

Photoinduced electron transfer in multicomponent arrays of a π -stacked fullerene porphyrin dyad and diazabicyclooctane or a fulleropyrrolidine ligand

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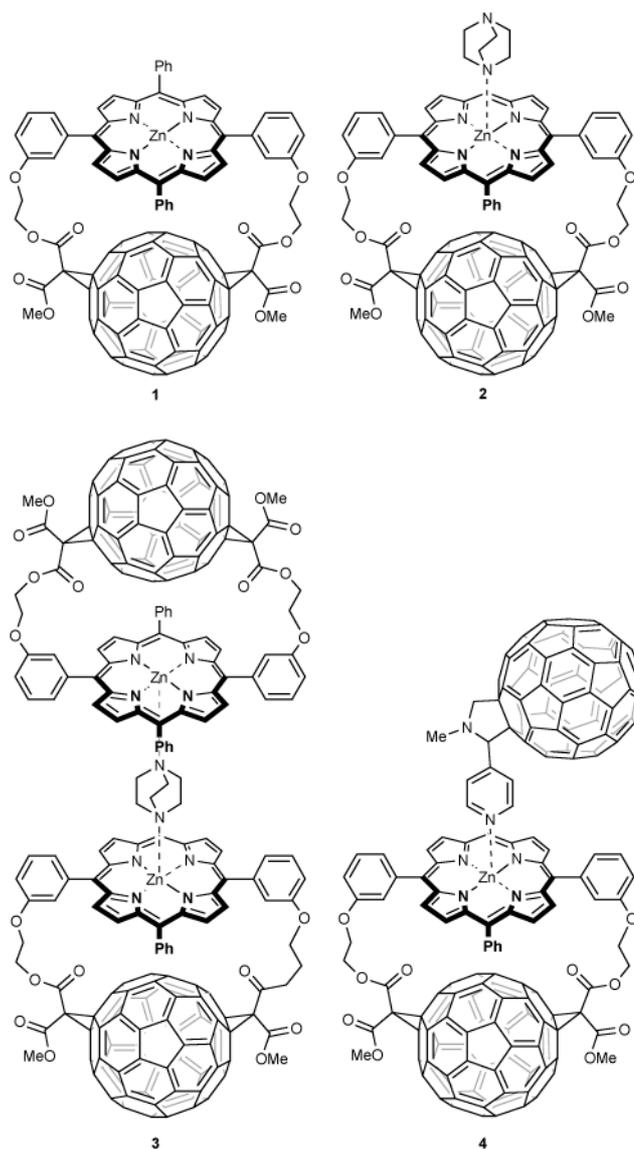
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The kinetics of photoinduced electron transfer in new multicomponent arrays of a π -stacked fullerene porphyrin dyad and diazabicyclooctane or a fulleropyrrolidine ligand have been determined and depend on the molecular architecture

Owing to the importance of converting sunlight into electric current, suitable models are needed for the mimicry of the primary events in natural photosynthesis. A viable approach to artificial photosynthesis is to organize the donor-acceptor couple *via* covalent linkage and, thereby, controlling the separation and electronic coupling. To optimize the performance of such artificial systems, incorporation of secondary electron donor or acceptor moieties into multicomponent arrays (triads, tetrads, pentads *etc.*) has attracted considerable attention. Recently, different alternatives to address the critical issue of organizing the donor-acceptor couples has been forwarded, for example the assembly of individual molecules, linked by weak intermolecular interactions such as van der Waals' forces, hydrogen bonding, salt bridges or by complexation with metals.¹ In this contribution we present the formation and photophysical properties of new rigid electroactive arrays that evolve from complexation of a π - π stacked C₆₀-based ZnTPP dyad **1**² with diazabicyclooctane (DABCO) or a pyridine-fullerene ligand.³

The facile and selective formation of triad **2** or pentad **3** is based on the pronounced concentration dependence of ZnTPPs to form either square pyramidal 1:1- or 2:1 complexes with diazabicyclooctane (DABCO), respectively.⁴ In analogy to related fullerene free TPPs⁴ at low concentrations (*e.g.* 10⁻⁶ M) the exclusive formation of **2** was observed as shown, for example, with the titration experiment depicted in Fig. 1. Owing to the complexation the absorptions of the TPP moiety undergo a bathochromic shift of 9–10 nm which is very characteristic for a 1:1 complex.⁴ The bathochromic shifts in 2:1 complexes are less pronounced (5–6 nm).⁴ At higher concentrations the formation of the pentad **3** prevails. Titration of a 4.3 × 10⁻² M solution of **1** in CDCl₃ with DABCO under ¹H NMR control showed the immediate appearance of one signal only for the 12 methylene protons of the axial ligand at δ -4.5 clearly demonstrating that exclusively **3** is formed. After the addition of 0.5 equiv. of DABCO only **3** can be detected in the NMR spectrum and all of free **1** is consumed. Upon formation of **3** the signals of the ZnTPP protons undergo an up-field shift of up to 0.5 ppm. Up-field shifts of up to 1 ppm for the ZnTPP C atoms and of 8.23 ppm for the C atoms of DABCO are observed in the ¹³C NMR spectrum of **3**. Addition of more DABCO results in the formation of **2** being in an equilibrium with **3** as demonstrated by the appearance of a second signal for the DABCO ligand at δ -2.50 belonging to the three outer methylene groups of **2**. Similarly, triad **4** was prepared by mixing equimolar solutions of **1** and the corresponding fulleropyrrolidine.^{3,5,6} The reversible formation of the complex was followed by visible and by ¹H NMR spectroscopies. In the former technique, a bathochromic shift of the porphyrin bands



was observed, in analogy to **2**, whereas in the proton NMR a considerable upfield shift of the pyridine 2-protons confirmed the presence of an equilibrium between **1** and the fulleropyrrolidine.⁵

