Photoactive Metallo-Conjugates for the Homogeneous Conversion of Solar-Light Energy

Settore scientifico-disciplinare: CHIM/03

Ph.D. student
PAOLO CAVIGLI

Ph.D. school Director
Prof. MAURO STENER

Thesis Supervisor
Dr. ELISABETTA IENGO
Dr. TATIANA DA ROS

ANNO ACCADEMICO 2012 / 2013
# Table of contents

Acknowledgements........................................................................................................iii
Summerize ....................................................................................................................iv
Riassunto........................................................................................................................vi
Chapter 1...........................................................................................................................1
  1.1 Natural photosynthesis.............................................................................................2
  1.2 Artificial photosynthesis .........................................................................................5
    1.2.1 Artificial photosynthetic systems obtained via metal-mediated strategies.....6
    1.2.2 Homogeneous photocatalytic H₂O oxidation metal-mediated systems........7
    1.2.3 Homogeneous photocatalytic H₂O and CO₂ reduction metal-mediated systems .................................................................9
  1.3 References..............................................................................................................12
Chapter 2..........................................................................................................................15
  2.1 Introduction............................................................................................................16
  2.2 Results and discussion .........................................................................................24
    2.2.1 Synthesis.......................................................................................................24
    2.2.2 Solution and solid state characterization .........................................................25
    2.2.3 Electrochemical and Photophysical characterization of dyads 3b–5b........32
  2.3 Conclusions ..........................................................................................................39
  2.4 References..............................................................................................................40
Chapter 3..........................................................................................................................43
  3.1 Introduction............................................................................................................44
  3.2 Results and discussion .........................................................................................47
    3.2.1 Pyridyl-functionalized fulleropyrrolidine monoadducts ............................47
    3.2.2 Re(I)(bipy)-Fullerene model complexes ......................................................51
    3.2.3 Re(I)(bipy)-porphyrin model complexes ......................................................54
    3.2.4 Triad: synthesis and characterization .........................................................56
3.2.5 Spectroscopic and Photophysical Properties ............................................. 66
3.3 Conclusions ................................................................................................... 72
3.4 References .................................................................................................... 73
Chapter 4 ............................................................................................................. 76
4.1 Introduction ................................................................................................... 77
4.2 Results and Discussion ............................................................................... 84
  4.2.1 Synthesis and characterization of the molecular components ............... 84
  4.2.2 Synthesis of two- and three-component (metallo)porphyrin systems ...... 87
  4.2.3 Two- and three-component (metallo)porphyrin-fullerene systems .......... 91
4.3 Photophysical investigation on the two- and three-component (metallo)porphyrin systems ................................................................. 99
4.4 Conclusions ................................................................................................ 106
4.5 References .................................................................................................. 106
Chapter 5 ............................................................................................................. 110
5.1 Introduction ................................................................................................ 111
  5.1.1 Rhenium(I)(diimine) complexes as photocatalysts for CO₂ reduction .... 112
  5.1.2 Liposomes as supramolecular scaffolds ............................................... 115
5.2 Results and discussion ............................................................................. 118
  5.2.1 Synthesis and characterization of 34 .................................................... 118
  5.2.2 Photochemistry experiments ............................................................... 120
5.3 Conclusions ................................................................................................ 132
5.4 References .................................................................................................. 132
Chapter 6 ............................................................................................................. 135
6.1 Experimental Methods ............................................................................. 137
6.2 Materials and synthesis .......................................................................... 138
6.3 References .................................................................................................. 154
Acknowledgements

I would like to thank Professor Enzo Alessio and Professor Maurizio Prato (University of Trieste) for supporting my PhD fellowship, for hosting me in their groups and for useful scientific discussions along this work.

Teresa Gatti, former colleague at the University of Trieste, is acknowledged for initiating part of the work presented.

I want to greatly acknowledge the group of Professor Franco Scandola (University of Ferrara), and more in particular Professor Maria Teresa Indelli, for the fruitful and helpful collaboration regarding the electrochemical and photophysical characterization of the systems reported in this work.

Professor Ennio Zangrando (University of Trieste) is acknowledged for the X-ray structures.

The group of Professor Dirk Guldi (University of Erlangen) is acknowledged for the near-infrared transient characterizations.

I would like to especially thank Professor Lies Bouwmann and Dr. Sylvestre Bonnet (University of Leiden) for giving me the chance to work in their group and supervising my research during my Erasmus period in Leiden.

I sincerely thank all the present and former members of Professor Enzo Alssio, Dr. Barbara Milani, Dr. Elisabetta Iengo, Professor Maurizio Prato and Dr. Tatiana da Ros (University of Trieste) research groups, who have accompanied me during this scientific adventure.

A special thank goes to my supervisors Dr. Elisabetta Iengo and Dr. Tatiana da Ros (University of Trieste) for all the constant support and help they gave me throughout these three years.
The work of the present PhD thesis is divided into six chapters.

In the first chapter, a general introduction on natural and artificial photosynthesis is presented, highlighting the key aspects and selected examples of metal-mediated systems proposed in the literature as synthetic candidates for performing relevant photocatalytic processes, such as water oxidation, H₂ evolution and CO₂ reduction are briefly described. Specific aspects related to the present work are separately presented in the introductory sections of the following chapters.

In the second chapter, the design and synthesis and characterization of a small library of dyads of the type zinc-monopyridylporphyrin-Re(I)-diimine-tricarbonyl complexes, together with a detailed electrochemical and photophysical investigation, are discussed. From the state-of-the-art results obtained for the dyad \( \text{fac-}[\text{Re(CO)}_3(\text{bipy})(\text{Zn-4'MPyP})](\text{CF}_3\text{SO}_3) \), a proper modification of the single components has been envisaged in order to improve the efficiency of the photoinduced charge separation process. With this aim, three different dyads have been designed. In two of them, electron-donor tert-butyl (t-Bu) groups (either three, or six, respectively) have been introduced on the meso-phenyl moieties of the zinc-porphyrin, in order to make the it a better electron donor. In the third dyad electron-withdrawing ethyl ester groups have been introduced on the bipy ligand, in order to make the rhenium fragment a better electron acceptor. The photophysical investigation proves that the latter system promotes the fast formation of a charge separated upon visible light irradiation.

In the third chapter, the synthesis and characterization of a new triad is reported. Starting from the rhenium(I) precursor \( \text{fac-}[\text{Re(CO)}_3(\text{dmsO-3})_3](\text{CF}_3\text{SO}_3) \), we present a variation on the synthetic pathway shown in the first chapter, in which the zinc-porphyrin is first coordinated to the rhenium(I)(CO)₃ fragment via an amido-bipyridyl linker unit, leaving the third apical position of the metal center free for the subsequent introduction of a pyridyl functionalized fullerene. The detailed NMR analysis, also in comparison with intermediate systems and appropriate model compounds, has elucidated several structural features of the adduct, and, in particular, highlighted the complexity deriving from the simultaneous presence of two stereogenic centers. A detailed photophysical investigation is also reported, that evidences the formation of the charge separated species, with the positive charge located on the zinc-porphyrin fragment and the negative charge located on the fullerene component.

The fourth chapter is focused on the development of new photoactive triads obtained by a metalloporphyrin-mediated self-assembling strategy. An aluminium-
monopyridylporphyrin platform has been successfully used to form, via based metal hard/soft discriminations, robust photoactive two-component and three-component systems, in one-pot reactions with quantitative yields. As complementary photoactive components, a ruthenium-porphyrin and either a free-base porphyrin or a fulleropyrrolidine, both suitably functionalized with a carboxylic acid group, have been employed. A complete characterization of the two-component and three-component systems is presented. The photophysical properties arising from the two- and three-component systems containing the three different types of porphyrins, investigated by stationary and nanosecond time-resolved emission techniques, are described.

In the fifth chapter, the preliminary investigations on the potential use of liposomes as supramolecular scaffolds for the anchoring of Re(bipy)-based catalysts and metalloporphyrin chromophores, and their potential employment in the photoreduction of CO₂ in water media has presented. Successful inclusion of a Re(bipy) complex, suitably functionalized with a pendant alkyl chain, alone or together with either a tetracationic or a tetraanionic zinc-porphyrin, on different types of liposomes is reported. The preliminary UV-vis surveys focused on the monitoring of the photogeneration of the One-Electron-Reduced species (OER), with either UV or visible light in buffer solution, and on the monitoring of the photostability of the systems, are described.

The sixth, and final chapter contains the experimental section.
Riassunto

Il lavoro di questa tesi di dottorato è diviso in sei parti

Nel primo capitolo, viene presentata una introduzione generale sulla fotosintesi naturale e artificiale, descrivendo e sottolineando l’aspetto fondamentale dei metalli e selezionando alcuni esempi dei sistemi metal-mediated proposti in letteratura come candidati per svolgere processi fotocatalitici come l’ossidazione dell’acqua, produzione di idrogeno e riduzione della CO\textsubscript{2}. Specifici aspetti riferiti al lavoro di questa tesi saranno trattati separatamente nelle sezioni introduttive dei singoli capitoli.

Nel secondo capitolo, viene discussa la sintesi e la caratterizzazione di una piccola libreria di diadi, basati su complessi del tipo zinco-porfirina(monopiridile)-Re(I)-diaminotricarbonile, insieme ad una dettagliata caratterizzazione elettrochimica e fotofisica. Partendo dallo stato dell’arte, in cui sono stati ottenuti risultati per la diade \textit{fac}-[Re(CO)\textsubscript{3}(bipy)(Zn-4’MPyP)](CF\textsubscript{3}SO\textsubscript{3}), è stata prevista una opportuna modificazione delle singole componenti con lo scopo di migliorare l’efficienza del processo di separazione di carica fotoindotto. Con questo obbiettivo, sono state pensate tre differenti diadi. In due di esse sono stati introdotti, sui gruppi meso-fenilici della zinco porfirina, rispettivamente tre a sei gruppi elettron donatori (tert-butilici), con l’intenzione di rendere la zinco porfirina un elettron donatore migliore. Nella terza diade sono stati introdotti sul legante bipiridile dei gruppi elettron attrattori, con l’intenzione di rendere il frammento di renio un migliore elettron accettore. La caratterizzazione fotofisica dimostra che quest’ultimo sistema è in grado di promuovere, sotto irraggiamento di luce visibile, una veloce formazione di uno stato a separazione di carica.

Nel terzo capitolo viene riportata la sintesi e la caratterizzazione di una nuova triade. Partendo dal precursore di renio(I) \textit{fac}-[Re(CO)\textsubscript{3}(dmso-O)](CF\textsubscript{3}SO\textsubscript{3}), viene riportata una variazione del processo sintetico mostrato nel primo capitolo, in cui la zinco porfirina viene prima coordinata al frammento di renio(I)(CO)\textsubscript{3} tramite funzionalizzazione del legante bipiridile per mezzo di un legame ammidico. In questo modo la posizione apicale del centro metallico rimane disponibile per la successiva introduzione di un monoaddotto fullerenico funzionalizzato con un gruppo piridinico. Un’analisi dettagliata della triade, sia in comparazione con gli intermedi sia con opportuni complessi modello, ha ben evidenziato alcune proprietà strutturali dell’addotto, in particolare evidenziando la complessità derivante dalla simultanea presenza di due centri stereogenici. Viene riportata una dettagliata caratterizzazione fotofisica che evidenzia la formazione di una specia a cariche separate con la carica positiva localizzata sul frammento zinco-porfirina e la carica negativa sulla componente fullerenica.
Il quarto capitolo è focalizzato sullo sviluppo di nuove triadi fotoattive ottenute per mezzo di una strategia di auto assemblaggio mediato da una metallo porfirina. Una alluminio-porfirina monopiridile, sfruttando la discriminazione basata sulla teoria hard/soft dei metalli, è stata utilizzata con successo nella la sintesi di solidi sistemi bi- e tri-componenti, ottenuti in un singolo passaggio e con rese quantitative. Come unità fotoattive complementari sono state impiegate una rutenio-porfirina e una porfina o un monoaddotto fullerenico entrambi funzionalizzati con un gruppo acido carbossilico. Viene presentata una completa caratterizzazione sia dei sistemi bi-componenti che tri-componenti. Infine, dei sistemi bi- e tri-componenti contenenti tre differenti di porfirine, vengono descritte le proprietà fotofisiche, ottenute da tecniche di emissione stazionaria e risolte nel tempo.

Nel quinto capitolo, viene descritto uno studio preliminare sull’uso di liposomi come scaffold supramolecolari per l’ancoraggio di catalizzatori basati su complessi Re(bipy) e di cromofori metallo porfirinici, con l’idea di un potenziale uso di questi sistemi per la fotoriduzione della CO₂ in soluzione acquosa. Viene riportata, con successo, l’inclusione, su differenti tipi di liposomi, di un complesso di renio(bipy), opportunamente funzionalizzato con una catena alchilica, sia da solo che in combinazione con zinco porfirine tetracationiche e tetraanioniche. Viene presentata una preliminare caratterizzazione UV-vis nella quale viene monitorata la fotogenerazione della specie ridotta del complesso di renio (OER), sia per irraggiamento UV che con luce visibile, e il monitoraggio della fotostabilità dei sistemi

Il sesto capitolo contiene la sezione sperimentale.
Chapter 1.

General Introduction
Modern civilization is strongly dependent upon fossil fuels, and non-renewable energy sources originally provided by the storage of solar energy performed by photosynthetic organisms. The success of photosynthesis stems from the fact that the raw materials and the energy needed for the process are available in unlimited amount; sunlight, water and carbon dioxide. In a recent report, the global energy consumption in 2008 was estimated in about $530 \times 10^{18}$ J, with 85% of that provided by combustion of fossil fuels. Even though the fossil fuels are consumed every year at the rate of 500000 times faster than Earth produces, the reserves of oil, gas and coal are expected for many years. For this reason, the great concern for the next decades is related to the potentially drastic effect of increased CO$_2$ concentration on global climate.

So, even though fossil fuels will continue to be a major source of energy, human society made a dramatic shift towards carbon neutral energy sources: hydroelectric, biomass and renewables, such as sun, wind, tide and wave. Among these, great importance has been focused on solar energy. It’s remarkable the fact that each day the sun blankets the earth providing society’s yearly energy demands in just over an hour. Actually, there are existing technologies, based on Si photovoltaic cell, capable to capture sunlight and produce electricity and the efficiency and robustness of these photovoltaic systems is improving daily. Nevertheless, these types of photovoltaic systems still represent an expensive way to generate electricity, in comparison with fossil fuels, and they are characterized by a theoretical limitation to the maximum efficiency. For this reason, for a long term sustainable future, it becomes necessary to develop new photovoltaic systems based on the same principles of natural photosynthesis.

1.1 Natural photosynthesis

Nature has developed several photosynthetic systems reflecting the wide variety of habitats, in which the photosynthetic organisms can be found in. However, each system is based on the same principles. The general structural organization, characterizing the photosynthetic organisms universally, is made of an antennae system to absorb light and funnel the excitation energy to the reaction centers (RCs) where a charge separation occurs. This process converts light energy to chemical energy. The use of antennae allows a multitude of pigment molecules to direct light excitation energy to each RC.

Great knowledge for the optimal design of highly efficient light-harvesting antenna has been collected by studying natural light-harvesting apparatus. Several major types of photosynthetic antennae exist, such as the green sulfur bacterial chlorosome, the higher plant light-harvesting complex II (LHClII), the purple bacterial light-harvesting complexes 1, 2 and 3 (LH1–LH3) and many others described in literature. The structures of the antenna systems can be very diverse, reflecting the wide difference of environments in
which the organisms have been found, but they are all based on the same principle of harvesting light energy in the form of coherent excited-state superpositions, referred to as excitons.\textsuperscript{10} In general, they are characterized by highly ordered arrays of pigments for the absorption and transmission of exciton energy via the Forster and Dexter transfer mechanisms.

One of the best understood photosynthetic system is the light-harvesting apparatus of purple non-sulfur bacteria, which typically consists of two pigment–protein complexes, light-harvesting complexes I and II (LHC I and LHC II). The precise arrangement of these complexes has been well elucidated by X-ray crystallography and electron microscopy. The spectroscopic characterization of these systems has revealed that the energy transfer occurs with a dramatic efficient transfer process, towards RC, of 95\%, which means that the energy absorbed by the antenna is almost quantitatively transferred to RC for the subsequent generation of the charge separated state.\textsuperscript{11} A schematic representation of light-harvesting apparatus of purple non-sulfur bacteria is reported in Figure 1.1, in which the cyclic arrangement of pigments in LHC I and LHC II and the reaction center consist of precise self-assemblies of $\alpha$-apoproteins, $\beta$-apoproteins, bacteriochlorophyll, carotenoids and other photoactive units. In this system it was found that the metal–ligand interactions between the histidine residues of the $\alpha$- and $\beta$-apoproteins and the Mg(II) ions at the center of the bacteriochlorophyll hold the chromophores in the right arrangement resulting in a strong exciton coupling, determining very efficient light harvesting and energy transfer processes. The energy is rapidly and efficiently transferred to LHCI and then to the reaction center. This last step is the slowest, but it crucial in order to prevent detrimental back reactions.\textsuperscript{12}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Figure 1.1. Left: schematic depiction of the photosynthetic apparatus of purple non-sulfur bacteria highlighting the arrangement of chromophores LHC II, LHC I and of the reaction center with a summary of the energy transfer processes. Right: enlargement of the reaction center and depiction of the electron transfer.}
\end{figure}

However, the structural aspects that determine the excellent light-harvesting quantum efficiency in natural photosynthesis, is not directly translated into high energy efficiency.
Quantum efficiency in natural photosynthesis is reported based on the probability that one absorbed photon is not wasted but converted into one charge-separated state. Indeed, most photosynthetic organisms can only absorb the higher energy photons of light irradiation (with wavelengths in a range of 700–900 nm, depending on the organism). Moreover, other energy losses contribute to the low quantum efficiency, such as relaxation of higher energy excited states to the lowest energy excited states for internal conversion, intra- and inter-complex Forster Resonance Energy Transfer (FRET), as well as the final conversion process of excitation energy into electrical energy by photoinduced electron transfer reactions.\(^{13}\)

The photosynthesis is recognized as that natural process that has produced oxygen for human life and most of the energy that human society is based on. The process is obtained by the light-driven water-splitting reaction. This reaction is high demanding in terms of energy, requiring, for the conversion of H\(_2\)O and CO\(_2\) to O\(_2\) four equivalents of oxidizing power. The green plants have solved this problem developing a system composed of two photosynthetic centers, PSII and PSI. Here, the solar energy is absorbed by chlorophyll, named P680, and transferred efficiently to the PSII reaction center, in which charge separation takes place. The special pair generated in the PSII RC already has, in principle, the redox potential to drive the formation of hydrogen. Instead, the reducing equivalent is passed along an electron transport chain to PSI (Figure 1.2), where it is excited by the energy of a second photon absorbed by a chlorophyll molecule, known as P700, to lift it to a reducing potential of −1 V or more. In this way, sufficient energy is accumulated to drive the fixation of CO\(_2\).
The P680$^{+}$ species generated in PSII drives the splitting of water at the ‘water oxidizing centre’ (WOC). The WOC is oxidized in one-electron steps from $S_0$ (the most reduced state) to $S_4$ (the most oxidized) by a repeatedly photo-oxidized chlorophyll center, which converts the collected light energy into redox potential energy. The catalyst has been well characterized by X-ray crystallography (Figure 1.2), and it acts by extracting electrons from a catalytic center composed of a cluster of four manganese (Mn$^{4+}$) ions and a calcium ion (Ca$^{2+}$). Nevertheless the mechanism of the reaction is still unknown.$^{14,15}$

### 1.2 Artificial photosynthesis

An ideal artificial photosynthetic system needs to be composed of five components, as shown in Figure 1.3. A light-harvesting antenna, for the solar light absorption, is the first component, that ideally should be constructed with a variety of chromophores to maximize absorption from the UV to the IR region. The antennae have to efficiently funnel the excitation energy toward a photosensitizer. At the photosensitizer, an initial charge separation takes place by generating one electron–hole pair. To maximize the lifetime of this charge-separated state additional donor and acceptor fragments may be included in order to increase the distance between the electron and hole, thus preventing the unwanted recombination and shuttle, instead, the charges toward the last components, i.e., the useful...
catalysts. Given the high degree of complexity of this designed system, a completely functional artificial system has not yet been achieved. Current research is focused on the optimization of antennae, photosensitizers, and catalytic systems, normally as separate or largely simplified object of studies.

**Figure 1.3.** Schematic cartoon for an ideal artificial photosystem.

### 1.2.1 Artificial photosynthetic systems obtained via metal-mediated strategies

As just described above, the natural photosynthetic systems are not perfect machines. One of the lacks of natural antennae is their incapacity to absorb the complete solar light spectrum, which results in a loss of ca. 50% of the incident solar irradiation. This limitation is called “green gap”. To truly take advantage of molecular artificial photosynthesis, light-harvesting antennae that absorb over the entire incident solar spectrum are desired. These antennae must be composed of a variety of strongly absorbing chromophores, that have to be spatially well-organized to promote an efficient and directional energy transfer to a redox center. Among the years, covalent synthesis has provided excellent models for studying directional energy transfer at fixed distances, but it is very demanding in terms of synthetic effort.\(^{16,17}\) For this reason self-assembling strategies are more appealing for the construction of multi-component light-harvesting antennae and redox centers. As well, the natural photosystems share a common motif, in which metal centers play both a role in directing the correct assembling of the photoactive components and also in behaving as catalytic photoactive centers. So, the metal–mediated approach is a very appealing choice for the development of artificial photosystems.\(^{18}\)

The metal-mediated approach has emerged over the years as a general, high yielding synthetic strategy that gives access to a variety of 2D and 3D fascinating supramolecular ensembles.\(^{19-22}\) One on the most attractive characteristics of this approach is that the design
of supramolecular structures can be guided by geometrical principles relaying on the highly directional and predictable nature of the metal to ligand coordination sphere and on the geometry of the rigid organic polytopic donors. Moreover, the choice of the metal ion and of its ancillary ligands, allow to modulate the thermodynamic and kinetic stability of the metal to ligand bond, thus complementing the geometrical control with a fine-tuning of the resulting supramolecular adducts stability, kinetics, and, not least, with the potential tailoring of the adducts with additional functional properties. Indeed, the metal fragments (that can be classical metal coordination compounds, large aromatic metallomacrocycles, metallodendrimers, polyoxometalates, etc), may be cleverly chosen in order to introduce some of the photoactive characteristics of interest (i.e., light harvesting, electron shifting, reaction catalysis), within the metal-directed assembling of the architectures. As well, the ancillary ligands may be usefully tailored in order to anchor the active species to a variety of supports. As a matter of facts, by following this design strategy, a great variety of antennae and photoactive components have been synthesized and studied.  

Few selected examples showing how the metal-mediated approach has been successfully implemented for the obtainment of multi-component photoactive systems, with specific reference to relevant photocatalytic processes, will be briefly described.

1.2.2 Homogeneous photocatalytic $\text{H}_2\text{O}$ oxidation metal-mediated systems

The solar light energy, after being harvested and converted in a charge separated state, employs catalytic centers in order to convert the oxidizing and reducing equivalents thus produced into chemical fuels. At the heart of both natural and artificial photosynthesis is the energetic demand of the water splitting half-reaction that consists in the conversion of two molecule of water into one molecule of dioxygen, with the concomitant delivery of four electrons and four protons:

$$2\text{H}_2\text{O} + 4\hbar\nu \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$$

In addition, the four oxidizing equivalents have to be delivered at a faster rate than non-productive back-electron transfer, in order to drive the catalytic turnover.

At the current state of the art synthetic water-oxidation catalysts generally do not compete with the rate, efficiency, and low overpotential exhibited by the protein-supported Mn$_4$Ca water-oxidation catalyst found in PS II.$^{34,35}$

One of the first synthetic molecular water-oxidation catalyst was reported by Meyer and co-workers in 1982. Known as the ‘blue dimer’, the bimetallic catalyst has the formula $\text{cis,cis-}[\text{(bpy)}_2(\text{H}_2\text{O})\text{Ru}^{\text{III}}\text{ORu}^{\text{III}}(\text{OH}_2)(\text{bpy})_2]^{4+}$ (Figure 1.4).$^{36}$
This discovery opened the field to the study of a variety of other catalysts, based on mononuclear Ru(II), Ir(III), and Fe(IV), as well as dinuclear Ru(II)-Mn(II), Mn(III,IV), and tetranuclear Ru(II), Mn(II), and Co(III) active centers. Recently, new catalysts based on a strict biomimicry of the Mn₄Ca cluster in PS II have been also developed.

The common issue for these homogeneous catalysts is the photooxidative decomposition of organic ligands. With this regard, tetranuclear Ru(II) oxygen evolving catalyst with robust all-inorganic polyoxometallate was recently introduced by Bonchio and coworkers (Figure 1.5). Ru₄–POM has been shown to oxidize water in the homogeneous phase with small overpotential (0.35 eV), high turnover frequency (> 450 h⁻¹), and no degradation.

A photocatalytically active metal-mediated system was reported for the first time in 2012 by Sun and co-workers, and is shown in Figure 1.6. The triad, upon visible light irradiation (λ > 400 nm) and in the presence of sodium persulfate as sacrificial oxidant, evolves O₂ with a TON of 38 after 70 minutes, while the non-assembled components exhibit only 8 turnover numbers. Oxidative quenching of the peripheral pyridyl-substituted Ru(bpy)₃²⁺ units by the sacrificial agent S₂O₇²⁻, followed by electron transfer to the central catalyst, drives O₂ evolution. Dissociation of the pyridyl axial ligands from the central metal catalyst results in a slow loss of catalytic activity.
1.2.3 Homogeneous photocatalytic H₂O and CO₂ reduction metal-mediated systems

In the natural photosynthesis the protons and electrons generated during water splitting are used to produce ATP and NADPH, respectively, which provide the chemical driving force for storing solar energy in the form of carbohydrates. Artificial photosynthetic systems are generally designed to catalyze the reduction of protons, thus converting the solar energy in the form of H₂. However, reduction of CO₂ is also a feasible process for the solar energy capture. The reductive side of artificial photosynthesis generating H₂ requires only two reducing equivalents, as opposed to the four oxidizing equivalents necessary for water oxidation, making the photocatalytic H₂ evolution a more surmountable task. A large number of robust catalysts have been reported based on mononuclear Co(II), Rh(II), Ir(III), or dinuclear Fe(II) active sites.⁴²,⁴³

Promising results from first generation metal-mediated photocatalysts composed of one photosensitizer attached to a catalyst, show that the assembled dyads generally outperform non-assembled control systems, in which the photosensitizer and catalyst are not connected. H₂ evolving cobaloxime catalysts are ideal platforms to construct dyads because an axial coordination site on Co(II) may be occupied by pyridyl-based ligands, without dramatically affecting the catalytic activity. A variety of cobaloxime photosensitizer-catalyst dyads has been reported, in which the photosensitizer is connected to the catalyst through a pyridyl substituent.⁴⁴–⁴⁷

In 2008, Fontecave and co-workers first reported H₂ evolution from dyads in which a Ru(bipy)₃ is coordinated to a cobaloxime, in the presence of Et₃N as the sacrificial reductant and Et₃NH⁺ as the protons source. (Figure 1.7).⁴⁵ Over a period of 4 h the dyad exhibited 104 turnovers, a value significantly higher compared with the non-assembled multi-component analogue.
One recent and interesting system was reported in collaboration between our group and the group of Scandola, in which a monopyridyl porphyrin was used as pivotal ligand for the three-component metal-mediated assembling of the sacrificial donor/sensitizer/catalyst system (Figure 1.8). Efficient quenching of the singlet excited state of the porphyrin sensitizer consequent to either the association with the catalyst or to the sacrificial donor has been observed in organic media, but a substantial amount of sensitizer is present as free, unquenched species in water/organic solvent mixture, that are actually used for the H₂ evolution experiments. Under these conditions, photocatalytic hydrogen evolution arises from a bimolecular reaction of the sensitizer triplet state with the sacrificial donor. This primary photoreaction yields the reduced photosensitizer, which further reacts bimolecularly with the catalyst, thereby triggering the photocatalytic hydrogen production, reaching maximum turnover numbers of 352. It is interesting to remark that this good result in terms of TN has been obtained using earth abundant metals. This a main goal for the future development of new photocatalytic systems.

In light of these observations, the system has been further developed by the same authors, by varying the nature of the photoactive partners involved. An efficient photocatalytic hydrogen evolution was observed in phosphate buffer by using mixed
Ru(bpy)$_3^{2+}$ as sensitizer, ascorbic acid as sacrificial donor, and a water-soluble Co(II)porphyrin as catalyst (Figure 1.9).\textsuperscript{49} In pure water, under continuous visible irradiation, TON up to 725 were achieved.

![Figure 1.9](image1.png)

**Figure 1.9.** Schematic depiction of the H$_2$ evolving system reported by Iengo, Scandola et al.\textsuperscript{49}

Re(I) complexes of the type $\text{fac-[Re(bpy)(CO)_3L]}^+$ ($L = \text{Cl, Br, P(OEt)}_3$) are well-known photocatalyst for CO$_2$ reduction operating under UV irradiation. In 2005 Ishitani and co-workers developed a first example of two-component system, in which the catalyst is sensitized with a Ru(bipy)$_3$ chromophore (Figure 1.8).\textsuperscript{50}

![Figure 1.10](image2.png)

**Figure 1.10.** Schematic depiction of the Ru-Re dyad reported by Ishitani.\textsuperscript{50}

The dyad has proved capable of visible light-driven photocatalytic CO$_2$ reduction. In a CO$_2$ saturated DMF : TEOA (5 : 1) solution, containing 1-benzyl-1,4-dihydronicotinamide as the sacrificial reductant, the system has shown 170 TN, after 16 h of irradiation at $\lambda \geq 500$ nm, whereas the non-assembled model system exhibited only 101.

The few examples reported briefly here, are designed to work as photocatalyst in homogeneous solution. The main difference between homogeneous and heterogeneous catalysis is the fact that in the case in homogeneous case, every single catalytic entity can act as a single active site. This makes homogeneous catalysts intrinsically more active and selective compared to the heterogeneous ones. On the other hand, most of the organic ligands connected to the metal catalysts usually show photodegradation, which leads to
relatively low efficiency (low TONs) compared with their heterogeneous counterparts. One possible solution was reported by Bonchio and coworkers, in regard to water oxidation. In order to combine the high rate of O₂ evolution of homogeneous catalysts with the robustness of heterogeneous catalysts, catalysts were prepared combining the tetranuclear Ru(II) oxygen evolving catalyst with robust all-inorganic polyoxometallate (POM). These polyanion ligands are excellent σ-donors stabilizing the high oxidation states required for water oxidation thus producing homogeneous catalyst with a much higher stability.⁴⁰

1.3 References

(1) Barber, J.; Tran, P. D. J. R. Soc. Interface 2013, 10, 1–16.


(41) Li, F.; Jiang, Y.; Zhang, B.; Huang, F.; Gao, Y.; Sun, L. Angew. Chemie Int. Ed. 
2012, n/a–n/a.


(45) Fihri, A.; Artero, V.; Razavet, M.; Baffert, C.; Leibl, W.; Fontecave, M. Angew. 

694, 2814–2819.

(47) McCormick, T. M.; Han, Z.; Weinberg, D. J.; Brennessel, W. W.; Holland, P. L.; 

19, 9261–71.

1842–4.

(50) Gholamkhass, B.; Mametsuka, H.; Koike, K.; Tanabe, T.; Furue, M.; Ishitani, O. 
Chapter 2.

