

Figure 5.1 Schematic representation of photochemical water splitting (artificial photosynthesis). Five fundamental components are needed: (1) an antenna for light harvesting, (2) a charge-separation system D–P–A (donor–photosensitizer–acceptor), (3) a catalyst for hydrogen evolution, (4) a catalyst for oxygen evolution, and (5) a membrane separating the reductive and the oxidative processes and enabling proton migration. (Reprinted from Ref. 3 with permission; © 2011 Wiley-VCH.)

Consequently, such an artificial photosynthetic system should include the following fundamental components: (1) an antenna for light harvesting, (2) a reaction center undergoing charge separation, (3) reduction, (4) oxidation catalysts as interfaces between the charge separation center and the final products, and (5) a membrane to provide physical separation of the products that allows proton migration to the reduction compartment (Fig. 5.1).

The overall complexity of a natural photosynthetic system largely exceeds the synthetic ability of any organic chemist. However, single photosynthetic tasks can be achieved by relatively “simple” artificial structures, i.e., relatively complex supramolecular systems. A successful conversion of light into a long-lived charge-separated state, which is necessary to allow an efficient charge transport, requires a highly engineered supramolecular system: The spatial location of the different structural components should be designed very precisely; the excited-state energy levels of each moiety must be perfectly matched; and the rates of any photophysical process must be known and thoroughly considered. In Nature, such an organization is the result of biological evolution; in artificial systems, it is the result of scientific progress. Our group has carried out research in the area of light harvesting and charge-separation systems, which are the key interface between sunlight and the final desired fuels.^{5,6} In the next sections, the related most recent results obtained in our laboratories are briefly described.

5.2.2 Ruthenium(II) complexes with π -extended ligands for solar energy harvesting

As illustrated in Fig. 5.1, the first step to initiate any photosynthetic process is sunlight harvesting. This goal can be achieved using a molecular antenna,

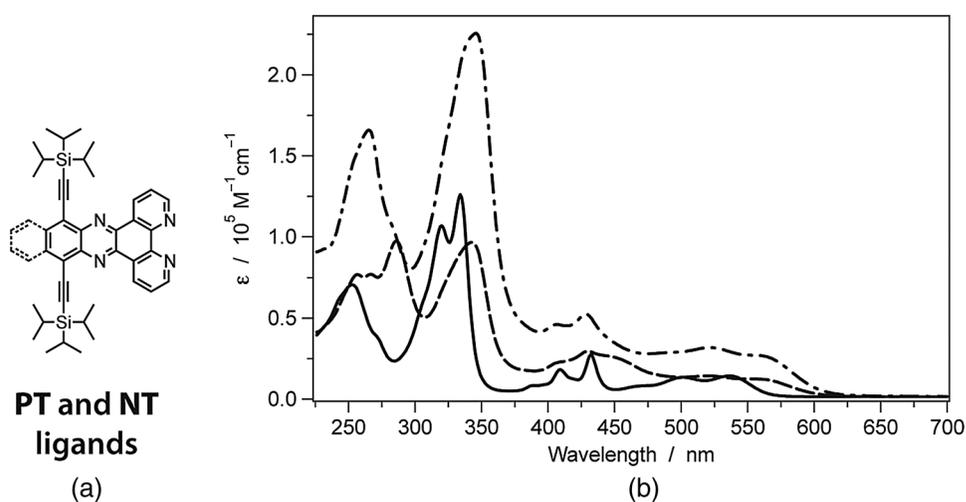


Figure 5.2 (a) Chemical structure of the extended phenanthroline ligands PT and NT (the extension of the NT structure is dashed) used for the synthesis of the heteroleptic and homoleptic Ru(II) complexes specially designed for light harvesting. (b) Absorption spectra of NT (solid line), $[\text{Ru}(\text{NT})_3]^{2+}$ (dashed line) and $[\text{Ru}(\text{NT})(\text{bpy})_2]^{2+}$ (dot-dashed line) in tetrahydrofuran at 298 K (bpy = 2,2'-bipyridine).