Picosecond excitation of triad **2** resulted in the rapid transformation of the ZnTPP singlet excited state into a new transient, which displays a broad absorption maximum around 680 nm. Since the absorption spectrum is in close agreement with that of dyad **1**, we conclude that a rapid intramolecular electron transfer to yield a charge-separated radical pair follows the initial excitation event. The lifetime of the charge-separated

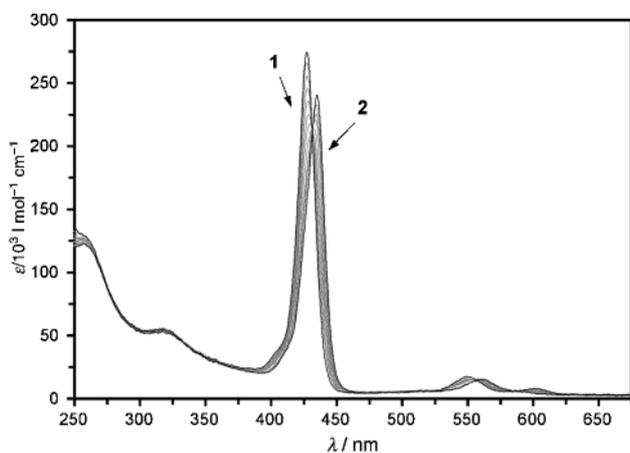


Fig. 1 Titration of **1** with DABCO in CH_2Cl_2 : The appearance of **2** and disappearance of **1** is monitored by UV-VIS-spectroscopy.

state in triad **2** (1980 ± 30 ps) gives rise to a significant enhancement over dyad **1** (619 ps). Interestingly, the transient absorption spectra still revealed the characteristics of the ZnTPP π -radical cation. A reasonable rationalization for this observation implements the close energy of the $\text{C}_{60}^{\bullet-}$ -ZnTPP $^{\bullet+}$ -DABCO and $\text{C}_{60}^{\bullet-}$ -ZnTPP-DABCO $^+$ states, as estimated by the oxidation potentials of the ZnTPP and DABCO electron donors. This leads to the assumption that the positive charge may be distributed over both moieties. In line with this assumption is the fact that the fullerene triplet quantum yield (*e.g.* the product of charge-recombination) did not change upon addition of the secondary electron donor (*i.e.* dyad **1** *cf.* triad **2**).

A qualitative similar picture was obtained with pentad **3**. Immediately after excitation of **3** in toluene the increase of absorbance between 600 and 800 nm is consistent with the formation of the radical pair, observed for dyad **1** and triad **2**. The kinetics of charge-recombination, as monitored around 660 nm, followed again first order kinetics, with a lifetime of 2280 ps.

As a viable alternative to DABCO (*e.g.* electron donor), addition of a fullerene derivative bearing a pyridine functionality (*e.g.* electron acceptor) to a toluene solution of dyad **1** was probed. In this context, the strong fluorescence quenching of **1** should be taken into account. Thus, addition of variable concentrations of the fullerene ligand ($0.5\text{--}5.0 \times 10^{-5}$ M) failed to show any meaningful effects on the fluorescence quantum yield of the resulting triad **4**. Photolysis (532 nm) of triad **4** in toluene or benzonitrile did not lead to any noticeable changes, relative to those described for dyad **1**. Owing to the rapid electron transfer occurring between the ZnTPP chromophore and the π - π stacked fullerene, the competing electron transfer route to the coordinated fullerene ligand is too slow that the latter reaction may contribute to the overall deactivation of the ZnTPP singlet excited state. Dramatic changes were,

however, noted upon generating the fullerene singlet excited state (excitation at 337 nm). Now photoinduced electron transfer can be activated from both fullerene moieties, namely, the covalently linked one, which is still very fast (*e.g.* within the time-resolution of the apparatus) and the coordinatively one. Since benzonitrile is used as a solvent, its ability to coordinate to the zinc center and, therefore, interference with the fullerene-ligand complexation equilibrium between dyad **1** and triad **4** should be considered. This divides a reaction between the photoexcited fullerene and the ZnTPP into two processes. In particular, a fast intramolecular reaction (*ca.* 10^{10} s $^{-1}$) between the fullerene singlet excited state in the coordinated complex (triad **4**) is followed by a much slower intermolecular reaction (1.7×10^{10} M $^{-1}$ s $^{-1}$) between the fullerene triplet excited state and the free dyad **1**. Spectroscopic evidence for this mechanism stems from the fact that the differential absorption changes reveal a two step formation of the $\text{C}_{60}^{\bullet-}$ /ZnTPP $^{\bullet+}$ radical pair grow-in around 1010 and 680 nm, respectively.

In conclusion, we have shown that the reversible complexation of diazabicyclooctane or a fulleropyrrolidine ligand by a π - π stacked C_{60} -ZnTPP dyad **1** is a viable concept to construct novel supramolecular architectures. Rapid photoinduced electron transfer reactions in these multicomponent assemblies lead to charge-separated states, whose lifetimes are markedly improved relative to dyad **1**.

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