Improving the efficiency of the photoinduced charge-separation process in rhenium(I)–zinc porphyrin dyads by simple chemical functionalization*

List of abbreviations

bipy = 2,2'-bipyridine
py = pyridine
4'MPyP = 5-(4'-pyridyl)-10,15,20-(phenyl)-porphyrin
3'-MPyP = 5-(3'-pyridyl)-10,15,20-(phenyl)-porphyrin
3-pic = 3-picoline
TPP-bipy = 5-[4-(4-Methyl-2,2'-bipyridine-4'-carboxyamidyl)phenyl]-10,15,20-(phenyl)-porphyrin
TPyP = 5,10,15,20-(4'-pyridyl)porphyrin
TPP = meso-tetraphenylporphyrin
tBu = tert-butyl
4'MPytBuP = 5-(4'-pyridyl)-10,15,20-(4'-tert-butylphenyl)porphyrin
4'MPydBuP = 5-(4'-pyridyl)-10,15,20-(3,5-di-tert-butylphenyl)porphyrin
4,4'-DEC-bipy = 4,4'-diethoxycarbonyl-2,2'-bipyridine
tBuTPP = meso-(4'-tert-butyl)-tetraphenylporphyrin
dBuTPP = meso-(3,5-di-tert-butyl)-tetraphenylporphyrin
Zn·TPP = zinc(II)-5,10,15,20-tetraphenylporphyrin
ZntBuPP = zinc(II)-meso-(3,5-di-tert-butyl)-tetraphenylporphyrin
ZndBuTPP = zinc(II)-meso-(3,5-di-tert-butyl)-tetraphenylporphyrin
MLCT = Metal-to-Ligand Charge Transfer
ISC = Inter System Crossing
CV = Cyclic Voltammetry

2.1 Introduction

Photoinduced charge separation is the key process for the conversion of solar light into chemical energy in the natural photosynthesis. The same principles have been applied for the construction of artificial photosynthetic systems for performing tantalizing reactions such as, CO₂ or water reduction.¹⁴ The simplest artificial system for charge-separating purposes is a two-component donor-acceptor combination (dyad), in which the donor unit
(D), following visible light absorption, induces an electron transfer to the acceptor unit (A) (Figure 2.1).

![Schematic representation of a Donor-Acceptor dyad.](image)

**Figure 2.1.** Schematic representation of a Donor-Acceptor dyad.

To this end, both covalent and non-covalent approaches have been widely employed to connect the two units. The covalent approach is well-suited to obtain robust and geometrically well defined structures, but, at the same time, it is very demanding in terms of synthesis, and in general low yielding.\(^5\)\(^\text{–}\)\(^13\) Vice versa, non-covalent strategies take advantages of milder reaction conditions, combinatorial flexibility, and repair capabilities. Among these, considerable interest has been given to the use of metal coordination for assembling molecular components into appropriate functional structures (‘metal-mediated’ approach).\(^13\)\(^\text{–}\)\(^20\)

Recently polypyridine-Re(I)-tricarbonyl complexes have shown attractive properties from a supramolecular point of view. In fact, Re(I) makes strong and inert bonds with N-based ligands, opening the possibility to include these complexes in more elaborate assemblies.\(^15\)\(^\text{–}\)\(^22\) Moreover, Re(I)(CO)\(_3\) (diimine) fragments have been widely studied as catalysts for CO\(_2\) reduction.\(^23\)\(^\text{–}\)\(^26\) These reasons make the Re(I) fragment a good candidate for the construction of supramolecular photoactive systems containing pyridyl functionalized chromophores, such as porphyrins or ruthenium(bipy)_3.

![Schematic depiction of some Ru(bipy)_3-Re(bipy)(L) conjugates.](image)

**Figure 2.2.** Schematic depiction of some Ru(bipy)_3-Re(bipy)(L) conjugates \(\text{fac-}[\text{Re}(\text{CO})_3(\text{bipy})(\text{M}+4\text{MPyP})](\text{CF}_3\text{SO}_3)\) (left) and \(\text{fac-}[\text{Re}(\text{CO})_3(3\text{-pic})(\text{M}+\text{TPP-bipy})](\text{CF}_3\text{SO}_3)\) (right).\(^13\)\(^14\)
In particular, the connection of porphyrins to fac-[Re(CO)$_3$](diimine)$^+$ fragments can occur in two different ways: either the diimine is conjugated to a peripheral group on the porphyrin (in this case the coordination sphere of Re(I) must be completed by a sixth ligand, either neutral or anionic), or the porphyrin itself behaves as a ligand through direct coordination of a peripheral meso-pyridyl group to the Re(I)(diimine) fragment. The group of Perutz has described compounds of the first type, and in particular adduct fac-[Re(CO)$_3$(3-pic)(M·TPP-bipy)](CF$_3$SO$_3$) (M = Mn or Zn) (Figure 2.2, right), obtained by reaction of a meso-tetraphenylmetalloporphyrin linked via an amide linker to 2,2'-bipyridine with the Re(I) precursor [ReBr(CO)$_5$], in the presence of picoline and silver triflate. Recently, our group has described the synthesis of compounds of the second type (Figure 2.3).

These structurally different systems have been obtained with a common synthetic strategy from a very convenient rhenium precursor, always developed in our group. The complex fac-[Re(CO)$_3$(dmso-O)$_3$](CF$_3$SO$_3$) (1), was efficiently prepared in one step from [ReBr(CO)$_5$] dissolved in acetone in presence of dimethylsulfoxide and silver triflate (AgCF$_3$SO$_3$). In general, it was demonstrated that this complex is a better precursor for the synthesis of Re(I) adducts of general formula fac-[Re(CO)$_3$(L-L)L](X), in which L-L and L are nitrogen-based ligands, when compared to the commonly used starting compounds [ReBr(CO)$_5$] and fac-[Re(CO)$_3$(CH$_3$CN)$_3$](X) (X = PF$_6$, BF$_4$, ClO$_4$). Indeed, 1 is much more versatile than [ReBr(CO)$_5$] as it allows for an efficient stepwise reaction (generally in mild conditions, and not needing the tedious work-up to remove silver salts, as very conveniently and once-for-all it is performed at the act of the precursor synthesis). In the first step the chelating diimine ligand of choice is introduced in the metal equatorial position, with isolation of the intermediate fac-[Re(CO)$_3$(L-L)(dmso-O)](CF$_3$SO$_3$), and in the second subsequent step a monodentate nitrogen-based ligand (among a potentially infinite variety) is coordinated in the apical position of the metal, also allowing for the parallel synthesis of the appropriate model compounds. Moreover, the O-bonded
dimethylsulfoxide ligands of \textbf{1} are more easily exchanged compared to the coordinated acetonitriles in \textit{fac-}[Re(CO)\textsubscript{3}(CH\textsubscript{3}CN)\textsubscript{3}](X). In addition, by changing the nature of the silver salt employed in for synthesis of \textbf{1}, it is possible to easily vary the nature of the counterion, thus tuning the solubility of \textbf{1} and of its final adducts. In Figure 2.4 the X-ray structures of \textbf{1}, of the intermediate \textit{fac-}[Re(CO)\textsubscript{3}(bipy)(dmso-O)](CF\textsubscript{3}SO\textsubscript{3}), and of one of its derivatives are reported.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{Schematic depiction of \textit{fac-}[Re(CO)\textsubscript{3}(dmso-O)](CF\textsubscript{3}SO\textsubscript{3}) (1, left), \textit{fac-}[Re(CO)\textsubscript{3}(bipy)(dmso-O)](CF\textsubscript{3}SO\textsubscript{3}) (centre) and \textit{fac-}[Re(CO)\textsubscript{3}(bipy)(4,4'-bipy)](CF\textsubscript{3}SO\textsubscript{3}) (right) and X-ray structures of the corresponding cations.\textsuperscript{37}}
\end{figure}

In terms of photophysical properties, the rhenium-diimine fragment possess a long-lived Re-(diimine) triplet MLCT excited state, that forms by UV irradiation after population of the corresponding singlet excited state and fast inter system crossing (ISC) (Figure 2.5). This characteristic makes this species a potentially interesting unit for the construction of photoactive dyad systems.
Figure 2.5. Schematic energy level diagram for a $\text{fac-}[\text{Re(CO)}_3\text{(diimine)}]$ fragment.

However, the high energy required in order to activate this excited state is detrimental in view of its possible practical applications. On the other hand, it is well known that the rhenium-diimine fragment can behave as a good electron acceptor moiety, as it possess a relatively accessible one-electron reduction potential, that can be appropriately tuned by varying the nature of the diimine and of the other ligands around the metal coordination sphere. Therefore, this metal fragment, coupled with appropriate photosensitizer/donor moieties may well serve as electron acceptor for the useful conversion of visible light.$^{38,39}$

In this context, the great varieties of appealing features of porphyrins and/or metalloporphyrins make them ideal partners for the construction of rhenium-mediated photoactive assemblies designed to emulate, at the molecular level, light-induced functions typical of biological systems such as antenna effect and photoinduced charge separation.$^{17,40,41}$

In the metalloporphyrin-rhenium conjugate developed by Perutz, bearing a 3-picoline as apical ligand (Figure 2.2), a fast photoinduced electron transfer process from the metalloporphyrin to the Re(I)-bipy fragment, after excitation of the porphyrin with visible light, was revealed by time-resolved infrared spectroscopy.$^{32}$ On the contrary, a detailed photophysical study on the free-base porphyrin-rhenium systems (Fb-Re) developed previously in our group showed no evidence for the occurring of photoinduced electron transfer processes from the attached porphyrin to the Re(bipy) fragment, upon visible light irradiation. As a matter of fact, and how it could be anticipated from electrochemical studies on model compounds, the energy level of the charge separated Fb$^+$-Re$^-$ in compounds such as $\text{fac-}[\text{Re(CO)}_3\text{(bipy)(4'MPyP)}](\text{CF}_3\text{SO}_3)$ (Figure 2.3) results to be energetically higher than that of the singlet excited state of the porphyrin, that gets populated after visible light irradiation (Figure 2.6). The moderate quenching of the porphyrin fluorescence emission observed for this system can be related uniquely to an
inter-system crossing process (ISC) promoted by the strong spin-orbit coupling with the rhenium atom (heavy-atom effect).

Figure 2.6. Energy level diagram for fac-[Re(CO)₃(bipy)(4'MPyP)](CF₃SO₃) and possible photophysical processes.

Modifications in either the relative orientation of the porphyrin and the bipyridyl units (e.g. fac-[Re(CO)₃(bipy)(3'MPyP)](CF₃SO₃), Figure 2.3) or in the number of peripheral Re(I)-bipy fragments attached to the porphyrin unit (e.g. fac-{Re(CO)₃(bipy)}₄(μ-4'TPyP)(CF₃SO₃)₄) was found to be detrimental as it leads to an increase in the energy of the charge-separated state and to a more efficient quenching of the Fb fluorescence by inter-system crossing. Upon insertion of Zn(II) in the porphyrin core of fac-Re(CO)₃(bipy)(4'MPyP)](CF₃SO₃), the photophysical behavior of the adduct changes appreciably. In particular, the zinc-porphyrin singlet excited state possess a higher energy than that of Fb, and, concomitantly the charge separated state ZnP⁺-Re⁻ is placed at lower energy compared to Fb⁺-Re⁻, and becomes almost isoenergetic with ¹⁺ZnP-Re (Figure 2.7).
Chapter 2

Still, there was no evidence for electron transfer process occurring upon selective irradiation of the zinc-porphyrin, whereas the addition of pyridine (that binds axially to zinc and thus affects the metalloporphyrin oxidation potential) lowers the energy of the charge separated state and a moderately efficient photo-induced electron transfer process could be observed (Figure 2.7 and Scheme 2.1).  

These results show that these systems have a borderline situation in terms of energetic levels, and slight modifications in the substitution pattern of the porphyrin chromophore and/or in the coordination sphere of the Re(I)-bipy fragment may increase the energy difference between the two states and, as a consequence, the efficiency of the photo-induced electron transfer process.
In this work, the design and synthesis of a small library of dyads, together with a detailed photophysical investigation, are presented. Starting from the results obtained for the dyad \( \text{fac-}[\text{Re(CO)}_3(\text{bipy})(\text{Zn-4'MPyP})](\text{CF}_3\text{SO}_3) \), a proper modification of the single components has been envisaged in order to improve the efficiency of the photoinduced charge separation process. With this aim, dyads 3b–5b have been designed. In 4b and 5b electron-donor tert-butyl (t-Bu) groups (either three, or six, respectively) have been introduced on the meso-phenyl moieties of the zinc-porphyrin in order to make the metalloporphyrin unit a better electron donor. In 3b electron-withdrawing ethyl ester groups have been introduced on the bipy ligand in order to make the rhenium fragment a better electron acceptor (Figure 2.8).

**Figure 2.8.** Functionalized rhenium(I)–zinc porphyrin dyads 3b–5b.
2.2 Results and discussion

2.2.1 Synthesis

4′MPyP, and the tBu-substituted monopyridylporphyrins 4′MPytBuP and 4′MPydBuP, were synthesized following the Adler-Longo procedure. 4′MPyP, 4′MPytBuP and 4′MPydBuP were obtained as microcrystalline violet solids by mixing 3 equivalents of benzaldehyde, 4-tert-butylbenzaldehyde and 3,5-di-tert-butylbenzaldehyde, respectively, with 1 equivalent of 4-pyridinecarboxaldehyde and 4 equivalents of pyrrole in propionic acid, followed by column chromatography of the resulting mixtures. The substituted bipy ligand 4,4′-DEC-bipy was prepared as described in the literature by esterification of (2,2'-bipyridine)-4,4′-dicarboxylic acid with ethanol.

![Scheme 2.2](image)

Scheme 2.2. Synthesis of dyad 3b with the yield of isolated products in each step. Reagents and conditions: (i) 4,4′-DEC-bipy, acetone, reflux, 1 h; (ii) 4′MPyP, CHCl₃, reflux, 8 h; (iii) Zn(OAc)₂·2H₂O, CHCl₃/MeOH, room temperature, overnight.

The new dyads 3b–5b were conveniently prepared via a common efficient stepwise procedure from the rhenium(I) precursor fac-[Re(CO)₃(dmso-O)]₃(CF₃SO₃) (1); the synthetic pathway for dyad 3b is reported in Scheme 2.2. The substituted bipyridyl ligand 4,4′-DEC-bipy, was introduced first, followed by the coordination of 4′MPyP. The intermediate products were isolated by precipitation, in good yield, and fully characterized. The last step was the quantitative insertion of the zinc ion inside the porphyrin core of the conjugate. The same procedure, and experimental conditions have been used for the high
yielding synthesis of dyads 4b and 5b, using the conventional 2,2'-bipyridine and the monopyridylporphyrins 4'MPyBuP and 4'MPydBuP, respectively. Dyads 3b–5b are purple solids soluble in a wide range of organic solvents.

For a better understanding of the spectroscopic properties of the above systems, some model compounds were also prepared (Figure 2.9). ZnTPP, the corresponding tBu-substituted TPPs Zn-tBuTPP and Zn-dtBuTPP, and fac-[Re(CO)₃(bipy)(py)](CF₃SO₃) were synthesized and purified according with the literature.³⁷,⁴²,⁴³ The rhenium complex fac-[Re(CO)₃(4,4'-DEC-bipy)(py)](CF₃SO₃) (6) was obtained as yellow microcrystalline solid in very good yield (85%) by treatment of fac-[Re(CO)₃(4,4'-DEC-bipy)(dmso-O)](CF₃SO₃) (2, see also Scheme 2.2) with a large excess of pyridine (DCM, room temperature, for 24 h).

![Schematic depiction of model compounds ZnTPP, Zn-tBuTPP, Zn-dtBuTPP, fac-[Re(CO)₃(bipy)(py)](CF₃SO₃) and fac-[Re(CO)₃(4,4'-DEC-bipy)(py)](CF₃SO₃) (6).](image)

2.2.2 Solution and solid state characterization

Dyads 3b–5b and the model complexes have been fully characterized in solution by a variety of techniques (ESI mass spectrometry, NMR, IR, UV-vis and emission spectroscopies); 4b and 6 were also characterized in the solid state (X-ray).
The ESI mass spectra of all compounds show a single peak of the corresponding molecular ion \([M – CF_3SO_3]^+\), with the correct isotopic distribution. As example, the ESI mass spectrum of 4b is reported in Figure 2.10.

![Figure 2.10](image)

Figure 2.10. ESI mass spectrum of fac-[Re(CO)₃(bpy)(Zn·4'MPytBuP)](CF₃SO₃) (4b); calculated for \([M – CF_3SO_3]^+\) 1272.3, found 1272.5. Inset: (left) calculated (program IsoPro3) and (right) experimental isotopic distribution of the molecular ion peak \([4b – CF_3SO_3]^+\).

A full NMR characterization in solution has been performed for dyads 3b–5b and the model compounds. A few representative features will be now described. In Figure 2.11 a comparison of the \(^1\)H NMR spectra (CDCl₃) of 6 and of the ligand 4,4'-DEC-bipy is reported. Relative integration of the proton resonances of the pyridyl and the bipyridyl diethyl ester fragments in the spectrum of 6 has the correct ratio. All the proton resonances of the bipy ligand in 6 are downfield shifted with respect to unbound 4,4'-DEC-bipy. This effect is due to the coordination to the metal center with a consequent deshielding effect, more pronounced for the protons closer to the metal center (\(\Delta\delta = +0.38\) for H₆,₆' and H₅,₅', while the resonances of H₃,₃' and those of the protons of ethyl ester groups are almost unchanged). Seemingly, coordination of pyridine or a pyridyl moiety to metal fragments, e.g. fac-Re(CO)₃(Br), induces normally a consistent downfield shift of the pyₐ proton resonances.\(^{15,22}\) On the contrary, in the \(^1\)H NMR spectrum of 6, the pyₐ doublet is upfield shifted (\(\Delta\delta = –0.44\)) as compared to unbound pyridine. This unusual behavior is caused by the shielding effect of the adjacent, and almost orthogonal, bipyridyl ligand.
In Figure 2.12 the downfield region of the $^1$H NMR spectrum (CDCl$_3$) of conjugate 3b is shown, in comparison with that of 4'MPyP. In the spectrum of 3b, all the resonances are resolved and display the correct relative integration (full assignment was done by means of a H–H COSY experiment). Once again, the py$_a$ doublet is upfield shifted ($\Delta \delta = -0.46$) as compared to the unbound porphyrin (Figure 2.12). This unusual feature, caused by the shielding effect of the bipyridyl ligand, as just described for the simpler model compound 6, and noted previously for fac-[Re(CO)$_3$(bipy)(Zn-4'MPyP)](CF$_3$SO$_3$), is common to all the dyads described here. Finally, the disappearance of the resonance at very high fields pertaining to the inner –NH porphyrin protons (at $\delta = -2.79$ ppm in the $^1$H NMR, CDCl$_3$, of the free-base analogue 3a (see also Scheme 2.2), is indicative of the presence of the zinc ion inside the porphyrin core. The H–H COSY spectrum (CD$_3$OD) of 5b is reported in Figure 2.13. In this spectrum the cross peak correlations of both the bipy and the pyridylporphyrin resonances, can be nicely observed. In particular, the doublet at $\delta = 8.79$ ppm can be assigned as the overlap of the resonances arising from the bipyridyl ligand.

*Zn-4'MPyP self-assembles in solution via axial coordination of the peripheral pyridyl group to the zinc center, generating broad and concentration dependent spectra, thus making a direct comparison not feasible.
protons $H_{3,3'}$ and the porphyrin protons $py_a$, as two cross peak correlations with $H_{4,4'}$ and $py_b$, respectively, can be detected.

Figure 2.12. Downfield region of the $^1$H NMR spectrum (CDCl$_3$, 400 MHz) of $4'MPyP$ (top) and conjugate $3b$ (bottom), and schematic depiction with the labeling scheme. Inset: highfield region of the $^1$H NMR spectrum of $3b$. 
Figure 2.13. Downfield region of the H-H COSY spectrum (CD$_3$OD, 500 MHz) of conjugate 5b, schematic depiction with labeling scheme. Proton resonances showing cross peak correlations are indicated with circles of the same color.

The IR spectra of dyads 3b-5b and the model compound 6 show the characteristic pattern of the $\{\text{fac-Re(CO)}_3\}^+$ fragment, with one carbonyl stretching band at $\nu = 2035$ cm$^{-1}$ and two carbonyl stretching bands, sometime overlapping, in the range of 1950–1930 cm$^{-1}$ (Figure 2.14). For both dyad 4 and model 6 an additional stretching band relative to the CO of the ester groups at $\nu = 1725$ cm$^{-1}$ is also present.
Figure 2.14. IR solution spectra (CHCl₃), limited to the CO stretching region, of \( \text{fac-}[\text{Re(CO)}₃(4,4'\text{-DEC-bpy})(\text{py})](\text{CF}_₃\text{SO}_₃) \) (6) (blue trace), \( \text{fac-}[\text{Re(CO)}₃(\text{bpy})(\text{Zn·4'MPydBuP})](\text{CF}_₃\text{SO}_₃) \) (5b) (red trace), and \( \text{fac-}[\text{Re(CO)}₃(4,4'\text{-DEC-bpy})(\text{Zn·4'MPyP})](\text{CF}_₃\text{SO}_₃) \) (3b) (black trace).

The absorption spectra of the dyads 3b-5b are practically identical and dominated in the whole spectral region by the zinc-porphyrin component, with an intense Soret band at ca. 420 nm. The insertion of zinc in the porphyrin ring is confirmed by the presence of only two additional weaker Q bands, between 500 and 700 nm, whereas in the free-base analogues 3a-5a the typical four Q band pattern is observed (Figure 2.15). The rhenium(bipy) unit absorbs in the UV region only, exhibiting a MLCT Re → bipy band at ca. 350 nm, partially hidden by the porphyrin Soret band tail, and intense ligand-centered transitions below 330 nm. Moreover, the dyads absorption spectra are a good superposition of those of the model compounds ZnTPP, except for a slight red shift of the Soret band (\( \Delta \lambda = 5 \) nm) consequence of the coordination of the pyridylporphyrin to the metal center, and \( \text{fac-}[\text{Re(CO)}₃(\text{bpy})(\text{py})](\text{CF}_₃\text{SO}_₃) \) (Figure 2.15). This fact indicates that there are no relevant interactions between the electronic ground states of the components within the dyads (i.e., (metallo)porphyrin and rhenium(bipy) fragment). The emission spectra of the dyads has been also recorded, and they are characterized by the typical fluorescence bands of the zincporphyrin unit, with intensities partially (for 4b and 5b) and almost totally (3b) quenched if compared with the emission of the corresponding zinc-tetraphenylporphyrins models (see below, Table 2.2 and Figure 2.18).
Figure 2.15. Absorption spectra (DCM, concentrations = $5.0 \times 10^{-5}$ M) of $dTBuTPP$ (black line), $fau-{[Re(CO)_{3}(bipy)(4'dtMPyP)](CF_{3}SO_{3})}$ (5a) (red line) and $fau-{[Re(CO)_{3}(bipy)(Zn·4'dtMPyP)](CF_{3}SO_{3})}$ (5b) (blue line) Inset: absorption spectra in the 500 – 700 nm range.

Single crystals of 4b and 6, suitable for X-ray diffraction, were obtained by slow diffusion of $n$-hexane into DCM solutions of the compounds. The X-ray molecular structures of 6 and of the cation of 4b are shown in Figure 2.16. The coordination bond lengths and angles are unexceptional and in agreement with those of similar rhenium(I) porphyrin conjugates previously described by our group (see Experimental Section for details).$^{36,45}$

Figure 2.16. X-ray structures of the cation of 2 (left) and of 6 with selected atom labeling scheme; colour code: C = gray, O = red, N = blue, Re = pink, Zn = white, S = pale yellow, F = green, H = yellow.
2.2.3 Electrochemical and Photophysical characterization of dyads 3b–5b.

In collaboration with Prof. M.T. Indelli (University of Ferrara), a detailed electrochemical and photophysical investigation on dyads 3b-5b has been carried out. The electrochemical properties of dyads 3b-5b were examined by cyclic voltammetry (CV) in DCM solutions focusing on the potential values for the first oxidation and reduction processes relative to the zinc-porphyrin and to the Re(bipy) fragments, respectively. In Figure 2.17 the CV of 3b is reported.

For comparison, the zinc-tetraphenylporphyrins, Zn·TPP and Zn·dBuTPP, and the rhenium model complexes 6 and fac-[Re(CO)₃(bipy)(py)](CF₃SO₃) were studied in the same experimental conditions. Some indicative results are summarized in Table 2.1. The data for dyad fac-[Re(CO)₃(bipy)(Zn·4'MPyP)](CF₃SO₃), previously investigated, are also reported for comparative purposes. The results obtained for the reference zinc-porphyrins clearly show that the introduction of the electron donor tBu substituents on the meso-phenyl rings has only a small effect on the oxidation potential of the metalloporphyrin. Conversely, the presence of the electron-withdrawing ethyl ester groups on the bipy ligand causes a large positive shift (ca. +0.4 V) in the reduction potential of the rhenium(bipy) unit, which thus becomes significantly easier to reduce. As expected by a comparison with similar systems, the voltammetric behavior of these systems indicate their supramolecular nature. In fact, comparing the redox potentials of 3b and 5b with those of the corresponding zinc-tetraphenylporphyrin models (oxidation waves) and those of the model complexes 6 and fac-[Re(CO)₃(bipy)(py)](CF₃SO₃) (reduction waves), the values are almost identical.
Table 2.1. CV data for dyads 3b and 5b and for the model compounds.\(^a\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(E_{1/2}) (red) V</th>
<th>(E_{1/2}) (ox) V</th>
<th>(E^{o}(S_1)) (b) eV</th>
<th>(\Delta G^{c}) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn-TPP</td>
<td>–1.38</td>
<td>+0.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn-dtBuTPP</td>
<td>–1.50</td>
<td>+0.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>fac-<a href="CF(_3)SO(_3)">Re(CO)(_3) (bipy)(py)</a>(^d)</td>
<td>–1.13</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fac-<a href="CF(_3)SO(_3)">Re(CO)(_3) (bipy)(Zn·4'MPyP)</a>(^d)</td>
<td>–1.16</td>
<td>+0.83</td>
<td>2.04</td>
<td>–0.05</td>
</tr>
<tr>
<td>fac-<a href="CF(_3)SO(_3)">Re(CO)(_3) (bipy)(Zn·4'MPyBuP)</a>(^d)</td>
<td>–1.15</td>
<td>+0.79</td>
<td>2.03</td>
<td>–0.09</td>
</tr>
<tr>
<td>fac-<a href="CF(_3)SO(_3)">Re(CO)(_3) (bipy)(Zn·4'MPyP)</a>(^d)</td>
<td>–0.71</td>
<td>+0.88</td>
<td>2.02</td>
<td>–0.42</td>
</tr>
</tbody>
</table>

\(^a\)All measurements were made in argon-purged DCM solutions at 298 K [0.1 M TBA(PF\(_6\)) as the supporting electrolyte, scan rate 200 mV/s, SCE as the reference electrode, and glassy carbon as the working electrode]. Half-wave potentials calculated as an average of the cathodic and anodic peaks (\(\Delta E_{pa} = 60–80\) mV). \(^b\)Estimated from the fluorescence spectrum. \(^c\)Free-energy change for photoinduced electron transfer from the excited \((S_1)\) zinc porphyrin unit to the rhenium unit. \(^d\)From ref. 36.

The supramolecular nature of the systems studied (as demonstrated by the additive nature of the spectroscopic and electrochemical properties of the molecular components) allows to build the energy level diagram of the excited states as a superposition of those of the components, with energetic values estimated from the corresponding fluorescence spectra (see below Figure 2.21). To this simple picture, possible states of intercomponent charge-transfer character should be added, that in the present case will be the ZnP\(^+\)–Re\(^−\) state. The energy of this state can be obtained as the difference in the potentials of the (oxidation) of the Zn-porphyrin component and of the (reduction) of the Re(bipy) component (Figure 2.21). The energy values inferred from electrochemical data (Table 2.1) for the ZnP\(^+\)–Re\(^−\) charge transfer state are 1.60 and 1.94 eV for 3b and 5b, respectively. Therefore, for 5b (and the same applies to 4b) the energy of the charge separated state is almost isoenergetic with respect to the singlet excited state \(S_1\) of the zinc-porphyrin with a (negligible) driving force for the electron transfer process (\(\Delta G = –0.09\)), and with only a slight improvement in comparison to fac-[Re(CO)\(_3\) (bipy)(Zn·4'MPyP)](CF\(_3\)SO\(_3\)) (\(\Delta G = –0.05\) eV).\(^36\) On the contrary, dyad 3b shows a \(\Delta G = –0.42\) eV, that makes this dyad the best candidate for the photo-induced charge separation (see also below the energy level diagram for 3b in Figure 2.21).

A detailed photophysical investigation on dyads 3b-5b was carried out in a DCM solution by stationary and time-resolved absorption/emission spectroscopy. For dyad 3b, some kinetic measurements were also performed in propionitrile and toluene for comparative purposes. The results of the emission experiments are collected in Table 2.2.
Following excitation in the visible region ($\lambda_{\text{exc}} = 550 \text{ nm}$), dyads 4b and 5b showed the typical zinc-porphyrin fluorescence. Comparative experiments carried out on optically matched solutions of 4b and 5b and of the corresponding zinc-porphyrin models at an excitation wavelength of 550 nm, clearly evidenced that the moderate fluorescence quenching observed for the rhenium dyads (both intensity and lifetime) is attributable, as previously discussed for fac-$\{\text{Re(CO)}_3(\text{bipy})(\text{Zn-4}'\text{MPyP})\}(\text{CF}_{3}\text{SO}_3)$, to the heavy-atom effect.\textsuperscript{36}

Table 2.2. Properties of dyads 3b–5b and of the model compounds.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ (em), nm</th>
<th>$\Phi_0/\Phi^b$</th>
<th>$\tau^c$ ns</th>
<th>$\tau_0/\tau^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn-TPP</td>
<td>599, 645</td>
<td></td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>Zn-tBuTPP</td>
<td>601, 648</td>
<td></td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>Zn-dtBuTPP</td>
<td>597, 647</td>
<td></td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>fac-${\text{Re(CO)}<em>3(\text{bipy})(\text{Zn-4}'\text{MPyP})}(\text{CF}</em>{3}\text{SO}_3)^d$</td>
<td>607, 650</td>
<td>1.6</td>
<td>0.9</td>
<td>2.0</td>
</tr>
<tr>
<td>3b</td>
<td>596, 644</td>
<td>8.3</td>
<td>$&lt;0.25$</td>
<td>&gt;6.8</td>
</tr>
<tr>
<td>4b</td>
<td>613, 650</td>
<td>2.0</td>
<td>0.7</td>
<td>2.3</td>
</tr>
<tr>
<td>5b</td>
<td>610, 650</td>
<td>1.9</td>
<td>0.6</td>
<td>2.8</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Selective excitation of the zinc porphyrin component in the Q-band region ($\lambda_{\text{exc}} = 550 \text{ nm}$), room temperature, and DCM solution. \textsuperscript{b}$\Phi_0$ and $\tau_0$ are respectively the fluorescence quantum yield and lifetime of the corresponding zinc-porphyrin model. \textsuperscript{c}Estimated error: $\pm0.1 \text{ ns}$. \textsuperscript{d}From ref. 36.

These results are consistent with CV measurements and confirm that the introduction of the electron-donor tBu substituents on the meso-phenyl rings has little effect on the oxidation potential of the porphyrin and consequently on the driving force for the photoinduced electron-transfer process. For this reason, in dyads 4b and 5b the charge separation does not occur. Evidently, the driving force for the electron transfer is too small so that the process is not fast enough to compete with the intersystem crossing in the porphyrin unit. By contrast, a strong quenching of the fluorescence intensity and lifetime (with respect to the reference model Zn-TPP) was observed for dyad 3b (Figure 2.18, and Table 2.2). Quenching of the fluorescence of Zn-TPP (or Zn-tBuTPP/Zn-dtBuTPP) in the presence of complex fac-$\{\text{Re(CO)}_3(\text{bipy})(\text{py})\}(\text{CF}_{3}\text{SO}_3)$, even at high concentrations (0.5 M), was not observed, thus confirming that a bimolecular electron-transfer process cannot occur because the lifetime of the zinc porphyrin singlet excited state is too short.
Figure 2.18. Emission fluorescence (DCM, 25°C, \( \lambda_{\text{exc}} = 550 \text{ nm} \)) of fac-\{Re(CO)\}_3(4,4'-DEC-bpy)(Zn-4'MPyP)(CF_3SO_3) (3b) (red curve) compared to that of ZnTPP (black curve).

