

## Self-organisation in photoactive fullerene porphyrin based donor–acceptor ensembles†

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Received (in Cambridge, UK) 7th March 2001, Accepted 1st May 2001

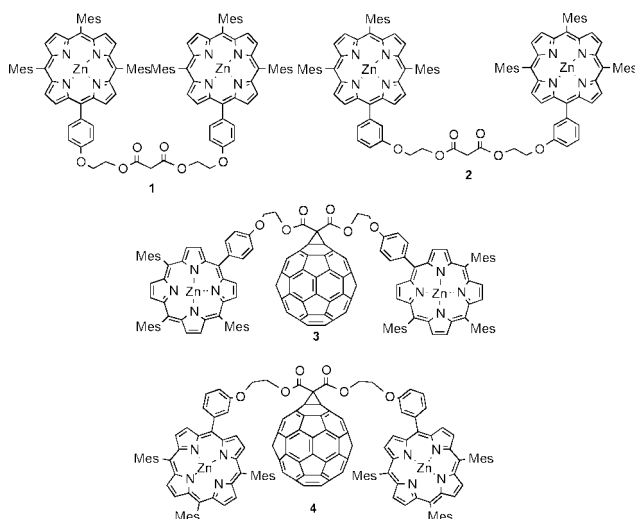
First published as an Advance Article on the web 22nd May 2001

Complexation of ZnP-C<sub>60</sub>-ZnP triads with diazabicyclooctane (DABCO) leads to rigid assemblies that display considerably prolonged charge-separated states.

Control over the separation, specific alignment and composition in donor–acceptor assemblies at a molecular level is a formidable task, especially in artificial reaction centres. Meaningful incentives can be lent from the organisation-principle in the bacterial photosynthetic reaction centre:<sup>1</sup> the different light- and redox-active components are embedded *via* noncovalent interactions into a protein matrix. In principal, biomimetic methodologies, such as hydrogen-bonding, donor–acceptor complexation, electrostatic interactions and  $\pi$ – $\pi$  stacking, guarantee the control over modulating the composition and, simultaneously, achieving well-defined and rigid architectures, with high directionality and selectivity.<sup>2</sup>

In the present communication we wish to present a simplistic but powerful means to regulate donor–acceptor separations and orientations. Successively, rigid, confined model ensembles are self-assembled, starting from a flexible ZnP-C<sub>60</sub>-ZnP system and DABCO.<sup>3,4</sup> The newly formed tetrads undergo, upon photoexcitation, efficient energy and electron transfer in toluene and *o*-dichlorobenzene solutions, respectively.

We selected for the current investigation the strongly fluorescing zinc tetraphenyl porphyrin (ZnP) chromophore as a photo-sensitive marker to monitor the extent of excited state interaction with the adjacent fullerene core. The porphyrinic precursors **1** and **2** were synthesised using a statistical approach,



starting with pyrrole and the corresponding benzaldehydes and subsequent reaction with malonyl chloride. In the final step,

† Electronic supplementary information (ESI) available: selected spectroscopic data. See <http://www.rsc.org/suppdata/cc/b1/b102141i/>

attachment to C<sub>60</sub> was achieved *via* modified Bingel-conditions.<sup>4a</sup>

New compounds **1–4** were completely characterised (see ESI†). The two different substitutional patterns of the phenyl-linkages (*i.e.* *para* vs. *meta*) were chosen to control possible orientations between the fullerene and porphyrin chromophores.

At first the porphyrin's emission in **3** and **4** was recorded in a variety of solvents and compared to that of a ZnP-ZnP reference (**1**). Most importantly, the *para*- and *meta*-linked ZnP-C<sub>60</sub>-ZnP systems both gave rise to a fairly strong emission quenching of the ZnP chromophore with fluorescence quantum yields ( $\Phi$ ) on the order of 0.001 (see Table 1). Although the solvent polarity differs quite substantially the emission intensity changed only marginally. For reference the emission quantum yield ( $\Phi$ ) of **3** in toluene and also in *o*-dichlorobenzene is about 0.04.

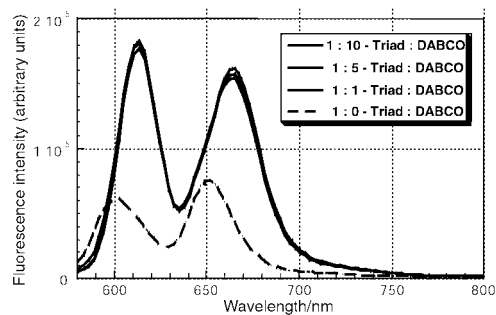
The anisotropy of the fullerene surface, as it prevails in the well-ordered but alternating assembly of electron rich hexagons with electron deficient pentagons, generally gives rise to marked 'through-space' interactions.<sup>5</sup> Thus, when structurally possible, fullerene-based ensembles adopt conformations in which the fullerene and the donor moieties come in close proximity, from which we hypothesise that the rapid deactivation of the <sup>1</sup>\*ZnP state in **3** and **4** implies a rate-determining transition to form the electron transfer mediating 'intramolecular exciplex'.

