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Reversible zinc phthalocyanine fullerene ensembles†

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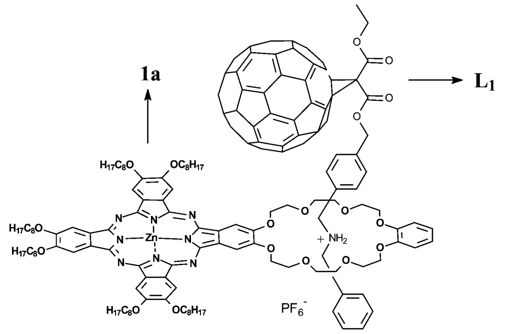
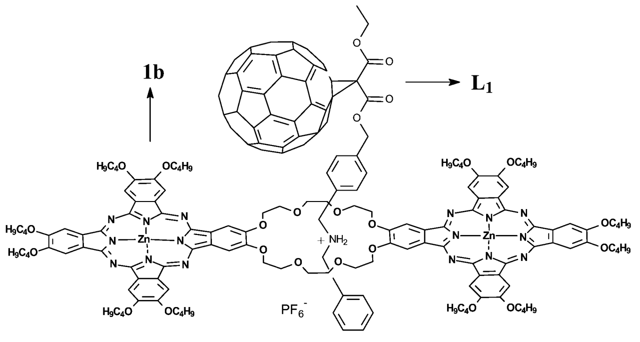
Novel zinc phthalocyanine (ZnPc)/fullerene ligand (L) ensembles are assembled following simple biomimetic principles, which upon photoexcitation give rise to *intra* complex electron transfer quenching of the ^{1*}ZnPc fluorescence.

In nature, covalently-bonded and self-assembled motifs are widely spread organization principles that regulate size, shape and function down to the nanometer scale. Exceptional and aesthetic illustrations for the sophistication of this course are protein shells—including those of the photosynthetic reaction center—with complex performances such as energy storage, protection and transport of inorganic or organic molecules.

To perform efficiently, the donor–acceptor organization by necessity must be weak enough to provide the means for reversible association/dissociation events, but, at the same time, strong enough to bind a given substrate selectively.[1] Considering these prerequisites, we have chosen for our current work a recognition motif that relies on threading a dibenzylammonium unit (*i.e.*, the anchor) through a dibenzo-24-crown-8 macrocycle (DB24C8) affording a reasonably stable pseudorotaxane-like complex.[2] Additionally, the anchor is attached to an electron accepting methanofullerene C_{60} (**L_1**)[3] and the macrocycle—DB24C8—bears either one (**1a, ZnPc**) or two (**1b, ZnPc-ZnPc**) unsymmetrically substituted zinc phthalocyanines.





Details regarding the synthesis and the ground state properties of ZnPc **1a** are described in a previous work.[4] Following the same methodology, that is, a crossover condensation of the tetracyano-DB24C8 and 4,5-dibutoxy-phthalonitrile in the presence of $Zn(OAc)_2{\cdot}2H_2O$ led to bisphthalocyanine ZnPc-ZnPc **1b** in 10% yield.‡ The synthesis of tetracyano-DB24C8 was carried out in two steps, (i) tetrabromination of the commercially available DB24C8 and (ii) conversion into the tetranitrile-derivative *via* Rosemund von Braun reaction.

The unique electron transfer properties of the new **ZnPc/C_{60}** couples rely on two central characteristics: (i) **ZnPc**s are excellent electron donor moieties with strong absorption light cross-sections in the visible region;[5] (ii) **C_{60}** and its derivatives are characterized by small reorganization energies in electron transfer reactions, which renders them very efficient electron acceptors.[6] The supramolecular combination of the two components should lead to very interesting donor–acceptor ensembles. These simple concepts led us to pursue a detailed photochemical investigation of the supramolecular arrangement of the novel **ZnPc-L** ensembles, **ZnPc-L_1** and **ZnPc-L_1-ZnPc**.

In the following, the photochemical details refer mainly to the **ZnPc-L_1** assembly, but stand also for **ZnPc-L_1-ZnPc**. The most important set of experiments involves fluorescence titration experiments, either steady-state or time-resolved, in which photoexcited **ZnPc** (**1a**) and **ZnPc-ZnPc** (**1b**) ($\sim 5.0 \times 10^{-6}$ M) are probed with variable concentrations of **L_1** (1.0–10.0×10^{-5} M). A progressive, non-linear quenching of the **ZnPc** fluorescence (*i.e.*, 670 nm excitation, 690 nm emission) reflects an *intra*complex and efficient quenching in the readily formed complexes—see Fig. 1.§