The lifetime of the residual emission is shorter (< 250 ps) than the instrumental response. These results clearly indicate that in dyad 3b there is an additional and efficient (100%) process for deactivation of the singlet excited state of zinc porphyrin that involves the rhenium(I) unit. Ultrafast absorption measurements were performed to obtain information on the quenching mechanism. When excitation of 3b was carried out at 560 nm, where light is selectively absorbed by the zinc-porphyrin, the spectral changes shown in Figure 2.19 were observed.

Figure 2.19. Transient spectral changes obtained for dyad 3b in a DCM solution (\( \lambda_{\text{exc}} = 560 \text{ nm} \)) in the 0–10 ps range (left) and in the 10–400 ps range (right).

The behavior is clearly biphasic, with different spectral changes taking place in the 0–10 and 10–400 ps time ranges (Figure 2.19). The initial spectrum of Figure 2.19, taken immediately after the excitation pulse (t = 0.9 ps), is typical for the zinc-porphyrin singlet excited state, a broad intense positive absorption in the 450–550 nm region and a relatively flat positive absorption throughout the 550–750 nm visible region with a superimposed bleaching of the ground-state Q bands at 565 (hidden within the excitation window) and 610 nm. Additional apparent bleaches at 625 and 670 nm are caused by
stimulated emission. In the 1−10 ps time interval (Figure 2.19, left), the spectral changes show a substantial recovery of the bleach in the 520−680 nm range, accompanied by an increase in the optical density of the positive absorption in the 620−700 nm range, where at 660 nm the typical absorption band of the radical cation of zinc-porphyrin can be recognized. We attributed these spectral changes to the formation of the charge-separated product ZnP⁺−Re⁻, in which the zinc-porphyrin chromophore is oxidized and the rhenium(bipy) unit is reduced. In the longer time range (Figure 2.19, right), the spectroscopic signatures of the charge-separated state disappear with a uniform decay of the whole spectrum toward the initial baseline with isosbestic points at zero differential absorbance. This indicates that ZnP⁺−Re⁻ convert quantitatively by charge recombination to the ground state. The ultrafast results demonstrate also that in 3b the deactivation process from the charge-separated state ZnP⁺−Re⁻, initially formed in a singlet spin state, toward formation of the 3⁺ZnP−Re triplet does not favorably compete with the charge recombination to the ground state because it requires a spin inversion (see below Figure 2.21). Kinetic analysis of the spectral changes at 660 nm yields a time constant of 4 ps for charge separation and 96 ps for the charge-recombination process (Figure 2.20).

Figure 2.20. Kinetic analysis of the changes of the transient spectrum of 3b at 660 nm in DCM.

These ultrafast experiments clearly show that in dyad 3b, in which 4,4'-DEC-bipy replaces bipy on the rhenium(I) acceptor fragment, an efficient and ultrafast intramolecular electron-transfer process occurs from the excited zinc-porphyrin to the rhenium(bipy) unit. These experimental evidences, that are summarized in terms of energy levels diagram in Figure 2.21, were well and usefully anticipated from the electrochemical and emission data (see above).
Consistent with the fast rate measured by ultrafast spectroscopy (time constant = 4 ps), the charge-separation process falls in the normal Marcus region according to the standard electron-transfer theory.\textsuperscript{48,49} Conversely, the rate for the charge-recombination process to the ground state is much slower (time constant = 96 ps) because it belongs to the Marcus inverted region ($\Delta G = -1.6$ eV). Since the energy of the charge-separated state depends strongly on the solvent polarity, photophysical characterization of 3b was repeated in a solvent of higher polarity (propionitrile, PrCN) and in one of lower polarity (toluene) compared to DCM. Stationary emission measurements clearly indicated that in both solvents, as in DCM, the fluorescence of zinc-porphyrin was almost completely quenched. Ultrafast laser experiments in PrCN and toluene gave transient spectral changes qualitatively similar to those observed in DCM (Figure 2.22), indicating that, in each case, a fast charge separation (i.e., formation of ZnP\textsuperscript{+}\textsuperscript{−}Re\textsuperscript{−}), followed by slower recombination, occurred. However, the kinetics of the processes were found to be solvent-dependent. This is particularly true for the charge-recombination process, which slows down with decreasing the solvent polarity. Kinetic analysis of the spectral changes (biexponential fitting performed at 660 nm; Figure 2.23) gives the values of the time constants for the charge-separation and charge-recombination processes reported in Table 2.3.
Figure 2.22. Transient spectral changes obtained for dyad 3b in toluene solution (λ_{exc}= 560 nm) in the 0–50 ps range (left) and in the 50–2000 ps range (right).

The observed solvent effect on the electron-transfer rates can be qualitatively explained in terms of standard electron-transfer theory as a consequence of the changes in the driving force and reorganization energy. In DCM, where ΔG = −0.42 eV, the charge-separation process, assuming that the reorganization energy has a value of ca. 1 eV, falls in the normal Marcus region, whereas the charge recombination belongs to the Marcus inverted region. As the solvent polarity decreases, the energy of the charge-separated state rises; as a consequence, the driving force for charge recombination to the ground state grows, while the reorganization energy diminishes. In the Marcus inverted region, both factors act in the same direction, and thus a strong decrease in the rate with decreasing solvent polarity is predicted for the charge-recombination processes.

Figure 23. Kinetic analysis of the changes of the transient spectrum of 3b at 660 nm in three different solvents.

On the other hand, for the charge-separation reactions that fall in the normal Marcus region, the two effects tend to compensate for each other, leading to prediction of much weaker solvent effects. The experimental results shown in Table 2.3 are consistent with these theoretical considerations: whereas the change from DCM to PrCN affects mainly the
recombination time constant, the low polarity of toluene leads to a noticeable increase of the time constants for both processes. Overall, the observed electron-transfer kinetics is satisfactorily accounted for in terms of standard electron transfer theory.

Table 2.3. Time constants ($\tau$) for the charge-separation (CS) and charge-recombination (CR) processes of dyad 3b in different solvents ($\varepsilon$ is the dielectric constant).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\tau^{CS}$ (ps)$^a$</th>
<th>$\tau^{CR}$ (ps)$^a$</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PrCN</td>
<td>5</td>
<td>25</td>
<td>27.7</td>
</tr>
<tr>
<td>DCM</td>
<td>4</td>
<td>96</td>
<td>9.1</td>
</tr>
<tr>
<td>Toluene</td>
<td>22</td>
<td>130</td>
<td>2.4</td>
</tr>
</tbody>
</table>

$^a$Experimental error: ±10%.

2.3 Conclusions

Ready-to-make dyads of the type $\text{fac-}[\text{Re(CO)}_3(bpy)(\text{Zn-pyridylporphyrin})](\text{CF}_3\text{SO}_3)$ have been investigated. Due to the strength and inertness of the Re(I)–N coordination bonds, the present adducts show a high stability in solution, at concentration at least $\geq 1 \times 10^{-5}$ M. These systems, in which the zinc-pyridylporphyrin units behaves as chromophores and electron-donor moieties and the $\text{fac-}[\text{Re(CO)}_3(bpy)]^+$ unit as electron acceptor, can be efficiently synthesized in a stepwise manner from the cationic rhenium(I) precursor $\text{fac-}[\text{Re(CO)}_3(\text{bpy})](\text{CF}_3\text{SO}_3)$. The modular procedure affords, with modest synthetic effort, tailor-made dyads whose properties can be tuned by changing, via appropriate functionalization, those of the bipy and porphyrin ligands. As previously anticipated, we demonstrate here that a simple chemical modification of dyad $\text{fac-}[\text{Re(CO)}_3(bipy)(\text{Zn-4'MPyP})](\text{CF}_3\text{SO}_3)$, i.e., functionalization of the bipy ligand with electron-withdrawing ethyl ester groups in the 4 and 4’ positions, greatly improves, as the rhenium unit becomes significantly easier to reduce, the thermodynamics of the photoinduced electron-transfer process. As a consequence, whereas dyad $\text{fac-}[\text{Re(CO)}_3(bipy)(\text{Zn-4'MPyP})](\text{CF}_3\text{SO}_3)$ shows no evidence for the formation of the charge-separated state $\text{ZnP}^+\text{Re}^-$ (unless when in the presence of excess pyridine),$^{36}$ in the new dyad 3b, an efficient and ultrafast intramolecular electron-transfer process occurs upon excitation with visible light. On the contrary, the introduction of electron-donor tBu groups (either three or six) on the meso-phenyl moieties of zinc-porphyrin has a negligible effect on the photophysics of the system. Ultrafast time-resolved experiments performed at 560 nm on dyad 3b in DCM afforded a time constant of 4 ps for the charge separation process and 96 ps for the subsequent charge recombination process. Moreover, experiments
performed in solvents of higher (propionitrile) or lower polarity (toluene) compared to DCM consistently suggest that the charge separation process occurs in the normal Marcus region, whereas the charge recombination belongs to the Marcus inverted region. The photophysical study of these dyads has shown a high stability towards possible photocleavage processes of the coordination bonds.

The photophysical results obtained for the systems presented in this work can be compared with those reported by Perutz even considering that the similarity of the molecular photoactive components of the two systems are structurally different. In the dyad \([\text{fac-} \text{Re(CO)}_3(3\text{-pic})(\text{Zn-TPP-bipy})](\text{CF}_3\text{SO}_3)\) reported by Perutz the photophysical analysis performed by time-resolved ultrafast IR spectroscopy has revealed the formation of the charge-separated excited state with a time constant of 5 ps and the occurring of the charge recombination process in ca. 40 ps.\(^{32,46}\) These values are comparable with those reported in this work. The flexible and mild synthetic strategy employed in the present work, makes the dyads of the type \([\text{fac-} \{\text{Re(CO)}_3(\text{bpy})(\text{Zn-pyridylporphyrin})\}](\text{CF}_3\text{SO}_3)\) amenable for further improvements. It should be noted here that, despite the short lifetime of the charge separated state, Perutz and coworkers have also demonstrated that \([\text{fac-} \text{Re(CO)}_3(3\text{-pic})(\text{Zn-TPP-bipy})](\text{CF}_3\text{SO}_3)\) is capable of promoting the photocatalytic reduction of \(\text{CO}_2\) to \(\text{CO}\) under solar light irradiation.\(^{33,34}\)

Presently, the appropriate experimental setup is being prepared in order to test dyad \(3b\) in the photoreduction reaction of \(\text{CO}_2\), under visible light irradiation.

### 2.4 References

1. Barber, J.; Tran, P. D. *J. R. Soc. Interface* 2013, 10, 1–16.


Chapter 3.

A rhenium-mediated triad for stepwise photoinduced electron transfer processes
List of abbreviations

OctylAmA = $\alpha$-aminoacid N-octylglycine
bipy = 2,2-bipyridine
bipyAc = 4’-methyl-2,2’-bipyridine-4-carboxylic acid
TPP-NH$_2$ = 5-(4’-aminophenyl)-10,15,20-(phenyl)-porphyrin
EDC·Cl = 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride
TPP-bipy = 5-[4-(4-Methyl-2,2’-bipyridine-4’-carboxyamidyl)phenyl]-10,15,20-(phenyl)-porphyrin
VT = Variable Temperature
CS = Charge-Separated
MLCT = Metal-to-Ligand Charge Transfer

3.1 Introduction

In the previous chapter the possibility to build a novel class of ready-to-make and highly robust dyads, of the type $f_{ac}$-[Re(CO)$_3$(bipy)(Zn-pyridylporphyrin)](CF$_3$SO$_3$) has been demonstrated. These dyads, as well as many others reported in literature, are usually characterized by a short lifetime of the charge separated state due to a fast charge recombination process. To overcome this problem, more multi-component systems are necessary (triads, tetrads, …) to allow for multistep electron transfer processes and thus get the opposite charges separated over longer distances. In this way the charge recombination process will slow down, and, ultimately, charge-separated (CS) states with longer lifetime will be obtained (Figure 3.1).

Figure 3.1. Schematic depiction of a photoinduced multistep electron transfer process in a three-component system (triad).

In this work, the design synthesis and characterization of a three-component system (triad) is presented. Starting from the metal-mediated modular approach successfully used
for the dyads described in the previous chapter, and exploiting the possibility to directly connect the photosensitizer/donor porphyrin unit to the acceptor Re(bipy) unit via a covalent coupling of the organic fragments, as described by Perutz,\textsuperscript{1–3} we designed a triad system in which the second electron acceptor will be introduced in the apical position of the rhenium center (Figure 3.2).

![Figure 3.2. Schematic depiction of the three-component system (triad).](image)

The final aim is that of possibly促进ing a multistep electron transfer in order to obtain a longer-lived charge separated state. Among the possible organic electron acceptors, fullerene has been chosen for a variety of reasons. \( C_{60} \) is an excellent electron acceptor in the ground state and can accept, reversibly, up to six electrons. Moreover, the localization of the charge over the large three-dimensional structure of \( C_{60} \) corresponds to a small reorganization energy, which tends to increase the rate of charge separation and decrease that of charge recombination.\textsuperscript{4–8} Fullerenes have been widely used in combination with porphyrins as electron acceptors.\textsuperscript{9,10} Good results, in terms of lifetime of charge-separated state, have been reported in literature, in many different systems, in which the porphyrin and the fullerene units were connected through either covalent\textsuperscript{6,11–14} or non-covalent linkers\textsuperscript{15–20}. One of the most successful triad has been reported by Imahori et al. (Figure 3.3), in which a free-base porphyrin and zinc-porphyrin have been linearly arranged and attached to \( C_{60} \), obtaining a system in which an energy transfer from the zinc-porphyrin to the free-base porphyrin is followed by an electron transfer from the excited free-base porphyrin to \( C_{60} \), with the formation of a charge separated state of 30 \( \mu \)s.\textsuperscript{14}

![Figure 3.3. Covalent triad reported by Imahori et al.\textsuperscript{14}](image)
While metalloporphyrin-fullerene conjugates have been investigated to a larger extent, examples of conjugates of fullerene coordinated to coordination metal complexes systems are quite rare. Usually, C\textsubscript{60} is functionalized with a peripheral nitrogen-based ligand that allows for the coordination to transition metals such as Cu(I), Ru(II) or Re(I).\textsuperscript{5,21-27} In the two examples reported in Figure 3.4, a fullerene is coordinated to a rhenium(I) center either \textit{via} a pyridyl ligand or \textit{via} a bipyridyl ligand. The photophysical properties of metal-fullerene donor-acceptor conjugates have been investigated. Many groups have demonstrated that the triplet MLCT excited state of the metal(diimine) fragment, generated by UV irradiation, is quenched by an energy transfer processes from the metal center to the C\textsubscript{60}. In parallel, for these systems, photoinduced electron transfer processes have never been fully proven for these systems.

\textbf{Figure 3.4.} Rhenium(I) complexes functionalized with fullerenes reported (left) by Nierengarten et al.\textsuperscript{27} and (right) by Paolucci et al.\textsuperscript{24}

In this work, the synthesis and characterization of a new triad is reported. Starting from the rhenium(I) precursor fac-\{Re(CO)\textsubscript{3}(dmso-O\textsubscript{3})(CF\textsubscript{3}SO\textsubscript{3})\}, we present a variation on the synthetic pathway previously developed by which the zinc-porphyrin is first coordinated to the rhenium(I)(CO\textsubscript{3}) fragment \textit{via} an amido-bipyridyl linker unit,\textsuperscript{28-31} leaving the third apical position of the metal center free for the subsequent introduction of a pyridyl functionalized fullerene (Figure 3.5).

46
3.2 Results and discussion

For this work two different pyridyl functionalized fullerenes monoadducts have been synthesized. For structural and photophysical characterization purposes, and also in order to investigate the coordination capabilities of the fullerenes towards the rhenium center, a series of model compounds have also been prepared, and will be briefly described in separate sections.

3.2.1 Pyridyl-functionalized fulleropyrrolidine monoadducts

Fullerenopyrrolidines have been obtained with the well-known Prato reaction, which consists of a 1,3-dipolar cycloaddition of azomethine ylide to C_{60}.\textsuperscript{32} In this reaction, the ylide can be generated \textit{in situ} by thermal ring opening of aziridines or by decarboxylation of the iminium salts derived from the condensation of \(\alpha\)-aminoacids and aldehydes (or ketones). The general schematic synthesis is reported in Scheme 3.1. The cycloaddition of azomethine ylides is a powerful and widely used methodology to functionalized fullerenes, since the resulting fulleropyrrolidines present high stabilities. Moreover, this reaction offer a great versatility, as it is possible to easily modify the groups attached to the pyrrolidine nitrogen and to the C_2 carbon of the fused pyrrolidine, and consequently vary the reactivity and solubility of the resulting monoadducts, without changing the physicochemical properties of pristine C_{60}.\textsuperscript{33,34} A minor drawback of this methodology is the not selective generation of a chiral center (carbon C_2 of the pyrrolidine, highlighted in Scheme 3.1) and as a consequence, the fullerenopyrrolidine derivatives are obtained as racemic mixtures.
Scheme 3.1. General schematic synthesis of fulleropyrrolidines by 1,3-dipolar cycloaddition.

For the synthesis of 7, the procedure reported in the literature, and very well studied in our group, in which N-methylglycine (sarcosine) and 4-pyridine carboxyaldehyde are used as starting materials, was followed (Scheme 3.2). For 8 the \(\alpha\)-aminoacid N-octylglycine (OctylAmA) was firstly synthesized from octylamine and benzy1-bromo-acetate, followed by deprotection of the carboxylic group with H\(_2\) on Pd/C. Both derivatives were isolated in good yield (the yields are based on C\(_{60}\) conversion), with values in line to that reported in the literature.\(^{34}\) It is worth to notice that the introduction of a long alkyl chain on the pyrrolidine nitrogen results in a significant increase in terms of solubility of the corresponding C\(_{60}\) monoadduct. Indeed, derivative 8 is well soluble in a variety of organic solvents, in particular chlorinated ones, in which 7 shows only a scarce solubility.

![Scheme 3.2. Schematic synthesis of pyridyl functionalized fulleropyrrolidines monoadducts 7 and 8 with yields based on C\(_{60}\) conversion. Reagent and conditions: (i) C\(_{60}\), toluene, reflux for 25 min.]

\[
\begin{align*}
\text{R'}NCOOH & + \text{RCHO} & \xrightarrow{\text{heating}} & \text{[\text{N}^\oplus]} & \xrightarrow{\text{C}_{60}} \\
\text{R} & = -\text{CH}_3 \\
\text{R} & = -(\text{CH}_2)_3\text{CH}_3 \\
\end{align*}
\]

7 and 8 have been characterized by ESI mass spectrometry and NMR spectroscopy. In particular, for 8, full assignment of the alkyl proton resonances was possible by means of 2D (H-H and H-C COSY, NOESY) NMR experiments; the H-C COSY (CDCl\(_3\)) of 8 is reported in Figure 3.6. As mentioned above, the cycloaddition reaction on C\(_{60}\) generates a chiral center on carbon C\(_2\) of the pyrrolidine ring, that reflects, in 8, in the fact that the pyrrolidine protons H\(_B\) and H\(_{B'}\), and all the germinal protons in the alkyl chain, are distereotopic (see labeling scheme of 8 in Figure 3.6; the (S)-enantiomer is depicted, but same reasoning stands for the (R)-enantiomer).
In the $^1$H NMR of 8 protons H$_B$/H$_{B'}$ and H$_C$/H$_{C'}$ give rise to pairs of well separated resonances at $\delta$(ppm) = 5.13/4.11 and 2.97/2.58, respectively. In addition, each diastereotopic proton cross-couples with its geminal counterpart, as evidenced from the multiplicities of the corresponding resonances (e.g. H$_B$/H$_{B'}$ give rise to two doublets), and from the correlations observed in the 2D H-H COSY (Figure 3.7). The non-equivalence of the diastereotopic protons becomes less evident gradually moving away from the stereogenic center, and already the two pairs of resonances of the geminal protons H$_D$/H$_{D'}$ and H$_E$/H$_{E'}$ are almost overlapped. By means of a 2D NOESY experiment, and by conventionally labeling as primed (') the protons residing on the same side of H$_A$, with respect to the plane defined by the pyrrolidine, it has been possible to distinguish between the two resonances of some of the diastereotopic proton pairs. For example, as shown in Figure 3.8, an nOe cross-peak correlation is evident between the resonance of H$_A$ and the doublet at $\delta$ = 4.11 ppm, unambiguously identifying the latter as pertaining to H$_{B'}$; seemingly an nOe cross-peak correlation is also evident between the resonance of H$_A$ and the multiplet at $\delta$ = 2.61 ppm, thus identifying H$_{C'}$. 

Figure 3.6. H-C COSY spectrum of 8 (CDCl$_3$, 500 MHz) and schematic depiction with proton labeling scheme.
Figure 3.7. H-H COSY spectrum of 8 (CDCl₃, 500 MHz) and schematic depiction with labeling scheme.

Figure 3.8. Partial NOESY spectrum of 8 (CDCl₃, 500 MHz), with relevant nOe cross-peaks highlighted with boxes.
3.2.2 \textit{Re(I)(bipy)-Fullerene model complexes}

The reactivity of 7 and 8 towards \textit{fac-}[Re(CO)$_3$(bipy)(dms-o)]$\text{[X]}$ ($X = \text{CF}_3\text{SO}_3$ or PF$_6$) was investigated and exploited to synthesize the model complexes 9 and 10 (Figure 3.9).

![Figure 3.9. Schematic depiction of model complexes 9a, 9b and 10.](image)

The influence of the nature of the counterion $X$ on the solubility of the resulting fullerene-rhenium(I) conjugates was initially evaluated by employing as starting rhenium precursor either \textit{fac-}[Re(CO)$_3$(dms-o)]$\text{[CF}_3\text{SO}_3$) or \textit{fac-}[Re(CO)$_3$(dms-o)]$\text{[PF}_6$), in combination with the less soluble fulleropyrrolidine 7. Bipy was coordinated to the metal center in the first step, as already described in the previous chapter, and 9\textit{a,b} were then isolated by repeated precipitation, after treatment of the corresponding intermediates \textit{fac-}[Re(CO)$_3$(bipy)(dms-o)]$\text{[X]}$ with a slight excess of 7 in 1,2-dichloroethane at reflux for three days (Scheme 3.3). The solubility of 9\textit{b}, in selected organic solvents, results significantly higher than that of 9\textit{a}, and this markedly different behavior can be ascribed to the different nature of the counterion $X$ in the two derivatives. Regrettably, despite the prolonged reaction time and the pretty high reaction temperature employed, both model compounds were isolated in very poor yields (\textit{ca.} 20\%), most probably due to the very low solubility of fulleropyrrolidine 7. On the contrary, 10 was obtained by treatment of \textit{fac-}[Re(CO)$_3$(bipy)(dms-o)]$\text{[PF}_6$ with 8 in DCM at reflux for 24 h, in good yield (Scheme 3.3). These experimental results led us to elect the fulleropyrrolidine monoadduct 8 and the countion PF$_6$, for the obtainment of the proposed triad target molecule (see below).
Scheme 3.3. Synthesis of model complexes 9a, 9b and 10. Reagents and conditions for 9: (i) 1,2-dichloroethane, reflux 3 days; Reagents and conditions for 10: (ii) DCM, reflux 24 h.

The model complexes 9a,b and 10 have been characterized in solution by ESI mass spectrometry and NMR spectroscopy, and in the solid state by IR spectroscopy. Only the characterization of 10 will be discussed, with highlight on the spectroscopic features that are relevant for the structural characterization of the subsequent more complex multi-component systems. The ESI-MS spectrum of 10 shows a single peak with the correct isotopic distribution for the molecular ion at m/z 1379.4 (calculated m/z for \([\text{M} - \text{PF}_6]^{+} \) 1379.2). In Figure 3.10 the comparison between the IR spectra of 10 and fac-[Re(CO)_3(bipy)(py)](PF_6) is reported. In this comparison, it is possible to notice that the coordination of the fullereopyrroldine monoadduct determines a slight shift at higher wavenumber of the stretching frequencies of the facial carbonyl ligands.

\(^{35}\)fac-[Re(CO)_3(bipy)(py)](PF_6) has been synthesized following a similar procedure reported for the synthesis of fac-[Re(CO)_3(bipy)(py)](CF_3SO_3), and also described in the previous chapter.
Figure 10. Selected region of the IR solid state spectra of \( \text{fac-}[\text{Re(CO)}_3(\text{bipy})(\text{py})](\text{PF}_6) \) (blue trace) and 10 (red trace).

In Figure 3.11 the \(^1\)H NMR (CDCl\(_3\)) of 10, that shows the correct relative integration of the signals, is reported; all the assignments have been done by 2D NMR experiments (H-H COSY, H-C COSY and NOESY). The chemical shifts and pattern of the proton resonances of 8 are not particularly affected by its coordination to the \( \{\text{fac-}[\text{Re(CO)}_3(\text{bpy})]\}^+ \) fragment except for that of the two pyridyl protons adjacent to the nitrogen atom (py\(_n\)), which is upfield shifted (\( \Delta \delta = -0.45 \)), as a result of the mutual perpendicular disposition of the pyridyl and bipyridyl groups (see also Chapter 2).\(^{35}\) The presence of a center of asymmetry on the fulleropyrrolidine ligand affects the pattern of the proton resonances of the bipy ligand, that loses its mirror plane and thus presents two non-equivalent halves. Two sets of resolved resonances of equal intensities for the bipyridyl protons can be detected, each set pertaining to one of the non-equivalent bipy halves (the H\(_{5,5'}\) proton signals are overlapped in a single multiplet), with each set identifying its own spin system and corresponding cross-peak correlations in the 2D H-H COSY spectrum (as indicated with the color code in the \(^1\)H NMR spectrum in Figure 3.11).
3.2.3 *Re(I)(bipy)*-porphyrin model complexes

The reactivity of porphyrin 13 (TPP-bipy), peripherally functionalized with a bipyridyl fragment, towards the rhenium(I) precursor fac-[Re(CO)$_3$(dmso-O)$_3$](PF$_6$) was conveniently investigated while performing the synthesis of model complex 15 (Scheme 3.4). First of all, 11 (TPP-NH$_2$) and 12 (bipyAc) were synthesized with procedures similar to those reported in the literature.$^{36,37}$ 11 was obtained by nitration of the *meso*-tetraphenylporphyrin, followed by reduction of the nitro group and purification by column chromatography (51% yield), whereas 12 has been obtained by oxidation of 4,4'-dimethyl-2,2'-bipyridine with SeO$_2$, leading to a mixture of oxidized products. The desired product 12 was collected by soxhlet extraction (36% yield). 13 was subsequently synthesized optimizing a procedure reported in literature, by a coupling reaction with EDC·Cl between 11 and 12 (Scheme 3.4).$^{38}$ fac-[Re(TPP-bipy)(py)](PF$_6$) (15a) was efficiently synthesized by coordination of the mono-substituted TPP-bipy ligand to fac-[Re(CO)$_3$(dmso-O)$_3$](PF$_6$), followed by replacement of the residual apical dmso-O with pyridine (Scheme 3.4). Synthesis of 15a, and the subsequent insertion step of the zinc(II) ion in the core of the porphyrin (15b), proceed both almost quantitatively.

Figure 3.11. Partial $^1$H NMR spectrum of 10 (CDCl$_3$, 500 MHz) and schematic depiction with labeling scheme.
Scheme 3.4. Synthesis of $\text{fac-}[\text{Re(Zn-TPP-bipy)}(\text{Py})](\text{PF}_6)$ (15b). Reagents and conditions: (i) EDC-Cl, pyridine, room temperature 2.5 h; (ii) $\text{fac-}[\text{Re(CO)}_3(\text{dms}-\text{O})_3](\text{PF}_6)$, CHCl$_3$, reflux 1.5 h; (iii) pyridine, CH$_2$Cl$_2$, reflux 4 h; (iv) Zn(OAc)$_2$·2H$_2$O, CHCl$_3$/MeOH, room temperature overnight.

15a and 15b were fully characterized by ESI mass spectrometry and NMR spectroscopy ($^1$H NMR and 2D NMR experiments, see Figure 3.12 and Figure 3.18, below). The relative integration of the proton resonances of the mono-substituted porphyrin and of the pyridine is correct. It is worth mentioning here that 15a and 15b both exists as mixtures of enantiomers. In fact, the ligand arrangement around rhenium metal center is, for both species, inherently asymmetrical, and of the type $\text{fac-MABCD}_3$ identifying the presence of a pair of (Clockwise and Anticlockwise) enantiomers, most presumably forming in equimolar quantities.
3.2.4 Triad: synthesis and characterization

The synthesis of the three-component systems 16 and triad (19) are reported in Scheme 3.5. 16 was obtained from intermediate 14, see also Scheme 3.4, by reaction with the fulleropyrrolidine monoadduct 8, as pure product in very good yield. For the reasons just mentioned above, 16 forms as a mixture of one-up-to four diastereoisomers (i.e., (C,S); (C,R); (A,S); (A,R)).
Scheme 3.5. Synthesis of 16 and of triad 19, with yields of the isolated products in each step. Reagents and conditions: (i) $\text{fac}^{-}[\text{Re(CO)}_3(\text{dmso-O})_3](\text{PF}_6)$, CHCl$_3$, reflux 2.5 h; (ii) 8, DCM, reflux, 1.5 h; (iii) Zn(OAc)$_2$·2H$_2$O, dichloroethane, reflux; (iv) Zn(OAc)$_2$·2H$_2$O, CHCl$_3$/MeOH, room temperature overnight; (v) $\text{fac}^{-}[\text{Re(CO)}_3(\text{dmso-O})_3](\text{PF}_6)$, CHCl$_3$, reflux 2.5 h; (vi) 2b, dichloroethane, reflux 20 h.
Chapter 3

Figure 3.13. ESI-MS of 16.

16 has been fully characterized in solution by ESI mass spectrometry, NMR, UV-vis and emission spectroscopies, and in the solid state by IR spectroscopy. The ESI-MS spectrum (Figure 3.13) show a single peak with the correct isotopic distribution for the molecular ion at m/z 2049.2 (calculated for [M – PF₆]+ 2049.2). In Figure 3.14, the comparison between the IR spectra of 16 and of its precursor 14 is reported. As already noticed for model complex 10, the coordination of the fulleropyrrolidine monoadduct determines a slight shift the stretching frequencies of the facial carbonyl ligands, that are found for 16 at higher wavenumbers with respect to 14. For 16, all the carbonyl stretching bands appear significantly broad, which may be a consequence (but not the only explanation) of the presence of a mixture of diastereoisomers. Finally, for both 16 and 14, an additional weak stretching band at 1675 cm⁻¹, related to the CO of the amide group, is also observable.
Figure 3.14. Selected region of the IR solid state spectra of fac-[Re(CO)₃(TPP-bipy)(dmso-O)](PF₆) (14) (blue trace), and fac-[Re(CO)₃(TPP-bipy)(8)](PF₆) (16) (red trace).

The UV-vis spectrum of 16 is dominated by the absorbance of the porphyrin unit with an intense Soret band at 420 nm and four weaker Q-band, in the region 500-700 nm, characteristic of a free-base porphyrin (Figure 3.15). Similarly, the fluorescence emission spectrum shows the typical bands of a free-base porphyrin. In particular, in Figure 3.15, the fluorescence of 16 is compared to that of tetraphenylporphyrin (TPP), showing a strong quenching of the porphyrin emission for 16.

Figure 3.15. Left: UV-vis absorption spectrum of 16 (DCM), with inset of the Q-bands region. Right: Emission spectrum of 16 (black curve) and TPP (red curve) in DCM (λₑₗₑ = 517 nm).

