A noncovalently linked, dynamic fullerene porphyrin dyad. Efficient formation of long-lived charge separated states through complex dissociation

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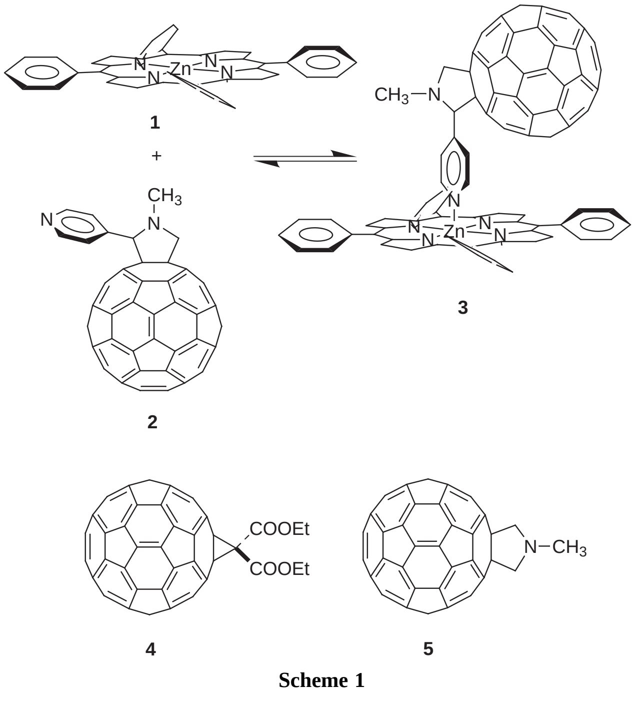
Photoexcitation of a Zn–tetraphenyl porphyrin–fullerene complex leads to electron-transfer with very long lifetimes of the charge-separated pairs.

Photoactive supramolecular systems, in which a donor and an acceptor moieties are non-covalently linked, are particularly appealing either as models for natural photosynthesis and for the conversion of light into electric current.[1–3] In essence, a rapid photoinduced electron-transfer (ET) should be followed by a diffusional splitting of the charge-separated radical pair, thus mimicking a key step in photosynthesis. Here, we describe the assembly of a rigidly connected dyad, in which a zinc tetraphenyl porphyrin [Zn(TPP)] is non-covalently linked to a C_{60} fullerene derivative *via* axial pyridine coordination to the metal.[4–6] Information associated with the photoprocesses has been achieved by optical spectroscopy, in full agreement with time-resolved EPR spectroscopy.

Ligand **2** (Scheme 1) was prepared by azomethine ylide cycloaddition to C_{60},[7,8] using sarcosine and 4-pyridine aldehyde as the starting materials.[9] Semiempirical (PM3) minimization gives 4.5 Å for edge-to-edge distance between the chromophores or 9.5 Å for center-to-center distance.

The absorption spectrum of Zn(TPP) (**1**) was measured at increasing concentrations of fullerene ligand **2** in different solvents. In non-coordinating solvents, such as toluene and dichloromethane, the spectra reveal a noticeable red-shift of the two Q-bands (in CH_2Cl_2: 548 → 559 nm; 588 → 598 nm), as well as a minor broadening of the Soret band. This effect is commonly attributed to the formation of pyridine-Zn(TPP) complexes.[10] In contrast, a similar addition of methanofullerene **4** or pyrrolidine **5** does not affect the porphyrin ground state absorption and, accordingly, the spectra of **1** and the respective fullerene derivative become virtually superimposable. In the more polar and coordinating solvents THF and benzonitrile, no dependence was observed of the spectral features of **1** from fullerene **2** concentrations, indicating a competition in the coordination of Zn between the fullerenic pyridine and the solvent. The ^{1}H NMR spectrum of a 1 : 1 mixture (3×10^{-3} M) of **1** and **2** in $CDCl_3$ shows that the pyridine 2-protons are shifted to δ 3.6 (from δ 8.7 in pure **2**), confirming that coordination of the Zn metal occurs through the pyridine nitrogen and not the pyrrolidine nitrogen, leading to **3** (Scheme 1).



