

## Photodynamics of a Constrained Parachute-Shaped Fullerene–Porphyrin Dyad

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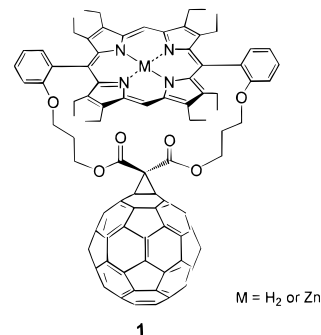
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The pronounced ability of fullerene C<sub>60</sub> to act as an electron and energy acceptor has led to the synthesis of a large number of compounds in which C<sub>60</sub> is covalently linked to photoactivatable groups which can serve as potential donors.<sup>1</sup> Such compounds are of interest as model systems for photosynthetic reaction centers<sup>2</sup> and also have potential applications in photodynamic therapy because of the highly efficient photosensitization of singlet molecular oxygen formation by C<sub>60</sub> and C<sub>60</sub> derivatives.<sup>3</sup> By far the largest number of such systems studied to date utilize porphyrins as antennas for efficient light capture in the visible region of the spectrum,<sup>4</sup> and a variety of linkers.<sup>5</sup> Photophysical studies as well as molecular modeling indicate that in conformationally flexible dyads the porphyrin (P) and C<sub>60</sub> moieties are in close proximity, due to  $\pi$ -stacking interactions, thus facilitating through-space interactions, as demonstrated by quenching of <sup>1</sup>P\* fluorescence and generation of fullerene-excited states (by energy transfer) or P<sup>+</sup>–C<sub>60</sub><sup>–</sup> ion-pair states (by electron transfer).<sup>2,4a,b,f–h</sup> These ion-pair states can be relatively long-lived, due to the small reorganization energy and strong thermodynamic driving force for back-electron transfer, which places this process within the

Marcus inverted region.<sup>4g,6</sup> Recently attention has focused on rigidly linked systems in which the porphyrin (P) and (C<sub>60</sub>) moieties are in enforced close proximity<sup>7,8</sup> or are forced apart by a saturated norbornylogous or steroid linker.<sup>9,10</sup> As part of a program to understand the nature of the dialogue between P and C<sub>60</sub> chromophores as the topology of P–C<sub>60</sub> dyads is systematically varied, we now report photophysical data for the parachute-shaped dyad **1** and the corresponding zinc complex **1-Zn**. We have reported previously the synthesis of **1** by Bingel–Hirsch addition of a strapped porphyrin malonate to C<sub>60</sub>.<sup>11</sup>



We observed that <sup>1</sup>P\* fluorescence is almost totally quenched in **1** and **1-Zn**.<sup>11</sup> Further insight into the photodynamic behavior of **1** and **1-Zn** has now been obtained from the measurement of fluorescence lifetimes in the picosecond time range,<sup>12</sup> quantum yields for formation of singlet molecular oxygen, O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>),<sup>13</sup> and transient absorption studies.<sup>14</sup> These data differ in several important aspects from related data reported for flexible dyads. As can be seen from the data collected in Table 1, the <sup>1</sup>P\* fluorescence for **1** and **1-Zn** (λ<sub>exc</sub> 550 nm, detection at 700 nm) are shortened by a factor between 1000 and 200, respectively, in the nonpolar solvent benzene and in the considerably more polar solvent THF compared with that for the model porphyrin derivatives **2** and **2-Zn** which lack the fullerene moiety. The dominant fluorescing species in the case of free base **1** is <sup>1</sup>P\*; the other very minor components to the fluorescence decay (τ 57 ps in benzene, 80 ps in THF) have not yet been identified. A possible explanation for the low amplitude component(s) is charge recombination fluorescence from a (partially) relaxed radical ion pair. For **1-Zn**, only a single fluorescing species is observed.