To quantify the relative contributions, stemming from *inter*molecular deactivation events, by which, for example, free **ZnPc**s and **L**s react with each other, we investigated different ratios of **1a**/**1b** and a methanofullerene, which lacks the dibenzylammonium anchor unit. Under these conditions no supramolecular association occurs! In fact, linear, *inter*molecular quenching dependence was noted, with rate constants that are close to diffusion. Upon correcting for the *inter*molecular part, the (I/I_o) *versus* the concentration of the ligand ($c_{\mathrm{Fullerene}}$) relationships were employed to extract the association constants (K_a) for the 1 : 1 **ZnPc-L** ensembles. Good agreement with the NMR-based values[4]—1.53×10^4 (**ZnPc-L_1**)—were obtained.

In time-resolved fluorescence decay measurements, photoexcited **ZnPc** (**1a**) and **ZnPc-ZnPc** (**1b**) gave rise to an interesting trend. Prior to the addition of **L_1**, the time-fluorescence profiles were best fitted by a mono-exponential decay component—with a lifetime of 3.1 ns. This picture

Table 1 Some selected properties of **ZnPc-L** ensembles

	K	k_{CS}	k_{CR}
ZnPc-L_1	1.4×10^4 M^{-1}	3.5×10^9 s^{-1}	6.6×10^5 s$^{-1\,a}$
ZnPc-L_1-ZnPc	1.9×10^4 M^{-1}	9.5×10^9 s^{-1}	7.6×10^5 s$^{-1\,a}$
ZnPc-L_2	4.8×10^3 M^{-1}		$\sim 10^9$ M^{-1} s$^{-1\,b}$

[a] *Intra*complex process. [b] *Inter*molecular process.

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† Electronic supplementary information (ESI) available: supporting spectra. See http://www.rsc.org/suppdata/cc/b2/b208516j/

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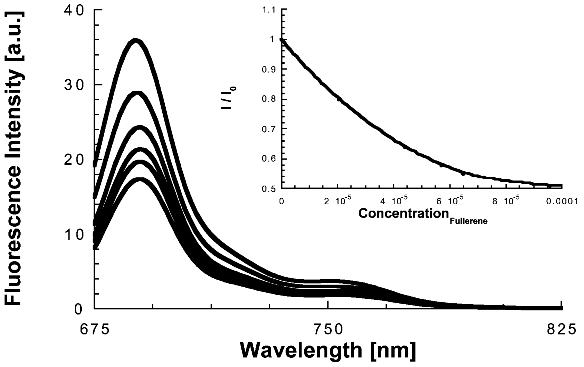


Fig. 1 Fluorescence spectra (λ_{exc} = 670 nm) of **1a** (8×10^{-6} M) and variable concentration of $\mathbf{L_1}$ (1.0–10.0 $\times 10^{-5}$ M) in dichloromethane. Insert depicts (I/I_o) *versus* $c_{\text{Fullerene}}$ relationship at the 690 nm fluorescence maximum.

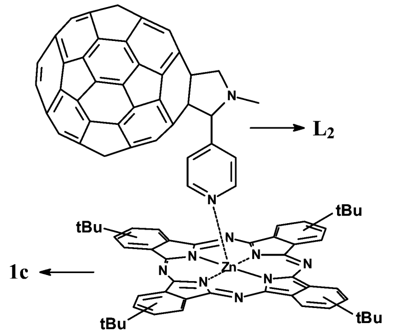
changed dramatically upon adding $\mathbf{L_1}$: in the presence of variable $\mathbf{L_1}$ concentrations, features connected with the long-lived ^{1*}ZnPc lifetime did not change. Instead, a second, short-lived component (0.28 ns for **ZnPc-L$_1$**) started to develop. During the titration assay, the weight of the short-lived part grew progressively, while that of the long-lived part simultaneously decreased. Clearly, this behavior suggests that static, *intra*complex electron transfer quenching inside the readily assembled **ZnPc-L$_1$** donor–acceptor ensemble exists, yielding a charge-separated state (*vide infra*). A good agreement was found between the so-measured electron transfer rates ($k_{\text{et}} = 1/t_{c\,=\,0} - 1/t_{c\neq 0}$) and those obtained by fluorescence quenching at high concentration of $\mathbf{L_1}$, namely, where the **ZnPc-L$_1$** complexation is close to completion.

Another important observation was that the addition of base (*i.e.*, quinuclidine) led to the destruction of the newly formed **ZnPc-L$_1$** ensemble, caused by selective deprotonation of the dibenzylammonium unit of $\mathbf{L_1}$. Quantitative restoration of the strongly quenched emission, for instance, is clear evidence for the reversible association/dissociation cycle.

