophotometer (Perkin Elmer) and on a Edinburgh FLS920 spectrofluometer (continuous 450 W Xe lamp), equipped with a Peltier-cooled Hamamatsu R928 photomultiplier tube (185-850 nm). The temperature of the solutions was varied with HAAKE F3-C digital heated/refrigerated water bath (Haake Mess-Technik GmbH u.Co., Germany) which can be manually connected to cuvette holder and controlled externally. Emission quantum yields were determined according to the approach described by Demas and Crosby[1] using Ruthenium ($\Phi_{em} = 0.028$ in air-equilibrated acid/H₂O solution, 1 N H₂SO₄) as standard. All the solvent (THF and cyclohexane) are spectrophotometric grade Sigma-Aldrich, (99+%) and were used as received.

5.3.2 AFM and TEM microscopic Characterisation

The samples for microscopic studies were prepared by heating cyclohexane solutions to 80 °C to break any kind of aggregate formed; the samples were then slowly cooled down to room temperature to induce the formation of the thermodynamically favoured nanostructures. For TEM analysis, a drop (10 µl) of each solution was placed on a carbon coated nickel grid (3.00 mm, 200 mesh). After drying at r.t., the samples were observed with a TEM Philips EM 208 microscope (accelerating voltage of 100 kV). The samples for AFM imaging were prepared by drop-casting each solution (10 µl) onto a freshly cleaved mica piece (0.5 cm × 0.5 cm), allowed to dry for a few minutes and then investigated by using Digital Instruments (Veeco) Nanoscope IIIa (Tapping Mode) with Veeco RTESP7 Tips. TEM measurements were performed together with Mr. Claudio Gamboz at Centro Servizi Polivalenti di Ateneo, Università di Trieste.
CHAPTER V

CHAPTER II
Assembly [91•84]ₙ, preparation of the blank. 20 μL of each solutions 1.4 mM, and 0.14 mM in CH₂Cl₂/o-Xylene (9:1) were drop casted on a freshly cleaved mica surface and dried under vacuum for one hour in order to completely remove the residual solvent.

Assembly [91•84]ₙ, preparation of samples. Solutions of 91 and 84 (in 1:1 molar ratio) were prepared in CH₂Cl₂/o-Xylene (9:1) at concentrations of 1.4 and 0.14 mM, respectively. 20 mL of each solution was then drop cast onto a freshly cleaved mica surface and heated at 145°C under argon atmosphere for 15 min. The samples were then dried under vacuum for 10 min to assure the complete removal of all residual solvent.

Assembly [91•84]ₙ, preparation of the blank. 20 μL of solutions 1.4 and 0.14 mM in CH₂Cl₂/o-Xylene (9:1) were drop casted each on a freshly cleaved mica surface and dried under vacuum for one hour in order to completely remove all the residual solvent.

Assembly [92•84]ₙ, preparation of samples. Solutions of 92 and 84 (in 1:1 molar ratio) were prepared in CH₂Cl₂/o-Xylene (9:1) at concentrations of 1.2 mm and 0.12 mm, respectively. 20 mL of each solution was then drop cast onto a freshly cleaved mica surface and heated at 145°C under argon atmosphere for 15 min. The samples were then dried under vacuum for 10 min to assure complete removal of the residual solvent.

Assembly [93•84]ₙ, preparation of samples. Twenty microliters of a solution of molecules 93 and 84 (1:1) in CH₂Cl₂/o-Xylene (9:1) at a concentration of 0.014 mM were drop casted onto freshly cleaved mica surfaces and heated at the respective temperature (65, 90, 120, 136, 145 195 °C) for 15 min under an Ar atmosphere. Then the samples were dried under vacuum for 10 min to ensure the complete removal of the residual solvent.

Molecule 91, 92, 93 and 84, preparation of the blanks. 20 μL of a solution of molecules 91, 92, 93 and 84 in CH₂Cl₂/o-Xylene (9:1) at the concentration of 0.14 mM (91, 92 and 93) and 0.12 mM (84) were drop casted on a freshly cleaved mica surfaces and heated at 145 °C for 15 minutes under argon atmosphere. Following this, the samples were dried under vacuum for 10 minutes to assure the complete removal of the residual solvent.

CHAPTER III
Assembly [(X)-104•84]ₙ, sample preparation: The solutions for the TM-AFM analysis were prepared by adding an aliquote of molecular units (R)-104 or (S)-104 at known concentration in THF, to a solution of molecule 84 in THF, stirred and diluted with CHX upon arriving to the final solvent ratio (95:5, 90:0 or 80:20) and heated in the same solvent mixture at 80 °C, all was stirred at the same temperature for ca.10 min. and then allowed to cool overnight (Final concentration: 2.3 mM). 30 μL of the solution obtained in this way was then drop-casted onto a freshly cleaved Mica surface and let dry by simple atmospheric evaporation.
Blank preparations: The solutions for the TM-AFM analysis were prepared by diluting an aliquote of molecular units (R)-104 or (S)-104, or 84 with CHX upon arriving to the final solvent ratio (95:5, 90:0 or 80:20) and heated in the same solvent mixture at 80 °C, all was stirred at the same temperature for ca.10 min. and then allowed to cool overnight (Final concentration: 2.3 mM). 30 µL of the solution obtained in this way was then drop-casted onto a freshly cleaved Mica surface and let dry by simple atmospheric evaporation.

CHAPTER IV

Assembly [109-111], preparation of samples. Twenty microliters of a solution of molecules 109 and 111 (1:1) in CHX at a concentration of 1.4 mM were drop cast onto freshly cleaved mica surfaces and dried by atmospheric evaporation.  

Assembly [110-111], preparation of samples. Twenty microliters of a solution of molecules 110 and 111 (1:1) in CHX at a concentration of 1.4 mM were drop cast onto freshly cleaved mica surfaces and dried by atmospheric evaporation. 

MWCNT-[109-111]n preparation of samples. Twenty microliters of a dispersion containing MWCNT-[109-111]n in CH2Cl2 at a concentration of 0.1 mg/mL were drop cast onto freshly cleaved mica surfaces and dried by atmospheric evaporation.

MWCNT-[110-111]n preparation of samples. Twenty microliters of a dispersion containing MWCNT-[110-111]n in CH2Cl2 at a concentration of 0.1 mg/mL were drop cast onto freshly cleaved mica surfaces and dried by atmospheric evaporation.

5.3.3 Thermogravimetric (TGA) characterizations

Thermogravimetric analyses were carried out on a TGA Q500 series V6.3 Build 189 produced by TA Instruments. The relative data were elaborated using Universal Analysis V4.1D software.

CHAPTER II

Operative procedure for compounds 91, 92 and 93. To perform the TGA analysis, 0.42 mg of compound were analysed on a platinum pan under nitrogen flow at 60 mL/min using the protocol here reported: (a) equilibration of the sample at 35 °C for 10 min, (b) temperature ramp of 2.00 °C/min until reaching 300 °C, and (c) equilibration of the sample at 50 °C.

Operative procedure for compound 93a. To perform the TGA analysis, 1.47 mg of the compound were analysed on a platinum pan under nitrogen flow at 60 mL/min using the protocol reported here: (a) equilibration of the sample at 45 °C for 10 min, b) temperature ramp of 5.00 °C/min until reaching 300 °C, and (d) equilibration of the sample at 50 °C.

CHAPTER IV

Operative procedure for assembly [109-111]n. To perform the TGA analysis, 1.52 mg of the
assembly [109-111] were analysed on a platinum pan under nitrogen flow at 60 mL/min using the protocol reported here: (a) equilibration of the sample at 45 °C for 10 min, b) temperature ramp of 5.00 °C/min until reaching 650 °C, and (d) equilibration of the sample at 50 °C.

**Operative procedure for assembly [110-111]** To perform the TGA analysis, 1.57 mg of the assembly [110-111] were analysed on a platinum pan under nitrogen flow at 60 mL/min using the protocol reported here: (a) equilibration of the sample at 45 °C for 10 min, b) temperature ramp of 5.00 °C/min until reaching 650 °C, and (d) equilibration of the sample at 50 °C.

**Operative procedure for composite material MWCNT-[109-111]** To perform the TGA analysis, 3.10 mg of the hybrid material MWCNT-[109-111] were analysed on a platinum pan under nitrogen flow at 60 mL/min using the protocol reported here: (a) equilibration of the sample at 50 °C for 120 min, b) temperature ramp of 5.00 °C/min until reaching 650 °C, and (d) equilibration of the sample at 50 °C.

**Operative procedure for composite material MWCNT-[110-111]** To perform the TGA analysis, 2.07 mg of the hybrid material MWCNT-[110-111] were analysed on a platinum pan under nitrogen flow at 60 mL/min using the protocol reported here: (a) equilibration of the sample at 50 °C for 120 min, b) temperature ramp of 5.00 °C/min until reaching 650 °C, and (d) equilibration of the sample at 50 °C.