A complete NMR characterization of 16 has been done by means of 1D and 2D NMR experiments. Relative integration of the proton resonances of the TPP-bipy and the fullerene moieties is correct. The ¹H NMR (dmso-d₆) of 16 is reported in Figure 3.16.
As expected from the presence of a (complex) mixture of diastereoisomers, a very crowded spectrum, especially in the aromatic region, with a large numbers of proton resonances and large overlapped portions can be observed. In particular, at least two sets of signals, more or less resolved, with different relative intensities, can be observed. This observation is particularly evident for the resonances of protons NH of the amide bridge, H₆ and H₅ of the bipy fragment, Hₐ and H₆ of the pyrrolidine ring, and the inner −NH of the porphyrin units (see also Figure 3.18). For the resonances of the bipyridyl protons H₅', an analogous splitting can be revealed by H-H COSY that unambiguously show one distinct correlation peak between each H₆' resonance, and that of the corresponding H₅' proton (Figure 3.17). The two bipyridyl protons H₃ and H₃' do not present any H-H correlation, while they show clear nOe correlations with the NH amide protons, thus revealing the presence of a total of four distinct singlets, two of which overlap with the resonances of the βH (δ = 8.85 ppm) and of the αH (δ = 8.12 ppm) protons, respectively (Figure 3.18). The proton resonances of the fulleropyrrolidine fragment and those of the protons inside the porphyrin macrocycle (labeled as 2NH), also appear split and not completely resolved. The overall split pattern of the resonances is even more evident when comparing the ^1H NMR of 16 with that of 15a (Figure 3.19).
Figure 3.17. Downfield region of the H-H COSY spectrum of 16 (dmso-$d_6$, 500 MHz).

Figure 3.18. Downfield region of the NOESY spectrum of 16 (dmso-$d_6$, 500 MHz), with some nOe correlations highlighted.
VT NMR experiments has been performed, but no appreciable variations of the signal linewidth and/or resolution were detected. A $^{13}$C NMR spectrum has also been recorded, but no useful information on the carbonyl resonances, which requires long acquisition times or higher sensitivity instruments, could be derived.

Despite the fact that from the NMR data just discussed, it appears as if two of the possible diastereoisomers of 16 are formed preferentially, and in different amounts, it is more likely that the complete mixture of the four isomers, displaying random proton resonance overlaps, is formed. In fact, if during the synthetic work-up 16 is collected in subsequent precipitation steps, while the solids deriving from each steps display the same ESI mass spectrum, with only a single correct molecular ion peak, their corresponding $^1$H NMR spectra show variations in the relative ratios of the resonances sets. Most likely, the four diastereoisomers form in similar proportions, but have a different solubility. Also, by varying the NMR solvent, the proton resonances present different resolution patterns. As example the $^1$H NMR of 16 in DMF-$d_6$, with only relevant proton resonances, is reported in Figure 3.20.
Direct insertion of the zinc ions in the free-base derivative 16 in order to obtain the target triad compound 19 was not successful. Different attempts performed by varying the amount of Zn(OAc)\(_2\)-2H\(_2\)O employed, the nature of the solvent, the reaction temperature and time, always resulted in mixtures of unreacted 16 and 19 (as ascertained by ESI-MS spectrometry). Alternatively, as reported in Scheme 6, the zinc ion was introduced, with standard conditions (Zn(OAc)\(_2\)-2H\(_2\)O in CHCl\(_3\)/MeOH), in the mono-substituted porphyrin (TPP-bipy), before the following porphyrin coordination step on the rhenium(I) center (Scheme 3.5). Afterwards, coordination of 8 to the metal center was accomplished and, conveniently, pure 19 was isolated by means of a simple filtration. In fact, the extremely low solubility of the triad in pure chlorinated solvents induced the precipitation of the product as soon as it is formed. The zinc triad 19 is only slightly soluble in chlorinated solvents. Adding small aliquots of methanol or pyridine, which may axially coordinate to the zinc ion, and thus break the \(\pi,\pi\) stacking interaction between porphyrin rings, resulted in a significant increase of solubility. Still, a complete NMR characterization has not been feasible, since the \(^1\)H NMR spectrum of 19 in mixed deuterated solvents is invariably too crowded, with most of the proton resonances overlapping in a small \(\Delta\delta\) range. The aromatic region of the H-H COSY spectrum of 19 (CDCl\(_3\)/MeOD) is shown in Figure 3.21.

It is possible to notice how, four sets of resolved resonances appear distinctly for some of the protons, and from those (and also by comparsion with the model systems just described), a partial NMR assignment was done. VT NMR experiments were performed, but at the highest temperature reachable (45 °C), no useful simplification of the spectrum occurred. Again, as already well discussed for 16, the presence of a mixture of distereoisomer is responsible for the high degree of complexity encountered in the NMR analysis of 19.
Figure 3.19. Downfield H-H COSY spectrum of 19 (CDCl₃/MeOD, 500 MHz), with partial assignments.

However, 19 was completely characterized in solution by ESI-MS spectrometry, UV-vis and emission spectroscopies, and in the solid state by IR. The ESI-MS spectrum, reported in Figure 3.22, shows uniquely the peak corresponding to the molecular ion of 19, with an exact match between the calculated mass isotopic distribution and the experimental one.

Figure 3.20. ESI-MS spectrum of 19 calculated for ([M - PF₆]⁻) 2112.6, found 2111.5. Inset: (left) calculated isotopic distribution (program IsoPro3) and (right) experimental isotopic distribution, of molecular ion peak.
Also for 19, the UV-vis spectrum is dominated by the absorbance of the porphyrin unit with the intense Soret band at 420 nm. Two weaker Q-bands, in the region 500-700 nm, characteristic of a zinc-porphyrin, and a shoulder at 311 nm, characteristic of the fulleropyrrolidine monoadduct, is also present (see below Figure 3.25). Similarly, the fluorescence emission spectrum shows the typical bands of a zinc-tetraphenylporphyrin. In particular, in Figure 3.23, the emission spectrum of 19 is compared with that of ZnTPP, showing a strong quenching of the fluorescence.

![Figure 3.21. Emission fluorescence of 19 (black curve) and ZnTPP (red curve) in DCM (λexc = 517 nm).](image)
3.2.5 Spectroscopic and Photophysical Properties

Triad 19 can be considered as the combination of three types of molecular subunits reported in Figure 3.24: a zinc-tetraphenylporphyrin (ZnTPP), a rhenium(I) complex (Re-bipy) and a functionalized fullerene (8).

![Figure 3.22. Subunits of triad 19.](image)

The triad absorption spectrum in dichloromethane (Figure 3.25, left) is a good superposition of those of the molecular components, aside from small red shifts (2-3 nm) of the porphyrins bands with respect of the ZnTPP unit due to coordination with Re(I) complex. This indicates that there is a weak electronic interaction between individual components in their ground state configuration. In the visible region, the spectrum is dominated by Zn-porphyrin unit, with two typical Q bands between 500 and 700 nm in addition to the Soret band centered at 430 nm (Figure 3.25). In this region, the rhenium unit does not absorb and the contribution of the fullerene unit is negligible.

In collaboration with Prof. M. T. Indelli (University of Ferrara) a detailed photophysical investigation of the new triad was carried out in dichloromethane solution, upon selective excitation of zinc-porphyrin chromophore, by stationary and time-resolved absorption and emission spectroscopy. At room temperature, a solution of the triad system shows the typical Zn porphyrin fluorescence with prominent vibronic bands at 599 and 648 nm (Figure 3.25, right). Comparative experiments carried out on optically matches solution of 19 and the ZnTPP model indicate that, in the triad, the zinc-porphyrin fluorescence is strongly quenched relative to that of the model compound. Single-photon counting experiments demonstrate that the fluorescence lifetime of 19 triad lies below the
instrumental time resolution (<250 ps). In order to obtain insight into the quenching mechanism, ultrafast spectroscopy experiments were performed in different solvents (dichloromethane, toluene, benzonitrile and tetrahydrofuran) and with different apparatus and excitation wavelengths.

**Figure 3.23.** Left: UV-Vis absorption spectrum of 19 (black curve), ZnTPP (red curve), 8 (blue curve) and Re-bipy (green curve). Right: Emission fluorescence of 19 (black curve) and ZnTPP (red curve) in DCM (λexc = 517 nm).

The transient spectral changes observed in dichloromethane upon excitation at 560 nm are shown in Figure 3.26. The initial spectrum, taken immediately after the excitation pulse (t ≈ 1ps) is that typical for the zinc-porphyrin singlet excited state, characterized by a broad intense positive absorption in the 450 – 550 nm range, a relatively flat positive absorption in the visible region in the 560 – 800 nm range with superimposed bleach of the ground-state Q bands (580 –600 nm). Additional apparent bleaches in the 650 –720 nm range are caused by stimulated emission.

**Figure 3.24.** Transient spectral changes obtained for triad 19 in a DCM solution (λexc = 560 nm) in the 0–10 ps range (left) and in the 50–2000 ps range (right).

The transient spectral changes show a biphasic behavior, taking place in the 1 – 10 ps and in the 10 – 2000 ps range. Figure 3.26 (left) shows the behavior in the first range
where a fast increase in the optical density in the 620-700 nm range and a reduction of Q-band bleach are observed. These spectral changes are relatively small, but the signatures of the radical cation of the zinc porphyrin (broad absorption bands in the 600–800 nm range) can be easily recognized, consistent with the formation of a charge separated state in which the zinc-porphyrin component is oxidized (ZnP$^+$). In the longer time range (10–2000 ps) a uniform decay of the ZnP$^+$ spectrum toward the initial baseline is observed clearly indicating that ZnP$^+$ converts quantitatively to the ground state. These results are consistent with an electron transfer mechanism for the excited singlet state of ZnP component. Kinetic analysis of the spectral changes at 650 nm (Figure 3.27) yields a time constant of 2 ± 1 ps for the first process (formation of ZnP$^+$) and 140 ± 10 ps for the second one (conversion to ground state).

![Figure 25. Kinetic analysis of spectral changes of 19 at 650 nm.](image)

In these measurements the spectral window (400-800 nm) investigated is limited by experimental apparatus (see Experimental Section). In order to obtain evidences on the nature of the charge separated state it is necessary extend the study to the infrared region. For these measurements, different equipment with a wider spectral window (400-1200 nm) was used in collaboration with the group of Prof. D. Guldi (University of Erlangen, Germany). Experiments in different solvents (toluene, THF and benzonitrile), by using 420 nm as excitation wavelength, were performed. The spectral changes observed in toluene are reported in Figure 3.28.
Immediately after excitation ($t = 0.1$ ps) of the ZnP component, its singlet excited state is formed. Evidences for the latter stem from the occurrence of an intense absorption with maxima at 462, 570 and 615 nm as well as a minima at 550, 600 and 620 nm corresponding to the bleach of the ground-state Q-bands and to the stimulated emission. In the early time scale (0 – 30 ps), spectral changes with signatures of radical cation $\text{ZnP}^+$ (maxima at 460, 625 and 675 nm and a minimum at 555 nm) and a maximum at 1025 nm, that corresponds to the typical absorption of the radical anion, $\text{C}_{60}^-$, are clearly discernible. These observations indicate that a charge separated product ($\text{ZnP}^+\text{-Re-C}_{60}^-$) in which the zinc porphyrin chromophore is oxidized and the fullerene unit is reduced is formed. Importantly, the $\text{ZnP}^+\text{-Re-C}_{60}^-$ features grow in a time scale that matches the decay of the ZnP singlet excited state indicating that a photoinduced electron transfer process from the ZnP excited state to C$_{60}$ component occurs. In a longer time scale, the spectroscopic signatures of the charge separated state disappear with a uniform decay of the whole spectrum toward the initial baseline. These results strongly suggest that $\text{ZnP}^+\text{-Re-C}_{60}^-$ converts quantitatively by charge recombination to the ground state. Qualitative similar spectral changes were observed also in THF and benzonitrile. Kinetics analysis of the spectral changes observed clearly indicates that, while the charge separation process is very fast (1-2 ps) and shows a kinetic behavior practically independent of the solvent, the charge recombination shows a strong dependence on the solvent, and is observed to be by far slower in toluene (in this solvent the charge-separated state may as well partially recombine via an ISC to the ZnP or C$_{60}$ triplet excited states). The values of the rate constants reported in Table 3.1 are obtained from kinetics analysis at three different wavelengths: 650, 465, 1020 nm.

Figure 3.26. Left: differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (420 nm, 200 nJ) of 19 in toluene (argon saturated) with several time delays, tween 0.1 and 6750.2 ps at room temperature. Right: time-absorption profiles of the spectra at 465, 650, and 1020 nm, monitoring the charge separation and charge recombination.
Table 1. Time constants ($\tau$) for the charge-separation (CS) and charge-recombination (CR) processes of 19 in different solvents ($\varepsilon$ is the dielectric constant).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\tau^{\text{CR}}$ (ps)</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzonitrile</td>
<td>125 ± 50</td>
<td>25.7</td>
</tr>
<tr>
<td>DCM</td>
<td>140 ± 10</td>
<td>9.1</td>
</tr>
<tr>
<td>THF</td>
<td>260 ± 40</td>
<td>7.6</td>
</tr>
<tr>
<td>Toluene</td>
<td>2800 ± 50</td>
<td>2.4</td>
</tr>
</tbody>
</table>

In conclusion, the interpretation of the transient spectral changes observed in the ultrafast absorption experiments as formation and decay of the charge separated product $\text{ZnP}^+\text{-Re}\text{-C}_{60}^-$, respectively, is straightforward. In all solvents investigated, no evidence of an intermediate species of the type $\text{ZnP}^+\text{-Re}^+\text{-C}_{60}^-$, in which the ZnP is oxidized and rhenium(bipy) fragment is reduced, was obtained. In order to discuss this point, it is useful to consider a simplified energy level diagram for the triad studied in dichloromethane (Figure 3.29, the excited states of the C$_{60}$ unit are omitted for clarity).

![Energy level diagram for 19 in DCM solution.](image)
In this diagram, in addition to the energy levels of the excited states of the ZnP unit, the intercomponent charge-transfer states must be added. Two types of charge transfer states, both containing the oxidized form of the zinc-porphyrin component can be considered; one, in which the rhenium(bipy) unit is reduced (ZnP$^+$-Re$^-$-C$_{60}$) and the other, in which the C$_{60}$ unit is reduced (ZnP$^+$-Re$^-$-C$_{60}$). The energy of these states can be obtained as the difference in the known potentials for oxidation of the ZnP unit ($E_{1/2}^{(ox)}(\text{ZnP/ZnP}^+)$ = +0.80 V vs SCE), for the reduction of the Re-bipy unit ($E_{1/2}^{(red)}(\text{Re/Re}^-)$ = −1.13V vs SCE) and for the reduction of C$_{60}$ ($E_{1/2}^{(red)}(\text{C}_{60}/\text{C}_{60}^-)$ = −0.55 eV vs SCE), respectively, with appropriate correction for the electrostatic work term. Within the limits of this type of calculation, both states are lower in energy than the singlet excited state of ZnP ($E(S_1)$ = 2.02 eV, estimated from the fluorescence spectrum), therefore the ZnP$^+$-Re$^-$-C$_{60}$ state is estimated to lie at 1.93 eV and the ZnP$^+$-Re-C$_{60}^-$ state at 1.35 eV (Figure 3.29). Qualitatively similar energy level diagrams are expected for the other solvents.

The important observation is that, upon excitation, an initial photoinduced charge separation (eq. 1) followed by a faster charge shift process (eq. 2) without accumulation of the intermediate product (ZnP$^+$-Re$^-$-C$_{60}$) is likely to occur:

\[
\begin{align*}
\text{ZnP}^\ast\text{-Re-C}_{60} &\rightarrow \text{ZnP}^+\text{-Re}^-\text{-C}_{60} \quad \Delta G = -0.09 \text{ eV} \quad (\text{eq. 1}) \\
\text{ZnP}^+\text{-Re}^-\text{-C}_{60} &\rightarrow \text{ZnP}^+\text{-Re-C}_{60}^- \quad \Delta G = -0.58 \text{ eV} \quad (\text{eq. 2})
\end{align*}
\]

The charge separated state, ZnP$^+$-Re-C$_{60}^-$, recombines to the ground state in a longer time scale (eq 3).

\[
\begin{align*}
\text{ZnP}^+\text{-Re-C}_{60}^- &\rightarrow \text{ZnP-Re-C}_{60} \quad \Delta G = -1.35 \text{ eV} \quad (\text{eq. 3})
\end{align*}
\]

The kinetics of the processes (eqs. 1, 2, 3) can be analyzed in the light of standard electron transfer theory. In the limit of weak-interaction (non-adiabatic regime), the rate constant for an electron transfer process from a donor to an acceptor is given by the following equation:

\[
k = \frac{2\pi}{\hbar} H_{DA}^2 FCWD \quad (\text{eq. 4})
\]

where $H_{DA}$ is the electronic coupling between donor and acceptor and $FCWD$ is the nuclear term (Franck-Condon weighted density of states) that accounts for the combined effects of the reorganizational energies and driving force. In principle, since the electron transfer processes (eqs. 1, 2 and 3) have different electronic factors as well as different
nuclear factors, a quantitative comparison between the rate constant values experimentally measured cannot be made. However, some remarkable comments can be useful to rationalize the kinetic data. Assuming approximately similar reorganizational energies for the charge separation and the charge shift processes (eq. 1 and 2), both processes belong to the normal Marcus region and the charge separation process (eq. 1) is likely to be slower, as it is more activated. Moreover, a better electronic factor could be expected for the charge shift process (eq. 2) that involves the C\textsubscript{60} unit directly connected to the rhenium unit via the pyridyl group, with respect to that for the photoinduced charge separation process (eq. 1), which involves the presence of an amide-bridge interposed between the ZnP and Re units. On the other hand, the fact that the charge recombination process to the ground state (eq. 3) is found to be by far slower than the charge separation (eq. 1), may be attributed mainly to two factors: i) a worse electronic term (the electron transfer occurs between two sites not directly connected) and ii) a larger exoergonicity (the process presumably fall in the Marcus inverted region).

From the data of Table 3.1, we may observe that the kinetic of charge-recombination process was found to be strongly solvent dependent with rate constants decreasing with decreasing solvent polarity. A similar solvent dependence has been observed for the charge recombination process occurring in dyad 4b described in Chapter 2, and can be qualitatively explained in terms of Marcus theory as a consequence of the changes in the driving force and reorganizational energy with changing the nature of the solvent. As the solvent polarity decreases, the energy of the charge-separated state rises; as a consequence, the driving force for charge recombination to the ground state grows, while the reorganization energy diminishes. In the hypothesis that the charge recombination belongs to the Marcus inverted region, both factors act in the same direction, and thus a strong decrease in the rate with decreasing solvent polarity is expected. On the other hand, for the charge separation that fall in the normal Marcus region, the two effects tend to compensate for each other, leading to a kinetic behavior independent of the solvent.

3.3 Conclusions

A triad system comprising a zinc-porphyrin chromophoric component and a fullerene unit coordinated around a central Re(bipy) fragment has been synthesized. Triad 19, despite being a three-component complex system, has been obtained in very good yield, and characterized. The NMR analysis, also in comparison with intermediate systems and appropriate model compounds, has elucidated several structural features of the adduct, and, in particular, highlighted the complexity deriving from the simultaneous presence of two stereogenic centers. The final triad 19 is very robust and, at the same time, possesses a
supramolecular nature in photophysical terms. All these, confirm the versatility of the rhenium-mediated strategy for the obtainment of multi-component systems. The photophysical behavior of 19 has also been investigated in detail. Electron transfer processes were detected and kinetically characterized by using a combination of emission spectroscopy and picosecond time-resolved absorption techniques. An ultrafast (τ = 1ps) photoinduced electron transfer from the zinc-porphyrin chromophore to the Re(bipy) unit can be postulated, followed by a faster charge shift process to the fullerene unit that therefore does not allows accumulation and detection of the ZnP⁺-Re⁻-C₆₀ intermediate species. Ultrafast absorption technique in the IR region allows to obtain a clear evidence for the formation of the charge separated species ZnP⁺-Re⁻-C₆₀⁻. The rate of charge separation is practically independent of the polarity of the solvent, whereas the kinetic of recombination, leading to the ground state, depends on the solvent, in agreement with a Marcus inverted behavior. For the less polar solvent (toluene) additional deactivation pathways (i.e., via the triplet states of the ZnP units and/or of the C₆₀ unit), cannot be excluded and should be explore further.

3.4 References


A metalloporphyrin-mediated approach for the efficient self-assembling of two- and three-component photoactive systems*

List of abbreviations

NDI = N-octyl-N-carboxy-naphthalenediimide
AlP = meso-(3,5-di-tert-butyl)-tetraphenylporphyrinato-(hydroxo)aluminium(III)
AlMPyP = 5-(4'-pyridyl)-10,15,20-(3,5-di-tert-butylphenyl)-porphyrinato-(hydroxo)aluminium(III)
RuP = meso-(4-tert-butyl)-tetraphenylporphyrinato-(carbonyl)ruthenium(II)
Fb = 5-(4-benzoic acid)-15-(3,5-di-tert-butylphenyl)-2,8,12,18-tetra-n-hexyl-3,7,13,17-tetramethylporphyrin
ba = benzoate
py = pyridine
TFA= trifluoroacetic acid

4.1 Introduction

As well explained in the introduction of this thesis and in the previous chapters, artificial systems mimicking the natural photoinduced processes are an important topic of research. In many of these artificial systems, porphyrins (and/or metalloporphyrins) play an important role as chromophores for the harvesting of solar light energy and as electron and/or energy vectors. In fact, besides their chemical resemblance to the chlorophylls of the natural systems, (metallo)porphyrins can be considered as ideal components for the construction of antennas for light harvesting and/or photoinduced electron transfer processes.

Supramolecular synthetic strategies have emerged in the last years as viable alternatives to covalent synthesis. In the literature it has been well demonstrated that with a suitable combination of non-covalent binding forces (coordination and hydrogen bonding among all), and with a judicious design of the geometry of the building blocks, it is possible to build relatively large, robust, and shape-persistent photoactive multicomponent architectures. On the other hand, while organic fragments used as building blocks for hydrogen-bonded assemblies may express a dual nature, i.e., one single fragment may bear both H-donor and H-acceptor moieties for multiple bonding, this peculiar feature is rarely found in organic components employed in metal-driven assemblies. Therefore, in the latter case it is inherently more difficult to construct asymmetric systems. This challenge becomes even more difficult to tackle if a one-pot high yielding self-assembling process of multi-component systems is addressed.
In this context, metalloporphyrins are an almost unique class of metal-coordination compounds, which can behave both as Lewis donors and acceptors in the formation of new coordination bonds. In fact, the tetapyrrolic macrocycle can be appropriately functionalized with a number of peripheral (either at the β pirrlic or at the meso postions) binding groups, and, at the same time, different metal ions can be inserted in the core (Figure 4.1).

![Figure 4.1. Schematic depiction of a metalloporphyrin.](image)

An additional bonus consists in the fact that a judicious choice of the central metal ion and of the external substitution pattern allows to fine-tune their physicochemical properties, including their antenna and redox features. Therefore, metalloporphyrins can potentially bind to metal fragments (that may be classical metal complexes or other metalloporphyrins) through the peripheral donor groups and, if the metal ion in the core is not coordinatively saturated, axially link to donor ligands through the inner metal (Figure 4.1). To this use, within the various metal centers that can be inserted in the core of the macrocycle, typical examples are zinc(II), ruthenium(II)(CO), and tin(IV)(OH)₂ (Figure 4.2).
Figure 4.2. Schematic depiction of possible axial coordination to the inner metal of some metalloporphyrins.

Zn(II)- and Ru(II)(CO)-porphyrins are capable of forming one additional axial bond, with a neat preference towards N-based ligands, while Sn(IV)(OH)$_2$-porphyrins can bind, with elimination of water, two additional O-based ligands (Figure 4.2). While zinc-porphyrins establish labile and relatively weak axial bonds, Ru- and Sn-porphyrins form kinetically more inert and robust axial bonds. More recently, Sanders and coworker have introduced the use of Al(III)(OH)-porphyrins as oxophilic building units for the formation of multiporphyrin arrays, either discrete or polymeric.$^{12-16}$ The high Lewis acidity of Al-porphyrins allows for the establishment of one kinetically inert and relatively stable bond with O-based ligands, and, at the same time, permits to introduce a Lewis base as additional sixth ligand, with a labile and relatively weak interaction (Figure 4.2).

The introduction of two or more attaching handles within the same metalloporphyrin (Figure 4.1, right) has been widely exploited to assemble discrete and infinite architectures of metalloporphyrins. Typical examples are cyclic structures formed by self-coordination of Zn(II)- or Ru(II)-porphyrins, bearing pendant pyridyl groups (Figure 4.3).$^{15,16}$
Figure 4.3. Examples of metalloporphyrin self-coordinated cyclic structures reported by (left) Hunter et al.\textsuperscript{15} and (right) Imamura et al.\textsuperscript{16}

More recently, the group of Sanders has reported on the formation of a cyclic trimer, obtained by self-coordination of an Al(III)-porphyrin functionalized at one peripheral \textit{meso} position with a benzoic acid moiety (Figure 4.4).\textsuperscript{17}

Figure 4.4. Self-coordinated cyclic structure reported by Sanders et al.\textsuperscript{17}

Despite the synthetic ease and the beauty of these large chromophoric arrays, they all lack the degree of complexity required to perform photoactive functions, as they contain a single type of component. Possible ways to overcome this limitation consist in either taking advantage of metal ions forming coordination bonds with distinct degree of inertness, in a precise stepwise manner, or in employing hard/soft discriminations between the metal ions and the axial donor ligands.\textsuperscript{17}

In this context, our group, has successfully exploited in the last years the exocyclic coordination ability of Zn(II)-\textit{cis}-dipyridylporphyrins to produce 2+2 zinc-porphyrin
metallacycles via coordination of the peripheral pyridyl groups to inert ruthenium(II) octahedral fragments (Figure 4.5). Subsequently, the Lewis acidity of the zinc ion has been used to efficiently combine the metallacycles with a series of pyridyl polytopic ligands (e.g., trans-dipyridylporphyrins or trans-dipyridylperylenebisimides), via axial coordination to the zinc ions (Figure 4.5). The two-step pathway employed, i.e., first coordination of the pyridyl groups to the inert Ru fragment, and second coordination of the pyridyl groups to the more labile Zn, allows to avoid the occurring of undesired scrambling reactions, even if both metals have similar affinities towards N-based ligands. The final architectures, that can be viewed as dyads in strict photophysical terms, are robust and capable of promoting distinct photoinduced processes, depending on the nature of the building units.

![Figure 4.5](image-url) Schematic depiction of multi-component porphyrin arrays reported by Iengo, Alessio and coworkers. Alternatively, the group of Sanders has reported on the preparation of a variety of self-assembled heterometallic oligoporphyrins, by cleverly tailoring the metalloporphyrins with metal ions and pendant arms possessing complementary but distinct affinities. One elegant example is reported in Figure 4.6. The two-component system is efficiently
assembled by selective coordination of the carboxylic pendant arms of the zinc(II)-
porphyrin to tin of a Sn(IV)-pyridylporphyrin, which in turn axially binds to the zinc-
porphyrin through its pendant pyridyl group.

![Figure 4.6. Example of self-assembled hetero-porphyrin two-component system reported by the group of Sanders.](image)

The work reported here, is focused on the development of new photoactive triads obtained by metalloporphyrin-mediated self-assembling strategies. The construction of a self-assembled metal-mediated three-component system is not obvious, as a very selective and simultaneous recognition events between the building units has to occur (Figure 4.7).

![Figure 4.7. Schematic depiction of a self-assembled three-component system.](image)

On this purpose, Al(III)-monopyridylporphyrin is a very promising platform for the construction of functional supramolecular arrays. In fact, this metalloporphyrin is characterized by the simultaneous presence of a Lewis acid (the Al center) and a Lewis basic (the *meso* pyridyl group) function (Figure 4.8), with different hard/soft characteristics. The aluminium center preferentially accepts hard ligands, whereas the pyridyl group coordinates preferentially to soft transition metals.
In a previous work by our group, a first accomplishment towards the challenging objective of a fully self-assembled triad was reported. The combination of one Al(OH)-monopyridylporphyrin with one Ru(CO)-porphyrin and with one naphthalenediimide equipped with carboxylic function, produced a self-assembled triad system, namely NDI-AlMPyP-RuP, as unique product (Figure 4.9). The assembling process is correctly guided by the complementarity of the metalloporphyrin affinities and those of the pendant groups. The photophysical behaviour of the triad has also been elucidated in details. The photophysical characterization of NDI-AlMPyP-RuP has shown the occurrence of a stepwise electron transfer, upon visible light excitation of the aluminium-porphyrin, that generates a charge separated state with the negative charge located on the naphthalenediimide acceptor and the positive charge located on the ruthenium-porphyrin donor, with a lifetime of few nanoseconds, indicating this system as one of the first example of triads obtained by self-assembly of molecular components via coordinative bonds uniquely (Figure 4.9).
Given this background, in this work the versatility of the self-sorting coordination abilities of the above metalloporphyrins, has been exploited to build three-component systems by simply varying the nature of one of the building blocks. In particular, two examples are presented, in which the naphthalene bisimide has been replaced either with a free-base porphyrin or with a series of fulleropyrrolidines, all suitably functionalized with a carboxylic acid group in order to maintain the selective binding motif just described (Figure 4.10).

**Figure 4.10.** Schematic depiction of free-base porphyrin Fb and fulleropyrrolidines monoadducts 23, 25 and 26.

### 4.2 Results and Discussion

#### 4.2.1 Synthesis and characterization of the molecular components

Prior to investigate the coordination of fullerenes towards the aluminium-porphyrin platform, a series of fulleropyrrolidine monoadducts containing a terminal carboxylic acid have been prepared (Figure 4.10). With this purpose amino acid 21 was synthesized from literature procedure (Scheme 4.1). The β-alanine tert-butyl ester was reacted with benzyl bromoacetate to protect the amino group. The desired mono alkylated derivative 20 was collected by column chromatography (yield ca. 35%). The subsequent hydrogenation, in presence of a catalytic amount of Pd/carbon, produced the desired unprotected amino acid 21. To obtain the fulleropyrrolidine monoadduct 22 by 1,3-dipolar cycloaddition on C₆₀, amino acid 21 was dissolved in toluene with p-formaldehyde and C₆₀ and refluxed for ca. 30 minutes. The fulleropyrrolidine monoadduct 24 was obtained by reaction of amino acid 21 with dihexyl ketone and C₆₀ in orthodichlorobenzene, at 170 °C for ca. 25 min. Pure 22
and 24 were purified by a plug of silica. A final step of deprotection on 22 and 24, in acidic conditions, afforded 23 and 25, respectively, in almost quantitative yields.

![Scheme 4.1. Synthesis of 23 and 25. Reagents and conditions: (i) NEt₃, dioxane, room temperature, 4 h; (ii) H₂, Pd/C, EtOH, room temperature, 12 h; (iii) p-formaldehyde and C₆₀, toluene, reflux, 30 min; (iv) dihexyl ketone and C₆₀, orthodichlorobenzene, 170 °C, 25 min; (v/vi) (i) TFA/DCM, room temperature, overnight.](image)

The fulleropirrolidine monoadduct 26 was instead directly obtained by cycloaddition of sarcosine and 4-carboxybenzaldehyde on C₆₀, followed by column chromatography, as reported in literature (Scheme 4.2). The solubility of the three fulleropyrrolidines is markedly different, and in particular 23 is totally insoluble in chlorinated solvents, 26 has a fair solubility, whereas 25, that bear two hexyl alkyl chains on the pyrrolidine ring, shows a good solubility. From these reasons, only 25 and 26 were further investigated.

![Scheme 4.2. Schematic synthesis of 26.](image)
Compounds 25 and 26 have been fully characterized by a variety of techniques in solution (NMR, UV-vis spectroscopies, and ESI mass spectrometry). The ESI mass spectra of both compounds show a single peak for the molecular ion [M–H]−. As example, the ESI-MS spectrum of 25 is reported in Figure 4.11.

![Figure 4.11. ESI mass spectrum of 25, calculated for C_{27}H_{33}N_{1}O_{2} ([M – H]^-) 1003.3, found 1002.3.](image)

A full NMR characterization in solution has been also performed and a few representative features will be shortly described. In Figure 4.12 the 1H NMR spectra (CDCl₃/CD₃OD) of 25 and 26 are reported. Compound 26 has a similar structure to that reported in Chapter 3 for the pyridyl fulleropyrrolidine monoadduct 8. In particular, the carbon C₂ on the pyrrolidine ring is a stereocenter and the monoadduct forms as a racemic mixture. For this reason H₈ and H₈' are diastereotopic and the corresponding proton NMR resonances are split. On the other hand, 25 is not chiral but the protons of its hexyl chains are enantiotopic. This fact is clearly evident for the first two protons (H₈ and H₈') that both presents signals split into two equally intense multiplets, mutually coupling in the 2D H-H COSY spectrum.
Chapter 4

Figure 4.12. $^1H$ NMR spectra (CDCl$_3$/CD$_3$OD, 500 MHz) of 26 (top) and of 25 (bottom), with the labeling scheme.