i.e., a molecule with high molar absorptivities across the entire sunlight spectrum that is capable of collecting and transferring all absorbed radiation on a single molecular center.⁷ Recently, we investigated a series of homoleptic and heteroleptic Ru(II) complexes designed for sunlight harvesting that take advantage of the high molar absorptivities of two differently π -extended phenanthroline ligands that bear two (tri-isopropylsilyl)ethynyl residues on the terminal phenyl rings [Fig. 5.2(a)].⁸

Both PT- and NT-based complexes show extended absorption bands with relatively high molar absorptivities [Fig. 5.2(b)], but they do not display strong luminescence. In fact, density functional theory (DFT) calculations show that the lowest electronic transitions are always centered on the triplet levels of the PT and NT ligands, which are poorly emissive. This assignment is unambiguously confirmed by experimental studies on the PT-based complexes at 77 K, which exhibit an emission band that is virtually identical to the phosphorescence of the PT free ligand. Both the homoleptic $[\text{Ru}(\text{PT})_3]^{2+}$ and the heteroleptic $[\text{Ru}(\text{PT})(\text{bpy})_2]^{2+}$ complexes (where bpy = 2,2'-bipyridine) also display weak luminescence at room temperature (RT) that is again assigned to a ligand-centered triplet (^3LC) state centered on the π -extended PT ligand. Notably, the two complexes equipped with the more π -extended NT ligand, $[\text{Ru}(\text{NT})_3]^{2+}$ and $[\text{Ru}(\text{NT})(\text{bpy})_2]^{2+}$, do not emit under any conditions because the triplet level is placed below 1 eV, where nonradiative decay processes are highly favored.

nonpolar media. In fact, despite the fact that the $\text{OPV} \rightarrow \text{C}_{60}$ electron transfer is always thermodynamically feasible [see the energy level diagram in Fig. 5.3(b)], this process occurs in the so-called Marcus inverted region¹⁸ and, therefore, it is much slower compared to the $\text{OPV} \rightarrow \text{C}_{60}$ energy transfer.

On the other hand, upon excitation of the fullerene moiety, no quenching of C_{60} singlet and triplet states is detected in low polar solvents (e.g., toluene and dichloromethane), since both fluorescence and sensitized singlet-oxygen luminescence spectra exhibit the same intensity as the individual C_{60} unit taken as reference. A completely different scenario is observed in benzonitrile solution, where a strong quenching of both singlet and triplets is detected, unambiguously proving that an $\text{OPV} \rightarrow \text{C}_{60}$ electron transfer process takes place in this polar medium since no other de-activation pathways are energetically allowed [Fig. 5.3(b)]. Electron transfer is feasible only in benzonitrile because the charge-separated state is lowered in polar solvents, due to the stabilization of the charges in a medium with a higher relative dielectric constant.

From the above-mentioned results, it is worth noting that by simply monitoring the C_{60} excited-state emission properties using Vis–NIR luminescence spectroscopy, one is able to detect photo-induced energy and electron transfer in multicomponent systems based on C_{60} and organic conjugated oligomers. Because of this relatively simple methodology, we were also able to investigate more-complex nanostructures such as OPV/C_{60} dendrimers containing (1) several C_{60} moieties as peripheral units and an OPV core¹⁹ or, alternatively, (2) rigid dendrimers with only one fullerene derivative as a central core and conjugated OPV external branches.²⁰ The photophysical and photo-induced processes of such complex structures are comparable with the prototypical $\text{OPV}-\text{C}_{60}$ dyad, but the efficiency of the $\text{OPV} \rightarrow \text{C}_{60}$ electron transfer is slightly affected by the specific dendrimer structure and generation, showing that in complex electron donor–acceptor nanosystems, the electron transfer dynamics can be finely tuned by molecular design, thanks to pure structural and physical factors. Such observations make these artificial photosystems somehow similar to the natural systems.