### 5.4 Detailed Experimental Procedures

1-Hexyluracil (94)

![Structure of 1-Hexyluracil](image)

To a suspension of uracil (2.8 g, 25 mmol) in DMSO (30 mL), dry K₂CO₃ (3.8 g, 27.5 mmol) was added and the suspension stirred for some minutes (15-20 min). 1-Bromohexane (3.5 mL, 25 mmol) was then added and the reaction mixture stirred for 20 h at 40 °C. The suspension was diluted with CHCl₃, washed with a 0.1M HCl aq. solution (20 mL × 3), H₂O (20 mL × 2), brine (20 mL), and dried over Na₂SO₄. The organic layer was concentrated and poured in cold hexane under vigorous stirring. The resulting precipitate was filtered and washed with cold hexane to afford compound 94 (2.1 g, 44 %) as a white solid. [¹] m.p. 91-95 °C; ¹H-NMR (200 MHz, CDCl₃): δ 10.1 (br, 1H; CONHCO), 7.1 (d,
3\(^1\)J(H,H) = 7.9 Hz, 1H; COCH\(_3\)), 5.7 (d, 3\(^1\)J(H,H) = 7.9 Hz, 1H; NCH\(_2\)), 3.7 (t, 3\(^1\)J(H,H) = 7.4 Hz, 2H; NCH\(_2\)(CH\(_2\))\(_2\)CH\(_3\)), 1.7 (t, 3\(^1\)J(H,H) = 7.4 Hz, 2H; NCH\(_2\)(CH\(_2\))\(_2\)CH\(_3\)), 0.9 (t, 3H; N(CH\(_2\))\(_3\); 13\(^1\)C-NMR (50 MHz, CDCl\(_3\)): \(\delta\) 164.14, 150.93, 144.37, 101.92, 48.78, 31.24, 28.92, 25.98, 22.39, 13.91; IR (cm\(^{-1}\)): \(\nu\) 3417.2, 3155.1, 3098.2, 3044.9, 2951.0, 2931.8, 2862.1, 2821.1, 1975.3, 1694.0, 1646.9, 1467.1, 1420.6, 1368.8, 1250.3, 1179.3, 989.5, 887.7, 816.5, 761.0, 726.0, 558.5; MS (70 eV, EI): Found 196 (M\(^+\)), C\(_{10}\)H\(_{16}\)N\(_2\)O\(_2\) requires = 196.09.

1-Hexyl-6-iodouracil (95)

To a solution of 1-Hexyluracil 94 (1.7 g, 8.7 mmol) in THF (55 mL), LDA (24 mL of a 1.8 M solution, 43.5 mmol) was added dropwise and the resulting solution stirred under Ar at -78 ºC for 1.5 h. I\(_2\) (11 g, 43.5 mmol) was added and the reaction mixture stirred for 2 h. The solution was then treated with AcOH (1.2 mL), and allowed to warm to r.t. The organic phase was diluted with CHCl\(_3\) (30 mL), washed with sat. aq. NaHCO\(_3\) solution (30 mL \(\times\) 3), sat. aq. Na\(_2\)SO\(_3\) solution (30 mL \(\times\) 3), brine (30 mL), and dried over Na\(_2\)SO\(_4\). Evaporation of the solvents in vacuo and purification of the crude by CC (AcOEt/cyclohexane 5:5) yielded compound 95 (1.68 g, 60%) as a white solid.\(^1\) m.p. 123-125 ºC; \(^1\)H-NMR (200 MHz, CDCl\(_3\)): \(\delta\) 8.6 (br, 1H; CONHCO), 6.4 (s, 1H; COCH\(_3\)), 4.0 (t, 3\(^1\)J(H,H) = 8.1 Hz, 2H; NCH\(_2\)(CH\(_2\))\(_2\)CH\(_3\)), 1.7 (t, 3\(^1\)J(H,H) = 8.1 Hz, 2H; NCH\(_2\)(CH\(_2\))\(_2\)CH\(_3\)), 1.3 (m, 6H; N(CH\(_2\))\(_2\)(CH\(_2\))\(_2\)CH\(_3\)), 0.9 (t, 3H; N(CH\(_2\))\(_3\)CH\(_3\); 13\(^1\)C-NMR (50 MHz, CDCl\(_3\)): \(\delta\) 161.04, 148.02, 115.73, 113.92, 53.84, 31.46; 28.85; 26.14; 22.69, 14.17; IR (cm\(^{-1}\)): \(\nu\) 3173.7, 3043.6, 1953.7, 1567.8, 1431.0, 1394.5, 1353.7, 1220.4, 1169.4, 1071.9, 1002.7, 827.4, 792.1, 750.9, 720.9, 635.4, 572.8, 537.0; MS (70 eV, EI): Found 322 (M\(^+\)), C\(_{10}\)H\(_{15}\)IN\(_2\)O\(_2\) requires = 322.14.
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1-Hexyl-3-(tert-butyloxycarbonyl)-6-iodouracil (96)

To a solution of 95 (1.60 g, 4.9 mmol) in anhydrous MeCN (10.0 mL), 1.3 mL of Py were added. After stirring the solution for 15 min at 55°C, BOC₂O (2.03 g, 14.3 mmol) was added and the whole solution stirred overnight at 55°C. H₂O (20 mL) was added to the mixture and the organic phase extracted with CHCl₃ (30 mL × 3) and dried over Na₂SO₄. Concentration of the organic layer under vacuum and purification of the crude by CC (cyclohexane/AcOEt 9:1) yielded 96 (0.75 g, 40%) as a dark brown oil.

[1] ¹H-NMR (200 MHz, CDCl₃) δ 6.43 (s, 1H; COC₅H₅), 4.04 (t, 3J(H,H) = 8.1 Hz, 2H; NC₅H₄(CH₂)₄CH₃), 1.68 (m, 2H; NCH₂(CH₂)₃CH₃), 1.58 (s, 9H, COC(C₂H₅)₃), 1.33 (m, 6H; N(CH₂)₅CH₃), 0.88 (t, 3H; N(CH₂)₅CH₃); ¹³C-NMR (50 MHz, CDCl₃): δ 158.4, 147.2, 146.2, 115.1, 113.3, 86.9, 54.2, 31.3, 28.6, 27.4, 25.9, 22.5, 13.9; IR (cm⁻¹) 3406.8, 2957.1, 2932.4, 1778.6, 1709.6, 1673.8, 1570.5, 1371.4, 1255.0, 1108.8, 845.3, 739.3; MS (ESI 5600; eV) Found 444.9 (M+Na)⁺, C₁₅H₂₃IN₂O₄Na requires = 445.26.

1,4-Bis[(trimethylsilyl)ethynyl]benzene (97)

To a degassed solution of dry Et₃N (8 mL) and dry THF (8 mL), 1,4-diiodobenzene (1 g, 3.03 mmol), [Pd(PPh₃)₄] (0.137 g, 0.12 mmol), and Cul (0.05 g, 0.24 mmol) were added and the mixture degassed a second time. TMSA (1.3 mL, 9.09 mmol) was added, the reaction mixture degassed one last time, and stirred overnight at 80 °C under Ar. The crude was filtered over celite, concentrated under vacuum and purified by CC (cyclohexane) yielding compound 97 (0.8 g, 98%) as a white solid. m.p. 107-110 °C; ¹H-NMR (200 MHz, CDCl₃): δ 7.3 (s, 4H; Ar-H), 0.25 (s, 18H, Si(CH₃)₃); ¹³C-NMR (50 MHz, CDCl₃): δ 131.84, 123.24, 104.68, 96.42, 0.14; IR (cm⁻¹): ν 2956.4, 2898.8, 2365.5, 2156.2, 1492.2, 1412.9, 1245.8, 1215.5, 845.7, 759.0, 698.1, 628.0, 551.5; MS (70 eV, EI): Found 270 (M⁺) C₁₆H₂₅Si₂ requires = 270.52.
1,4-Diethynylbenzene (98)

To a solution of TMS-protected ethynylbenzene derivative 97 (0.7 g, 2.6 mmol) in MeOH (20 mL), a 1M KOH aq. solution was added and the mixture stirred at r.t. for 40 min. H₂O (10 mL) was added and the organic phase extracted with CHCl₃ (10 mL × 5) and dried over Na₂SO₄. Evaporation of the solvent under vacuum yielded compound 98 as a white crystalline solid in a quantitative yield. [4] m.p. 86-89 ºC; ¹H-NMR (200 MHz, CDCl₃): δ 7.4 (s, 4H; Ar-H), 3.2 (s, 2H; acetylene-H); ¹³C-NMR (50 MHz, CDCl₃): δ 132.04, 122.59, 83.12, 79.21; IR (cm⁻¹): ν 3435.3, 3264.6, 2925.5, 2854.2, 2346.2, 2366.5, 1628.4, 1412.5, 1263.5, 835.6, 707.1, 676.8, 640.4, 547.2; MS (70 eV, EI): Found 126 (M⁺) C₁₀H₆ requires = 126.15.