The Al(OH)-tetraphenylporphyrin, AlP, the Al(OH)-monopyridylporphyrin, AlMPyP, and the Ru(CO)-tetraphenylporphyrin, RuP (Figure 4.13), have been obtained by reaction of either AlMe$_3$ or Ru$_3$(CO)$_{12}$, followed by column chromatography, with the corresponding free base porphyrins (prepared by the Adler-Longo procedure), as reported earlier.$^{12,32-35}$ The free-base porphyrin Fb (Figure 4.13) was already available in our laboratories.

Figure 4.13. Schematic depiction of the molecular components AlP, AlMPyP, RuP and Fb.
4.2.2 Synthesis of two- and three-component (metallo)porphyrin systems

The quantitative and selective one-pot self-assembly of the stable two- and three-component photoactive systems, 27 and 28, has been efficiently achieved at room temperature, in CHCl₃ solution as reported in Scheme 4.3. In particular, coordination of the carboxylic group to the Al(OH)-porphyrins, occurs with the loss of one molecule of H₂O, thus leading to the attachment of a benzoate group.

Scheme 4.3. Self-assembly of the two- and three-component component systems 27 and 28, with labeling scheme.
With specific regard to 28, as the different (metallo)porphyrins are compatible in terms of solubility, and the kinetics of the coordination bonds involved are fast, the resulting assembling process occurs almost instantly and in very mild conditions. In fact, the simple mixing in chlorinated solvents at room temperature of the individual compounds (in a stoichiometric ratio), leads, almost instantaneously, to the formation of the desired products, collected by precipitation, in almost quantitative yields. The assembled dyad and triad are robust and remain intact for concentrations \( \geq 5 \times 10^{-5} \) M (in chlorinated solvents).

27 and 28 have been fully characterized in solution by means of 1D and 2D NMR spectroscopy in CDCl₃, UV-vis absorption and emission experiments in CH₂Cl₂ solutions (see also the photophysical characterization below). Mass analysis attempted with two different techniques (ESI and MALDI), has proved particularly challenging and only afforded molecular peaks corresponding to fragmentation, as it is often the case with side-to-face metalloporphyrin assemblies.

In Figure 4.14 the \(^1\)H NMR spectra of 27 and 28, as compared to that of free Fb, are reported. Despite the great number of proton resonances present (particularly in the aromatic region), full assignment was possible; relative integrations are consistent with the adducts stoichiometries. As expected, the main consequence of the axial coordination to the metalloporphyrins, is a substantial up-field shift of the proton resonances of the axially bound ligand, as already described previously for other side-to-face assembled.\(^{36-38}\) Indeed, the proton resonances of both Fb (within 27 and 28) and AlMPyP (within 28) are remarkably up-field shifted, the effect being more dramatic for the resonances of the protons closer to the shielding cone of the facing porphyrin. The \( \Delta \delta \) for the benzoate protons of Fb in 27, a and b are \(-2.95\) and \(-1.13\), respectively. These values are in perfect agreement with those already reported for AlP(ba) (see below Figure 4.22).\(^{12}\) A further upfield shift of these protons is observed in 28 (\( \Delta \delta = -3.33 \) and \(-1.28\), for protons a and b, respectively), and this additional contribution reasonably originates from the extra anisotropic effect of the facing Ru(CO)-porphyrin. Similarly, and as already reported earlier for NDI-AlMPyP-RuP (see Figure 4.9), the resonances of the pyₐ and pyₚₜ protons of AlMPyP in 28 show a \( \Delta \delta \) of \(-7.15\) and \(-2.00\), respectively.\(^{26}\) In this case the shift is more pronounced than that observed for the benzoate protons, because the pyridyl group is closer to the facing metalloporphyrin, with respect to the benzoate. These anisotropic shielding effects are also clearly evident from the spreading on a wide ppm range of the \( \beta \) pírrolic proton resonances of AlMPyP and from the chemical shifts of the proton of hexyl and methyl substituents (\( R' \) and \( R'' \), respectively) of Fb. For example, while in unbound Fb, the non-equivalent -CH₃ groups give raise to two very close singlets, and the resonances of the non-equivalent hexyl chains are not resolved, when Fb is axially bound to the Al-porphyrin the following occurs: i) the singlet corresponding to the -CH₃ groups in the 13 and 17 positions, gets up-field shifted; ii) hexyl proton resonances are split into two
equally intense sets, with the set at higher fields pertaining to the hexyl protons closer to the facing Al-porphyrin. A 2D NOESY NMR experiment performed on 28 did not indicate any spatial correlation between the protons of the alkyl groups of the Fb unit and those of RuP. This fact, together with the presence of one single resonance for the Hmeso protons of Fb, suggests that the free-base and the ruthenium-porphyrin, within 28, assume, in solution, a parallel average orientation.
Figure 4.14. Partial $^1$H NMR spectra (CDCl$_3$, 500 MHz) of Fb (top), 27 (middle), and 28 (bottom) (see Scheme 4.4 and 4.5 for labeling).
Qualitative $^{1}$H NMR experiments have been performed in order to nicely prove how the different coordination binding motives are efficiently directing the self-assembling process, and how the Al-monopyridyl porphyrin is playing the central pivotal role in this process. $^{1}$H NMRs of approximately 1:1 mixtures of Fb/AlMPyP or Fb/RuP or AlMPyP/RuP have been recorded first, and then re-recorded after the addition of ca. one equivalent of the missing partner as schematically depicted by the three reaction pathways, 1, 2, and 3 in Scheme 4.4. Indeed, the final outcome is always the desired three-component assembly 28. The difference in the three reaction pathways lays in the fact that for 1 and 2 an intermediate two-component system forms (Fb-AlMPyP or AlMPyP-RuP, respectively), whereas for 3 there is no interaction between the starting units, Fb and RuP, and the donor/acceptor pivotal AlMPyP has to be added, so as to establish the useful chemical connections.

Scheme 4.4. Possible reaction pathways 1, 2 and 3, leading to the same three-component system 28.
4.2.3 Two- and three-component (metallo)porphyrin-fullerene systems

Following the metal-mediated approach just described, the two-component systems 29, 30, and the three-component system 31 were prepared (Figure 4.15).

The presence of the two alkyl chains in 25 provide for a good solubility of 25 in chlorinated solvents, thus allowing to follow the formation of 29 directly in an NMR (CDCl₃) sample. A ¹H NMR titration has been performed starting from a 1.5 mM solution of 25 in CDCl₃ by adding progressive aliquots of solid AlP. The occurring of the fullerene axial coordination to the aluminium center can be observed with the expected upfield shift of the signals of the proton closer to the porphyrin aromatic plane ($\Delta\delta = -1.00$ and $-4.73$, for $H_A$ and $H_1$, respectively). Nevertheless, even above the one to one ratio of 25 and AlP, the presence of additional signals, that can be assigned to an excess of unreacted 25 and to a species containing the Al-porphyrin else than free AlP, can also be detected (in a ratio 2:1). The ¹H NMR spectrum registered after the addition of 1.5 eq of AlP is reported in Figure 4.16.
Figure 4.16. $^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 29 with labeling scheme. Inset: Downfield region of the spectrum. Proton resonances of 25, 29, and of a third species, postulated to be CF$_3$COO-AlP, are identified with blue, red and green circles, respectively.

The reaction has been also performed at reflux in chlorinated solvents, with and without anhydrous sodium sulfate (to eliminate the H$_2$O liberated during the reaction), but analogous $^1$H NMR were obtained. Several attempts of purification, by either crystallization (with different combination of solvents) or by column chromatography, have been made without success. One plausible explanation of the behaviour observed is that fulleropirrolidine 25 contains a not negligible amount of residual TFA (used for the deprotection of the –COOH group). If this is the case, then the trifluoroacetic acid acts as a competitive ligand for axial coordination to the aluminium center, and a species of the type CF$_3$COO-AlP (Figure 4.16), is concomitantly form, together with 29. A partial confirmation of this hypothesis comes from a very recent 1D $^{19}$F NMR experiment performed on 25, in which the presence of a singlet at –75.3 ppm (typical of TFA ) is clearly evident (Figure 4.17). $^{19}$F NMR experiments on solutions of mixed 25 and AlP are planned.
On the contrary, the simple mixing in solution of 26 and AIP in a stoichiometric ratio leads to the formation of the desired product instantaneously at room temperature in chlorinated solvents, which can be collected by precipitation, almost quantitatively. The $^1$H NMR spectra of 26 and 30 are reported in Figure 4.18. Relative integration between the fullerene and porphyrin proton resonances confirms the formation of a 1:1 complex. The full coordination of the fullerene unit is confirmed by the characteristic upfield shifts observed for the $a$ and $b$ proton resonances, ($\Delta \delta = -2.96$ and $-1.04$, respectively). A, progressive less pronounced, shielding effect is noticeable also for the pyrrolidine resonances of protons $H_A$, $H_B$ and $H_B'$, and for the methyl group (Figure 4.18).

![Figure 4.17. $^{19}$F NMR spectrum (CDCl$_3$, 500 MHz) of 25.](image)

![Figure 4.18. $^1$H NMR spectrum (CDCl$_3$/CD$_2$OD, 500 MHz) of 26 (top) and $^1$H NMR spectrum (CD$_2$Cl$_2$, 500 MHz) of 30 (bottom), with labeling scheme.](image)
The UV-vis absorption spectrum of 30 shows the bands, at 418 nm (Soret), 548 and 587 nm (two Q-bands), characteristic of the AlP component. This fact indicates that the coordination of 26 does not affect the electronic ground state of AlP. In the UV region it is possible to observe the contribution of 26 (Figure 4.19).

![Absorbance vs Wavelength](image)

**Figure 4.19.** UV-vis spectra (DCM) of 30 (red trace) and AlP (black trace).

The quantitative self-assembly of 31 has been also obtained by the simple mixing in solution at room temperature of the individual compounds in a stoichiometric ratio. 31 has been fully characterized in solution by means of 1D and 2D NMR experiments. In Figure 4.20 ¹H NMR spectrum of 31 (the comparison with those of 27, and 30) is reported. All the assignments have been made by means of 2D experiments, and the corresponding resonances show the correct relative integrations.
Figure 4.20. $^1$H NMR spectrum (CDCl$_3$/CD$_3$OD, 500 MHz) of 27 (top) and $^1$H NMR spectra (CD$_2$Cl$_2$, 500 MHz) of 30 (middle) and 31 (bottom), with labeling scheme.
In Figure 4.21 the emission spectrum of 31 (upon selectively excitation of AlP component in the Q bands region) is reported. It can be noted that the porphyrin fluorescence is almost totally quenched if compared with those of unbound AlP, indicating the occurrence of an efficient interaction between the excited state of the porphyrin and the fullerene.

![Emission fluorescence](image)

**Figure 4.21.** Emission fluorescence (DCM, 25°C, \( \lambda_{\text{exc}} = 550 \text{ nm} \)) of 31 (blue trace) and of AlP (black trace).

A photophysical investigation on 31 is currently ongoing, in order to elucidate the nature of such interaction (i.e., energy and/or electron transfer). However, in the meantime, two papers on similarly structured systems have been reported by Ito and coworkers (Figure 4.22). 30,31

![Molecular structures](image)

**Figure 4.22.** Al(III)-porphyrin dyad and triads reported by Ito et al. 30,31

For both cases the formation of the fullerene radical anion, after excitation of the Al-porphyrin, has been observed, but the mechanism of its formation was not fully
understood. Also, quite surprisingly, no appreciable differences, in terms of formation and life-time, could be observed between the triad the corresponding dyads.

For future photophysical investigations, the two-component system 32, and the model compounds AlP(ba) and RuP(py) have been also prepared (Figure 4.23).

![Figure 4.23](image)

**Figure 4.23.** Schematic representation of the two-component system 32 and the model compounds AlP(ba), and RuP(py) used in the present study.

32 was prepared by simple mixing of 8 (see also Chapter 3) and RuP in a 1:1 ratio, and isolation of the pure product by crystallization in almost quantitative yield. In this case it was possible to obtain an ESI mass spectrum (Figure 4.24), in which the peak of molecular ion of 32 is found at 1348.1.

![Figure 4.24](image)

**Figure 4.24.** ESI-MS of 32 calculated for [(M-H)]: 1347.1 found:1348.1

32 has been also characterized by 1D and 2D NMR experiments. In Figure 4.25 the $^1$H NMR is reported. The coordination of 8 is evident by the large upfield shift of the pyridyl proton resonances py$_a$ and py$_b$, as usual, consequent to the anisotropy of the porphyrin core ($\Delta \delta = -7.15$ and $-1.76$, respectively).
4.3 Photophysical investigation on the two- and three-component (metallo)porphyrin systems

In collaboration with Prof. M. T. Indelli (University of Ferrara), a detailed photophysical behavior of the two- and three-component (metallo)porphyrin systems, 27 and 28, have been thoroughly investigated, also in comparison with model compounds representative of the individual components (namely, Fb, AlP(ba), and RuP(py), (see Figure 4.13), and will be discussed separately for clarity reasons.33

The absorption spectrum of 27 (red curve in Figure 4.26) is in good agreement with the superposition of the spectra of the molecular components. However, the absorption bands of Fb and AlP(ba) are overlapping; therefore, a selective excitation of the single chromophores (either Fb or AlP) is not feasible. Convenient excitation wavelengths are 508 and 548 nm, at which the light is predominantly absorbed by the free-base porphyrin (80%) and by the aluminium porphyrin (87%), respectively.
Figure 4.26. Absorption spectra (CH\textsubscript{2}Cl\textsubscript{2}) of 27 (red), AlP(ba) (black) and Fb (blue).

A supramolecular adduct, of two or more components, is a system in which the electronic ground states of the species, forming the adduct, do not interact. In this manner it is possible to consider the photophysics properties of the supramolecular molecule as the sum of the properties of each component. In this context, a simplified energy level diagram for 27 can be derived from the spectroscopic properties of the models Fb and AlP(ba) (Figure 4.27). In the diagram the high-lying charge transfer state, \textit{Fb}^\text{+}–\textit{AlP}^\text{−}, has been omitted for clarity. In fact, the energy of this state, obtained from the redox potentials measured for 27 (\textit{E}^\text{red} = −1.44 V \text{vs SCE} for \textit{Fb} and \textit{E}^\text{ox} = +0.84 V \text{vs SCE} for \textit{AlP(ba)} including the appropriate electrostatic work term), is too high in order to be accessible (2.15 eV). On the contrary, the diagram clearly suggests that an energy transfer pathway is available for the deactivation of the singlet state of the aluminium porphyrin unit.

Figure 4.27. Energy level diagram of 27.
The room-temperature emission spectra of 27 in dichloromethane solution, measured at two different excitation wavelengths (λ = 508 and 548 nm) are reported in Figure 4.28. A comparison with the emission spectra of the corresponding models (inset of Figure 4.28) clearly shows that 27 exhibits the fluorescence emissions of both chromophores, and the relative intensities strongly depend on the excitation wavelength. This behaviour is apparent from the fluorescence contour measurements (Figure 4.29).

![Figure 4.28. Emission spectrum of 27 in dichloromethane, measured at two different excitation wavelengths (λ = 508 nm, excitation of Fb (dotted line); λ = 548 nm, excitation of AlP (continuous line)). Inset: normalized emission spectra of Fb (dotted line) and of AlP(ba) (continuous line).](image1)

Quantitative spectrofluorimetric measurements indicate that upon excitation at 548 nm (where the light is predominantly absorbed by AlP) the aluminium–porphyrin fluorescence is strongly quenched (50%) compared to the corresponding model AlP(ba), and a sensitized fluorescence of the free-base unit is clearly observed (Figure 4.30).

![Figure 4.29. Fluorescence contour map of 27 (λ_{exc} = 508 nm, CH_{2}Cl_{2}, room temperature).](image2)
Figure 4.30. Emission spectra of: (left) 27 (continuous line) and AlP(ba) (dotted line) (optically matched solutions, CH₂Cl₂, λₑₓ = 548 nm); (right) 27 (continuous line) and of Fb (dotted line) (optically matched solutions, CH₂Cl₂, λₑₓ = 548 nm).

This result strongly suggests that the mechanism for the quenching of the aluminium–porphyrin fluorescence in 27 is a singlet–singlet energy transfer process from the AlP to the Fb component (Fb–AlP* → Fb*–AlP). To obtain an estimate for the efficiency of this energy transfer process (\( \eta_{\text{ent}} \)), a relative method, compatible with the use of stable (\( 5 \times 10^{-5} \) M) solutions, was adopted. Relative-emission-intensity measurements were performed on 27 and Fb (solutions optically matched at the excitation wavelength) by using 548 nm as the excitation wavelength, at which, in the case of 27, the light is predominantly (87%) absorbed by the AlP unit. The ratio of the emission intensities measured at 695 nm, the wavelength of the maximum fluorescence of Fb, gives a value of \( \eta_{\text{ent}} \approx 0.5 \) for the efficiency of the process. The comparison between the excitation spectrum of the Fb fluorescence and the absorption spectra is consistent with this result. The photophysical behavior of 27 is summarized in Figure 4.27.
The absorption spectrum of 29 is shown in Figure 4.31, together with the spectra of the model compounds. As can be seen from Figure 4.31, a selective excitation of the individual components is not feasible. Convenient excitation wavelengths are: 508, 532, and 548 nm, at which light is substantially absorbed by Fb (68%), RuP (59%), and AlMPyP (64%), respectively.

![Figure 4.31. Absorption spectra (CH₂Cl₂) of 28 (green), Fb (blue), RuP(py) (orange), and AlP(ba) (black).](image)

As already seen for the model 27, a simplified energy level diagram for 28, can be derived from the photophysical properties of the molecular components and model compounds, as shown in Figure 4.32. From electrochemical analysis of the components, a charge separated state can be localized at 1.80 eV corresponding to Fb–Al−Ru⁺ (E^{red} = −1.21 V vs SCE for AlMPyP(ba) and E^{ox} = 0.78 V vs SCE for RuP(py) including the appropriate electrostatic work term), in which the AlMPyP unit is reduced and the RuP unit is oxidized.

![Figure 4.32. Energy level diagram of 28.](image)
After the excitation of the aluminium–porphyrin chromophore, two quenching pathways are available: a singlet–singlet energy transfer process to the free-base unit (Fb–Al*–RuP → Fb*–Al–RuP) and an electron transfer from the ruthenium–porphyrin to the excited singlet state of the aluminium–porphyrin (Fb–Al*–RuP → Fb–Al–RuP*). The photophysical study was aimed at the discrimination of the occurring process.

In dichloromethane, upon excitation of the AlMPpyP unit (548 nm), the aluminium–porphyrin fluorescence is totally (> 99%) quenched (Figure 4.33), and the quenching process is not accompanied by the appearance of a sensitized free-base porphyrin fluorescence.

**Figure 4.33.** Emission spectra of 28 (continuous) and AlP(ba) (dashed), optically matched solutions, CH₂Cl₂, at λ<sub>exc</sub> = 548 nm.
This result clearly indicates that the quenching is due to the electron transfer process \( \text{Fb–Al}^*\text{–Ru} \rightarrow \text{Fb–Al}^*\text{–Ru}^* \), which prevails over the energy transfer process \( \text{Fb–Al}^*\text{–Ru} \rightarrow \text{Fb}^*\text{–Al}^*\text{–Ru} \) (Figure 4.32). Single-photon counting experiments demonstrate that the Al-based residual emission decays with a lifetime \( \leq 250 \) ps (Figure 4.34).

![Emission decay (with superimposed lamp profile) monitored at 615 nm for 28 in CHCl₃. The solid line represents the fit of the data points to a two-exponential decay law (see text). The values obtained from the fit are (pre-exponential factors in parentheses): \( \tau_1 = 250 \) ps (85%); \( \tau_2 = 5 \) ns (15%).](image)

**Figure 4.34.** Emission decay (with superimposed lamp profile) monitored at 615 nm for 28 in CHCl₃. The solid line represents the fit of the data points to a two-exponential decay law (see text). The values obtained from the fit are (pre-exponential factors in parentheses): \( \tau_1 = 250 \) ps (85%); \( \tau_2 = 5 \) ns (15%).

From this value a rate constant of \( k_{el} > 4 \times 10^9 \) s\(^{-1}\) can be estimated. To obtain a complete photophysical characterization of the system, experiments were carried out by using different excitation wavelengths. Upon excitation at 508 nm, at which light is substantially absorbed by the free-base component, the typical free-base fluorescence is quenched (65%). The most likely mechanism is an intersystem crossing to the triplet excited state by a heavy-atom effect \( (\text{Fb}^*\text{–Al–Ru} \rightarrow \text{Fb}^*\text{–Al–Ru}) \). As discussed in our previous works, this effect, that is, the enhancement of a formally spin-forbidden deactivation process of the singlet state of a free-base porphyrin by spin–orbit coupling, is a general feature observed for porphyrin arrays containing Ru atoms.\(^{39}\) On the other hand, upon excitation of the ruthenium–porphyrin, which quantitatively populates the ruthenium–porphyrin triplet state, a stepwise triplet–triplet energy transfer from the ruthenium to the aluminium and consequently to the free-base porphyrin is expected to occur (Figure 4.32). Laser flash photolysis experiments (\( \lambda_{exc} = 532 \) nm) show that the transient spectrum observed immediately after the laser pulse (10 ns) is the triplet–triplet absorption spectrum of the Fb component (Figure 4.35), which indicates that the stepwise energy transfer process is fast (\( \leq 10 \) ns).
Figure 4.35. Triplet difference absorption spectra obtained in laser flash photolysis experiments (CH$_2$Cl$_2$) of: (left) Fb; (right) 28.

The different photophysical behaviour of 27 and 28 is very schematically summarized in Figure 4.36.

Figure 4.36. Schematic representation of the photoinduced processes occurring in 27 and 28 upon excitation of the Al-porphyrin component.

4.4 Conclusion

In this work, a metallolporphyrin metal-mediated self-assembly strategy, based on hard/soft discriminations has been successfully used to form robust photoactive two-component and three-component systems in quantitative yields. The selective synthetic approach described here is in principle a powerful and viable tool for the construction of easy-to-make libraries of three-component photoactive arrays with desired built-in properties. The photophysical properties of the (metallo)porphyrin systems 27 and 28 have been investigated by using stationary and nanosecond time-resolved emission techniques, and the results were interpreted in terms of photoinduced intercomponent processes. Noticeable differences are found between the two systems. In the two-component system, an energy transfer from the singlet excited state of the aluminium–porphyrin to that of the free-base porphyrin takes place efficiently. On the other hand, when the ruthenium–
Chapter 4

porphyrin component is added to give the three-component system, the electron-transfer process \( \text{Fb–Al}^\bullet–\text{Ru} \rightarrow \text{Fb–Al}–\text{Ru}^+ \) prevails over the energy-transfer process in the deactivation of the singlet state of the aluminium–porphyrin unit. The photophysical characterization of the two- and three-component metalloporphyrin-fullerene systems is currently under investigation.

4.5 References


Chapter 5.

Functionalization of water-soluble liposomes with rhenium(I)(bipy) and zinc-porphyrin units for photocatalysis applications*  

* The work discussed in this chapter has been performed during a six-month stay in the laboratories of Prof. L. Bouwman and Dr. S. Bonnet, and supported by an Erasmus Placement fellowship.
List of abbreviations

bipy = 2,2’-bipyridine
phen = 1,10-phenanthroline
ZnTPPyMe = zinc(II)-meso-tetra-(4’-pyridinium)-porphyrin
ZnTPPS = zinc(II)-meso-(4’-sulfonato)-tetraphyloporphyrin
TEOA = triethanolamine
TEA = triethylamine
(NA)DMPG = Sodium 1,2-dimyristoyl-sn-glycero-3-phosphoglycerol
DMPC = 1,2-dimyristoyl-sn-glycero-3-phosphocholine
eDMPC(Cl) = 1,2-dimyristoyl-sn-glycero-3-ethylphosphocholine chloride
MLCT = Metal-to-Ligand-Charge-Transfer
OER = One-Electron-Reduced species
TN = Turnover Number
DLS = Dynamic Light Scattering

5.1 Introduction

As pointed out along this thesis, there are extensive efforts being made in the field of artificial photosynthesis. Actually, one of the most problematic consequences related to the consumption of fossil fuels is the constant and progressive increase of CO\textsubscript{2} concentration into the atmosphere. The dramatic consequences of this situation (desertification, high sea level, loosing of ice caps) have been widely predicted by many researchers. For this reason, in parallel with the constant search for renewable energies, it is concomitantly urgent to find viable ways to sequester and/or to convert the massive amounts of CO\textsubscript{2} released into the atmosphere. Among these, the artificial photocatalytic conversion of CO\textsubscript{2} into liquid fuels is a critical goal that would positively impact the global carbon balance by recycling CO\textsubscript{2} into usable fuels. Great interest has been focused on CO production as a chemical feedstock for industrial processes like the hydroformylation and the Fischer–Tropsch reactions.\textsuperscript{1,2} Artificial homo- and heterogeneous systems for the conversion of CO\textsubscript{2} into liquid fuels have been deeply investigated in the last decades and, despite great improvements were made, still no robust artificial solutions have been found.

In the literature many studies have been reported, with very many groups actively contributing at present. One of the pioneering systems was reported by Tinnemans et al. He
proposed bi-component systems based on tetraaza-macrocycles of cobalt(II) or nickel(II) as catalysts combined with ruthenium(bipy)₃ as photosensitizer.³ Many other photocatalysts have been proposed, based on the similar systems, in which variation on the tetraaza-macrocyclic ring and/or photosensitizer have been reported, such those of Fujita and coworker.⁴⁵ Kimura et al. also developed systems in which the photosensitizer (Ru(bipy)₃ or Ru(phen)₃) was covalently linked to the tetraaza-macrocyclic metal complex and presented a catalytic efficiency very similar to the bi-component systems, but with increased photostability (Figure 5.1).⁶⁻⁸ Other systems based on cobalt complexes and metalloporphyrins, or related metallo-macrocycles (metallocorrins, metallalphalocyanines and metallocorroles), have been also investigated.⁹⁻¹³

**Figure 5.1.** Example of Ru(bipy)₃-tetraaza-macrocycle of Ni(II) conjugate reported by Kimura et al.⁸

### 5.1.1 Rhenium(I)(diimine) complexes as photocatalysts for CO₂ reduction

In the early 1980s, Lehn and co-workers reported for the first time on the homogeneous photochemical reduction of CO₂ to CO using a simple molecular photocatalyst, fac-[Re(CO)₃(bipy)(L)] (L = Cl⁻ or Br⁻) in DMF/TEOA.¹⁴¹⁵ They found that the rhenium(I) catalyst has a higher selectivity for CO production as compared to other photocatalytic systems, for which the CO₂ photoreduction outcome may include side products, such as formate or H₂. Since then, octahedral rhenium(I)(CO)₃(bipy) fragment, bearing one labile ligand L in the last apical position has become one of the most widely studied catalyst for the photochemical reduction of CO₂ to CO (Figure 5.1).¹⁴⁻²⁶

![Rhenium(I)(diimine) complexes as photocatalysts for CO₂ reduction](image)

**Figure 5.2.** Examples of rhenium(I)(CO)₃(bipy) complexes studied for the photocatalytic conversion of CO₂ to CO.

L = Cl⁻, Br⁻, CN⁻, NSC⁻, PR₃, py, ...
R = -(CH₂)ₙCH₃
- COO(CH₂)ₙCH₃
X = OT⁺, PF₆⁻, NO₃⁻
In terms of spectral properties, and as already discussed in the previous Chapters, Re(I)bipy complexes show a typical absorption band related to the Re → bipy MLCT transition in the 350 – 400 nm region. This band can be positioned at relatively different wavelengths, depending on the nature of the apical ligand and/or the functionalizations on the bipyridyne. When the triplet MLCT excited state is populated by UV irradiation in the presence of sacrificial electron donors (typically amines, like TEOA or TEA), an electron transfer process from the donor occurs (reductive quenching) to yield $[\text{Re}^I \text{bipy} \cdot \text{CO}_3 \text{L}]^-$ (where bipy’ is a radical anion), the so-called one-electron-reduced species (OER). From the OER, the complex is either recovered (by charge recombination to the ground state, with the occurring of possible intermediate steps of photodissociation and re-association of the apical ligand L, or it undergoes photodegradation (for example with formation of permanently reduced species) (Figure 5.3)

![Figure 5.3. Schematic depiction of the cycle occurring upon UV of a neutral \( [\text{Re(CO})_3\text{(bipy)(L)}] \) complex in the presence of a sacrificial electron donor (SD).](image)

Depending on the nature of the ligand L, the stability of the OER in solution can be tuned. If the OER is sufficient stable, it can be accumulated in solution, and its formation can be monitored by UV-vis spectroscopy. An example, reported by Hori and coworkers, is shown in Figure 5.4.\(^\text{18}\) The absorption spectra shows the formation and progressive increase of the characteristic bands (at around 500 nm), plus a weak broad band at longer wavelength, attributed to the radical anion located on the bipy ligand.
Figure 5.4. UV–vis absorption spectroscopic changes of a DMF/TEOA (5/1, v/v) solution containing 2.5 mM fac-[Re(CO)$_3$(bpy)(P(OEt)$_3$)]$^+$ irradiated at 365 nm.$^{21}$

As well documented in the literature, the formation of the OER is the primary step of the catalytic cycle of the photoreduction of CO$_2$ to CO. Nevertheless, despite several groups have tried to elucidate the complete mechanism of the reaction, the catalytic cycle is not yet completely disclosed and many questions are still open. In particular, one of the crucial points is the source of the second electron that is necessary to reduce the CO$_2$. Ishitani et al. have recently performed a systematic study, in which he argues that the second electron is provided by a second molecule of Re(bpy)(CO)$_3$L (Figure 5.5).$^{21}$ These data suggest the possibility of the formation of a binuclear rhenium dimer intermediate, and have been supported by theoretical studies by Agarwal.$^{25,26}$

Figure 5.5. Catalytic cycle proposed by Ishitani for the photoreduction of CO$_2$ to CO by the fac-[Re(CO)$_3$(bipy)(NCS)] catalyst, in the presence of the sacrificial donor TEOA.$^{21}$
The photocatalytic systems based on mononuclear rhenium complex have shown a very high selectivity toward CO production (no hydrogen is detected in the experiments), but also limitations in terms of efficiency and turnover number TN (with 48 being the highest value obtained), as a consequence of the catalyst photodegradation.\textsuperscript{14} Moreover, Re(bipy)-based catalysts are highly demanding in terms of light energy required for activation. So, in the last years, several studies have been made in order to couple this type of catalysts with chromophores absorbing in the visible region. The groups of Ishitani, Perutz and Bian have been active on this topic, and developed systems with either Re(bipy) fragments appended to a chromophoric unit (ruthenium(bipy)\textsubscript{3} or metalloporphyrins) by covalent bonds or investigated bi-component mixed systems.\textsuperscript{20,24,27,28} Some relevant examples are reported in Figure 5.4. One of the best results, in terms of catalytic efficiency, was reported by Ishitani with a TN of 232 (Figure 5.6, left).

The idea to sensitize the catalyst with a chromophore with a virtually free light energy source seems to be a promising direction in order to obtain an efficiency improvement and practical applications, but several aspects still needs to be addressed. For example, great efforts are still necessary in order to increase the photosensitizer and the catalyst photostability, which represents one of the stronger limitations of these systems. Moreover, it is worth to remark here that, up to date, all the Re(bipy) based catalysts are employed in environmentally not sustainable organic solvents. It would be very interesting and challenging, to promote the photoreduction of CO\textsubscript{2} in homogeneous water solution.