In general a more efficient quenching (~ two-fold) was noted for the *meta*- (**4**) relative to the more electron-rich *para*-linked derivatives (**3**). A possible interpretation for this evidently solvent-independent outcome relates to the different substitution pattern given on the phenyl ring and the subsequent impact that stems from an electronic interaction with the fullerene core.† The *meta*-isomer is clearly more susceptible to interactions between the fullerene core and the porphyrin moiety. In line with this purely structural assumption is the observation that a weakly emitting transition around 800 nm was found only for the *meta*-linked ZnP-C<sub>60</sub>-ZnP (**4**) in toluene. This NIR emission originates from a charge transfer state, despite its quantitative cancellation in stronger polar solvents, such as THF, *o*-dichlorobenzene and benzonitrile.

Time-resolved transient absorption spectroscopy was conducted to probe the fate of the photoexcited ZnP chromophore and to inspect the identity of the resulting products. In

**Table 1** Photophysical properties of *para*- and *meta*-linked ZnP-C<sub>60</sub>-ZnP (1.3 × 10<sup>-5</sup> M) in different solvents

Solvent	$\tau$ <sup>1</sup> *ZnP		$\Phi$ <sup>1</sup> *ZnP × 10 <sup>3</sup>		$\Phi$ ZnP <sup>+</sup> -C <sub>60</sub> <sup>-</sup>	
	(3)	(4)	(3)	(4)	(3)	(4)
Toluene			1.62	0.83	0.018	0.008
THF	122 ns	70 ns	1.50	0.79	0.02	0.012
<i>o</i> -dichlorobenzene	106 ns	75 ns	1.46	0.81	0.019	0.014
Bzcn	101 ns	58 ns	1.18	0.64	0.016	0.009



**Fig. 1** Emission spectrum of **4** ( $1.3 \times 10^{-5}$  M) in *o*-dichlorobenzene (dashed line) and upon addition of various DABCO equivalents (*i.e.*, 1, 5 and 10); excitation wavelength 550 nm.

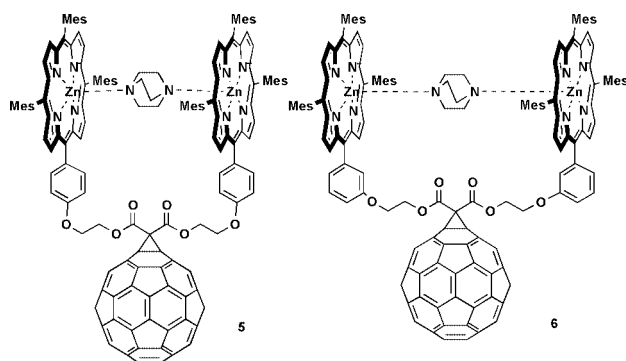
**Table 2** Influence of DABCO on the photophysical properties of *para*- and *meta*-linked **ZnP-C<sub>60</sub>-ZnP** ( $1.3 \times 10^{-5}$  M)

Solvent	DABCO <sup>a</sup>	( $\Phi$ ) <sup>1</sup> *ZnP	( $\tau$ ) ZnP <sup>+</sup> -C <sub>60</sub> <sup>-</sup>	( $\Phi$ ) ZnP <sup>+</sup> -C <sub>60</sub> <sup>-</sup>
<b>3</b> Toluene	0	$1.62 \times 10^{-3}$	—	0.018
	5	$2.50 \times 10^{-3}$	— <sup>b</sup>	— <sup>b</sup>
<i>o</i> -DCB <sup>c</sup>	0	$1.46 \times 10^{-3}$	290 ns	0.019
	5	$2.29 \times 10^{-3}$	702 ns	0.082
<b>4</b> Toluene	0	$0.83 \times 10^{-3}$	—	0.008
	5	$2.14 \times 10^{-3}$	— <sup>b</sup>	— <sup>b</sup>
<i>o</i> -DCB <sup>c</sup>	0	$0.81 \times 10^{-3}$	150 ns	0.014
	5	$2.40 \times 10^{-3}$	724 ns	0.086

<sup>a</sup> Equivalents of DABCO. <sup>b</sup> Triplet excited state. <sup>c</sup> *o*-Dichlorobenzene.