1,3,5-Tris[(trimethylsilyl)ethynyl]benzene (99)

To a degassed solution of dry Et₃N (10 mL), 1,3,5-tribromobenzene (1.0 g, 3.17 mmol), [Pd(PPh₃)₄] (0.150 g, 0.13 mmol), and CuI (0.048 g, 0.25 mmol) were added and the mixture degassed a second time. TMSA (10 mL, 12.70 mmol) was added, the reaction mixture degassed one last time, and stirred overnight at 80 ºC under Ar. The crude was filtered over celite, concentrated under vacuum and purified by CC (cyclohexane) yielding compound 99 (1.19 g, 97%) as a brown solid. [3] m.p. 64-67 ºC; ¹H-NMR (200 MHz, CDCl₃): δ 7.5 (s, 3H; Ar-H), 0.2 (s, 27H; Si(CH₃)₃); ¹³C-NMR (50 MHz, CDCl₃): δ 134.94, 123.69, 103.19, 95.63, 0.02; IR (cm⁻¹): ν 3435.9, 2959.2, 2899.3, 2857.8, 2165.3, 1579.5, 1410.8, 1250.5, 1162.4, 1108.8, 980.7, 882.5, 843.1, 760.6, 700.7, 680.5, 652.2; MS (70 eV, EI): Found 366.72 (M⁺) C₂₁H₃₀Si₃ requires = 366.72.
1,3,5-Triethynylbenzene (100)

To a solution of TMS-protected ethynylbenzene derivative 99 (0.09 g, 0.25 mmol) in MeOH (3.3 mL), a 1M KOH aq. solution was added and the mixture stirred at r.t. for 40 min. H₂O (5 mL) was added, the organic phase extracted with CHCl₃ (5 mL × 5), and dried over Na₂SO₄. Evaporation of the solvent under vacuum yielded compound 100 as a brown crystalline solid in a quantitative yield.³ m.p. 95-97 °C; ¹H-NMR (200 MHz, CDCl₃): δ 7.6 (s, 3H; Ar-H), 3.1 (s, 3H; acetylene-H); ¹³C-NMR (50 MHz, CDCl₃): δ 135.68, 122.95, 81.68, 78.79; IR (cm⁻¹): ν 3436.4, 3296.2, 3280.6, 2925.7, 1788.3, 1580.4, 1413.4, 1250.9, 884.5, 677.8, 663.7, 612.7; MS (70 eV, EI): Found 149 (M⁺) C₁₂H₆ requires = 150.18.

1,3,6,8-Tetrabromopyrene (101)

A solution of pyrene (2 g, 9.8 mmol) in nitrobenzene (40 mL) was stirred at 120 °C for 30 min. Following this, Br₂ (2.3 mL, 44 mmol) was added dropwise. The mixture was vigorously stirred for 4 h and then EtOH (50 mL) was slowly added and the mixture stirred 1 h at r.t. The precipitate formed was filtered off, washed with EtOH and dried under vacuum yielding 101 (4 g, 79%) as a pale-green solid insoluble in all common organic solvents.² m.p. > 220 °C; IR (cm⁻¹): ν 3436.3, 1592.0, 1466.2, 1453.1, 1227.2, 1054.7, 987.8, 873.8, 839.3, 811.9, 691.5, 674.4, 495.5; MS (70 eV, EI, TFA): Found 518 (M⁺) C₁₆H₈Br₄ requires = 519.85.
1,3,6,8-Tetrakis[(trimethylsilyl)ethynyl]pyrene (102)

To a degassed solution of dry iPr₂NH (20 mL) and dry THF (20 mL), tetrabromopyrene derivative 101 (1 g, 1.93 mmol), [Pd(PPh₃)₂Cl₂] (0.067 g, 0.096 mmol) and CuI (0.018 g, 0.096 mmol) were added and the resulting solution degassed a second time. Finally, TMSA (1.6 mL, 11.5 mmol) was added, the reaction mixture degassed one last time and the final mixture stirred overnight at 80 °C under Ar. Notably, after a few minutes the reaction colour changed from green to intense orange. The resulting mixture was filtered over celite and extensively washed with CH₂Cl₂ (30 mL) and MeOH (30 mL). Removal of the solvents under vacuum and purification of the crude by CC (heptane) yielded 102 (1.16 g, 88%) as a bright orange solid.² m.p. > 220 °C; ¹H NMR (200 MHz, CDCl₃): δ 8.7 (s, 4H; H₄, H₅, H₉, H₁₀), 8.4 (s, 2H; H₂, H₇), 0.5 (s, 36H; Si(CH₃)₃); ¹³C-NMR (50 MHz, CDCl₃): δ 134.55, 131.99, 126.98, 123.5, 118.64, 102.93, 101.46, 0.32; IR (cm⁻¹): ν 3436.1, 2959.3, 2151.7, 1417.7, 1249.1, 1105.0, 890.6, 842.9, 759.8, 641.9; MS (70 eV, EI): Found 586 (M⁺), C₃₆H₄₂Si₄ requires = 587.06.

1,3,6,8-Tetraethynylpyrene (103)

Trimethylsilylethynylpyrene derivative 102 (0.17 g, 0.59 mmol) was dissolved in a 1:1 MeOH/CH₂Cl₂ mixture (20 mL) and 4 mL of a 1M KOH aq. solution added. The mixture was stirred overnight at r.t. As the reaction proceeded a yellow precipitate appeared. H₂O (10 mL) was then added to the mixture and the organic phase extracted with CHCl₃ (10 mL × 5) and dried over Na₂SO₄. Evaporation of the solvent under vacuum yielded 103 as a yellow solid in a quantitative yield, which resulted insoluble in all common organic solvents.² m.p.: the compound burns at 190 ºC; ¹H-NMR (200 MHz, CDCl₃:CD₂OD): δ 8.7 (s, 4H; H₄, H₅, H₉, H₁₀), 8.4 (s, 2H; H₂, H₇), 3.7 (s, 4H; acetylene-H); IR (cm⁻¹): ν 3435.7, 3280.8, 2100.5, 1600.7, 1468.6, 1115.8, 905.5, 831.9, 670.0, 608.8, 473.2; MS (70 eV, EI):
CHAPTER V

Found 298 (M⁺), C₂₃H₁₈ requires = 298.34. NOTE: The low solubility of the compound did not allow to perform the \(^{13}\)C-NMR.

1,4-Bis[(1-hexyl-3-tert-butyloxy carbonyl)-6-ethynyl-uracil]benzene (91)

To a degassed solution of dry Et₃N (2.5 mL) and THF (2.5 mL), 96 (0.19 g, 0.35 mmol), [Pd(PPh₃)₄] (0.013 g, 0.013 mmol) and CuI (0.004 g, 0.026 mmol) were added and the mixture degassed a second time. 98 (0.020 g, 0.16 mmol) was then added, the reaction mixture degassed one last time, and stirred overnight at r.t. under Ar. The crude mixture was then filtered over celite, concentrated under vaccum and purified by CC (cyclohexane/AcOEt 8:2) yielding 91 (0.023g, 70%) as a white solid.

\[^{1}H\text{-NMR}\ (200\text{ MHz, CDCl}_3): \delta 7.57\text{ (s, 4H; Ar-H)}, 6.05\text{ (s, 2H; COCH)}, 4.03\text{ (t, }^{3}J(H,H) = 7.4\text{ Hz, 4H; NCH}_2(CH_2)_3), 1.77\text{ (m, 4H; NCH}_2(CH_2)_3(CH_3)), 1.60\text{ (s, 18H; COC(CH}_3)_3)}, 1.33\text{ (m, 12H; N(CH}_2)_3(CH_2)_3(CH_3)), 0.86\text{ (t, 6H; N(CH}_2)_3(CH_3)); }^{13}\text{C-NMR (50 MHz, CDCl}_3): \delta 159.5, 148.6, 147.6, 137.3, 132.3, 122.3, 107.1, 98.9, 87.1, 82.8, 47.4, 31.5, 28.8, 27.5, 26.6, 22.7, 14.1; IR (cm}\text{⁻¹): }\nu 3442.8, 2958.5, 2929.1, 2860.7, 2363.5, 2220.7, 1779.9, 1714.4, 1682.7, 1596.2, 1447.6, 1370.6, 1257.9, 1150.2, 843.4; MS (70 eV, EI): Found 514 (M⁺ − 2 BOC), C₄₀H₄₀N₂O₈ − 2 BOC requires = 514.62.

1,3,5-Tris[(1-hexyl-3-tert-butyloxy carbonyl)-6-ethynyl-uracil]benzene (92)

To a degassed solution of dry Et₃N (3 mL) and THF (3 mL), 96 (0.24 g, 0.13 mmol), [Pd(PPh₃)₄] (0.012 g, 0.011 mmol) and CuI (0.005 g, 0.022 mmol) were added and the mixture degassed a second time. 99 (0.020 g, 0.44 mmol) was then added, the reaction mixture degassed one last time, and stirred overnight at 40 °C under Ar. The crude mixture was then filtered over celite, concentrated under vacuum and purified by CC (cyclohexane/AcOEt 7:3) yielding 92 (0.055g, 39%) as a white solid.\[^{3}\]
1H-NMR (200 MHz, CDCl3): δ 7.71 (s, 3H; Ar-H), 6.04 (s, 3H; COCH), 4.01 (t, 3J(H,H) = 7.4 Hz 6H; NCH2(CH2)4CH3), 1.76 (br, 6H; NCH2CH2(CH2)3CH3), 1.60 (s, 27H; COC(CH3)3), 1.33 (m, 18H; N(CH2)2(CH2)3CH3), 0.85 (t, 9H; N(CH2)2CH3); 13C-NMR (50 MHz, CDCl3): δ 159.1, 149.2, 147.9, 136.9, 136.0, 122.5, 107.9, 96.2, 87.2, 82.2, 47.5, 31.9, 27.1, 21.0, 14.0; IR (cm⁻¹): ν 3379.9, 3092.1, 2957.2, 2928.8, 2222.7, 1785.4, 1715.9, 1678.3, 1598.9, 1432.5, 1389.0, 1370.8, 1256.1, 1147.7, 842.9, 816.9. MS (5600 eV, ESI): Found 733.4 (M⁺ − 3 BOC), 755.4 (M + Na⁺ − 3 BOC), C57H72N6O12 − 3 BOC requires = 732.87, C57H72N6O12Na − 3 BOC requires = 755.87.