### 5.1.2 Liposomes as supramolecular scaffolds

The self-assembly of lipid molecules in aqueous solution, usually results in the formation of amphiphilic bilayers, with the hydrophilic polar heads of the lipids oriented towards the aqueous phase and the hydrophobic portions forming the core of the bilayer. When the bilayers are closed in a spherical shape, they are called vesicles, whereas artificial synthesized vesicles are named liposomes. Liposomes formed by phospholipids
have been widely used to mimic the functions and the shape of biological membranes. Lately, they have also been used to develop carrier systems, reaction containers, sensors as well as supramolecular scaffolds.\textsuperscript{29–31} In particular, liposomes can work as supramolecular supports (via electrostatic or hydrophobic interactions) in order to obtain a high content of the desired active species on the surface and/or in the membrane.

In the last years, in the group of Prof. L. Bouwman and Dr. S. Bonnet (University of Leiden, The Netherlands), in whose laboratories the work here presented was carried out, has developed great expertise on the potential use of liposomes as supramolecular scaffolds.\textsuperscript{32,33} In one of their studies, they reported on the preparation of negatively charged and neutral liposomes in the presence of a Ru(II)(polypiridyl) complex containing a S-bonded cholestanol-thioether hybrid ligand. Several of such complexes embed in the membrane via hydrophobic interactions of the cholestanol portions of the S-ligand, while the Ru-(polypiridyl)(thioether) heads remain exposed on the surface. The complexes get released in solution after visible light irradiation (that causes the cleavage of the Ru-sulfur bond and the formation of a Ru-(polypirdyl)(aqua) species, Figure 5.7). When negatively charged lipids where employed to form the liposomes, the aqau complexes retain some (electrostatic) interactions with the liposome surface, that allows for its (thermally- driven) back coordination to the S-ligand.\textsuperscript{32}

![Figure 5.7. Schematic representation for light-triggered release of Ru(II) complexes anchored on liposomes: (a) with anionic DMPG lipids or (b) with neutral DMPC lipids.\textsuperscript{32}](image)

Given this background, in this work, preliminary investigations on the potential use of liposomes as supramolecular scaffolds for the anchoring of Re(bipy)-based catalysts and metalloporphyrin chromophores, and their potential employment in the photoreduction of CO\textsubscript{2} in water media, will be presented.
For these objectives two different Re(bipy) systems were investigated, as shown in Figure 5.8. The first one is a neutral complex designed in order to interact with the hydrophobic bilayer of the liposomes thanks to the back pendant lipophilic alkyl chain, while the second is cationic and may establish useful electrostatic interactions with the surface of negatively charged liposomes. For comparative purposes, in both cases negatively charged lipids were employed. As a matter of facts, the initial results obtained with the cationic complex suffer of irreproducibility issues, most probably connected to the fact that a mono-charged species is not capable of establishing efficient interactions with the liposome surface. Therefore, only the studies made on the neutral complex \( \text{fac-[Re(CO)}_3(bipyR)(NSC)] \) (34) will be discussed here.

**Figure 5.8.** Schematic depiction of the Re(bipy) complexes investigated in the present work, and schematic depiction of their supramolecular interactions with (either neutral or anionic) liposomes.

Also, some preliminary results regarding two bi-component photosentitizer/catalyst systems anchored on the liposome scaffolds will be also described. Both the systems are designed to contain the rhenium catalyst 34, but differs in the photosentitizer component, that were chosen to be either a poly-cationic or a polyanionic zinc-porphyrin photosentitizer, as very schematically depicted in Figure 5.9.
5.2 Results and discussion

5.2.1 Synthesis and characterization of 34

For the obtainment of complex 34, the bipyridyl ligand 33 has been firstly prepared by a coupling reaction between 11 and dodecyl amine (Scheme 5.1). The ligand, thus prepared, was then reacted with fac-[Re(CO)₃(dms-O)₃](CF₃SO₃), followed by the coordination of thiocyanate (Scheme 5.1). 34 was collected in high yield by a simple extraction of the aqueous phase with diethyl ether, and fully characterized by ESI-MS, IR and NMR spectroscopy (1D and 2D experiments).
Scheme 5.1. Synthesis of 33 and complex 34. Reagents and conditions: (i) EDC-Cl, pyridine, room temperature, 2.5 h; (ii) acetone, room temperature 2 h; (iii) KSCN, methanol/water, 70 °C, 4h.

The IR spectrum of the product 34, reported in Figure 5.10, shows the typical pattern of the three *facial* C=O stretching at 2022 and 1905 cm\(^{-1}\). Moreover, it is possible to observe the stretching of the C=O of the amide group, and that of C=N, from N-bonded thiocyanate at 1671 and 2100 cm\(^{-1}\), respectively.

![Figure 5.10](image.png)

Figure 5.10. Selected region of the IR spectrum (solid state) of 34.

In Figure 5.11 the comparison between the \(^1\)H NMR spectra (CDCl\(_3\)) of 33 and 34 is reported, with all the proton resonances unambiguously assigned by a H-H COSY experiment. As expected, most of the aromatic protons are downfield shifted, as a consequence of the coordination to the metal center. The chemical shifts of the protons of the alkyl chain do not present significant variations in 34 with respect to 33.
5.2.2 Photochemistry experiments

In Figure 5.12 the UV-vis spectrum of 34 in DMF is reported. The spectrum shows the characteristic absorption band related to the MLCT at 384 nm, as reported in literature for similar systems.\textsuperscript{21}

---

**Figure 5.11.** $^1$H NMR spectra (CDCl$_3$, 500 MHz) of 33 (top) and 34 (bottom) and schematic depiction of 34 with labeling scheme.

**Figure 5.12.** Absorption spectrum of 34 (DMF, concentration = $1.0 \times 10^{-4}$ M).
Preliminary photoreduction experiments have been performed, following the typical experimental conditions reported in literature. A 0.1 mM solution of 34 in DMF was prepared, placed in a 1-cm quartz cuvette, and continuously purged with argon. The sacrificial electron donor TEOA was added in the ratio DMF:TEOA 5:1. Typically, in the literature the organic solution is irradiated selectively by a laser source. In the present experiments the irradiation source is positioned on the top of the cuvette, using a custom-built set up, that consists of an optic fiber connected to a Xe white lamp, with a cut off filter at 335 nm. At regular interval of times (every minute, unless otherwise stated) the absorption spectrum between 300 – 800 nm has been recorded.

As previously explained, the MLCT excited state that forms upon UV-light irradiation can be reductively quenched by a sacrificial electron donor. The quenching process generates the one-electron-reduced species (OER), the formation of which can be monitored by UV-vis spectroscopy (Figure 5.13).

![Figure 5.13. Absorption spectra of 34 and 34(OER) (initial concentration = 1.0 x 10^-4 M).](image)

As reported in Figure 5.13 the OER is characterized by three typical absorption bands at 365, 492 and 525 nm. In Figure 5.14 the UV-vis spectral changes observed under continuous irradiation of a DMF solution of 34 in the presence of TEOA, are reported. The formation of the OER with time is clearly evident, with its characteristic three absorption bands growing in intensity with time. Moreover, an isosbestic point is present at 331 nm.
Figure 5.14. UV-vis absorption spectra of a photoirradiated $1.0 \times 10^{-4}$ M solution of 34 (DMF:TEOA 5:1, $\lambda_{\text{in}} > 335$ nm). Spectra reported from $t = 0$ min to $t = 6$ min.

The kinetic analysis at 525 nm indicates that the OER is continuously accumulated in solution until a maximum amount is reached, after 6 min of irradiation (Figure 5.15). After this time, maintaining the irradiation, a slow but progressive decrease of the bands related to the OER are observed (Figure 5.15), without any appreciable new absorptions appearing. This experimental evidence may be related both to photodegradation processes and/or to the permanent photodissociation of the apical NCS ligand, which hampers the recovery of 34.

Figure 5.15. Kinetic analysis at $\lambda = 525$ nm upon continuous irradiation of a $1.0 \times 10^{-4}$ M solution of 34 (DMF:TEOA 5:1).

This phenomenon is even more evident by looking at the kinetic analysis during an ON/OFF irradiation experiment, in which the irradiation was switched off after 50 minutes, the solution was kept in the dark and monitored till the total disappearance of the OER
absorptions was reached (10 minutes). At this time the irradiation was switched on again (Figure 5.16, top). What it can be observed is that only a small amount of OER species is reformed. Few relevant absorption spectra are also reported (Figure 5.16, bottom).

![Figure 5.16. Top: Kinetic analysis at $\lambda = 525 \text{ nm}$ upon intermittent irradiation of a $1.0 \times 10^{-4} \text{ M}$ solution of 34 (DMF:TEOA 5:1). Bottom: comparison between UV-vis spectra of 34 at different time: $t = 8 \text{ min}$ (b); $t = 50 \text{ min}$ (c); $t = 60 \text{ min}$ (d); $t = 66 \text{ min}$ (e).]

After these preliminary studies, the measurements have been repeated in aqueous solution using liposomes as supramolecular scaffolds. Incorporation of 34 in the liposome scaffolds is obtained during the liposomes preparation. To do that, chloroform stock solutions of 34 (0.4 mM) and DMPG (5 mM) were mixed in a ratio of ca. 1:10, slowly dried, freeze-thawed with a phosphate buffer at pH = 10.92, and finally filter-extruded to give the desired liposomes (see also Experimental Section). Liposomes, so prepared, were characterized with DLS, obtaining an average diameter of 108.8 nm. Qualitative results indicating the successful incorporation of 34 in the liposomes (from now on the conjugated system will be referred as 34:DMPG) can be derived from a comparison of the (yellow) buffer solution containing the supramolecular 34:DMPG system (Figure 5.17, left) and the buffer solution containing undissolved 34 (Figure 5.17, right).
Using the same experimental setup previously described for the surveys done in DMF, UV photoirradiation experiments have been carried out on solutions of 34:DMPG (0.1 mM:1.25 mM) in the presence of 50 mM TEOA, as sacrificial electron donor at pH = 10.92. These conditions (which from now on will be referred as “standard”, and not further specified) have been chosen after several preliminary experiments, in which the concentration of TEOA, the pH and the nature of the buffer were screened. In particular, a strong dependence on pH was observed. In fact, for pH ≤ 10, no evidences of spectral changes, upon continuous irradiation, were apparent. Most likely, at pH ≤ 10 the TEOA is still partially protonated, it does loose its reducing-agent character.

By collecting UV-vis spectra during irradiation, an increase of the absorptions at 365 and 525 nm and a decrease of that at 300 nm, can be detected (Figure 5.18, left). By comparing these spectral modifications with those observed for 34 in DMF, it is possible to presume that these bands are related to the formation of the OER species. Still, the comparison between the two systems, at the same concentration, clearly shows that the maximum amount of OER species accumulated in solution upon irradiation is considerable lower for the liposome system. The reason for these different behaviors may be multifarious, and includes a decreased stability of the OER species, a partial seclusion (and therefore inaccessibility) of 34 inside the membrane, a pH effect, and slower kinetics of the processes.

† In the liposomes formation process, 34 could be, as shown in the cartoon of Figure 5.5, embedded in the membrane with the metal “head” (Re(bipy)) on the surface, as well as completely included inside the membrane, precluding the reductive quenching by TEOA.
Chapter 5

Figure 5.18. UV-vis absorption spectral changes during irradiation of 34:DMPG in standard conditions ($\lambda_{irr} > 335$ nm). Spectra collected every minute, and reported from $t = 0$ min to $t = 25$ min (left). Comparison between the spectrum of 34:DMPG before UV irradiation (black curve) and after 25 min of irradiation (red curve), with inset of the 350 – 600 nm range (right).

On the other hand, a very encouraging aspect rely in the fact that the slower kinetic of the OER formation (the maximum amount of OER detected is reached after 20 minutes, see kinetic analysis in Figure 5.19) is also accompanied by a prolonged life-time of the same species (no decrease of its absorptions are observed, upon continuous irradiation, for up to at least 2 h).

Figure 5.19. Kinetic analysis at $\lambda = 525$ nm upon continuous irradiation of a 34:DMPG in standard conditions.

This is also confirmed by an ON/OFF irradiation experiment (the kinetic analysis of which is reported in Figure 5.30), that shows how the same amount of OER is reformed for at least two ON/OFF cycles (for a total irradiation time of 4 h). The slight deviations observed are related to the experimental conditions.‡

‡ The analyzed solutions are subject to progressive evaporation with time, as a consequence of the argon flux, that determines a background increase of absorbance in the whole spectral range. A linear correction has been applied, but after 4 h it is not effective anymore.
Another set of experiments have also been performed in order to tackle the not trivial issue of decreasing the light energy required to activate the catalyst. The idea is to irradiate selectively a photosentitizer with visible light and, by reductive or oxidative quenching of its excited state, to induce an electron transfer toward the rhenium complex, thus promoting the formation of the OER by employing the solar energy.

In this particular, two bi-component systems each composed of 34 and of one photosensitizer, capable to absorb in the visible region, and at the same time to anchor on the liposome scaffolds, have been explored. As photosensitizers, ZnTPPS and ZnTPPyMe have been chosen (Figure 5.21).

The two zinc-porphyrins are tetra-cationic and tetra-anionic, respectively and has been attached to the liposome scaffolds, via electrostatic interactions. For these purposes, negatively (Na-DMPG) and positively (DMPC:eDMPC:Cl) charged liposomes,
respectively, have been prepared in phosphate buffer at pH 10.92. Phosphate buffer solutions of the two zinc-porphyrins were also prepared. Finally, the solutions were mixed, thus obtaining the two supramolecular systems ZnTPPyMe:DMPG and ZnTPPS:DMPC:eDMPC, with relative component concentrations of 3.3μM:1.25mM and 3.3μM:1.25mM:1.25mM, respectively. The successful anchoring of the two zinc-porphyrins on the liposome surfaces is indicated by a blue-shift of the Soret absorption band in their UV-vis spectra (ca. 5 nm for both porphyrins). For the subsequent photochemical investigations, two different monochromatic LEDs were chosen as light source of irradiation, according to the best λ-match with the absorption maximum of the zinc-porphyrin Soret band (449 nm for ZnTPPyMe and 420 nm for ZnTPPS, respectively). The experiments have been carried out in phosphate buffer at pH 10.92, in the presence of TEOA (50 mM). All these parameters, from now on, will be referred as “standard”, and not further specified. Firstly the systems composed only by the zinc-porphyrin anchored on the liposomes were investigated.\footnote{For time matters the corresponding homogeneous systems (zinc-porphyrin in DMF/TEOA), and (zinc-porphyrin plus 34 in DMF/TEOA) were not investigated.}

The results for ZnTPPyMe:DMPG are reported in Figure 5.22. A progressive decrease with time of the zinc-porphyrin Soret maximum absorption band, at λ = 445 nm, can be observed. This photobleaching corresponds to a reductive quenching of the singlet excited state of the zinc-porphyrin by TEOA. Indeed, if the same experiment is carried out in the absence of sacrificial electron donor, the photobleaching does not occur. As soon as the irradiation is switched off, the Soret band absorption is restored, but with a remarkable ipsochromic shift from 449 to 429 nm. Concomitantly, a new set of weak bands (between 500 and 600 nm), with a pattern typical of the Q bands of a free-base porphyrin, arises (Figure 5.23, left).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Figure5.22}
\caption{UV-vis absorption spectra of ZnTPPyMe:DMPG recorded every minute upon irradiation and reported from t = 0 min to t = 40 min, in standard conditions.}
\end{figure}
For comparative purposes, an experiment in the absence of liposomes has also been carried out. The occurring of the photobleaching is observed also in this case, but the original absorption spectrum of ZnTPPyMe is almost totally recovered, without any shift (Figure 5.23, right), when the irradiation is switched off. It can be therefore concluded that continuous irradiation in the presence of liposomes induces a progressive de-metallation of the zinc-porphyrin macrocycle.

![Figure 5.23](image_url)

**Figure 5.23.** Left: Comparison between UV-vis spectra of ZnTPPyMe:DMPG before irradiation (black curve) and after irradiation (red curve), in standard conditions. Right: Comparison between UV-vis spectra of ZnTPPyMe before irradiation (black curve) and after irradiation (red curve).

After these preliminary surveys, the same experiments were repeated introducing 34 in the system. To do that, first 34:DMPG liposomes were prepared as described above, and subsequently ZnTPPyMe was added. The UV-vis spectral changes upon irradiation of 34:ZnTPPyMe:DMPG were then monitored (Figure 5.24). The photobleaching of the zinc-porphyrin is still occurring, but no spectroscopic signatures related to the OER can be detected (i.e., there is no evidence of the desired electron transfer process from the photosentisizer to 34). Most likely, the energetic levels, and more in particular the relative redox potentials, of the components are not thermodynamically suited.
Analogous studies were then performed using the tetra-anionic \textit{ZnTPPS} as photosensitizer in place of \textit{ZnTPPyMe}. \textit{ZnTPPS} was combined with positively charged liposomes (prepared mixed DMPC/eDMPC in a 1:1 ratio, and following the usual process). Again, a preliminary survey without 34 was initially performed, and it shows that also in this case a photobleaching process is occurring, that indicating indicates the efficient reduction of the zinc-porphyrin excited state by TEOA (Figure 5.25). Though, in comparison with the previous system, there is no evidence of absorption recovery when the irradiation is switched off. The same behavior was observed in a blank experiment in absence of liposomes. This fact indicates that \textit{ZnTPPS} progressively decomposes during the reductive quenching process.

**Figure 24.** UV-vis absorption spectra of 34:ZnTPPyMe:DMPG recorded every minute upon irradiation and reported from \(t = 0\) min to \(t = 40\) min, in standard conditions.

**Figure 5.25.** Photoirradiated UV-vis absorption spectra of ZnTPPS:DMPC:eDMPC, in standard conditions; spectra collected every minute and reported from \(t = 0\) min to \(t = 30\) min.
After these preliminary studies, and as already done for ZnTPPyMe, 34 was introduced in the system. For this purpose, first 34:DMPC:eDMPC liposomes were prepared, and subsequently ZnTPPyMe was added.

Upon selective light irradiation in standard conditions, the intensity and position of the Soret band is maintained (i.e., no photobleaching occurring), while two weak absorption shoulders appear at 525 and 365 nm, as shown in Figure 5.26. These spectral features may well be related to the formation of the OER species.

![Figure 5.26](image)

**Figure 5.26.** Left: Comparison between the spectra of 34:DMPC:eDMPC, in standard conditions, before irradiation (black curve) and after 15 min of irradiation (red curve), with inset of the 350 – 600 nm range.

If this is the case, the desired two-step electron transfer process has occurred (Figure 5.27), with two possible mechanism that cannot be ruled out at this stage. One possibility is that first the excited state of the zinc-porphyrin (populated by light irradiation) is reductively quenched by the sacrificial donor and then a very fast electron transfer from the radical anion of the porphyrin to the Re(bipy) occurs. Alternatively, the excited state of the zinc-porphyrin transfer one electron to the Re(bipy) complex, and then the porphyrin radical cation is oxidatively quenched by the sacrificial donor.
Figure 5.27. Schematic cartoon of the two-step electron transfer processes leading to the formation of the OER after visible light irradiation of the porphyrin photosensitizer in the supramolecular $34:ZnTPPS:DMPC:eDMPC$ system, in the presence of TEOA.

It must be noted here, that the UV-vis spectrum of $34:ZnTPPS:DMPC:eDMPC$ is a good superposition of those of $ZnTPPS:DMPC:eDMPC$ and $34:DMPC:eDMPC$ (Figure 5.28). Therefore, by irradiating the system with a $\lambda_{exc} = 420$ nm, ca. 25% of the light is absorbed by $34$. For this reason an experiment on $34:DMPC:eDMPC$ was also performed in order to evaluate if the LED light source chosen may directly activate the photoreduction of $34$. Such experiment confirms the formation of a very small amount of OER. Therefore, for the $34:ZnTPPS:DMPC:eDMPC$ system, a certain amount of OER is generated by direct reduction of the excited state of $34$. Still, from the kinetic analysis, it is evident that the OER species is substantially generated from excited state of the $ZnTPPS$ (Figure 5.28).

Figure 5.28. Left: absorption spectra of $34:ZnTPPS:DMPC:eDMPC$ (black curve), of $ZnTPPS:DMPC:eDMPC$ (red curve) and of $34:DMPC:eDMPC$ (blue curve) in phosphate buffer solution at pH = 10.92. Right: Kinetic analysis at $\lambda = 525$ nm upon continuous irradiation, in standard conditions, of $34:ZnTPPS:DMPC:eDMPC$ (black curve) and $34:DMPC:eDMPC$. 
5.3 Conclusions

This work represent a preliminary survey on the photophysical response of Re(bipy) complexes anchored on liposome scaffolds, in aqueous solution. The UV-vis experiments show that it is possible to generate the One-Electron-Reduced species (OER), with UV-irradiation of the supramolecular system. Most interestingly, this is also the case for the bi-component photosensitizer/Re(bipy) system 34:ZnTPPS:DMPC:eDMPC, in which a visible (low energy) light source is employed. The accumulation of the OER upon irradiation in the water media is dramatically lower if compared with that detected for 34 in DMF. Nevertheless, the liposome scaffolds are crucial in order to bring the neutral catalyst 34 in aqueous media, and especially they seem to contribute in greatly improving the photostability of the system. Also, Ishitani and coworkers have demonstrated that the accumulation of the OER in solution is not necessarily a requisite in order to catalyze the photoreduction of CO₂. In fact, they showed that while fac-[Re(CO)_3(bipy)(CN)] is able to form a great amount of OER upon UV irradiation, the same complex is completely inactive in the photoconversion of CO₂ to CO.¹ At the same time, the same group has reported that fac-[Re(CO)_3(bipy)(Cl)], for which negligible amounts of OER get accumulated, shows a photoactivity with TN of 19.¹ These considerations support the that if a photosensitizer/catalyst system is capable of promoting the formation of the active species, though the latter does not get appreciably accumulated, it is still worthwhile to test the system in the actual photocatalytic process of interest. This is especially true if with systems exhibiting improved features, such as lower activation energies, increased photostabilities, and environment compatibility.

Therefore, these preliminary results can be considered as very encouraging starting points for the potential applications of these supramolecular systems, and related ones, in various photocatalytic conversions, in water media.

5.4 References


Chapter 6.

Experimental Section
List of abbreviations

NaDMPG = Sodium 1,2-dimyristoyl-sn-glycero-3-phosphoglycerol
DMPC = 1,2-dimyristoyl-sn-glycero-3-phosphocholine
eDMPCCl = 1,2-dimyristoyl-sn-glycero-3-ethylphosphocholine chloride
TPPyMe = meso-tetra-(4’-pyridinium)-porphyrin
TPPS = meso-(4’-sulfonato)-tetrapheylporphyrin
TPP = meso-tetraphenylporphyrin

$t$BuTPP = meso-(4-tert-butyl)-tetraphenylporphyrin
drBuTPP = meso-(3,5-di-tert-butyl)-tetraphenylporphyrin

4’MPyP = 5-(4’-pyridyl)-10,15,20-(phenyl)-porphyrin
4’MPytBuP = 5-(4’-pyridyl)-10,15,20-(4-tert-butylphenyl)porphyrin
4’MPydrBuP = 5-(4’-pyridyl)-10,15,20-(3,5-di-tert-butylphenyl)porphyrin
Fb = 5-(4-benzoic acid)-15-(3,5-di-tert-butylphenyl)-2,8,12,18-tetra-n-hexyl-3,7,13,17-tetramethylporphyrin

RuP = meso-(4-tert-butyl)-tetraphenylporphyrinato-(carbonyl)ruthenium(II)
AIP = meso-(3,5-di-tert-butyl)-tetraphenylporphyrinato-(hydroxo)aluminium(III)

AlMPyP = 5-(4’-pyridyl)-10,15,20-(3,5-di-tert-butylphenyl)-porphyrinato-(hydroxo)aluminium(III)

4,4’-DEC-bipy = 4,4’-diethoxycarbonyl-2,2’-bipyridine

ESI = Electro Spray Ionization
DLS = Dynamic Light Scattering
PTFE = Polytetrafluoroethylene
LUV = Large Unilamellar Vesicles
PDI = PolyDispersity Index
6.1 Experimental Methods.

**NMR.** Mono- and bidimensional NMR experiments ($^1$H, $^{13}$C, $^{19}$F, H-H COSY, H-C COSY, NOESY, HMBC) were recorded on either a Bruker DPX 300 (300 MHz), or a JEOL Eclipse 400FT (400 MHz) or a Varian 500 (500 MHz) spectrometer. All spectra were run at room temperature; $^1$H chemical shifts were referenced to the peak of residual non deuterated solvent ($\delta$ (ppm) = 7.26 (CHCl$_3$), 5.32 (CH$_2$Cl$_2$), 2.04 (acetone-$d_6$), 3.30 (CH$_3$OH), 2.50 (dmso), 4.33 (CH$_3$NO$_2$), 8.74 (pyridine), 7.19 (toluene) and 8.03 (DMF)). $^{13}$C chemical shifts has been referenced to the peak of residual non deuterated solvent ($\delta$ (ppm) = 7.26 (CHCl$_3$), 5.32 (CH$_2$Cl$_2$)). $^{19}$F chemical shifts were referred to the internal CFCl$_3$ standard.

**Mass.** ESI mass spectrometry measurements were performed on a Perkin-Elmer API spectrometer at 5600 eV by Dr. Fabio Hollan, Department of Chemical and Pharmaceutical Sciences, University of Trieste, Italy.

**IR.** Solution (CHCl$_3$) and Nujol IR spectra were recorded in 0.1 mm cells with NaCl and KBr windows, respectively, on a Perkin-Elmer Fourier transform infrared/Raman 2000 instrument in the transmission mode. Solid IR spectra were recorded on a Varian 660-IR FT-IR spectrometer in conjunction with a Pike GladiATR™ accessory provided with a germanium crystal.

**Absorption.** UV/vis absorption spectra were recorded with a Jasco V-570 UV/vis/near-IR and a Varian Cary50 spectrophotometer.

**Emission.** Emission spectra were acquired on a Spex-Jobin Ivon Fluoromax-2 spectrofluorimeter, equipped with Hamamatsu R3896 tubes. Nanosecond emission lifetimes were measured using a TCSPC apparatus (PicoQuant Picoharp300) equipped with subnanosecond LED sources (280-600 nm range; 500-700 ps pulse width) powered with a PicoQuant PDL 800-B variable-pulsed (2.5-40 MHz) power supply. The decays were analyzed by means of PicoQuant FluoFit Global Fluorescence Decay Analysis Software. Fluorescence contour measurements were performed with a Spectrofluorometer Edinburgh Instrument FLS920.

**Transient absorption.** Femtosecond time-resolved experiments were performed using a pump-probe setup based on a Spectra-Physics Hurricane Ti:sapphire laser source and an Ultrafast Systems Helios spectrometer. Nanosecond transient absorption spectra were measured with an Applied Photophysics laser flash photolysis apparatus, with frequency doubled (532 nm, 330 mJ), Surelite Continuum II Nd/YAG laser (halfwidth 6-8 ns). Photomultiplier (Hamamatsu R928) signals were processed by means of a LeCroy 9360 (600 MHz, 5 Gs/sec) digital oscilloscope. The 560 nm pump pulses were generated with a
Spectra Physics 800 optical parametric amplifier. Probe pulses were obtained by continuum generation on a sapphire plate (useful spectral range: 450–800 nm). The effective time resolution was ca. 300 fs, the temporal chirp over the white-light 450–750 nm range was ca. 200 fs, and the temporal window of the optical delay stage was 0-1000 ps. The time-resolved spectral data were analyzed with Ultrafast Systems Surface Explorer Pro software.

**DLS.** DLS experiments were performed on a Malvern Instruments Zetasizer operated at 633 nm.

**X-ray.** Crystallographic data for compound 4b were collected at the X-ray diffraction beamline of the synchrotron Elettra (Trieste) at 100 K, $\lambda = 1.0000$ Å; those for 6 were collected on a Nonius DIP-1030H single-crystal diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å) at room temperature. Cell refinement, indexing, and scaling of the data sets were performed using programs Denzo and Scalepack. Both structures were solved by direct methods and subsequent Fourier analyses and refined by the full matrix least-squares method based on F$^2$ with all observed reflections. The triflate anion in 4b was found to be disordered over two positions, each refined with occupancy of 0.50. Hydrogen atoms were placed at calculated positions. All of the calculations were made using WinGX, version 1.80.05.

**Photochemistry measurement.** Irradiation experiments were performed in a quartz UV-vis cell irradiated from the top using a custom-built LED light source equipped with either a LED ($\lambda_{\text{max}} = 420$ nm, $\Delta\lambda_{1/2} = 10$ nm) or an OSRAM Opto Semiconductors LD W5SM LED ($\lambda_{\text{max}} = 449$ nm, $\Delta\lambda_{1/2} = 25$ nm). 3mL samples in a quartz UV-vis cell were deaerated inside the spectrometer for 30 minutes by slowly bubbling argon through the solution, and irradiated while thermostated under stirring and a constant flow of argon, also inside the spectrometer. The photoreaction was then monitored by UV-vis spectroscopy perpendicular to the irradiation beam.

### 6.2 Materials and synthesis

**Materials.** All reagents were purchased from Sigma-Aldrich and used without further purification, unless otherwise stated. Deuterated solvents were purchased from CIL. NaDMPG, DMPC and eDMPCCl lipids were purchased from Avanti Polar Lipids and stored at −20 °C. TPyP and H$_2$TPPS·2HCl were obtained from Frontier Scientific. The corresponding zinc adducts, [ZnTPPyMe](Cl$_4$) and (Na$_4$)[ZnTPPS] respectively, were synthesized and purified following the literature procedure. TPP, tBuTPP, d$t$BuTPP, 4$'$MPyP, 4$'$MPyrBuP and 4$'$MPyd$'$BuP were synthesized and purified as described in the
literature.\textsuperscript{6,7} RuP\textsuperscript{8}, AlP\textsuperscript{9} and AlMPyP\textsuperscript{10,11} were prepared in accordance with literature procedures. The free-base porphyrin, Fb, was kindly furnished by Dr. E. Iengo. 4,4′-DEC-bipy was also prepared as described in the literature.\textsuperscript{12} Complexes fac-[Re(CO)\textsubscript{3}(dmso-O\textsubscript{3})][X] (1a X = CF\textsubscript{3}SO\textsubscript{3}\textsuperscript{−}, 1bX = PF\textsubscript{6}\textsuperscript{−}), fac-[Re(CO)\textsubscript{3}(bipy)(dmso-O\textsubscript{3})][CF\textsubscript{3}SO\textsubscript{3}] and fac-[Re(CO)\textsubscript{3}(bipy)(py)][CF\textsubscript{3}SO\textsubscript{3}] were prepared as previously described.\textsuperscript{13,14}

**fac-[Re(CO)\textsubscript{3}(4,4′-DEC-bipy)(dmso-O\textsubscript{3})][CF\textsubscript{3}SO\textsubscript{3}] (2).** 1 (100 mg, 0.15 mmol) and 4,4′-DEC-bipy (50 mg, 0.17 mmol) were dissolved in acetone (15 mL). The solution, initially colorless, was refluxed for 1 h under argon atmosphere and turned yellow. Concentration to ca. 7 mL followed by addition of n-hexane (3 mL) induced in a few days the formation of pale yellow microcrystals, that removed by filtration, washed with n-hexane, and vacuum-dried. Yield: 77 mg (65%). \textsuperscript{1}H NMR (δ, 400 MHz, CD\textsubscript{3}NO\textsubscript{2}): 9.32 (d, \(J = 5.7\) Hz, 2H, H\textsubscript{6,6}′), 9.08 (s, 2H, H\textsubscript{3,3}′), 8.25 (d, \(J = 5.6\) Hz, 2H, H\textsubscript{5,5}′), 4.52 (q, \(J = 7.1\) Hz, 4H, CH\textsubscript{2}), 2.60 (s, 6H, CH\textsubscript{3}dmso-O\textsubscript{3}), 1.45 (t, \(J = 7.1\) Hz, 6H, CH\textsubscript{3}).