Transient absorption studies show that formation of P<sup>+</sup>, λ<sub>max</sub> ~670 nm,<sup>4h</sup> occurs on excitation of **1** at 532 nm within the time resolution of the experiment (20–40 ps) in both nonpolar (toluene)

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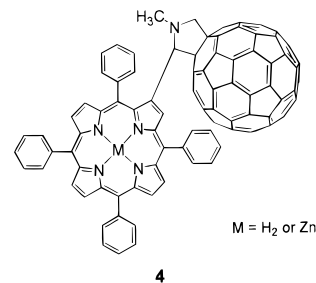
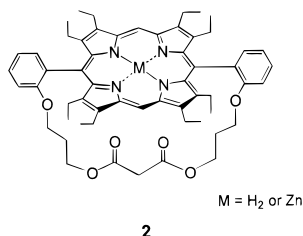
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**Table 1.** Fluorescence Lifetimes, Lifetimes of Ion-Pair States, and Quantum Yields of Singlet Molecular Oxygen Formation

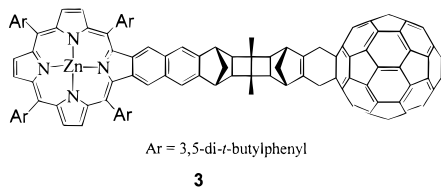
compounds	fluorescence lifetimes $\tau$ (ns) <sup>a,b</sup>		lifetimes of ion-pair states (ns) <sup>c</sup>			singlet oxygen quantum yield $\Phi_{\Delta}^d$	
	benzene	THF	toluene	THF	benzonitrile	toluene	CH <sub>2</sub> Cl <sub>2</sub> <sup>e</sup>
<b>1</b>	0.014 (0.904)	0.023 (0.819)	3.5	0.314	0.155	0.22 ± 0.02	< 0.01
<b>1-Zn</b>	0.009 (0.99)	0.013 (0.99)	1.015	0.099	0.069	< 0.01	< 0.01
<b>2</b>	13 (0.98)	11.3 (0.907)				0.77 ± 0.08	0.95 ± 0.09
<b>2-Zn</b>	1.81 (0.94)	1.8 (0.94)				0.76 ± 0.08	0.80 ± 0.08

<sup>a</sup>  $\lambda_{\text{exc}} = 550$  nm,  $\lambda_{\text{obs}} = 700$  nm for **1** and **2**,  $\lambda_{\text{obs}} = 587$  nm for **1-Zn** and **2-Zn**. <sup>b</sup> Numbers in parentheses are relative amplitudes. <sup>c</sup>  $\lambda_{\text{exc}} = 532$  nm,  $\lambda_{\text{obs}} = 670$  nm. <sup>d</sup>  $\lambda_{\text{exc}} = 532$  nm,  $\lambda_{\text{obs}} = 1270$  nm, TPP ( $\Phi_{\Delta} = 0.67 \pm 0.14$ ) in toluene used as reference. <sup>e</sup> Corrected for refractive index and  $O_2(^1\Delta_g)$  radiative lifetime differences between sample and reference.



and polar (THF, benzonitrile) solvents. Although  $C_{60}^{-*}$  ( $\lambda_{\text{max}} \approx 1040$  nm)<sup>13</sup> was not directly detected due to experimental limitations, we assume it is formed along with  $P^{+*}$ . Thus, extremely rapid electron transfer to give a charge-separated radical ion pair is the dominant pathway decay of  $^1P^*$  in **1** as well as of **1-Zn** in nonpolar as well as polar solvents, which is unprecedented for P- $C_{60}$  dyads.<sup>2,4,9</sup> The ion-pair state in turn decays by back-electron transfer to regenerate ground-state starting materials, except in toluene where  $C_{60}$  triplet states are formed.  $C_{60}$  triplet excited states in the free base dyads were detected *only in toluene* by transient absorption ( $\lambda_{\text{max}} \approx 720$  nm)<sup>14</sup> and through sensitized  $O_2(^1\Delta_g)$  formation,  $\Phi = 0.22 \pm 0.02$ . It is particularly noteworthy that the lifetime of the charge separated state of **1** and of **1-Zn** (see Table 1) is longer in toluene than in the more polar solvents THF or PhCN. This is clear evidence that back-electron transfer occurs in the Marcus inverted region,<sup>6</sup> due to the strong effect of solvent polarity on the difference in energy of the charge-separated ion-pair state and the ground state. Since  $-\Delta G^\circ$  for back-electron transfer is considerably larger in nonpolar *vis à vis* polar solvents,  $k_{-et}$  consequently increases with an increase in solvent polarity.