1,3,6,8-Tetrakis[(1-hexyl-3-tert-butyloxycarbonyl)-6-ethynyl-uracil]pyrene (93)

To a degassed solution of dry Et3N (2.5 mL) and THF (2.5 mL), 96 (0.16 g, 0.29 mmol), [Pd(PPh3)4] (0.010 g, 0.008 mmol) and CuI (0.003 g, 0.016 mmol) were added and the mixture degassed a second time. 103 (0.015 g, 0.042 mmol) was then added, the reaction mixture degassed one last time, and stirred overnight at 40 °C under Ar. The crude mixture was then filtered over celite, concentrated under vaccum and purified by CC (cyclohexane/AcOEt 8:2) yielding 93 (0.010 g, 10%) as an orange powder. 1H-NMR (200 MHz, CDCl3): δ 8.66 (s, 4H; H4, H5, H9, H10), 8.45 (s, 2H; H2, H7), 6.26 (s, 4H; COC(CH3)3), 4.20 (t, 8H; N(CH2)2(CH2)3CH3), 1.91 (m, 8H; NCH2CH2(CH2)3CH3), 1.58 (s, 36H; COC(CH3)3), 1.32 (m, 24H; N(CH2)2(CH2)3CH3), 0.79 (t, 3J(H,H) = 7.5 Hz 12H; N(CH2)2CH3); 13C-NMR (50 MHz; CDCl3): δ 159.4, 148.8, 147.5, 137.1, 135.2, 133.3, 128.0, 123.8, 117.5, 107.7, 96.8, 87.6, 87.4, 47.7, 31.6, 29.2, 27.7, 26.7, 22.8, 14.2. MS (5600 eV, ESI): Found 1498.3 (M + Na⁺), 1397.5 (M + Na⁺ − 1 BOC), 1297.5 (M + Na⁺ − 2 BOC), 1197.5 (M + Na⁺ − 3 BOC), 1097.7 (M + Na⁺ − 4 BOC), 1075.7 (M − 4 BOC), C84H98N8O16Na requires = 1498.72, C84H98N8O16 Na − 1 BOC requires = 1397.66, C84H98N8O16 Na − 2 BOC requires = 1298.49, C84H98N8O16 Na − 3 BOC requires = 1198.37, C84H98N8O16 Na − 4 BOC requires = 1098.26, C84H98N8O16 − 4 BOC requires = 1075.26.
1,3,6,8-Tetrakis(1-hexylurac-6-yl)ethynylpyrene (93a).

To a degassed solution of dry THF (5 mL) and Et₃N (5 mL), 1-hexyl-6-iodouracil 95 (0.270 g, 0.84 mmol), [Pd(PPh₃)₄] (4 mg, 0.034 mmol), and CuI (13 mg, 0.068 mmol) were added and the resulting mixture degassed a second time. 1,3,6,8-Tetraethynylpyrene 103 (0.05 g, 0.17 mmol) was added, the solution degassed one last time, and stirred overnight at 45 °C under Ar. Notably, after some minutes the reaction colour changed and a red precipitate appeared. The suspension was then concentrated in vacuo and the crude purified by several precipitations from CHCl₃ upon addition of MeOH yielding compound 93a (0.082 g, 46%) as a dark red solid.

[5] 1H-NMR (400 MHz, C₅D₅N): δ 9.03 (s, 4 H; H₄, H₅, H₉, H₁₀), 8.90 (s, 2 H; H₂, H₇), 6.64 (s, 4 H; COC₃H), 4.37 (br, 8 H; NC₃H₂(CH₂)₄CH₃), 2.01 (m, 8 H; NCH₂C₆H₂(CH₂)₃CH₃), 1.53 (m, 8 H; N(CH₂)₂C₆H₂(CH₂)₂CH₃), 0.81 (t, 12 H, N(CH₂)₅C₆H₃), four imidic protons are missing due to the exchange with pyridine; 13C-NMR (50 MHz, C₅D₅N): δ 169.67, 152.14, 137.85, 133.64, 131.88, 126.68, 121.41, 118.21, 109.09, 96.41, 88.86, 47.09, 32.13, 27.16, 26.32, 23.26, 14.53; IR (cm⁻¹): ν 3442.6, 3164.0, 3034.1, 2954.8, 2919.3, 2850.8, 2202.9, 1690.2, 1600.0, 1581.9, 1456.2, 1243.3, 1170.5, 1114.1, 825.2, 618.7; MS (5600 eV, ESI): Found 1075.4 (M)⁺, 1098.3 (M + Na)⁺; C₆₄H₆₆N₈O₈ requires = 1075.26, C₆₄H₆₆N₈O₈Na requires = 1098.26.

2,6-Di(acetylamino)-4-bromo-pyridine (104)

To a solution of pyridine (1.4 mL, 17.5 mmol) and Ac₂O (2.5 mL, 26.4 mmol), 4-Bromo-2,6-diaminopyridine (0.45 g, 2.14 mmol) was added and the reaction mixture stirred overnight at r.t. The mixture was then diluted with CHCl₃ (10 mL), washed with H₂O (10 mL × 5), brine (20 mL), and dried over Na₂SO₄. Solvent evaporation and precipitation with Et₂O yielded compound 104 in a quant. yield as a yellow solid.[6] m.p. 210-215 °C; 1H-NMR (200 MHz, CD₂OD/CDCl₃, 1:1): δ 7.7 (s, 2H; Py-H), 4.3 (s, 2H; CH₃CONH-Py), 1.9 (s, 6H; CH₃CONH-Py); 13C-NMR (50 MHz, CD₂OD/CDCl₃, 1:1):
δ 171.08, 151.20, 135.53, 112.67, 23.93; IR (cm⁻¹): ν 3311.5, 3124.7, 1685.7, 1577.9, 1538.1, 1415.5, 1367.2, 1280.8, 1237.7, 1199.7, 1035.0, 996.7, 861.4, 777.4, 746.9, 693.0, 603.0, 561.3, 549.1; MS (70 eV, EI): Found 273 (M⁺), C₉H₁₀BrN₃O₂ requires = 272.

2,6-Di(acetylamino)-4-[(trimethylsilyl)ethynyl]pyridine (105)

To a degassed solution of dry Et₃N (40 mL), dry THF (6 mL) and and dry DMF (1 mL), 104 (0.44 g, 1.6 mmol), [(Pd(PPh₃)₄] (0.074 g, 0.06 mmol), and CuI (0.024 g, 0.128 mmol) were added and the solution degassed a second time. TMSA (0.44 mL, 3.2 mmol) was then added and the reaction mixture degassed one last time, and stirred overnight at 85 ºC under Ar. The resulting dark mixture was filtered over celite and washed with toluene (10 mL), CH₂Cl₂ (20 mL), and MeOH (20 mL). Removal of the solvents under vacuum and purification of the crude by CC (cyclohexane/AcOEt 5:5) yielded compound 75 (0.33 g, 60%) as a yellow crystalline solid. m.p. 85-90 ºC; ¹H-NMR (200 MHz, CDCl₃): δ 8.4 (br, 2H; CH₃CONH-Py), 7.8 (br, 2H; Py-H), 2.0 (s, 6H; CH₃CONH-Py), 0.2 (s, 9H; Si(CH₃)₃); ¹³C-NMR (50 MHz, CDCl₃): δ 168.36, 149.49, 135.88, 111.91, 102.44, 99.97, 24.83, 0.11; IR (cm⁻¹): ν 3422.9, 3276.1, 2960.2, 2161.9, 1681.5, 1611.9, 1557.9, 1416.0, 1370.0, 1276.1, 1249.7, 1206.9, 1145.0, 1033.4, 996.7, 983.5, 953.7, 848.1, 760.2, 625.8, 569.6, 539.3; MS (70 eV, EI): Found 289 (M⁺), C₁₄H₁₉N₃O₂Si requires = 289.41.