**fac-[Re(CO)\textsubscript{3}(4,4′-DEC-bipy)(4'MPyP)][CF\textsubscript{3}SO\textsubscript{3}] (3a).** 4'MPyP (50 mg, 0.09 mmol) and 2 (60 mg, 0.08 mmol) were dissolved in chloroform (15 mL), and the solution was heated to reflux for 8 h. After concentration to ca. 8 mL, n-hexane (10 mL) was added to induce precipitation of the product as a purple solid, which was collected by filtration, washed thoroughly with n-hexane, and vacuum-dried. Yield: 70 mg (72%). \textsuperscript{1}H NMR (δ, 400 MHz, CDCl\textsubscript{3}): 9.58 (d, \(J = 5.6\) Hz, 2H, H\textsubscript{6,6}′), 9.15 (s, 2H, H\textsubscript{3,3}′), 8.83 (m, 6H, βH), 8.76 (d, \(J = 6.2\) Hz, 2H, py\textsubscript{a}), 8.65 (d, \(J = 3.3\) Hz, 2H, βH), 8.43 (d, \(J = 4.7\) Hz, 2H, H\textsubscript{5,5}′), 8.28 (d, \(J = 6.1\) Hz, 2H, py\textsubscript{b}), 8.19 (d, \(J = 8.0\) Hz, 2H, oH), 8.17 (d, \(J = 7.5\) Hz, 4H, oH), 7.74 (m, 9H, \(m+p\)H), 4.55 (q, \(J = 7.1\) Hz, 4H, CH\textsubscript{2}), 1.47 (t, \(J = 7.1\) Hz, 6H, CH\textsubscript{3}), –2.88 (s, 2H, NH). ESI-MS: calc'd for C\textsubscript{62}H\textsubscript{46}N\textsubscript{7}O\textsubscript{7}Re ([M – CF\textsubscript{3}SO\textsubscript{3}]\textsuperscript{+}): 1186.3, found: 1186.5. Selected IR bands (cm\textsuperscript{-1}, CHCl\textsubscript{3}): 2037 (s, C=O fac), 1931 (s, br, C=O fac), 1733 (m, C=O).

**fac-[Re(CO)\textsubscript{3}(bipy)(4'MPyBuP)][CF\textsubscript{3}SO\textsubscript{3}] (4a).** 4'MPyBuP (90 mg, 0.12 mmol) and fac-[Re(CO)\textsubscript{3}(bipy)(dmso-O\textsubscript{3})][CF\textsubscript{3}SO\textsubscript{3}] (60 mg, 0.09 mmol) were dissolved in chloroform (25 mL). The mixture was heated to reflux for 8 h and then concentrated in vacuo to ca. 15 mL. The product precipitated as a purple solid upon addition of diethyl ether until saturation and was collected by filtration, washed with diethyl ether, and vacuum-dried. Yield: 87 mg (71%). \textsuperscript{1}H NMR (δ, 400 MHz, acetone-\textit{d}\textsubscript{6}): 9.70 (d, \(J = 5.3\) Hz, 2H, H\textsubscript{6,6}′), 9.03 (d, \(J = 6.4\) Hz, 2H, py\textsubscript{a}), 8.95 (d, \(J = 8.3\) Hz, 2H, H\textsubscript{3,3}′), 8.85 (m, 8H, βH), 8.61 (t, \(J = 7.7\) Hz, 2H, H\textsubscript{4,4}′), 8.34 (d, \(J = 6.5\) Hz, 2H, py\textsubscript{b}), 8.18 (d, \(J = 8.1\) Hz, 2H, oH), 8.15 (d, \(J =
8.0 Hz, 4H, oH), 8.12 (t, J = 8.0 Hz, 2H, H₅,₅′), 7.85 (m, 6H, mH), 1.60 (s, 27H, tBu), −2.86 (s, 2H, NH). ¹H NMR (δ, 400 MHz, CDCl₃ + 10 μL of MeOD): 9.25 (d, J = 4.6 Hz, 2H, H₆,₆′), 8.65 (d, J = 8.3 Hz, 2H, H₂,₆), 8.48 (d, J = 6.5 Hz, 3H, H₃,₃′), 8.31 (t, J = 8.0 Hz, 2H, H₄,₄′), 8.06 (d, J = 6.5 Hz, 2H, H₃,₅), 7.97 (d, J = 8.1 Hz, 2H, oH), 7.95 (d, J = 8.2 Hz, 2H, oH), 7.79 (t, J = 6.7 Hz, 1H, H₅,₅′), 7.63 (d, J = 8.4 Hz, 2H, mH), 7.61 (s, J = 8.4 Hz, 4H, oH), 1.46 (s, 27H, tBu). ESI-MS. calcd for C₆₈H₆₁N₇O₃Re ([M – CF₃SO₃]⁺): 1210.5, found: 1210.4. Selected IR bands (cm⁻¹, CHCl₃): 2038 (s, C=O fac), 1930 (s, br, C=O fac).

fac-[Re(CO)₃(bipy)(4′MPydBuP)](CF₃SO₃) (5a). 4′MPydBuP (180 mg, 0.18 mmol) and fac-[Re(CO)₃(bipy)(dmso-O)](CF₃SO₃) (90 mg, 0.14 mmol) were dissolved in chloroform (20 mL). The mixture was heated to reflux for 8 h and then concentrated in vacuo to ca. 8 mL. The dropwise addition of n-hexane (5 mL) induced precipitation of the product as a microcrystalline purple solid, which was collected by filtration, recrystallized from acetone/n-hexane and vacuum-dried. Yield: 150 mg (76%). ¹H NMR (δ, 400 MHz, CDCl₃): 9.26 (d, J = 4.7 Hz, 2H, H₆,₆′), 9.17 (d, J = 8.4 Hz, 2H, H₃,₃′), 8.95 – 8.85 (m, 6H, βH), 8.61 (d, J = 4.9 Hz, 2H, βH), 8.53 (d, J = 6.5 Hz, 2H, pya), 8.48 (t, J = 7.2 Hz, 2H, H₄,₄′), 8.21 (d, J = 6.5 Hz, 2H, pyb), 8.03 (d, J = 1.8 Hz, 2H, oH), 8.01 (d, J = 1.8 Hz, 4H, oH), 7.83 (t, J = 6.5 Hz 2H, H₅,₅′), 7.78 (m, 3H, pH), 1.50 (s, 54H, tBu), −2.78 (s, 2H, NH). ESI-MS. calcd for C₆₈H₆₁N₇O₃Re ([M – CF₃SO₃]⁺): 1378.6, found: 1378.9. Selected IR bands (cm⁻¹, CHCl₃): 2038 (s, C=O fac), 1930 (s, br, C=O fac). UV-vis (λ_max, nm, CH₂Cl₂): 425, 521, 558, 594, 650.

**Zincated Adducts.** The insertion of zinc into the free-base porphyrins and rhenium(I) pyridylporphyrin conjugates was performed according to this general procedure: a concentrated chloroform solution of each adduct was treated overnight with an 8-fold molar excess of Zn(CH₃COO)₂·2H₂O dissolved in a minimum amount of methanol. The solvent was evaporated in vacuo and the solid redissolved in chloroform. The product was precipitated by the addition of n-hexane, removed by filtration, washed thoroughly with cold methanol and diethyl ether, and vacuum-dried. Yield: >85%. The compounds were characterized by ¹H NMR, UV-vis and IR spectroscopy and ESI-MS.

fac-[Re(CO)₃(4,4′-DEC-bipy)(Zn·4′MPyP)](CF₃SO₃) (3b). Yield: 92%. ¹H NMR (δ, 400 MHz, CDCl₃): 9.49 (d, J = 5.7 Hz, 2H, H₆,₆′), 9.12 (s, 2H, H₃,₃′), 8.90 (m, 6H, βH), 8.69 (d, J = 5.1 Hz, 2H, βH), 8.59 (d, J = 6.4 Hz, 2H, pya), 8.38 (d, J = 5.5 Hz, 2H, H₅,₅′), 8.28 (d, J = 6.1 Hz, 2H, pyb), 8.18 (d, J = 8.2 Hz, 2H, oH), 8.16 (d, J = 7.2 Hz, 4H, oH), 8.01 (d, J = 1.8 Hz, 2H, oH), 7.83 (t, J = 6.5 Hz 2H, H₅,₅′), 7.78 (m, 3H, pH), 1.50 (s, 54H, tBu), −2.78 (s, 2H, NH). ESI-MS.
Chapter 6

7.73 (m, 9H, m+pH), 4.52 (q, 4H, CH₂), 1.47 (t, 6H, CH₃). ESI-MS. calcld for C₆₂H₄₃N₇O₇ZnRe ([M – CF₃SO₃]⁺): 1248.2, found: 1248.4. Selected IR bands (cm⁻¹, CHCl₃): 2038 (s, C=O fac), 1945 (s, br, C=O fac), 1935 (s, br, C=O fac), 1726 (m, C=O). UV-vis (λmax, nm, CH₂Cl₂): 423, 500, 598.

**fac-[Re(CO)₃(bipy)(Zn-4'MPydBuP)][(CF₃SO₃)] (4b)**. Yield: 85%. ¹H NMR (δ, 400 MHz, CD₂OD): 9.54 (d, J = 5.6 Hz, 2H, H₆₆,₆'), 8.85 (d, J = 4.7 Hz, 2H, H₃,₃'), 8.82 (m, 6H, H), 8.76 (d, J = 6.5 Hz, 2H, pyₐ), 8.57 (d, J = 4.7 Hz, 2H, βH), 8.44 (t, J = 8.0 Hz, 2H, H₄,₄'), 8.19 (d, J = 6.5 Hz, 2H, pyₐ), 8.07 (d, J = 5.9 Hz, 2H, oH), 8.05 (d, J = 5.9 Hz, 4H, oH), 7.97 (t, J = 6.7 Hz, 2H, H₃,₃'), 7.77 (m, 6H, mH), 1.60 (s, 18H, tBu), 1.59 (s, 9H, tBu). ESI-MS. calcld for C₆₈H₇₀N₇O₇ZnRe ([M – CF₃SO₃]⁺): 1272.3, found: 1272.5. Selected IR bands (cm⁻¹, CHCl₃): 2036 (s, C=O fac), 1932 (s, br, C=O fac), 1935 (s, br, C=O fac), 1726 (m, C=O). UV-vis (λmax, nm, CH₂Cl₂): 423, 500, 600 nm. Crystals of 4b suitable for X-ray diffraction were obtained by the slow diffusion of n-hexane into a dichloromethane solution of the compound. Crystal data: C₆₉H₇₀F₃N₇O₇ReSZn, MW = 1422.86, triclinic, space group P1⁻ a = 8.7260(8) Å, b = 9.8370(9) Å, c = 40.956(3) Å, α = 84.227(10)°, β = 84.429(11)°, γ = 72.995(7)°, V = 3336.3(5) Å³, Z = 2, Dc = 1.416 g/cm³, μ = 4.750 mm⁻¹, F(000) = 1436, θ range = 2.11–26.76°. Final R1 = 0.0925, wR2 = 0.2276, and S = 1.194 for 838 parameters and 5036 unique reflections [R(int) = 0.0640], of which 3766 with I > 2σ(I), max positive and negative peaks in ΔF map 1.538 (close to the disordered triflate) and −1.731 e/Å³.

**fac-[Re(CO)₃(bipy)(Zn-4'MPydBuP)][(CF₃SO₃)] (5b)**. Yield: 87%. ¹H NMR (δ, 500 MHz, CDCl₃): 9.26 (d, J = 4.3 Hz, 2H, H₆₆,₆'), 8.93 – 8.85 (m, 8H, βH+pyₐ), 8.57 (d, J = 4.5 Hz, 2H, H₃,₃'), 8.47 (d, J = 5.7 Hz, 2H, βH), 8.41 (t, J = 8.0 Hz, 2H, H₄,₄'), 8.18 (d, J = 5.4 Hz, 2H, pyₐ), 8.03 – 7.95 (m, 6H, oH), 7.83 (t, J = 8.0 Hz, 2H, H₅,₅'), 7.73 (s, 3H, pH), 1.48 (s, 54H, tBu). ¹H NMR (δ, 500 MHz, CDCl₃): 9.26 (d, J = 4.3 Hz, 2H, H₆₆,₆'), 8.85 (d, J = 5.7 Hz, 2H, H₃,₃'), 8.47 (d, J = 5.7 Hz, 2H, βH), 8.41 (t, J = 8.0 Hz, 2H, H₄,₄'), 8.18 (d, J = 5.4 Hz, 2H, pyₐ), 8.03 – 7.95 (m, 6H, oH), 7.83 (t, J = 8.0 Hz, 2H, H₅,₅'), 7.73 (s, 3H, pH), 1.48 (s, 54H, tBu). ESI-MS. calcld for C₆₈H₇₀N₇O₇ZnRe ([M – CF₃SO₃]⁺): 1440.5, Found: 1440.5. Selected IR bands (cm⁻¹, CHCl₃): 2036 (s, C=O fac), 1932 (s, br, C=O fac), 1935 (s, br, C=O fac), 1726 (m, C=O). UV-vis (λmax, nm, CH₂Cl₂): 423, 551, 594.

**fac-[Re(CO)₃(4,4'-DEC-bipy)(py)][(CF₃SO₃)] (6)**. To a dichloromethane (20 mL) solution of complex 2 (50 mg, 0.06 mmol) pyridine was added (30 μL, 0.3 mmol). The
A dichloromethane solution (100 mL) of benzyl bromoacetate (3 mL, 19.1 mmol) was added dropwise to a dichloromethane (150 mL) solution of n-octylamine (9 mL, 54.5 mmol) at 0 °C and stirred overnight. The mixture was extracted with distilled water (6 × 50 mL) and purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate 9:1. A catalytic amount of Pd/C (10% w/w) was added. The solution was left under stirring overnight under hydrogen atmosphere. The mixture was filtrated on Celite and the solvent removed in vacuo to obtain the product as a white solid. Yield: 720 mg (20%). \(^1H\) NMR (δ, 500 MHz, CD$_3$OD): 3.49 (s, 2H, H$_A$), 2.55 (t, J = 7.1 Hz, 2H, H$_1$), 1.38–1.29 (m, 12H, H$_2$–H$_7$), 0.88 (t, J = 7.1 Hz, H$_8$).

N-methyl-2(4-pyridine)-3,4-fulleropyrrolidine (7).\(^{15}\) A toluene (200 ml) solution of of C$_{60}$ (250 mg, 0.35 mmol), pyridine-4-carboxaldehyde (150 mg, 1.40 mmol) and N-methylglycine (62 mg, 0.70 mmol) was stirred at reflux temperature for 25 minutes, after which the solvent was removed in vacuo. The solids were purified with a plug of silica gel initially eluted with toluene to recover unreacted C$_{60}$ and then with toluene/ethyl acetate
N-octyl-2(4-pyridine)-3,4-fulleropyrrolidine (8). C₆₀ (250 mg, 0.350 mmol), pyridine-4-carboxaldehyde (0.21 mL, 1.73 mmol) and and OctylAmA (130 mg, 0.69 mmol) were dissolved in 200 mL toluene () and stirred at reflux for 25 minutes, then the solvent was removed in vacuo. The product was purified by column chromatography on silica gel initially eluted with toluene to recover unreacted C₆₀ and then with toluene/ethyl acetate 95:5. Yield: 185 mg (55%). ¹H NMR (δ, 500 MHz, CDC1₃): 8.68 (d, J = 5.3 Hz, 2H, py₃), 7.76 (s, 2H, py₅), 5.13 (d, J = 9.4 Hz, 1H, H₅), 5.05 (s, 1H, H₆), 4.15 (d, J = 9.4 Hz, 1H, H₇), 3.16 (dt, J = 11.9, 8.5 Hz, 1H, H₈), 2.59 (ddd, J = 12.4, 8.4, 4.4 Hz, 1H, H₉), 2.06 – 1.82 (m, 2H, H₁₀), 1.75 – 1.50 (m, 2H, H₁₁), 1.50 – 1.18 (m, 10H, H₁₂), 0.92 (t, J = 6.9 Hz, 3H, CH₃). ¹³C NMR (δ, 50 MHz, CDC1₃): 13.96, 22.55, 27.35, 28.15, 29.6, 31.68, 53.36, 66.71, 81.18, 124.28, 155.36. UV-vis (λ_max, nm, cyclohexane): 216, 254, 308, 323, 429.

fac-[Re(CO)₃(bipy)(dmso-O)](PF₆). fac-[Re(CO)₃(dmso-O)₃](PF₆) (100 mg, 0.15 mmol) and 2,2’-bipyridine (31 mg, 0.2 mmol) were dissolved in acetone (15 mL). The solution, initially almost colorless, was refluxed for 1 h under argon atmosphere and turned yellow. Concentration in vacuo to ca.10 mL followed by addition of a few drops of diethyl ether induced the formation of yellow microcrystals, that were removed by filtration, washed with diethyl ether and vacuum-dried. Yield: 84 mg (85%). ¹H NMR (δ, 500 MHz, CD₂JNO₂): 9.15 (d, J = 4.8 Hz, 2H, H₆,₆’), 8.55 (d, J = 8.2 Hz, 2H, H₃,₃’), 8.37 (t, J = 8.1, 1.5 Hz, 2H, H₅,₅’), 7.80 (t, J = 8.1, 2H, H₄,₄’), 2.62 (s, 6H, CH₃ dmso-O).

fac-[Re(CO)₃(bipy)(7)](CF₃SO₃) (9a). 7 (50.4 mg, 0.053 mmol) was added to a solution of fac-[Re(CO)₃(bipy)(dmso-O)](CF₃SO₃) (44.9 mg, 0.069 mmol) in 1,2-dichloroethane (15 mL). The mixture was stirred at reflux for 72 h. A brown solid was precipitated after concentration in vacuo followed by addition of diethyl ether, and vacuum-dried. Yield: 20 mg (20%). ¹H NMR (δ, 500 MHz, CD₂JCl₂): 9.17 (dd, J = 5.5, 0.8 Hz, 2H, H₆,₆’), 8.42 (d, J = 8.2 Hz, 2H, H₃,₃’), 8.29 (t, J = 8.1, 2H, H₅,₅’), 8.19 (d, J = 5.5 Hz, 2H, py₅), 7.79 (m, 4H, py₅+H₄,₄’), 4.99 (m, 3, H₆+H₇), 4.29 (d, J = 9.6 Hz, 1H, H₉),
2.73 (s, 3H, CH₃). Selected IR bands (cm⁻¹, solid state): 2028 (s, C=O fac), 1916 (s, br, C=O fac). ESI-MS calcd for C₈₁H₁₇N₄O₃Re ([M - CF₃SO₃]⁺) 1281.6, found 1281.4.

fac-[Re(CO)₃(bipy)](7)[PF₆] (9b). 7 (25.4 mg, 0.026 mmol) was added to a solution of fac-[Re(CO)₃(bipy)(dmso-O)][PF₆] (22.9 mg, 0.035 mmol) in 1,2-dichloroethane (10 mL). The mixture was stirred at reflux for 72 h. A brown solid was precipitated after concentration in vacuo followed by addition of diethyl ether, and vacuum-dried. Yield: 10 mg (20%). ¹H NMR (δ, 500 MHz, CD₂Cl₂): 9.19 (dd, J = 5.5, 0.8 Hz, 2H, H₆,₆'), 8.39 (d, J = 8.2 Hz, 2H, H₅,₅'), 8.28 (t, J = 8.1, 2H, H₃,₃'), 8.15 (d, J = 5.5 Hz, 2H, pyₐ), 7.85 (m, 4H, pyₐ+H₄,₄'), 5.04 (m, 3, H₆+H₇), 4.25 (d, J = 9.6 Hz, 1H, H₇), 2.71 (s, 3H, CH₃). Selected IR bands (cm⁻¹, solid state): 2030 (s, C=O fac), 1918 (s, br, C=O fac). ESI-MS calcd for C₈₁H₁₇N₄O₃Re ([M – PF₆]⁺) 1281.4, found 1281.4.

fac-[Re(CO)₃(bipy)](8)[PF₆] (10). 8 (50.4 mg, 0.053 mmol) was added to a solution of fac-[Re(CO)₃(bipy)(dmso-O)][PF₆] (44.9 mg, 0.069 mmol) in anhydrous dichloromethane (15 mL). The mixture was stirred at reflux for 24 h. A brown solid was precipitated after concentration in vacuo followed by addition of diethyl ether, and vacuum-dried. Yield: 50 mg (60%). ¹H NMR (δ, 500 MHz, CDCl₃): 9.07 (dd, J = 5.5, 0.8 Hz, 1H, H₆,₆'), 8.99 (dd, J = 5.4, 0.8 Hz, 1H, H₆,₆'), 8.71 (d, J = 8.2 Hz, 1H, H₃,₃'), 8.67 (d, J = 8.2 Hz, 1H, H₃,₃'), 8.27 (td, J = 8.1, 3.0, 1.6 Hz, 2H, H₅,₅'), 8.19 (d, J = 5.5 Hz, 2H, pyₐ), 7.81 (d, J = 6.1 Hz, 2H, pyₐ), 7.72 (dd, J = 7.6, 5.5, 1.1 Hz, 1H, H₄,₄'), 7.65 (dd, J = 7.5, 5.5, 1.1 Hz, 1H, H₄,₄'), 5.06 (d, J = 9.7 Hz, 1H, H₇), 5.04 (s, 1H, H₆'), 4.10 (d, J = 9.6 Hz, 1H, H₇), 2.96 (dt, J = 11.7, 8.3 Hz, 1H, H₅), 2.61 - 2.53 (m, 1H, H₄'), 1.95 - 1.78 (m, 2H, H₆), 1.68 - 1.55 (m, 2H, H₇), 1.49 - 1.28 (m, 10H, H₃,₃, CH₃). ¹³C NMR (δ, 50 MHz, CDC₁₃): 14.42, 22.34, 27.24, 28.14, 29.31, 31.87, 53.57, 66.62, 79.95, 126.08, 127.08, 128.71, 141.51, 151.62, 152.53. Selected IR bands (cm⁻¹, solid state): 2032 (s, C=O fac), 1918 (s, br, C=O fac). ESI-MS calcd for C₈₁H₃₂N₄O₃Re ([M – PF₆]⁺) 1379.2, found 1379.4.

fac-[Re(CO)₃(bipy)(py)][PF₆]. fac-[Re(CO)₃(bipy)(dmso-O)][PF₆] (30 mg, 0.046 mmol) was dissolved in CH₂Cl₂ (15 mL). After addition of pyridine (37 μL, 0.46 mmol), the solution was stored at ambient temperature for 2 days and then concentrated in vacuo to ca. 5 mL. Yellow microcrystals of the product formed upon addition of a few drops of diethyl ether and were removed by filtration, washed with diethyl ether and vacuum-dried. Yield: 22 mg (73%). Selected IR bands (Nujol, cm⁻¹): 2026 (s, C=O fac), 1921 and 1907 (s,
br, C=O fac). $^1$H NMR (δ, CD$_3$NO$_2$): 9.32 (d, 2H, H$_{6,6'}$), 8.44 (dd, 2H, H$_{3,3'}$), 8.36 (m, 4H, H$_{4,4'}$ + py$_{c}$), 7.87 (m, 3H, H$_{5,5'}$ + py$_{c}$), 7.35 (t, 2H, py$_{b}$).

4'-Methyl-2,2'-bipyridine-4-carboxylic Acid (11, bipyAc).$^{12}$

A suspension of SeO$_2$ (0.76 g, 6.93 mmol) and 4,4'-dimethyl-2,2'-bipyridine (1.05 g, 5.60 mmol) in 1,4-dioxane (60 mL) was stirred at reflux for 24 h. The hot mixture was filtered through Celite® to remove elemental selenium. The filtrate was cooled to room temperature and the solvent removed in vacuo. The residual yellow solid was suspended in 95% ethanol (40 mL). A solution of AgNO$_3$ (1.10 g, 6.33 mmol) in water (10 mL) was added. The yellow suspension was stirred rapidly and 1.0 M NaOH (25 mL) was added dropwise over 20 min. The black reaction mixture was stirred rapidly for 15 h. Ethanol was removed in vacuo and the aqueous residue was filtered to remove Ag$_2$O and elemental silver. The solids were washed with 1.3 M NaOH (2 ×10 mL) and water (10 mL). The filtrate was extracted with dichloromethane (4 × 25 mL) to remove unreacted bipyridine and adjusted to pH 3.5 with 1:1 (v/v) 4.0 M HCl/acetic acid, which produced a white precipitate. After the mixture was kept at −10 °C overnight, the white solid was collected, vacuum-dried, placed into thimble of a Soxhlet apparatus, and continuously extracted with dry acetone for 72 h. A pure white product was obtained by removal of acetone in vacuo. Yield: 0.45 g (36%). $^1$H NMR (δ, 500 MHz, acetone- $d_6$): 9.03 (s, 1H, H$_3$), 8.87 (d, $J$ = 4.9 Hz, 1H, H$_6$), 8.57 (d, $J$ = 4.9 Hz, 1H, H$_6$), 8.35 (s, 1H, H$_3$), 7.91 (dd, $J$ = 4.9, 1.6 Hz, 1H, H$_3$), 7.30 (d, $J$ = 4.9 Hz, 1H, H$_3$), 2.47 (s, 3H, CH$_3$). Selected IR bands (cm$^{-1}$, solid state): 1708 (s, C=O), 1288 (m, C-O).

5-(4'-aminophenyl)-10,15,20-triphenylporphyrin (12, TPP-NH$_2$).$^{16,17}$
To a solution of TPP (200 mg, 0.326 mmol) in trifluoroacetic acid (20 mL), NaNO₂ (45 mg, 0.65 mmol) was added. The solution reaction was stirred for 3 min at room temperature and quenched with water (200 mL). The aqueous solution was extracted with dichloromethane (6 × 50 mL). The organic layer was washed twice with saturated water solution of NaHCO₃, twice with distilled water, dried over anhydrous Na₂SO₄ and filtrated. The solvent was removed in vacuo. The crude was purified by column chromatography on silica gel eluted with chloroform, collecting the first fraction that contains unreacted TPP and the reaction intermediate 5-(4-nitrophenyl)-10,15,20-triphenylporphyrin, TPP-NO₂). After evaporation of the solvent, the residue was dissolved in concentrated HCl (20 mL) and SnCl₂ (440 mg, 1.95 mmol) was added. The mixture was heated to 65 °C for 1 h under argon atmosphere. The reaction was quenched pouring, carefully, cold water (200 mL) into the flask. The aqueous solution was neutralized NH₄OH until pH 8 and extracted with dichloromethane until the water phase was colorless. The organic layer was dried over anhydrous Na₂SO₄ and filtrated. The solvent was removed in vacuo. The residue was purified by column chromatography on silica gel and collected as the second band with chloroform. Yield: 205 mg (51%). ᵃH NMR (δ, 500 MHz, CDCl₃): 8.94 (d, J = 4.7 Hz, 2H, βH), 8.83 (s, 6H, αH), 8.28 – 8.17 (m, 6H, oH), 8.00 (d, J = 8.3 Hz, 2H, oNH), 7.84 – 7.70 (m, 9H, m+pH), 7.07 (d, J = 8.3 Hz, 2H, mNH), 4.03 (s, 1H, NH₂), -2.75 (s, 2H, NH).

Selected IR bands (cm⁻¹, solid state): 1617 (m, δN-H), 1288 (s, br, N-C).

5-{4-(4-Methyl-2,2′-bipyridine-4′-carboxyamidyl)phenyl}-10,15,20-(phenyl)-porphyrin (13, TPP-bipy).¹⁸

BipyAc (132.3 mg, 0.62 mmol) and 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (144.7 mg, 0.75 mmol, EDC-Cl) were dissolved in pyridine (7 mL). The solution was stirred for 10 min under argon atmosphere at room temperature. TPP-NH₂ (190.3 mg, 0.30 mmol) was added and the mixture stirred at room temperature for 2.5 h. The reaction was quenched with distilled water (20 mL). The purple precipitate was collected by filtration, washed with distilled water (80 mL) and vacuum-dried. The product was purified on a plug of silica gel eluting with CHCl₃:EtOH 98:2. Yield: 225 mg (90%).
**Chapter 6**

$^1$H NMR (δ, 500 MHz, CDCl$_3$): 8.95 (d, $J = 5.0$ Hz, 1H, H$_6^\alpha$), 8.94 (s, 1H, H$_3^\gamma$), 8.89 (dd, $J = 13.8$, 4.7 Hz, 4H, $\beta$H), 8.85 (s, 4H, $\beta$H), 8.63 (d, $J = 4.9$ Hz, 1H, H$_6^\alpha$), 8.49 (s, 1H, NH$_{am}$), 8.38 (s, 1H, H$_3$), 8.27 (d, $J = 8.3$ Hz, 2H, oNH), 8.23 (dd, $J = 7.6$, 1.4 Hz, 6H, oH), 8.11 (d, $J = 8.2$ Hz, 2H, mNH), 8.01 (dd, $J = 4.9$, 1.7 Hz, 1H, H$_5^\gamma$), 7.81 – 7.73 (m, 9H, m+pH), 7.24 (d, $J = 5.5$ Hz, 1H, H$_3$), 2.51 (s, 3H, CH$_3$), -2.75 (s, 2H, NH). Selected IR bands (cm$^{-1}$, solid state): 1654 (m, C=O), 1605 (m, $\delta$N=H).

*fac-[Re(CO)$_3$(TPP-bipy)(dms-O)](PF$_6$) (14).* TPP-bipy (75 mg, 0.092 mmol) and *fac-[Re(CO)$_3$(dms-O)$_3$](PF$_6$) (45 mg, 0.070 mmol) were dissolved in chloroform (15 mL). The mixture was stirred at reflux for 1.5 h under argon. The purple product was collected by filtration after concentration of the solution and addition of diethyl ether and vacuum-dried. Yield: 60 mg (60%). $^1$H NMR (δ, 500 MHz, dms-O$_6$): 11.29 (s, 1H, NH$_{am}$), 9.38 (d, $J = 5.5$ Hz, 1H, H$_6^\alpha$), 9.30 (s, 1H, H$_3^\gamma$), 9.03 (d, $J = 5.7$ Hz, 1H, H$_6^\alpha$), 8.95 (s, 1H, H$_3$), 8.93 – 8.76 (m, 8H, $\beta$H), 8.35 (d, $J = 5.6$ Hz, 1H, H$_3^\gamma$), 8.33 – 8.26 (m, 4H, o+mNH), 8.26 – 8.19 (m, 6H, oH), 7.90 – 7.81 (m, 9H, m+pH), 7.77 (d, $J = 5.4$ Hz, 1H, H$_3$), 2.67 (s, 3H, CH$_3$), 2.54 (s, 6H, CH$_3$ dms-O), -2.90 (s, 2H, NH). $^1$H NMR (δ, 500 MHz, CDCl$_3$): 9.44 (s, 1H, NH$_{am}$), 9.16 (d, $J = 5.6$ Hz, 1H, H$_6^\alpha$), 8.96 – 8.84 (m, 9H, $\beta$H+H$_3^\gamma$), 8.83 (d, $J = 5.6$ Hz, 1H, H$_6^\alpha$), 8.50 (s, 1H, H$_3$), 8.30 (d, $J = 6.2$ Hz, 1H, H$_3^\gamma$), 8.28 (d, $J = 3.2$ Hz, 4H, o+mNH), 8.26 – 8.20 (m, 6H, oH), 7.84 – 7.72 (m, 9H, m+pH), 7.47 (d, $J = 6.2$ Hz, 1H, H$_3$), 2.71 (s, 3H, CH$_3$), 2.60 (d, $J = 3.9$ Hz, 6H, CH$_3$ dms-O), -2.59 (s, 2H, NH). Selected IR bands (cm$^{-1}$, solid state): 2030 (s, C=O), 1918 (s, br, C=O fac), 1901 (s, br, C=O fac), 1677 (m, C=O), 966 (m, S=O). ESI-MS calcd for C$_{59}$H$_{57}$N$_7$O$_4$ ([M – PF$_6$ – dms-O]+) 1096.3, found 1096.4.