The occurrence of photoinduced electron transfer upon photoexcitation of the zinc-bound dyad **1-Zn** at long wavelengths in both polar and nonpolar solvents fits the pattern of previously studied Zn-bound porphyrin- $C_{60}$  dyads, with the unique exception of **3** in toluene, where singlet-singlet energy transfer and not electron transfer is observed.<sup>9</sup> The magnitude of  $k_{et}$  in both **1** and



**1-Zn**, approaching  $10^{11}$  s<sup>-1</sup>, is unprecedented and obviously reflects the enforced proximity of P to  $C_{60}$ . The behavior of the photoexcited free base dyad **1** is even more remarkable, in that electron transfer is again the predominant decay mode of  $^1P^*$  in both nonpolar and polar solvents. Typically, the dominant decay mode of photoexcited conformationally flexible dyads in nonpolar solvents (such as toluene or benzene) is energy transfer to give an energetically low-lying fullerene singlet excited state. In the particularly well-studied case of **4**,<sup>48</sup> the latter was detected by time-resolved fluorescence spectra and had a lifetime  $\tau_f$  of  $\sim 1.3$  ns, typical of that for fullerenes lacking an attached porphyrin moiety. Such fullerene singlets typically undergo intersystem crossing to give fullerene triplets, which can be directly detected

spectroscopically and by sensitized singlet oxygen formation.<sup>2-4</sup> In polar solvents such as benzonitrile, P- $C_{60}$  dyads typically undergo rapid photoinduced electron transfer (typically  $k_{et} \approx 10^{10}$  s<sup>-1</sup>), sometimes in competition with slightly slower singlet-singlet energy transfer (as with **4**) to give fullerene singlet excited states; for **4**, the lifetime of the latter was shortened to 74 ps due to quenching by electron transfer from the ground-state porphyrin, providing an alternate route to the charge-separated ion-pair state.<sup>48</sup> Such solvent-dependent photophysical behavior is typical of most P- $C_{60}$  dyads studied to date.<sup>2,4a,b,f-h</sup> Thus, the fact that electron transfer completely dominates the behavior of **1** in nonpolar as well as polar solvents is unprecedented and must again be attributed to the special topology of this system. In toluene, the ion-pair state of **1** is apparently sufficiently destabilized so that it lies energetically above the P- $^3C_{60}^*$  state, so that decay to the latter with a spin flip becomes energetically feasible. There is no evidence that this process involves the intermediacy of discrete P- $^1C_{60}^*$  states.

It is instructive to compare the lifetimes of the charge-separated state of **1** and **1-Zn** (155 and 69 ps, respectively) with that of Zn-dyad **3** (420 ns), **4** (290 ps), and **4-Zn** (50 ps), all in benzonitrile. Although back-electron transfer is almost surely occurring in the Marcus inverted region in all cases, increasing the distance between the chromophores as in **3** clearly slows down the process and enhances the lifetime of the ion-pair state, which is highly desirable for model photosynthetic reaction centers. Larger multicomponent arrays constructed from **1** should have very interesting electronic properties.

Thus, the unique orientation of the porphyrin and fullerene moieties in **1** facilitates electron transfer over energy transfer in both nonpolar and polar media. In the case of **1**, the interchromophoric dialogue following electronic excitation is restricted to through-space as opposed to through-bond interactions.

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