2,6-Di(acetylamino)-4-ethynylpyridine (106)

To a solution of TMS-protected ethynylpyridine derivative 105 (0.4 g, 1.38 mmol) in MeOH (15 mL), a 1M KOH aq. solution was added and the mixture stirred at r.t. for 40 min. H₂O (10 mL) was added and the organic phase extracted with CHCl₃ (10 mL × 5) and dried over Na₂SO₄. Evaporation of the solvent under vacuum yielded compound 106 as a yellow crystalline solid in a quantitative yield. m.p. 208-213 ºC; ¹H-NMR (200 MHz, CD₃OD/CDCl₃, 1:1): δ 7.8 (br, 2H; Py-H), 4.3 (br, 2H; CH₃CONH-Py), 3.2 (s, 1H; acetylene-H), 2.0 (s, 6H; CH₃CONH-Py); ¹³C-NMR (50 MHz,
CD$_3$OD/CDC$_3$, 1:1): δ 169.79, 149.79, 134.16, 111.72, 81.31, 24.09; IR (cm$^{-1}$): ν 3319.0, 3253.2, 3124.4, 2115.1, 1715.6, 1669.5, 1612.1, 1561.0, 1415.9, 1365.6, 1278.1, 1235.7, 1202.7, 1037.5, 998.9, 876.0, 853.6, 724.9, 703.3, 673.7, 636.7, 562.4; MS (70 eV, EI): Found 217 (M$^+$), C$_{11}$H$_{11}$N$_3$O$_2$ requires = 217.22.

1,4-Bis(dodecyloxy)-2,5-bis[2,6-di(acetylamino)pyridin-4-yl]-ethynyl]benzene (84)

To a degassed solution of dry Et$_3$N (4 mL) and THF (4 mL), 107 (0.2 g, 0.29 mmol), [Pd(PPh$_3$)$_4$] (0.014 g, 0.012 mmol), and CuI (4 mg, 0.023 mmol) were added and the mixture degassed a second time. 2,6-Diacetylamino-4-ethynylpyridine (106) (0.16 g, 0.73 mmol) was then added, the reaction mixture degassed one last time, and refluxed overnight at 85 ºC under Ar. The crude mixture was then filtered over celite, concentrated under vacuum and purified by CC (cyclohexane/AcOEt, 5:5, then AcOEt) yielding 123 (0.121 g, 40 %) as a bright yellow solid. m.p. > 240 ºC; $^1$H-NMR (200 MHz, CDCl$_3$): δ 8.1 (s, 4H; Py-H), 7.6 (s, 4H; CH$_3$CONH-Py), 7.0 (s, 2H; Ar-H), 4.1 (t, $^3$J(H,H) = 8.1 Hz, 4H; Ar-OC$_2$H$_5$(CH$_2$)$_3$CH$_3$), 2.2 (s, 12H; C$_3$H$_3$CONH-Py), 1.9 (m, 4H; Ar-OC$_2$H$_5$(CH$_2$)$_3$CH$_3$), 1.3 (br, 36H; Ar-O(CH$_2$)$_2$(CH$_2$)$_3$CH$_3$), 0.9 (t, 6H; Ar-O(CH$_2$)$_2$(CH$_2$)$_3$CH$_3$); $^{13}$C-NMR (50 MHz, CDCl$_3$): δ 168.28, 153.66, 149.45, 136.13, 117.33, 113.62, 111.49, 92.95, 90.57, 69.83, 32.11, 29.83, 29.56, 29.51, 29.29, 26.14, 24.97, 22.88, 14.32; IR (cm$^{-1}$): ν 3285.3, 2959.1, 2925.6, 2220.3, 2162.1, 1708.1, 1685.4, 1612.1, 1554.9, 1419.2, 1249.8, 869.7, 843.0, 759.1, 642.1; MS (70 eV, EI): Found 877 (M$^+$), C$_{52}$H$_{72}$N$_6$O$_6$ requires = 877.16.

(R)-2,2'-Dimethoxy-1,1-binaphthalene ((R)-109)

To a stirred mixture of (R)-Binol (3.00 g, 10.5 mmol) and K$_2$CO$_3$ (3.18 g, 23.0 mmol) in dry DMF (60 ml) at 80 °C under N$_2$, MeI (3.27 g, 23.0 mmol) was slowly added, and the mixture was stirred for 16 h at 80°C. After cooling to 20°C, H$_2$O (360ml) was added, and the aq. phase was extracted with CH$_2$Cl$_2$ (3 times, 100 ml). The combined organic layers were washed with 0.5 M KOH (120 ml), H$_2$O (120 ml), and sat. aq. NaCl soln. (120 ml), dried over MgSO$_4$, and evaporated. Reprecipitation from
Acetone/H₂O afforded 109 in quantitative yield as a white coloured solid. [7] m.p. 223 °C. [α]D = +54° (c=1.0, CHCl₃). ¹H-NMR (200 MHz, CDCl₃): δ 3.74 (s, 6H; OCH₃), 7.10-7.30 (m, 6H; Ar-H₆,₇,₈), 7.44 (d, J(H,H) = 9.0 Hz, 2H; Ar-H₅); 7.85 (m, 2H; Ar-H₃), 7.95 (d, J(H,H) = 9.0 Hz, 2H; Ar-H₄). ¹³C-NMR (50 MHz, CDCl₃): δ 56.86, 114.21, 119.56, 123.48, 125.22, 126.26, 127.89, 129.19, 129.36, 133.98, 154.92; IR (cm⁻¹): ν 3044, 2933, 2836, 1618, 1590, 1506, 1461, 1354, 1264, 1250, 1091, 811; MS (70 eV, EI): Found: 314.2 (M⁺), C₂₂H₁₈O₂ requires 314.38.

(S)-2,2'-Dimethoxy-1,1'-binaphthalene ((S)-109)

To a stirred mixture of (S)-Binol (3.00 g, 10.5 mmol) and K₂CO₃ (3.18 g, 23.0 mmol) in dry DMF (60 ml) at 80 °C under N₂, MeI (3.27 g, 23.0 mmol) was slowly added, and the mixture was stirred for 16 h at 80 °C. After cooling to 20 °C, H₂O (360 ml) was added, and the aq. phase was extracted with CH₂Cl₂ (3 times, 100 ml). The combined organic layers were washed with 0.5 M KOH (120 ml), H₂O (120 ml), and sat. aq. NaCl soln. (120 ml), dried over MgSO₄, and evaporated. Reprecipitation from Acetone/H₂O afforded 109 in quantitative yield as a white coloured solid. [7] m.p. 223 °C. [α]D = -54.9° (c=1.0, CHCl₃). ¹H-NMR (200 MHz, CDCl₃): δ 7.95 (d, J(H,H) = 9.0 Hz, 2H; Ar-H₄); 7.44 (d, J(H,H) = 9.0 Hz, 2H; Ar-H₅); 7.10-7.30 (m, 6H; Ar-H₆,₇,₈); 3.74 (s, 6H; OCH₃); 7.85 (m, 2H; Ar-H₃), 7.95 (d, J(H,H) = 9.0 Hz, 2H; Ar-H₄). ¹³C-NMR (50 MHz, CDCl₃): δ 154.92, 133.98, 129.36, 129.19, 127.89, 126.26, 125.22, 123.48, 119.56, 114.21, 56.86. IR (cm⁻¹): ν 3044, 2933, 2836, 1618, 1590, 1506, 1461, 1354, 1264, 1250, 1091, 1064, 811. MS (70 eV, EI): Found: 314.2 (M⁺), C₂₂H₁₈O₂ requires 314.38.

(R)-3,3-diiodo-2,2'-Dimethoxy-1,1'-binaphthalene ((R)-110)

A solution of (R)-109 (4.32 g, 7.63 mmol) in THF (220 ml) was cooled to –78 °C under N₂, and 1.6 M BuLi (4.77 ml, 7.63 mmol) in hexane was slowly added. After stirring for 1 h, sat. aq. NH₄Cl soln. (40 ml) was added, and the mixture was allowed to warm to 20 °C. Et₂O (300 ml) was added, and the organic layer was washed with H₂O (4 times, 150 ml) and sat. aq. NaCl soln. (50 ml) dried over
MgSO₄ and evaporated. Purification through CC (hexane/AcOEt 10 : 1) gave (R)-110 (1.90 g, 45%) as a cream coloured solid.¹⁰¹ m.p. 197°C. [α]⁰²0 = +41.5 (c = 0.5, CHCl₃). ¹H-NMR (200 MHz, CDCl₃): 8.70 (s, 2H, Ar-H₂); 7.96 (d, ³J(H,H) = 8.0 Hz, 2H, Ar-H₂), 7.58 (t, ³J(H,H) = 7.48 Hz, 2H, Ar-H₂), 7.43 (t, ³J(H,H) = 7.6 Hz, 2H, Ar-H₂), 7.46 (d, ³J(H,H) = 8.4 Hz, 2H, Ar-H₂), 3.58 (s, 6H, CH₃); ¹³C-NMR (50 MHz, CDCl₃): 180.42, 154.65, 140.09, 134.03, 132.37, 127.30, 125.98, 125.58, 97.33, 92.62, 61.41; IR (KBr): 2931, 2823, 1619, 1593, 1508, 1464, 1390, 1352, 1262, 1146, 1089, 1054, 1018, 896, 812, 752. MS (70 eV, El): Found: 566.3 C₁₂H₁₇O₂I₂ requires 566.17.