particular, the instantaneously formed ZnP singlet–singlet absorption, which is in reference **1** subject to a slow intersystem crossing (2.5 ns) to the triplet excited state, decays rather rapidly ( $\sim 100$  ps) following the completion of the short laser pulse in **3** and **4** (18 ps; 532 nm). Furthermore, this fast deactivation is coupled with a synchronously occurring grow-in of a new transient absorption, which in all solvents revealed a set of VIS and NIR maxima at  $\sim 650$  and 1030 nm, respectively.<sup>5</sup> These features resemble the spectral fingerprints of the one-electron oxidised ZnP and the one-electron reduced fullerene, respectively. From this we conclude that the resulting ZnP<sup>+</sup>-C<sub>60</sub><sup>-</sup> radical pair is formed *via* a photoinduced electron transfer from the ZnP singlet excited state to the electron accepting fullerene. The charge-separated state, formed with moderate quantum yields, decayed on a time scale of a few hundred nanoseconds to regenerate the ground state.

Addition of DABCO to a toluene and *o*-dichlorobenzene solution of triads **3** and **4** led to a strong reactivation of the ZnP emission (Fig. 1 and Table 2). Taking the emission reactivation into account the ZnP in both tetrads disclose nearly the same fluorescence quantum yields. Parallel picosecond experiments, which indicate prolonged <sup>1</sup>\*ZnP singlet lifetimes ( $\sim 185$  ps) in **5** and **6** compared with **3** (106 ps) and **4** (75 ps), further



corroborated the emission studies. Both effects can be rationalised in terms that complexation of DABCO to the vacant sites of the two ZnP (*i.e.* dz<sup>2</sup>-orbitals)<sup>3</sup> increases the donor–acceptor separation considerably (*i.e.* triad *vs.* tetrad). The bridging motif with the monomeric compounds **5** and **6** was confirmed by

molecular modelling using semi-empirical methods. The formation of coordination oligomers can be largely excluded since no dependence of the spectroscopic properties on the DABCO concentration was observed for  $1.3 \times 10^{-5}$  M solutions of **3** and **4**. The amplification of the emission between the triads and corresponding tetrads is less prominent in toluene ( $\epsilon = 2.38$ ) than in *o*-dichlorobenzene ( $\epsilon = 9.93$ ). To follow up on this issue, the pathway of ZnP deactivation was examined by revisiting the pico- and nanosecond experiments. In *o*-dichlorobenzene, the typical radical ion fingerprints, formed concurrently with the <sup>1</sup>\*ZnP decay, unmistakably attest to an electron transfer mechanism.

On the contrary, the absorption features noted upon excitation of a toluene solution are fundamentally different. In fact, new broad absorption maxima at 360 and 720 nm are an exact match of the fullerene triplet features.<sup>5</sup> The above experiments, considered in concert, infer that a rapid intramolecular energy transfer, from the <sup>1</sup>\*ZnP (2.06 eV) to the energetically lower lying <sup>1</sup>\*C<sub>60</sub> (1.79 eV),<sup>5</sup> prevails in toluene with a quantum yield of 0.57. This is then followed by an efficient *intersystem crossing* to generate the triplet excited state (1.50 eV)<sup>5</sup> with a unimolecular rate constant of  $7.1 \times 10^8$  s<sup>-1</sup>. The energy transfer pathway in **5** and **6** is in sharp contrast to the excited state behaviour seen for **3** and **4**, disclosing even in toluene the spectral characteristics of the ZnP<sup>+</sup>-C<sub>60</sub><sup>-</sup> radical pair.

The forward electron transfer is, however, not the only parameter affected by the increased donor–acceptor separation (*i.e.* triad *vs.* tetrad): in addition, markedly higher quantum yields ( $\Phi$ ) and longer lifetimes ( $\tau$ ) of the ZnP<sup>+</sup>-C<sub>60</sub><sup>-</sup> radical pair were noted. Interestingly, the back electron transfer dynamics in **5** and **6** gives rise to approximately the same rate constant of  $1.3 \times 10^6$  and  $1.4 \times 10^6$  s<sup>-1</sup>, respectively, reflecting the nearly equal donor–acceptor separations in these rigid systems.

In conclusion, we have shown by spectroscopic and photochemical means that a simple complexation of DABCO to a series of flexible **ZnP-C<sub>60</sub>-ZnP** triads, and thereby affording the corresponding tetrads, is a powerful tool to control the design and photophysical properties of rigidly, confined donor–acceptor systems. §

## Notes and references

‡ Further support for this difference can be deduced from the ground state absorption spectra, which in the case of the *meta*-substituted isomer reveals a marked red-shift of the *Soret*- and *Q*-band transitions (*e.g.*, in toluene 550  $\rightarrow$  552 nm; 588  $\rightarrow$  590 nm).

§ This work was supported by the Office of Basic Energy Sciences of the Department of Energy and the Stiftung Volkswagenwerk. This is document NDRL# 4294 from the Notre Dame Radiation Laboratory.

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