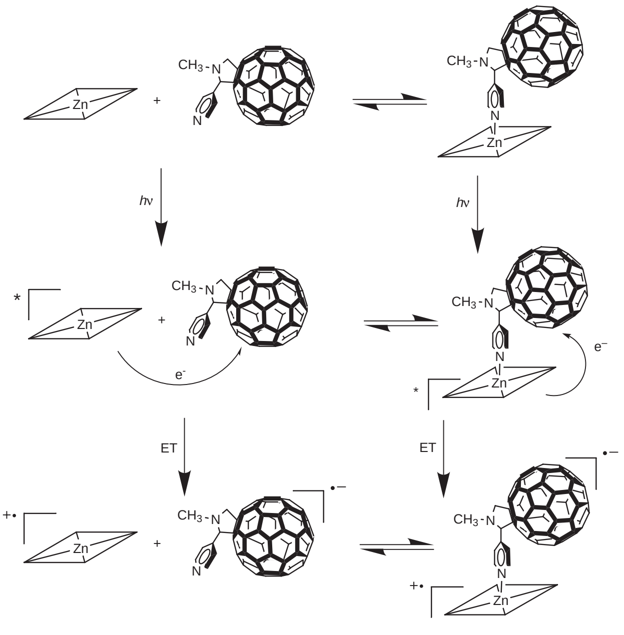
Scheme 1

Zn(TPP) displays a high lying (2.06 eV) and strongly emitting (Φ = 0.04) singlet excited state, $^1(\pi–\pi^*)$ Zn(TPP).[11] However, substantially lower emission yields were noticed upon excitation of ($\mathbf{1} + \mathbf{2} \rightleftharpoons \mathbf{3}$) in solution relative to the Zn(TPP) reference. The emission quantum yields of the $^1(\pi–\pi^*)$ ZnTPP (**1**) (1.0×10^{-5} M) strongly decreased with progressing fullerene ligand **2** concentrations. Toluene and dichloromethane solutions of **1**, in the presence of 1.3×10^{-5} M **2**, gave rise to quantum yields (Φ) of 0.0156 and 0.0152, respectively. These values refer to kinetics much faster than diffusion, thus pointing toward intramolecular processes.

Time-resolved photolysis was carried out to complement the steady-state experiments and to characterize the resulting photoproducts. Irradiation into the porphyrin Q-bands yielded the characteristic $^1(\pi–\pi^*)$ Zn(TPP) absorptions, which decayed (τ = 2.5 ns), in the absence of any fullerene ligand **2**, into the energetically lower lying $^3(\pi–\pi^*)$ Zn(TPP) state (1.53 eV). A systematic addition of fullerene ligand **2** led to a substantial reduction of the singlet state lifetime. More importantly, the $^1(\pi–\pi^*)$ Zn(TPP) transforms into a new product with broad absorption features between 600 and 800 nm, which is a known characteristic for a one-electron oxidized porphyrin, $[\mathrm{Zn(TPP)}^{\cdot+}]$. In addition, the charge-separated radical pair was unequivocally identified *via* the NIR-fingerprint absorption of $(C_{60}{}^{\cdot-})$ at 1010 nm.

While the insufficient polarity of toluene prevents an appreciable stabilization of the radical pair, in moderately polar dichloromethane a lifetime of 8.6 μs was measured. In contrast, parallel experiments using **4** or **5** instead of **2** did not result in any measurable $(C_{60}{}^{\cdot-})/[\mathrm{Zn(TPP)}^{\cdot+}]$ absorptions.

In benzonitrile and THF, differential absorption changes in the NIR reveal the participation of two components in the formation of the $(C_{60}{}^{\cdot-})$. The faster process clearly evolves from an intramolecular ET process, while the slower one involves intermolecular quenching of the lower lying $^3(\pi–\pi^*)$ Zn(TPP) state. For the bimolecular quenching reaction a rate constant of 1.7×10^{10} dm^3 mol^{-1} s^{-1} was resolved. Kinetic



Scheme 2

analysis of the 1010 nm transient absorption ($C_{60}^{\bullet-}$) gives rise to a remarkable lifetime of the separated radical pair in deoxygenated benzonitrile of several hundred microseconds.