(S)-3,3-diiodo-2,2'-Dimethoxy-1,1'-binaphthalene ((S)-110)

A solution of (S)-109 (4.32g, 7.63 mmol) in THF (220 ml) was cooled to – 78°C under N₂, and 1.6 M BuLi (4.77 ml, 7.63 mmol) in hexane was slowly added. After stirring for 1 h, sat. aq. NH₄Cl soln. (40 ml) was added, and the mixture was allowed to warm to 20°C. Et₂O (300 ml) was added, and the organic layer was washed with H₂O (4 times, 150 ml) and sat. aq. NaCl soln. (50 ml) dried over MgSO₄ and evaporated. Purification through CC (hexane/AcOEt 10 : 1) gave (S)-110 (1.52 g, 35%) as a cream coloured solid.¹⁰¹ M.p. 197°C. [α]⁰²0 = +41.5 (c = 0.5, CHCl₃). ¹H-NMR (200 MHz, CDCl₃): 8.70 (s, 2H, Ar-H₂); 7.96 (d, ³J(H,H) = 8.0 Hz, 2H, Ar-H₂), 7.58 (t, ³J(H,H) = 7.48 Hz, 2H, Ar-H₂), 7.43 (t, ³J(H,H) = 7.6 Hz, 2H, Ar-H₂), 7.46 (d, ³J(H,H) = 8.4 Hz, 2H, Ar-H₂), 3.58 (s, 6H, CH₃); ¹³C-NMR (50 MHz, CDCl₃): 180.42, 154.65, 140.09, 134.03, 132.37, 127.30, 125.98, 125.58, 97.33, 92.62, 61.41; IR (KBr): 2931, 2823, 1619, 1593, 1508, 1464, 1390, 1352, 1262, 1146, 1089, 1054, 1018, 896, 812, 752. MS (70 eV, El): Found: 566.3 C₁₂H₁₇O₂I₂ requires 566.17.

(R)-3,3'-Diethyl-2,2'-dimethoxy-1,1'-binaphthalene ((R)-111)

To a degassed solution of 3,3'-diiodo-2,2'-dimethoxy-1,1'-binaphthalene (R)-110, (1.132 g, 2.0 mmol) and [Pd(PPh₃)₂Cl₂] (144 mg, 0.2 mmol) in benzene (10 mL) and Et₃N (12 mL) was added TMSA (4 mL, 328.3 mmol) and CuI (76 mg, 0.4 mmol). After heated to reflux overnight, the reaction mixture was cooled to r.t. The solid was filtered off and the filtrate was evaporated to dryness. The
residue was dissolved in THF (30 mL) and methanol (30 mL) and to this solution was added anhydrous K₂CO₃. After stirred for ~1 h, the product was extracted with dichloromethane and washed with H₂O three times. The organic layer was dried over anhydrous MgSO₄, and the organic volatiles were removed in vacuo. The crude product was purified by silica gel column chromatography with an eluent of ethyl acetate/hexane (1:5 v/v) to give light yellow solid of \((R)-111\) (0.47 g, 65%).[^1] \([\alpha]^{20}_{D} = -7.5\) (c= 0.5, CHCl₃) ¹H-NMR (200 MHz, CDCl₃): δ 8.20 (s, 2H, Ar-H₂), 7.85 (d, 3J(H,H) = 7.95, 2H, Ar-H₂), 7.40 (t, 2H, Ar-H₂), 7.27 (t, 3J(H,H) = 7.90, 2H, Ar-H₂), 7.09 (d, 1H, Ar-H), 8.43, 2H, Ar-H, 2H), 3.66 (s, 6H, CH₃), 3.37 (s, 2H, C-H); ¹³C-NMR (50 MHz, CDCl₃): δ 155.94, 135.29, 134.02, 130.02, 127.78, 127.43, 125.62, 125.35, 124.82, 116.15, 81.55, 80.53, 61.13. IR: (cm⁻¹) ν: 3436, 3292, 3057, 2956, 2917, 2850, 1730, 1588, 1458, 1247, 1109, 842. MS (70 eV, EI): Found: 362.1 C₂₀H₁₈O₂ requires 362.15.

\((S)-3,3′-Diethynyl-2,2′-dimethoxy-1,1′-binaphthalene \((S)-111\)\)

To a degassed solution of 3,3′-diiodo-2,2′-dimethoxy-1,1′-binaphthalene \((S)-110\) (1.130 g, 20 mmol) and [Pd(PPh₃)₂Cl₂] (140 mg, 0.2 mmol) in benzene (10 mL) and Et₃N (12 mL) was added TMSA (4 mL, 328.3 mmol) and Cul (76 mg, 0.4 mmol). After heated to reflux overnight, the reaction mixture was cooled to r.t. The solid was filtered off and the filtrate was evaporated to dryness. The residue was dissolved in THF (30 mL) and methanol (30 mL) and to this solution was added anhydrous K₂CO₃. After stirred for ~1 h, the product was extracted with dichloromethane and washed with H₂O three times. The organic layer was dried over anhydrous MgSO₄, and the organic volatiles were removed in vacuo. The crude product was purified by silica gel column chromatography with an eluent of ethyl acetate/hexane (1:5 v/v) to give light yellow gummy solid of \((S)-111\) (590 mg, 75%).[^1] \([\alpha]^{20}_{D} = +7.5\) (c= 0.5, CHCl₃) ¹H-NMR (200 MHz, CDCl₃): δ 8.20 (s, 2H, Ar-H₂), 7.85 (d, 3J(H,H) = 7.95, 2H, Ar-H₂), 7.40 (t, 2H, Ar-H₂), 7.27 (t, 3J(H,H) = 7.40, 2H, Ar-H₂), 7.09 (d, 1H, Ar-H), 8.43, 2H, Ar-H, 2H), 3.66 (s, 6H, CH₃), 3.37 (s, 2H, C-H); ¹³C-NMR (50 MHz, CDCl₃): δ 155.94, 135.29, 134.02, 130.02, 127.78, 127.43, 125.62, 125.35, 124.82, 116.15, 81.55, 80.53, 61.13. IR: (cm⁻¹) ν: 3436, 3292, 3057, 2956, 2917, 2850, 1730, 1588, 1458, 1247, 1099, 842. MS (70 eV, EI): Found: 362.1 C₂₀H₁₈O₂ requires 362.15.
(R)-6,6’-(2,2’-dimethoxy-1,1’-binaphthyl-3,3’-diyl)bis[ethyne-2,1-diyl-(1-hexyluracil)] ((R)-108)

To a degassed solution of dry Et₃N (2.0 mL) and THF (2.0 mL), 95 (0.040 g, 0.12 mmol), [Pd(PPh₃)₄] (0.010 g, 0.008 mmol) and CuI (0.003 g, 0.017 mmol) were added and the mixture degassed a second time. Compound (R)-111 (0.020 g, 0.05 mmol) was then added, the reaction mixture degassed one last time, and stirred overnight at r.t. under Ar. The crude mixture was concentrated under vacuum and purified by CC (cyclohexane/AcOEt 7:3) yielding (R)-108 (0.024 g, 65%) as a light yellow powder. m.p. 193 °C; [α]₂¹ D = -66° (CH₂Cl₂; c=1)

H-NMR (200 MHz, CDCl₃): δ 9.26 (s, 2H; NH), 8.26 (s, 2H; Ar-H₄), 7.92 (d, J(H,H) = 7.95, 2H; Ar-H₂), 7.50 (t, J(H,H) = 7.47, 2H; Ar-H₂), 7.37 (t, J(H,H) = 7.62, 2H; Ar-H₂), 7.15 (d, J(H,H) = 8.30, 2H; Ar-H₂), 6.13 (s, 2H; CH), 4.13 (t, J(H,H) = 7.38, 4H; NCH₂(CH₂)₄CH₃), 3.61 (s, 6H; OCH₃), 1.81 (m, 4H; NCH₂CH₂(CH₂)₄CH₃), 1.32 (m, 12H; N(CH₂)₃CH₂CH₂CH₃), 0.79 (m, 6H; N(CH₂)₃CH₂CH₃); ¹³C-NMR (50 MHz; CDCl₃): δ 162.6, 155.5, 150.8, 138.9, 134.9, 130.2, 128.6, 126.4, 125.8, 124.9, 114.8, 107.1, 97.8, 84.4, 61.8, 47.1, 31.8, 29.2, 26.6, 22.8, 14.3, 14.2; IR (KBr) ν = 3424.4, 2956.8, 2917.9, 2850.3, 1731.4, 1619.6, 1591.8, 1462.9, 1379.7, 1264.7, 1250.3, 1180.4, 1091.9, 1065.7, 1020.0, 896.8, 811.2, 747.3, 542.2; MS (5600 eV, ESI): Found: 751.4 [M⁺+1] and 773.4 [M⁺+Na⁺], C₄₆H₄₆N₄O₆ requires 750.34.