*fac-[Re(CO)$_3$(TPP-bipy)(py)](PF$_6$) (15a).* *fac-[Re(CO)$_3$(TPP-bipy)(dms-O)](PF$_6$) (47 mg, 0.037 mmol) and pyridine (15 μL, 0.15 mmol) were dissolved in DCM (15 mL). The mixture was stirred at reflux for 4 h. The solution was concentrated *in vacuo* to ca. 10 mL and the same amount of diethyl ether was added to induce precipitation. The purple product was collected by filtration and vacuum-dried. Yield: 44 mg (93%). $^1$H NMR (δ, 500 MHz, CDCl$_3$): 10.81 (s, 1H, NH$_{am}$), 9.24 (d, $J = 5.6$ Hz, 1H, H$_6^\alpha$), 9.21 (s, 1H, H$_3^\gamma$), 8.95 – 8.85 (m, 9H, $\beta$H+H$_6^\alpha$), 8.73 (s, 1H, H$_3$), 8.38 (d, $J = 6.2$ Hz, 1H, H$_5^\gamma$), 8.32 (d, $J = 6.2$ Hz, 2H, py$_a$), 8.28 – 8.20 (m, 10H, oH+ o+mNH), 7.86 (t, $J = 7.5$ Hz, 1H, py$_c$), 7.84 – 7.74 (m, 9H, m+pH), 7.53 (d, $J = 6.2$ Hz, 1H, H$_3$), 7.43 (t, $J = 7.5$ Hz, 2H, py$_b$) 2.78 (s, 3H, CH$_3$), -2.59 (s, 2H, NH).
**fac-[Re(CO)3(ZnTPP-bipy)(py)](PF6) (15b).** 15a (44 mg, 0.035 mmol) was dissolved in chloroform (10 mL) and Zn(CH3COO)2·2H2O (19 mg, 0.105 mmol) dissolved in MeOH (2 mL) was added. The mixture was stirred overnight at room temperature. The solvent was removed in vacuo and the solid washed with methanol, filtrate, and vacuum-dried. Yield: 42 mg (95%). 1H NMR (δ, 500 MHz, CDCl3 + 10 μL of CD3OD): 9.25 (d, J = 5.6 Hz, 1H, H6), 8.98 (s, 1H, H3′), 8.89 (d, J = 5.7 1H, H6′), 8.85 – 8.75 (m, 8H, βH), 8.50 (s, 1H, H3), 8.28 (d, J = 6.2 Hz, 1H, H5′), 8.19 – 8.04 (m, 12H, oH+ o+mNH + py), 7.79 (t, J = 7.5 Hz, 1H, py), 7.72 – 7.56 (m, 9H, m+pH), 7.52 (d, J = 6.2 Hz, 1H, H3), 7.32 (t, J = 7.5 Hz, 2H, pyb) 2.64 (s, 3H, CH3).

**fac-[Re(CO)3(TPP-bipy)(8)](PF6) (16).** fac-[Re(CO)3(TPP-bipy)(dmso-O)](PF6) (49 mg, 0.037 mmol) and 8 (36 mg, 0.037 mmol) were dissolved in 1,2-dichloroethane (15 mL). The mixture was stirred at reflux for 18 h. The solution was concentrated in vacuo to ca. 10 mL and the same amount of diethyl ether was added to induce precipitation. A brown pure product was collected by filtration, and vacuum-dried. Yield: 57 mg (70%). 1H NMR (δ, 500 MHz, dmso-d6): 10.88 (s, 1H, NHam), 10.75 (s, 1H, NHam), 9.51 – 9.45 (m, 1H, H6), 9.19 (m, 1H, H6), 8.90 – 8.74 (m, 9H, βH+H3′), 8.71 (s, 1H, H3′), 8.40 (d, J = 6.0 Hz, 2H, py), 8.33 (s, 1H, H3), 8.29 (d, J = 5.9 Hz, 1H, H5), 8.26 – 8.13 (m, 8H, oH+H3+H5′), 8.10 (d, J = 8.0 Hz, 2H, oNH2), 8.02 (d, J = 8.3 Hz, 2H, mNH2), 7.93 – 7.81 (m, 9H, m+pH), 7.78 (d, J = 5.9 Hz, 1H, H5), 7.70 (d, J = 5.9 Hz, 1H, H3), 7.63 (d, J = 4.7 Hz, 2H, pyb), 5.07 (s, 1H, H8), 5.02 (s, 1H, H8), 4.73 (d, J = 9.1 Hz, 1H, H8), 4.51 (d, J = 8.9 Hz, 1H, H8), 3.82 – 3.60 (m, 1H, H8b), 3.04 – 2.90 (m, 1H, Hc), 2.59 – 2.53 (m, 1H, Hc), 2.43 – 2.32 (m, 3H, CH3), 1.89 – 1.68 (m, 1H, Hδ), 1.66 – 1.52 (m, 1H, Hδ), 1.49 – 1.26 (m, 10H, Hβ-Hδ), 1.02 – 0.76 (m, 3H, Hδ), -2.98 (d, 2H, NH). Selected IR bands (cm⁻¹, solid state): 2036 (s, C=O fac), 1940 (s, br, C=O fac), 1914 (s, br, C=O fac), 1674 (m, C=O). ESI-MS calcd for C314H63N9O3Re ([M – PF6⁺] 2049.2, found 2049.0.

**5-[4-(4-methyl-2,2′-bipyridine-4′-carboxyamidylphenyl)-10,15, 20-triphenyl porphyrin ligand (17, ZnTPP-Bpy).** A chloroform solution (25 mL) of TPP-Bpy (148 mg, 0.18 mmol) was treated overnight with 2.5 eq. of Zn(CH3COO)2·2H2O (99 mg, 0.45 mmol) dissolved in the minimum amount of methanol (3 mL). The solution was dried in vacuo. The product was purified by column chromatography on aluminium oxide eluted with chloroform/n-hexane 80:20, and vacuum-dried. Yield: 128.6 mg (81%). 1H NMR (δ, 500 MHz, CDCl3): 8.98 (dt, J = 8.0, 4.0 Hz, 2H, βH), 8.95 (s, 6H, βH), 8.94 (d, J = 4.9 Hz, 1H, H6), 8.91 (s, 1H, H3′), 8.62 (d, J = 4.8 Hz, 1H, H6), 8.50 (s, 1H, NH), 8.37 (s, 1H, H3), 8.26 (d, J = 8.3 Hz, 2H, oNH), 8.25 – 8.20 (m, 6H, oH), 8.08 (d, J = 8.1 Hz, 2H, mNH), 7.56 (m, 9H, m+pH), 7.32 (t, J = 7.5 Hz, 2H, pyb) 2.64 (s, 3H, CH3).
7.97 (d, J = 3.4 Hz, 1H, H$'_5$), 7.80 – 7.71 (m, 9H, m+pH), 7.24 (s, 1H, H$_3$), 2.51 (s, 3H, CH$_3$). ESI-MS calcd for C$_{56}$H$_{38}$N$_7$O$_4$Zn ([MH]$^+$) 888.2, found 888.3.

fac-[Re(CO)$_3$(ZnTPP-Bpy)(dms-O)](PF$_6$)$_3$ (18). ZnTPP-Bpy (119 mg, 0.134 mmol) and fac-[Re(CO)$_3$(dms-O)](PF$_6$) (79 mg, 0.121 mmol) were dissolved in chloroform (50 mL). The mixture was stirred at reflux for 4 h under argon. The product was isolated by precipitation from concentrated solution and diethyl ether. Yield: 125 mg (75%) $^1$H NMR ($^1$H, 500 MHz, CDCl$_3$): 9.30 (s, 1H, NH$_{am}$), 9.06 (d, J = 5.4 Hz, 1H, H$_6'$), 8.97 (dd, J = 10.8, 4.5 Hz, 4H, H$'$_4), 8.93 (s, 4H, H$'$_3), 8.82 (d, J = 5.6 Hz, 1H, H$_6$), 8.71 (s, 1H, H$_3'$), 8.44 (s, 1H, H$_3$), 8.27 – 8.22 (m, 6H, oH), 8.20 (d, J = 7.9 Hz, 2H, oNH), 7.97 (d, J = 7.7 Hz, 2H, mNH), 7.82 – 7.70 (m, 10H, m+pH + H$'_5$), 7.47 (d, J = 5.3 Hz, 1H, H$_5$), 2.71 (s, 3H, CH$_3$), 2.55 (s, 6H, CH$_3$ dms-O). Selected IR bands (cm$^{-1}$, solid state): 2030 (s, C=O fac), 1913 (s, br, C=O fac), 1670 (m, C=O), 950 (m, S=O). ESI-MS calcd for C$_{59}$H$_{37}$N$_7$O$_4$ReZn ([M – PF$_6$ – dms-O]$^+$) 1158.2, found 1158.2.

fac-[Re(CO)$_3$(ZnTPP-bipy)(8)](PF$_6$) (19). fac-[Re(CO)$_3$(ZnTPP-Bpy)(dms-O)](PF$_6$) (65 mg, 0.047 mmol) and 8 (45 mg, 0.047 mmol) were dissolved in 1,2-dichloroethane (10 mL). The mixture was refluxed for 20 h. The brown solid s formed during the reaction was collected by filtration and vacuum-dried. Yield: 85 mg (80%) ESI-MS calcd for C$_{134}$H$_{61}$N$_9$O$_4$ReZn ([M – PF$_6$]$^+$) 2112.6, found 2112.5.

2-((3-(tert-butoxy)-3-oxopropyl)amino)acetic acid (20).

$\beta$-alanine-$t$-butylester (1.0 g, 5.50 mmol) and triethylamine (1.5 mL, 11.0 mmol, NEt$_3$) were dissolved in dichloromethane (50 mL). Benzyl bromoacetate (0.86 mL, 5.50 mmol) was added dropwise within 5 h at room temperature. The solvent was removed under reduced pressure, the crude was redissolved in 100 mL of CHCl$_3$ and extracted with brine ($\times$3). The organic phase was dried over anhydrous Na$_2$SO$_4$. The product was purified with column chromatography in silica gel eluting first with Petroleum ether and then Ethyl acetate/Petroleum ether (1:1), and vacuum-dried. Yield 512 mg (32%). $^1$H-NMR ($^1$H, 500
MHz, CDCl\textsubscript{3}: 7.37-7.33 (m, 5H, H\textsubscript{Ph}), 5.17 (s, 2H, H\textsubscript{Bz}), 3.48 (s, 2H, H\textsubscript{A}), 2.87 (t, J = 6.0 Hz, 2H, H\textsubscript{1}), 2.45 (t, J = 6.0 Hz, H\textsubscript{2}), 2.39 (bs, 1H, NH), 1.44 (s, 9H, Boc).

2-((3-(tert-butoxy)-3-oxopropyl)amino)acetic acid (21).

To a solution of 20 (512 mg) in MeOH (30 mL) a catalytic amount (50 mg) of Pd/C (10% w/w) was added. The solution was left under stirring overnight under hydrogen atmosphere. The mixture was filtrated on Celite and the solvent removed in vacuo to obtain the product as a white solid. Yield 360 mg (> 99%). \textsuperscript{1}H-NMR (\textdelta, 500 MHz, CD\textsubscript{3}OD): 3.50 (s, 2H, H\textsubscript{A}), 3.23 (t, J = 7.1 Hz, 2H, H\textsubscript{1}), 2.70 (t, J = 7.1 Hz, 2H, H\textsubscript{2}), 1.47 (s, 9H, Boc).

1-(propionyl-(\textit{t}-butyl)-ester)-3,4-fulleropyrrolidine (22). C\textsubscript{60} (250 mg, 0.35 mmol), 21 (138 mg, 0.68 mmol) and formaldehyde (60 mg, 1.97 mmol) were refluxed in toluene (240 mL) for 30 min. The solvent was eliminated in vacuo and the product purified by a plug of silica gel eluted with toluene, and vacuum-dried. Yield 90 mg (30%). \textsuperscript{1}H-NMR (\textdelta, 500 MHz, toluene-d\textsubscript{8}): 3.92 (s, 4H, H\textsubscript{A}), 3.10 (t, J = 8.9 Hz, 2H, H\textsubscript{2}), 2.69 (t, J = 8.9 Hz, 2H, H\textsubscript{1}), 1.51 (s, 9H, tBu). \textsuperscript{13}C NMR (\textdelta, 50 MHz, CDCl\textsubscript{3} + drops of CS\textsubscript{2}): 28.17, 35.40, 50.25, 67.62, 70.46, 80.65. ESI-MS: calcd for M: 892.1, found: 891.88. UV-vis (\lambda\textsubscript{max}, nm, toluene): 325, 433, 704.

1-(2-carboxyethyl)-3,4-fulleropyrrolidine (23). 22 (100 mg, 0.11 mmol) was dissolved in dichloromethane (10 mL) and 10 mL of trifluoroacetic acid were added. The reaction mixture was diluted with additional 10 mL of DCM and extracted with brine (\times2) to remove the excess of TFA. The organic phase containing a brown solid in suspension was recovered and the solvent removed in vacuo obtaining in the product in quantitative yield. \textsuperscript{1}H NMR (\textdelta, 500 MHz, pyridine-d\textsubscript{5}): 3.31 (s, 4H\textsubscript{A}), 2.48 (t, J = 7.2 Hz, 2H\textsubscript{2}), 2.09 (t, J = 7.2 Hz, 2H\textsubscript{1}). ESI-MS: calcd for M: 835.77, found: 834.9. UV-vis (\lambda\textsubscript{max}, nm, CH\textsubscript{2}Cl\textsubscript{2}): 229, 255, 322, 427.

1-(propionyl-(\textit{t}-butyl)-ester)-2-dihexyl-3,4-fulleropyrrolidine (24). C\textsubscript{60} (253 mg, 0.35 mmol), 21 (144 mg, 0.71 mmol) and dihexyl ketone (454 mg, 2.29 mmol) were
dissolved in orthodichlorobenzene (20 mL) and heated for 25 min at 170 °C. The reaction was monitored by TLC (silica gel, toluene:n-hexane 1:1). The product was purified in a plug of silica gel and unreacted C₆₀ was eluted first with cyclohexane. While the product was eluted as second with cyclohexane:toluene 1:1. The solid was purified by reprecipitation from carbon disulfide, washed with distilled methanol three times, and vacuum-dried. Yield: 101 mg (27%). ¹H NMR (δ, 500 MHz, CDCl₃): 4.78 (s, 2H, H₅), 3.76 (t, J = 6.9 Hz, 2H, H₂), 2.77 (t, J = 6.8 Hz, 2H, H₁), 2.71 – 2.57 (m, 2H, H₆), 2.49 – 2.38 (m, 2H, H₇), 1.88 – 1.72 (m, 4H, H₈), 1.56 (s, 9H, t-Bu), 1.48 – 1.39 (m, 4H, H₉), 1.38 – 1.22 (m, 8H, H₁₀+H₁₁), 0.90 (t, J = 7.0 Hz, 6H, H₁₂). ¹³C NMR (δ, 50 MHz, CDCl₃): 13.78, 22.12, 24.57, 30.28, 31.59, 35.40, 36.89, 43.73, 62.68

1-(2-carboxyethyl)-2-dihexyl-3,4-fulleropyrrolidine (25). 24 (95 mg, 0.090 mmol) was dissolved in dichloromethane (5 mL) and 5 mL of trifluoroacetic acid (TFA) were added. The mixture was stirred overnight at room temperature checking the completion of the reaction via TLC (silica gel, toluene). The solvent was eliminated in vacuo and the solid was purified by reprecipitation from carbon disulfide, washed with distilled methanol and vacuum-dried. Yield 80 mg (90%). ¹H NMR (δ, 500 MHz, CDCl₃): 4.89 (s, 2H, H₅), 3.95 (s, 2H, H₂), 2.96 (t, J = 6.3 Hz, 2H, H₁), 2.78 – 2.66 (m, 2H, H₆), 2.62 – 2.50 (m, 2H, H₇), 1.99 – 1.70 (m, 4H, H₈), 1.56 – 1.25 (m, 12H, H₁₀–H₁₁), 0.91 (t, J = 6.9 Hz, 6H, H₁₂). ¹³C NMR (δ, 50 MHz, CDCl₃): 13.93, 22.18, 24.72, 29.75, 31.44, 32.60, 35.66, 43.55, 61.06. ESI-MS calcd for C₂₇H₃₃N₂O₂ ([M – H]⁻) 1003.3, found 1002.3. UV-vis (λmax, nm, CH₂Cl₂): 229, 256, 315, 430.

1-methyl-2-(4-carboxybenzyl)-3,4-fulleropyrrolidine (26).¹⁹ C₆₀ (125 mg, 0.174 mmol), sarcosine (31.3 mg, 0.35 mmol) and 4-carboxybenzaldehyde (130 mg, 0.87 mmol) were dissolved in toluene (200 ml) and stirred at reflux under argon for 3.5 h. The solvent was evaporated and the crude mixture was purified by silica gel column chromatography using toluene to elute unreacted C₆₀ followed by toluene:ethyllacetate 90:10. Yield: 49 mg (31%). ¹H NMR (δ, 500 MHz, CDCl₃ + drops of CD₃OD): 8.11 (d, J = 8.4 Hz, 2H, a), 7.90 (s, 2H, b), 5.00 (d, J = 9.4 Hz, 1H, H₅), 5.00 (s, 1H, H₆), 4.28 (d, J = 9.5 Hz, 1H, H₇), 2.80 (s, 2H, CH₃). ¹H NMR (δ, 500 MHz, dmso-d₆): 13.11 (s, 1H, NH), 8.14 (d, J = 8.2 Hz, 2H, a), 8.04 (d, J = 7.9 Hz, 2H, b), 5.32 (s, 1H, H₅), 5.20 (d, J = 9.6 Hz, 1H, H₆), 4.44 (d, J = 9.6 Hz, 1H, H₇), 2.85 (s, 3H, CH₃). ESI-MS calcd for C₇₀H₁₁N₂O₂ ([M – H]⁻) 897.1, found 896.1. UV-vis (λmax, nm, CH₂Cl₂): 229, 254, 309, 422.
**Fb-AlP (27).** **AIP (30 mg, 2.72 × 10⁻⁶ mmol) and Fb (27.5 mg, 2.72 × 10⁻⁶ mmol)** were dissolved in CHCl₃ (30 mL). The violet solution was stirred at room temperature for a few minutes. The color of the solution changes to deeper violet almost instantly. Concentration of the solution in vacuo to approximately half of its original volume and the subsequent addition of n-hexane induced the precipitation of the product as a violet powder, that was collected by filtration, washed with n-hexane, and vacuum-dried (52 mg, 90% yield). ¹H NMR (δ, 500 MHz, CDCl₃): 10.10 (s, 1H, Hmeso), 9.24 (s, 8H, βAl), 8.27 (d, 2H, b), 5.61 (d, 2H, a), 3.93 (m, 4H, H1), 3.79 (m, 4H, H1'), 2.42 (s, 6H, CH₃), 2.14 (m, 4H, H2), 2.11 (m, 4H, H2'), 2.01 (s, 6H, CH₃'), 1.68 (m, 4H, H3), 1.63 (m, 4H, H3'), 1.49 (s, 90H, tBuFb + tBuAl), 1.49 (m, H4 +H4' +H5 +H5'), 0.89 (m, 6H, H6), 0.87 (m, 6H, H6'). UV-vis (λmax, nm, CH₂Cl₂): 502, 548, 581.

**Fb-AlMPyP-RuP (28).** **AlMPyP (15 mg, 1.51 × 10⁻³ mmol), Fb (15.2 mg, 1.51 × 10⁻³ mmol), and RuP (15.3 mg, 1.51 × 10⁻³ mmol)** were dissolved in CHCl₃ (30 mL). The solution was stirred at room temperature for a few minutes, and the solution turned from red-violet to deep violet almost instantly. Concentration of the solution in vacuo to approximately half of its original volume and the subsequent addition of n-hexane induced the precipitation of the product as a red-violet powder, that was isolated by filtration, washed with n-hexane, and vacuum-dried (45 mg, 95% yield). ¹H NMR (δ, 500 MHz, CDCl₃): 10.07 (s, 1H, Hmeso), 9.03 (s, 2H, β4Al), 9.01 (s, 2H, β3Al), 8.82 (s, 2H, β2Al), 8.76 (s, 8H, βRu), 8.23 (d, 4H, oRu), 8.11 (d, 4H, oRu'), 8.02 (d, 2H, oAl), 7.87 (d, 4H, oFb), 7.80 (m, 5H, pAl +mRu), 7.64 (m, 9H, pFb +p'Al +m'Ru + β1Al), 7.01 (d, 2H, b), 6.15 (br. d, 2H, pyb), 5.23. (d, 2H, a), 3.90 (m, 4H, H1), 3.76 (m, 4H, H1'), 2.42 (s, 6H, CH₃), 2.10 (m, 4H, H2), 2.01 (m, 4H, H2'), 1.97 (d, 2H, pya), 1.65 (s, 6H, CH₃'), 1.49 (108H, s, tBuFb + tBuAl + tBuRu), 1.40 (m, H3 +H3' +H4' +H5 +H5'), 0.86 (m, 6H, H6), 0.84 (m, 6H, H6'). UV-vis (λmax, nm, CH₂Cl₂): 504, 545, 570.

**25-AIP (29).** **AIP (15 mg, 0.014 mmol) and 25 (12.3 mg, 0.014)** were dissolved in 10 mL of anhydrous dichloromethane. The solution was stirred at room temperature under argon for 4 h. The solvent was removed in vacuo and the solid was purified by recrystallization from dichloromethane and n-hexane, and vacuum-dried.

**26-AIP (30).** **AIP (30 mg, 0.027 mmol) and 26 (24.3 mg, 0.027)** were dissolved in 20 mL of anhydrous dichloromethane. The solution was stirred at room temperature under
argon for 4 h. The solvent was removed in vacuo and the solid was purified by recrystallization from dichloromethane and n-hexane, and vacuum-dried. Yield 50 mg (93%). $^1$H NMR ($\delta$, 500 MHz, CD$_2$Cl$_2$): 9.10 (s, $J = 5.4$ Hz, 8H, $\beta$H), 8.05 (d, $J = 61.5$ Hz, 8H, oH), 7.85 (t, $J = 1.8$ Hz, 4H, pH), 6.88 (s, 2H, H$_{2,6}$), 5.14 (d, $J = 8.0$ Hz, 2H, H$_{3,5}$), 4.66 (d, $J = 9.4$ Hz, 1H, H$_B$), 4.41 (s, 1H, H$_A$), 3.92 (d, $J = 9.4$ Hz, 1H, H$_C$), 2.39 (s, 3H, CH$_3$), 1.52 (s, $J = 25.4$ Hz, 72H, t-Bu). $^{13}$C NMR ($\delta$, 50 MHz, CD$_2$Cl$_2$): 39.37, 69.46, 82.46, 120.73, 129.31, 132.01. UV-vis ($\lambda_{max}$, nm, CH$_2$Cl$_2$): 418, 548, 587.

27-AlMPyP-RuP (31). AlMPyP-RuP (30 mg, 0.015 mmol) and 26 (16 mg, 0.015 mmol) were dissolved in chloroform (30 mL). The solution was stirred at room temperature for a few minutes, and the solution turned from red-violet to violet almost instantly. Concentration of the solution in vacuo to approximately half of its original volume and the subsequent addition of n-hexane induced the precipitation of the product as a red-violet powder, which was collected by filtration, washed with n-hexane, and vacuum-dried. Yield 44 mg (95%). $^1$H NMR ($\delta$, 500 MHz, CD$_2$Cl$_2$): 9.05 – 8.91 (m, 4H, $\beta$3Al), 8.78 (s, 8H, $\beta$Rup), 8.74 – 8.69 (m, 2H, $\beta$2Al), 8.26 (d, $J = 7.9$ Hz, 4H, oRuP), 8.12 (d, $J = 7.9$ Hz, 4H, o$\beta$RuP), 8.05 – 7.87 (br, m, 6H, oAlP+o$\beta$AlP), 7.82 (d, $J = 8.0$ Hz, 4H, mRuP), 7.79 (s, 3H, pAlP+p$\beta$AlP), 7.72 (d, $J = 7.9$ Hz, 4H, mRuP), 7.52 (d, $J = 4.9$ Hz, 2H, $\beta$1AlP), 6.69 (br, s, 2H, b), 6.00 (d, $J = 5.5$ Hz, 2H, py$_b$), 4.81(d, $J = 7.9$ Hz, 2H, a), 4.61 (d, $J = 9.4$ Hz, 1H, H$_B$), 4.29 (s, 1H, H$_A$), 3.87 (d, $J = 9.4$ Hz, 1H, H$_B$), 2.20 (s, 3H, CH$_3$), 1.89 (d, $J = 5.3$ Hz, 2H, py$_d$), 1.60 (s, 36H, t-BuRuP), 1.44 (s, 54H, t-BuAlP). UV-vis ($\lambda_{max}$, nm, CH$_2$Cl$_2$): 417, 545.

RuP-8 (32). RuP (13.5 mg, 0.014 mmol) and 8 (13.3 mg, 0.014 mmol) were stirred in chloroform (10 mL) at room temperature for 30 min. The solution was concentrated under vacuum to ca. 5 mL, metanol was added to induce precipitation of the product, that was collected by filtration, washed thoroughly with methanol, and vacuum-dried. Yield: 24.5 mg (92%). $^1$H NMR ($\delta$, 500 MHz, CDCl$_3$): 8.59 (dd, $J = 10.2$, 4.8 Hz, 8H, $\beta$H), 8.16 (d, $J = 6.9$ Hz, 4H, oH), 7.77 (d, $J = 7.7$ Hz, 4H, mH), 7.71 (d, $J = 6.6$ Hz, 4H, oH), 7.59 (d, $J = 7.7$ Hz, 4H, mH), 5.66 (s, 2H, py$_b$), 4.61 (d, $J = 5.6$ Hz, 1H, H$_B$), 3.90 (s, 1H, H$_A$), 3.57 (d, $J = 9.7$ Hz, 1H, H$_C$), 2.05 – 1.92 (m, 1H, H$_1$), 1.84 – 1.75 (m, 1H, H$_1$), 1.58 (s, 36H, t-Bu), 1.57 (s, 2H, py$_d$), 1.43 – 1.35 (m, 2H, H$_2$), 1.33 – 1.08 (m, 8H, H$_4$ – H$_7$), 1.15 – 1.10 (m, 1H, H$_3$), 1.06 – 0.94 (m, 1H, H$_3$), 0.87 (t, $J = 7.2$ Hz, 3H, H$_8$). $^{13}$C NMR ($\delta$, 50 MHz, CDCl$_3$): 14.24, 22.40, 27.48, 29.13, 29.65, 31.47, 52.35, 65.30, 78.42, 122.83, 123.04, 131.59, 133.45, 134.04. ESI-MS: calcd for M: 1347.1, found: 1348.2. UV-vis ($\lambda_{max}$, nm, CH$_2$Cl$_2$): 416, 537, 573.
**N-dodecyl-4'-methyl-[2,2'-bipyridine]-4-carboxamide (33, BipyR).** BipyAc (135.2 mg, 0.63 mmol) and 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (149.2 mg, 0.77 mmol, EDC-Cl) were dissolved in 7 mL of pyridine. The solution was stirred for 15 min under argon atmosphere at room temperature. Dodecylamine (59.8 mg, 0.32 mmol) was added and the mixture was stirred at room temperature for 2.5 h. The reaction was quenched with distilled water (10 mL). The precipitate was collected by filtration, washed with distilled water (50 mL) and vacuum-dried. The product was purified on a plug of silica gel eluting with CHCl₃:EtOH 95:5. Yield: 99 mg (80%). ¹H NMR (δ, 500 MHz, CDCl₃): 8.80 (dd, J = 5.0, 0.8 Hz, 1H, H₂), 8.58 (s, J = 0.9 Hz, 1H, H₃), 8.55 (d, J = 5.0 Hz, 1H, H₄), 8.29 (s, 1H, H₅), 7.78 (dd, J = 5.0, 1.7 Hz, 1H, H₆), 7.19 (d, J = 5.0 Hz, 1H, H₇), 6.39 (s, 1H, NH), 3.49 (dt, J = 7.2, 6.0 Hz, 2H, H₈), 2.46 (s, 3H, CH₃), 1.70 – 1.60 (m, 2H, H₉), 1.43 – 1.20 (m, 18H, H₃-H₁₁), 0.88 (t, J = 7.0 Hz, 3H, H₁₂). ¹³C NMR (δ, 50 MHz, CDCl₃): 13.59, 20.96, 29.33, 39.70, 116.52, 121.77, 125.39, 147.38, 148.87, 150.0.

**fac-[Re(CO)₃(bipyR)(NSC)] (34).** fac-[Re(CO)₃(dmsO-0)](CF₃SO₃) (52.0 mg, 0.080 mmol) and BipyR (30.2 mg, 0.080 mmol) were dissolved in dry acetone (10 mL) and stirred at room temperature for 2 h. The solution, initially colorless, turned to yellow. After solvent evaporation the residual oil was redissolved in methanol (9 mL) and KSCN (23.5 mg, 0.24 mmol) dissolved in water (2 mL) was added. The reaction was maintained at 70 °C for 4 h. An orange solid was collected after extraction of the water phase with diethyl ether and removal of the solvent in vacuo. Yield: 60 mg (87%). ¹H NMR (δ, 300 MHz, CDCl₃): 9.02 (d, J = 5.7 Hz, 1H, H₂), 8.76 (d, J = 5.6 Hz, 1H, H₃), 8.33 (s, 1H, H₄), 8.11 (s, 1H, H₅), 7.88 (d, J = 5.6 Hz, 1H, H₆), 7.37 (d, J = 5.5 Hz, 1H, H₇), 7.18 (s, 1H, NH), 3.65 – 3.31 (m, 2H, H₈), 2.43 (s, 3H, CH₃), 1.79 – 1.64 (m, 2H, H₉), 1.46 – 1.16 (m, 18H, H₃-H₁₁), 0.88 (t, J = 6.6 Hz, 3H, H₁₂). ¹³C NMR (δ, 50 MHz, CDCl₃): 14.12, 22.68, 27.06, 29.21, 29.35, 29.59, 29.63, 31.91, 40.84, 120.35, 124.83, 128.87, 151.81, 152.96, 153.49, 154.53, 162.43. Selected IR bands (cm⁻¹, solid state): 2923 (m, C=H), 2100 (s, C=O), 2022 (s, br, C=O fac), 1925 (s, br, C=O fac), 1677 (m, C=O). UV-vis (λmax, nm, DMF): 384 nm.

**Liposome preparation.** Aliquots of NaDMPG from chloroform/methanol 3:1 stock solutions (5 mM) or of DMPC and eDMPCCl from chloroform stock solutions (5 mM), in a 1:1 ratio, were evaporated on a rotary evaporator to give a lipid film on a glassware. The film was hydrated by addition of phosphate buffer (Na₂HPO₄, 50 mM + aliquots of NaOH 0.1 M, final pH = 10.92) to give final lipid concentrations of 2.5 mM. The mixture was
vortexed, freeze-thawed five times, and extruded through 0.2 μm PTFE filters five times at 50 °C to give uniform LUVs. DLS (common value for a range of samples): NaDMPG sample, Z-avg 108.8 nm, PDI 0.059; 1:1 eDMPCCl/DMPC sample, Z-avg 127.5 nm, PDI 0.120.

34:DMPG have been prepared mixing aliquots of DMPG stock solution (5 mM) with 34 stock solution in chloroform (0.4 mM) obtaining liposomes in buffer phosphate (pH = 10.92) with a final concentration of DMPG and 34 of 2.5 and 0.2 mM respectively. Z-avg 116.2 nm, PDI 0.135.

34:DMPC:eDMPC have been prepared mixing aliquots of DMPC:eDMPC stock solution (5 mM) with 34 stock solution in chloroform (0.4 mM) obtaining liposomes in buffer phosphate (pH = 10.92) with a final concentration of DMPC:eDMPC and 34 of 2.5:2.5 and 0.2 mM respectively. Z-avg 118.3 nm, PDI 0.130.

ZnTPPyMe:DMPG and 34:ZnTPPyMe:DMPG have been obtained by DMPG and 34:DMPG respectively adding ZnTPPyMe direct on the sample cuvette for a concentration of porphyrin 3.3 μM.

ZnTPPS:DMPC:eDMPC and 34:ZnTPPS:DMPC:eDMPC have been obtained by DMPC:eDMPC and 34:DMPC:eDMPC respectively adding ZnTPPS direct on the sample cuvette for a concentration of porphyrin 3.3 μM.

6.3 References