5.2.4 A photosynthetic multicomponent system with an antenna and a charge separation module

Recently, we proposed a multifunctional supramolecular system with 12 light-harvesting Zn(II) -porphyrin (ZnP) units grafted onto an exafunctionalized fullerene center ($\text{h-C}_{60}(\text{ZnP})_{12}$). A monosubstituted fullerene (F) is then noncovalently linked to the Zn(II) ion of the porphyrin units through a pyridine residue, creating the self-assembled supramolecular nanostructure ($\text{h-C}_{60}(\text{ZnP})_{12}\text{F}_n$) schematized in Fig. 5.4.²¹

In this system, only the monosubstituted C_{60} derivative (F) plays an active role (i.e., electron acceptor) in the cascade of photo-induced events.

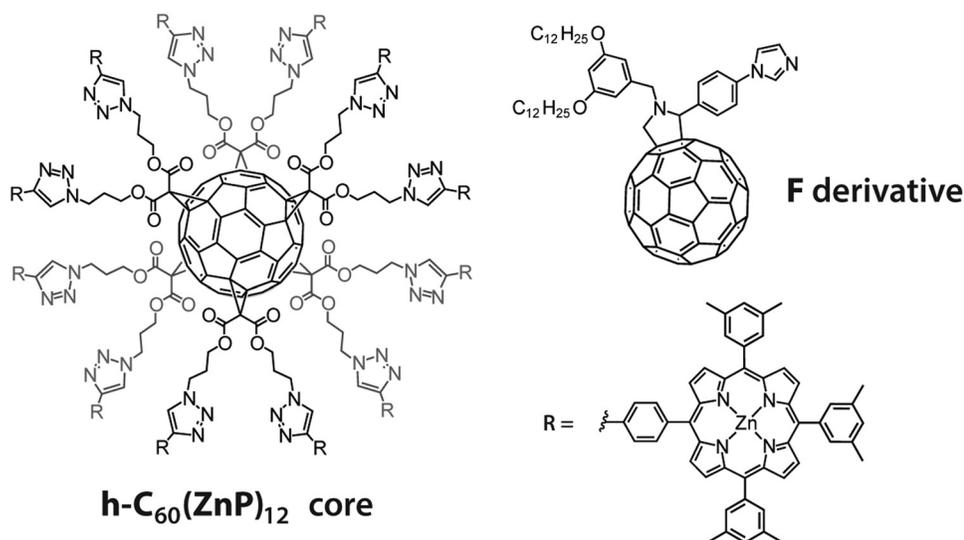


Figure 5.4 Chemical structure of the $h\text{-C}_{60}(\text{ZnP})_{12}$ core and the C_{60} derivative (F), which are able to self-assemble, forming a supramolecular nanostructure. In this system, the light-harvesting process is achieved in high yields by the 12 porphyrin moieties. The charge separation is obtained by electron transfer from a Zn(II)-porphyrin to a proximate noncovalently linked monosubstituted fullerene; hole hopping occurs between nearby porphyrins.

The hexa-substituted C_{60} moiety serves as a nanoscaffold for the twelve-porphyrin cluster, which simultaneously serves as a light-harvesting antenna and an electron donor. In benzonitrile, a charge-separated state occurring for 300 ns is observed. Such unexpectedly long lifetime is attributed to hole hopping over the porphyrin electron donor antennas, a process that also takes place in natural photosystems.

5.2.5 Beyond fullerene: cyanobuta-1,3-dienes as unconventional electron acceptors

We recently examined the electron-accepting capabilities of differently substituted cyanobuta-1,3-dienes as potential alternatives to more conventional acceptors (e.g., quinone-, perylenediimide- or C_{60} -based derivatives) to be used in multicomponent systems featuring photo-induced electron transfer.⁶

The structures of the two novel aniline-substituted pentacyano- (PCBD) and tetracyano-buta-1,3-dienes (TCBD) acceptors are reported in Fig. 5.5 together with three dyads, as representative examples of the investigated multicomponent systems involving a Zn(II)-porphyrin as an electron donor.