(S)-6,6’-(2,2’-dimethoxy-1,1’-binaphthyl-3,3’-diyl)bis[ethyne-2,1-diyl-(1-hexyluracil)] ((S)-108)

To a degassed solution of dry Et₃N (2.0 mL) and THF (2.0 mL), 95 (0.040 g, 0.12 mmol), [Pd(PPh₃)₄] (0.010 g, 0.008 mmol) and CuI (0.003 g, 0.017 mmol) were added and the mixture degassed a second time. Compound (S)-111 (0.020 g, 0.05 mmol) was then added, the reaction mixture degassed one last
time, and stirred overnight at r.t. under Ar. The crude mixture was concentrated under vacuum and purified by CC (cyclohexane/AcOEt 7:3) yielding (S)-108 (0.020 g, 55%) as a light yellow powder. m.p. 193 °C; [α]D21 = +66° (CH2Cl2; c=1) 1H-NMR (200 MHz, CDCl3): δ 9.26 (s, 2H; NH), 8.26 (s, 2H; Ar-H4), 7.92 (d, 3J(H,H) = 7.95, 2H; Ar-H6), 7.50 (t, 3J(H,H) = 7.47, 2H; Ar-H6), 7.37 (t, 3J(H,H) = 7.62, 2H; Ar-H6), 7.15 (d, 3J(H,H) = 8.30, 2H; Ar-H8), 6.13 (s, 2H; CH), 4.13 (t, 3J(H,H) = 7.38, 4H; NCH2(CH2)4CH3), 3.61 (s, 6H; OCH3), 1.81 (m, 4H; NCH2C2H2(CH2)3CH3), 1.32 (m, 12H; N(CH2)2(C2H5)3CH3), 0.79 (m, 6H; N(CH2)5C3H3); 13C-NMR (50 MHz; CDCl3): δ 162.6, 155.5, 150.8, 138.9, 134.9, 130.2, 128.6, 126.4, 125.8, 124.9, 114.8, 107.1, 97.8, 84.4, 61.8, 47.1, 31.8, 29.2, 26.6, 22.8, 14.3, 14.2; IR (KBr) ν = 3424.4, 2956.8, 2917.9, 2849.0, 2103.4, 1731.4, 1619.6, 1591.8, 1462.9, 1379.7, 1250.3, 1180.4, 1091.9, 1065.7, 1020.0, 896.8, 811.2, 747.3, 542.2; MS (5600 eV, ESI): Found: 751.4 [M+1] and 773.4 [M+Na+] C46H46N4O6 requires 750.34.

1,6-dibromopyrene (115)

Pyrene (10 g; 50.0 mmoles) was dissolved in CCl4 (150.0 mL) at room temperature until complete dissolution. Then Br2 (5.4 mL of pure Br2 diluted in 200 mL of CCl4) was carefully added with a syringe pump to the solution that becomes red. All stirred overnight at room temperature. Filtration of the reaction mixture to afford a pink precipitate that was crystallized 5 times with toluene to obtained the most insoluble component 115 as a pink solid (6.3 g; 35%).101 m.p. 229 °C; 1H-NMR (400 MHz; CDCl3): δ 8.45 (d, 2H; 3J(H,H) = 9.02, Ar-H2), 8.25 (d, 3J(H,H) = 8.11, 2H; Ar-H3), 8.15 (t, 3J(H,H) = 9.46 4H, Ar-H6), 13C-NMR (50 MHz; CDCl3): 125.5; 150.5, 160.1, 165.5, 187.5, 198.7, 210.3, 215.7; IR (cm⁻¹): 2964.3, 2916.2, 2849.0, 2355.4, 834.1, 754.3; MS (EI 70 eV; CH2Cl2) found 360.1 (M⁺); C16H16Br2 requires 360.14.
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1,6-diethynylpyrene (117)

\[
\begin{array}{c}
\text{CH}_2\text{H} \\
\text{H} \\
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\text{3} \\
\text{4} \\
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\text{10} \\
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\]

1,6-dibromopyrene 115 (0.050 g; 0.14 mmol), TMSA (0.5 mL), \([\text{Pd(PPh}_3]_4\)) (0.010 g; 0.01 mmol) and CuI (0.005 g; 0.03 mmol) were sealed in a microwaves tube with THF (1.0 mL), toluene (1.0 mL) and Et$_3$N (1.0 mL) all was heated at 120 °C for 1 h minutes under microwave irradiation at 200 MHz of power.

The reaction mixture has been evaporated under reduced pressure and dissolved in 2.0 mL of a (1:1) mixture of THF and MeOH. Then 1.0 mL of a 1M acqueous solution of NaOH was added dropwise. a yellow precipitate immediately appeared and the solution was stirred for two hours. The reaction mixture has been purified by means of precipitation with MeOH to afford the final compound (0.024 g; 65%) as a yellow solid.

\[\text{mp } 1H-NMR (200 MHz; CDCl}_3): \delta 8.60 (d, J(H,H) = 9.01, 2H, Ar-H); 8.18 (m, 6H, Ar-H$_{3,4,5}$); 3.65 (s, 2H, C-H); \]

\[\text{13C-NMR (50 MHz; CDCl}_3): 132.7, 131.6, 130.7, 128.5, 126.5, 125.3, 117.5, 83.3, 82.7; IR (cm$^{-1}$): 2916.8, 2849.3, 1730.8, 1637.2, 1470.4, 1264.1, 1179.2, 1104.1, 1047.9, 990.1; MS (EI 70 eV; CH$_2$Cl$_2$) found 250.1 (M$^+$); requires C$_{20}$H$_{20}$ 250.2.

1,8-diiodopyrene (118)

\[
\begin{array}{c}
\text{H} \\
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\text{2} \\
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\]

Pyrene (5.0 g; 24.7 mmol) was dispersed in AcOH (150.0 mL) at 90 °C. Then H$_2$O (16.0 mL), Iodine (6.27 g; 24.7 mmol), KIO$_4$ (2.11 g; 9.80 mmol) and Sulfuric Acid (1.67 mL) were carefully added. The solution becomes red. Filtration of the reaction mixture afforded a brown precipitate that was then purified by crystallization with hot toluene to afford 118 pure (2.8 g; 25 %),\[\text{mp } 1H-NMR (200 MHz; CDCl}_3): 8.60 (d, J(H,H) = 8.12, 2H, Ar-H$_2$); 8.40 (s, 2H, Ar-H$_{10}$); 8.07 (s, 2H, Ar-H$_4$); 7.90 (d, J(H,H) = 8.12, 2H, Ar-H$_4$); \]

\[\text{13C-NMR (50 MHz; CDCl}_3): 137.2, 133.5, 132.5, 131.8, 128.0, 126.5, 124.8, 97.8; IR (cm$^{-1}$): 2916.81, 2849.3, 1730.8, 1637.2, 1470.4, 1264.1, 1179.2, 1104.1, 1047.9, 990.1; MS (EI 70 eV; CH$_2$Cl$_2$) found 454.1 (M$^+$); C$_{16}$H$_{16}$I$_2$ requires 454.15.
1,8-diethynylpyrene (120)

1,8-dibromopyrene 118 (0.050 g; 0.11 mmol), TMSA (0.5 mL), [Pd(PPh₃)₄], (0.010 g; 0.01 mmol) and CuI (0.005 g; 0.03 mmol) were sealed in a microwaves tube with THF (1.0mL), toluene (1.0 mL) and Et₃N (1.0 mL) all was heated at 120 °C for 14 minutes, under microwave irradiation at 200 MHz of power.

The reaction mixture has been evaporated under reduced pressure and dissolved in 2.0 mL of a (1:1) mixture of THF and MeOH. Then 1.0 mL of a 1M aqueous solution of KOH was added dropwise. A dark brown precipitate immediately appeared and the solution was stirred for two hours. The reaction mixture has been purified by means of precipitation with MeOH to afford the final compound 120 (0.020 g; 75 %) as a brown solid. mp 131 °C ¹H-NMR (200 MHz; CDCl₃): δ 8.69 (s, 2H; Ar-H₁₀); 8.16 (dd, 3J(H,H) = 9.0 Hz, 4H; Ar-H₁,₂); 8.08 (s, 2H; Ar-H₉); 3.65 (s, 2H, C-H); ¹³C-NMR (100 MHz; CDCl₃): 132.28, 131.55, 130.50, 128.11, 126.39, 125.02, 123.89, 117.33, 83.12, 82.47; IR (cm⁻¹):, MS (EI 70 eV; CH₂Cl₂) found 250.1 (M⁺); requires C₂₀H₂₀ 250.2.

Zn(II)-5-(4-iodophenyl)-10,15,20-trimesitylporphyrin (121)

4-iodobezaldehyde (0.500 g ; 2.72 mmol), pyrrole (0.76 mL; 10.9 mmol) and mesylaldehyde (1.207 g; 8.16 mmol) were dissolved in 1.0 L of distilled CHCl₃ all was stirred under Ar for 15 min. then also BF₃/Et₂O (0.9 mL) was added. The solution becomes immediately violet. After one hour also DDQ (1.8 g; 8.16 mmol) was added and all was stirred for another hour. Finally also Et₃N (0.7 mL) was added and the reaction mixture was evaporated and subjected to a preliminary CC using as mobile phase Cyclohexane and CHCl₃ (8:2) to separate the mixture of different porphyrins. The overall mixture (0.3 g) was then dissolved in a mixture of MeOH and CHCl₃ (10 mL each) and 10 mL of an
acqueous solution of Zn(AcO)$_2$ (0.700 g 5.0 mmol) were added in the dark and all was stirred at room temperature overnight. The reaction mixture was then extracted with CHCl$_3$ and H$_2$O and the final compound purified by means of CC using as mobile phase CHX and CH$_2$Cl$_2$ (8:2) to afford 121 (0.100 g; 7.0 %) as a pink solid. m.p >300 °C. $^1$H-NMR (200 MHz; CDCl$_3$): 8.85 ($d$, $^3J$ (H,H) = 4.69, 2H, Pyr-H) 8.75 ($d$, $^3J$ (H,H) = 4.69, 2H, pyr-H); 8.7 (s, 2H, pyr-H); 8.15 ($d$, $^3J$ (H,H) = 4.81, 2H, Ar-H); 7.95 ($d$, $^3J$ (H,H) = 8.42, 2H, Ar-H); 7.28 (s, 6H, Ar-H); 2.60 (s, 9H, CH$_3$); 1.80 (s, 18H, CH$_3$); $^{13}$C-NMR (50 MHz; CDCl$_3$): 150.2, 149.9, 143.9, 149.8, 139.5, 139.2, 139.1, 137.7, 134.6, 132.1 131.5, 131.4, 131.0, 130.6, 127.9, 121.4, 119.2, 119.0, 84.1, 22.1, 22.0, 21.8; IR (cm$^{-1}$) : 3049.8, 2917.7, 2849.1, 1744.4, MS (ESI 5600 eV; MeOH) found 929.9 (M$^+$); C$_{53}$H$_{45}$IN$_4$NaZn requires 929.4.