According to the above results, two different pathways can be envisioned for the ET processes (Scheme 2). The excitation of the porphyrin chromophore is followed by fast intramolecular ET inside the complex (right-hand pathway in Scheme 2). Alternatively, the free porphyrin is excited, undergoing intermolecular ET when the acceptor molecules approach closely enough during the molecular diffusion (left hand side pathway in Scheme 2). The former process is likely to occur in all solvents. However, in coordinating media, the solvent can displace **2** from the Zn metal, thus making intermolecular ET more effective. This latter ET process is slow enough to allow the excited porphyrin to convert from the singlet to triplet state by ISC.

Experiments performed by time resolved EPR (TREPR) fully support the mechanisms proposed in Scheme 2. The TREPR spectrum of (**1** + **2** $\rightleftharpoons$ **3**) dissolved in THF (1×10^{-4} M) and detected at 180 K with 1 μs delay from the laser pulse is shown in Fig. 1. The spectrum consists of a broad signal superimposed to a narrow derivative-like EPR signal, displaying A/E spin polarization pattern (A and E mean absorption and emission), that is assigned to the singlet-born spin correlated radical pair (SCRP),[12,13] arising here from the CS state ($C_{60}^{\bullet-}$)/[Zn(TPP)$^{\bullet+}$] inside the complex and generated by intramolecular electron transfer. The spin system responsible for the narrow signal is described as two unpaired electrons weakly coupled by small spin exchange and electron–electron dipolar interactions, characterized by J and D constants, respectively. The spectrum is given by two doublets of lines with antiphase spin polarization pattern.[12] In our case, the low-field doublet is centered at the g value of ZnTPP$^{\bullet+}$ radical cation (2.0026)[14] and the high-field doublet at the g value of $C_{60}^{\bullet-}$ radical anion (1.9986).[15] The effect of the unresolved hyperfine interaction is taken into account by a linewidth contribution to the spectrum lines. Estimated linewidths are 1 and 0.1 mT for $C_{60}^{\bullet-}$ and Zn(TPP)$^{\bullet+}$, respectively.[14,15] Since Zn(TPP)$^{\bullet+}$ radical cation has a large inhomogeneous linewidth, while that of the fullerene (with little hyperfine interaction due to protons) is much smaller, the doublet due to the porphyrin radical cation is practically undetectable in the spectrum. Experimental and calculated spectra due to ($C_{60}^{\bullet-}$)/[Zn(TPP)$^{\bullet+}$] singlet-born SCRP are shown in Fig. 1.

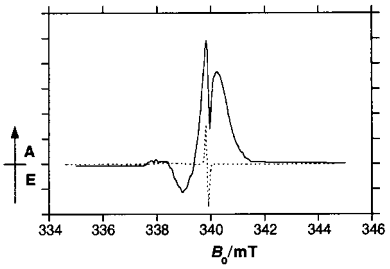


Fig. 1 TREPR spectrum (solid line) observed 1 μs after the laser pulse excitation of (**1** + **2** $\rightleftharpoons$ **3**) dissolved in THF at 180 K. A Lambda Physik LPX 100 XeCl excimer laser (λ = 308 nm, 10 mJ pulse^{-1}) fed a Rhodamin G6 dye laser with emitting light at 581 nm (pulse duration 20 ns). The signal was taken directly from the microwave preamplifier immediately after the detection diode and fed into a EG&G Boxcar Averager mod. 162 equipped with a mod. 164 plug-in. It was operative with an integration window of 50 ns. Positive and negative signals indicate absorptive (A) and emissive (E) polarizations, respectively. Microwave frequency: $\omega/2\pi$ = 9.5256 GHz. Microwave field: B_1 = 0.023 mT.

The broad spectrum of Fig. 1 is attributed to the triplet-born radical ion pair[16] that is generated by intermolecular electron transfer between unlinked Zn(TPP)$^{\bullet+}$ cation and $C_{60}^{\bullet-}$ anion mediated by solvent molecules and stabilized by Coulomb attraction. Details on the spectrum simulation will be reported elsewhere. The separation between the outermost lines amounts to 2|D|, where D represents the dipolar coupling constants. If the classical expression of the point dipole model is used for D, from the measured value of $D = -1.72$ mT the estimated center-to-center distance of 11.7 Å between cation and anion is obtained.

The narrow transient signal detected at 339.9 mT was fitted by a single exponential function with decay time constant of 12 μs, this value being in good agreement with that measured by optical methods (11 μs, 1×10^{-5} M in THF).

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