Further insight into the *intra*complex electron transfer mechanism was lent from transient absorption measurements, in which a short—8 ns—laser pulse resulted in the near exclusive excitation of **1a** and **1b**. The resulting singlet excited states are transformed with time constants of 3.2×10^8 s^{-1} into the long-lived triplet manifolds ($\tau \sim 50$ µs). Characteristics are the triplet–triplet absorption features as they are displayed in Fig. S1 (see ESI†). Quite different are the absorption features found after exciting **ZnPc-L$_1$**, for example, with a 50 ns delay. Three major transient features are noted—Fig. S2 (see ESI†): of fundamental importance is the presence of the 1040 nm absorption band, which is the characteristic fingerprint absorption of the one-electron reduced form of $\mathbf{L_1}$. The other two features, that is, maxima at 500 and 860 nm, correspond to the one-electron oxidized zinc phthalocyanine π-radical cation. This clearly suggests the charge-separated radical pair as the product of the fast ^{1*}ZnPc deactivation in **ZnPc-L$_1$** (*vide supra*). The efficiency for the **ZnPc**$^{\cdot+}$-C$_{60}^{\cdot-}$ formation is with ~0.9 quite high, and documents the promising feature of these donor–acceptor organisations.

Fitting the decay of the **ZnPc**$^{\cdot+}$/**C$_{60}$**$^{\cdot-}$ characteristics to a mono-exponential rate law allowed the determination of the radical pair lifetime as 1.5 µs for **ZnPc-L$_1$** and 1.3 µs for **ZnPc-L$_1$-ZnPc**. In line with the thermodynamics in dichloromethane ($-\Delta G_{\text{CR}} \sim 1.11$ eV), product of the back electron transfer is the singlet ground state. As reference points, the triplet energies of ^{3*}ZnPc (1.26 eV) and ^{3*}C$_{60}$ (1.5 eV) should be considered, which are placed higher than that of the charge-separated radical pair.

We also thought it interesting to probe a more labile way of coordinating C$_{60}$ to **ZnPc**. Accordingly, we pursued the coordination of a pyridine-linked C$_{60}$-ligand ($\mathbf{L_2}$) to **ZnPc** (**1c**).[7] The coordination constant, K (4.8×10^3 M^{-1}), appears to be conceivably affected by the cavity size of the **Pc** macrocycle, which weakens the in plane Zn–N$_{\text{pyrrole}}$ coupling, but strengthens likewise the axial Zn–N$_{\text{pyridine}}$ bond. We found that the weak equilibrium between dissociation and association of the 'metal–pyridine' bond facilitates, after photoexcitation and rapid *intra*complex electron transfer, the crucial break-up of the radical pair, **ZnPc**$^{\cdot+}$-$\mathbf{L_2}^{\cdot-}$, into the free radical ions, **ZnPc**$^{\cdot+}$ and $\mathbf{L_2}^{\cdot-}$. The lifetime of the latter is governed by a nearly diffusion-controlled, *inter*molecular back electron transfer of ~10^9 M^{-1}s^{-1}. By contrast, the stronger binding in **ZnPc-L$_1$** and **ZnPc-L$_1$-ZnPc** prevents this splitting and, hereby, limits the radical pair lifetime to *intra*molecular processes.



In summary, biomimetic organization principles provide the means for an evident trend towards the facile preparation of precise donor–acceptor architectures, **ZnPc / C$_{60}$**. Microsecond-lived charge-separated states, **ZnPc**$^{\cdot+}$-C$_{60}^{\cdot-}$, are the products of efficient *intra*complex electron transfer. A comparison with covalently linked **ZnPc-C$_{60}$** dyads, in which lifetimes of around 3 ns were found,[8] shows that the current examples of supramolecular architectures are suitable candidates as integrative components in solar energy conversion.

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Notes and references

‡ Selected data for **1b**: ^{1}H-NMR (CDCl$_3$, 300 MHz, 25 °C, TMS): δ = 8.34, 7.96 (2 × br s, 16H, Pc ring), 4.8–3.3 (several m, 48H, OCH$_2$), 2.3–1.0 ppm (5 × m, 84H, aliphatic); UV/vis (CHCl$_3$): $\lambda_{\max}$ (log ε) = 293 (4.93), 343 (4.99), 629 (4.92), 677 nm (4.98); MS: MALDI-TOF: m/z: 2309 [M$^+$], 2332 [M + Na]$^+$, 2348 [M + K]$^+$.

§ No fullerene emission—**^{1*}C$_{60}$** (1.76 eV) —, as it may stem from an exothermic transduction of singlet excited state energy—**^{1*}ZnPc** (1.80 eV) —, was detected.

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