1,6-Bis-[(Zn(II)-5-(1-phen-4-yl)-10,15,20-trimesitylporphyryl)ethynyl]pyrene (112)

Compound 121 (0.038 g; 0.040 mmol) was dissolved in 1 mL of THF then 1 mL of Et$_3$N was added and the whole solution was degassed with a “freeze thaw pump” cycle. After this [Pd(PPh$_3$)$_4$] (0.005g; 0.05 mmol) and CuI (0.02 g; 0.10 mmol) were added and the suspension was subjected to another degassing cycle. Finally also compound 117 (0.005 g; 0.018 mmol) was added and all was degassed for the last time. All was stirred at room temperature overnight under Ar atm. The reaction mixture was then evaporated and subjected to CC using as mobile phase CHX and CH$_2$Cl$_2$ (8:2) to afford the final compound as a red solid (0.018 g; 60 %)$^{121}$ m.p. $^1$H-NMR (200 MHz; CDCl$_3$): 8.95 (m, 6H, pyr-H); 8.80 ($d$, $^3J$ (H,H) = 4.64, 4H, pyr-H); 8.7 (s, 8H, pyr-H); 8.30 ($m$, 10H, Ar-H ); 8.16 ($d$, $^3J$ (H,H) = 8.42, 4H, Ar-H); 7.30 ($s$, 12H, Ar-H); 2.60 ($s$, 18H, CH$_3$); 1.85 ($s$, 36H, CH$_3$); $^{13}$C-NMR (50 MHz; CDCl$_3$): 150.2, 149.9, 149.7, 143.9, 139.5, 139.2, 139.2, 137.6, 134.5, 132.1, 131.5, 131.3, 131.1, 131.0, 130.5, 127.9, 121.4, 119.2, 119.0, 84.1, 22.1, 22.0, 21.9; IR (cm$^{-1}$) 2956.3, 2917.7, 2849.3, 1732.7, 1507.1, 1456.0, 909.1, 735.7; MS (MALDI; DCTAB) found 1855 (M$^+$); C$_{126}$H$_{98}$N$_8$Zn$_2$ requires 1855.1.

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1,8-Bis-[ (Zn(II)-5-(1-phen-4-yi)-10,15,20-,trimesitylporphyryl)ethynyl]pyrene (113)

![Diagram of 1,8-Bis-[ (Zn(II)-5-(1-phen-4-yi)-10,15,20-,trimesitylporphyryl)ethynyl]pyrene (113)]

Compound 121 (0.070 g; 0.084 mmol) was dissolved in 2.0 mL of THF then 1.0 mL of Et$_3$N was added and the whole solution was degassed with a “freeze thaw pump” cycle. After this [Pd(PPh$_3$)$_4$] (0.005 g; 0.05 mmol) and CuI (0.02 g; 0.10 mmol) were added and the suspension was subjected to another degassing cycle. Finally also compound 120 (0.012 g; 0.028 mmol) was added and all was degassed for the last time. All was stirred at room temperature overnight under Ar atm. The reaction mixture was then evaporated and subjected to CC using as mobile phase CHX and CH$_2$Cl$_2$ (8.2) to afford the final compound as a red solid (0.020 g; 55%).

$^1$H-NMR (200 MHz; CDCl$_3$): 9.30 (s, 4H, Ar-H); 9.10 (d, $^3$J(H,H) = 4.64, 2H, pyr-H); 9.00 (d, $^3$J(H,H) = 4.64, 4H, pyr-H); 8.90 (s, 8H, pyr-H); 8.5 (m, 14H, Ar-H); 7.30 (s, 12H, Ar-H); 2.90 (d, 18 H, C$_2$H$_5$); 2.00 (d, 36H, C$_2$H$_5$).

$^{13}$C-NMR (50 MHz; CDCl$_3$): 150.1, 149.9, 149.8, 139.5, 139.2, 137.6, 134.8, 132.4, 132.1, 131.8, 131.3, 131.1, 127.8, 119.2, 119.0, 96.2, 89.8, 22.1, 22.0, 21.8; IR (cm$^{-1}$) 2915.1, 2826.4, 1650.7, 1556.2, 1455.2, 1185.4; MS (MALDI; DCTAB) found 1855 (M$^+$); C$_{126}$H$_{98}$N$_8$Zn$_2$ requires 1855.1.

5.5 BIBLIOGRAPHY

APPENDIX: Selected $^1$H and $^{13}$C spectra

1,4-Bis[(1-hexyl-3-tert-butyloxycarbonyl)-6-ethynyl-uracil]benzene (91)
1,3,6,8-Tetrakis[(1-hexylurac-6-yl)ethynyl]pyrene (93a).

![Diagram of the molecule](image)

![NMR Spectrum](image)
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1,3,5-Tris[(1-hexyl-3-tert-butoxycarbonyl)-6-ethynyl-uracil]benzene (92)

![Chemical structure](image)

![NMR spectrum](image)
1,3,6,8-Tetrakis[(1-hexyl-3-tert-butyloxycarbonyl)-6-ethynyl-uracil]pyrene (93)
1,4-Bis(dodecyloxy)-2,5-bis[(2,6-di(acetylamino)pyridin-4-yl)-ethynyl]benzene (84)

\[
\begin{align*}
\text{H-N} & \quad \text{C}_{12}\text{H}_{25}\text{O} \\
\text{H-N} & \quad \text{C}_{12}\text{H}_{25}\text{O} \\
\text{H-N} & \quad \text{C}_{12}\text{H}_{25}\text{O} \\
\text{O} & \quad \text{N-H} \\
\text{O} & \quad \text{N-H} \\
\text{O} & \quad \text{N-H} \\
\text{O} & \quad \text{N-H}
\end{align*}
\]
(R)-6,6'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis[ethyne-2,1-diyl-(1-hexyluracil)] ((R)-108)
1,6-Bis-[ (Zn(II)-5-(1-phen-4-yl)-10,15,20-trimesitylporphyril)ethynyl]pyrene (112)
1,8-Bis-[Zn(II)-5-(1-phen-4-yl)-10,15,20-trimesitylporphyryl]ethynylpyrene (113)
Curriculum Vitae

Tomas Marangoni was born in Pordenone (Italy) in 1984. He obtained his Laurea degree “summa cum laude” in Pharmaceutical Sciences in 2008 from the University of Trieste, working under the co-direction of Prof. Maurizio Prato and Dr. Davide Bonifazi, onto the preparation novel photoactive H-bond based nanostructures. After the graduation, he joined the group of Dr. Davide Bonifazi in FUNDP institution in Namur (Belgium) for three months as visiting student, to work on the functionalization of nucleobases derivatives for the preparation of supramolecular materials. In 2009, he started his Ph.D. in the group of Prof. Maurizio Prato (University of Trieste) under the supervision of Dr. Davide Bonifazi. During his Ph.D., he enjoyed an Erasmus fellowship at the University of Warwick (United Kingdom) in the group of Dr. Giovanni Costantini (May-October 2011), aimed to the study of H-bonded based supramolecular nanostructures, by means of solid-liquid interface and Ultra High Vacuum (UHV) Scanning Tunneling Microscopy (STM).
List of Publications:

1) Yoosaf, K; Llanes-Pallas, A; Marangoni, T; Belbakra, A; Marega, R; Botek, E; Champagne, B; Bonifazi, D; Armaroli, N. From Molecular to Macroscopic Engineering: Shaping Hydrogen-Bonded Organic Nanomaterials, Chem. Eur. J. 2011, 17, 11, 3262-3273.

2) Marangoni, T; Mezzasalma, S. A.; Llanes-Pallas A.; Yoosaf, K; Bonifazi, D; Armaroli, N. Thermosolutal Self-Organization of Supramolecular Polymers into Nanocraters, Langmuir 2011, 27, 4, 11513-1523.


Poster presentations

1) Marangoni, T; Mezzasalma, S.; Bonifazi, D; Armaroli, N. Supramolecular Chemistry conference 2012: Supramolecular Assemblies at Surfaces: Nanopatterning, Functionality, Reactivity (20-23 February 2012, Lanzarote, Spain) From Molecular to Macroscopic Engineering: Shaping Hydrogen-Bonded Organic Nanomaterials