

Parallel (Face-to-Face) Versus Perpendicular (Edge-to-Face) Alignment of Electron Donors and Acceptors in Fullerene Porphyrin Dyads: The Importance of Orientation in Electron Transfer

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The role of the spatial arrangement of donor–acceptor couples in electron transfer is a subject of primary interest to understand the properties of fundamental systems such as those generating the natural photosynthetic process^{1–3} and the one-dimensional array of DNA base pairs aligned face-to-face to make π – π stacks.⁴ The rates of electron transfer (ET) depend considerably on the wave function mixing, which is gauged by the electronic coupling $|V|$ between the electron donor and the electron acceptor.^{1–3} Despite the qualitative understanding reached in recent years, the challenge to directly tune π – π interactions to modify $|V|$ awaits in depth exploration.

Here we report the ET rates due to two fundamentally different orientations of a zinc tetraphenyl porphyrin (ZnTPP) and a fullerene moiety. A full and comprehensive account will be given of the effects of the face-to-face versus edge-to-face alignment on the intramolecular ET rates. In particular, we are able to determine that the magnitude of π – π interactions is the crucial parameter that controls rates, efficiencies, and mechanisms of ET. As model compounds for this investigation we chose the previously reported dyad **1**,⁵ where ZnTPP is attached in the *trans*-2 position, and the new dyad **2**, with an *equatorial* bridging of ZnTPP.

The regioselective synthesis of **2** was accomplished via a tether directed,⁶ 2-fold cyclopropanation of C₆₀ with bismalonate **3**. The latter was obtained from the statistical co-condensation of **4** with

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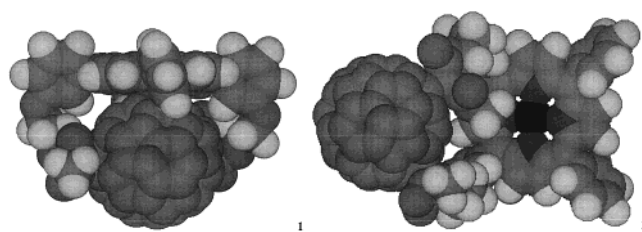


Figure 1.

benzaldehyde and pyrrole under Lindsey conditions⁷ and subsequent chromatographic separation from the constitutional isomer **5** (Scheme 1).

Irradiation of **2** with a short 532 nm laser pulse resulted in the immediate *Q*-band bleaching of the porphyrin and the concomitant formation of broad absorption characteristics, especially in the region between 550 and 750 nm. These spectral features are representative of the porphyrin singlet excited state. In contrast to the slow *intersystem crossing* dynamics in ZnTPP **3**, the ¹*-(π – π)ZnTPP absorption decays rapidly and monoexponentially in dyad **2** (Table 1). The singlet lifetimes and the fluorescence quantum yields in **2** are subject to a marked solvent dependence. Particularly interesting are the strong solvent effects of dichloromethane. In analogy with previous work,⁹ such variations may hint at an ET mechanism mediated by a solvent molecule situated in the cavity between ZnP and C₆₀.

Formation of the charge-separated radical pair (i.e., C₆₀^{•–}–ZnTPP^{•+}) was confirmed by transient absorption spectroscopy. The one-electron reduced form of C₆₀ displayed its fingerprint absorption in the NIR (1060 nm), in good agreement with an *equatorial* reference. The π -radical cation of ZnTPP was seen with its strongest absorption in the visible (700 nm).

In general, the ET rates in the *equatorial* dyad **2** are ca. 10 times slower than those reported for the *trans*-2 dyad **1**. In an effort to correlate the different ET kinetics with the structure of the dyad and to assess the location of possible solvent molecules, we carried out molecular dynamics investigations.⁸ Six randomly selected and superimposed conformers of each dyad (Figure S2) support three critical aspects: (1) Due to the double linkage, the variability of relative orientation of the two chromophores within each dyad is very limited. In **1**, the face-to-face alignment is completely locked. In **2**, only two types of face-to-edge orientations (*vertical* and *horizontal*) were found. NOE measurements (S3) further showed that the “horizontal” conformation has a very low population (0.2%) relative to the preferred “vertical” conformation (99.8%). Both systems have therefore strong conformational rigidity. (2) The face-to-face alignment in **1** with the shortest interplanar distance (3 Å) leads to an appreciable π – π stacking, whereas the edge-to-face alignment in **2** prohibits effective π – π interactions (Figure 1). (3) **2** can accommodate between the two moieties a solvent molecule such as toluene.

The red shift of the *Soret*–*Q*-band transitions and the lower extinction coefficients, relative to ZnTPP **3**, are good fingerprints of the presence of electronic coupling (Table S4). Unquestionably, the interactions in the π – π stacked dyad **1** are significantly stronger than those noted for **2**.

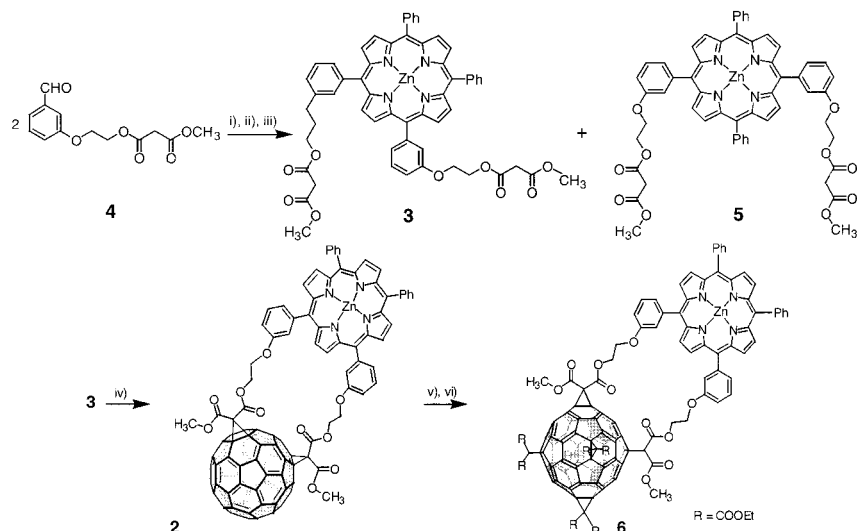
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Scheme 1. Synthesis of the Equatorial Dyad **2** and the Mixed Hexakisadduct **6**^a

^a Conditions: (i) 2 equiv of Ph-CHO, 4 equiv of pyrrole, $\text{BF}_3 \cdot \text{Et}_2\text{O}$, room temperature; (ii) *p*-chloranile, reflux; (iii) ZnCl_2 , THF, reflux; (iv) C_{60} , 2 equiv of iodine, DBU, toluene, room temperature; (v) DMA, toluene, room temperature; (vi) $\text{BrCH}(\text{COOEt})_2$, DBU, room temperature.

Table 1. Summary of the Photophysical Parameters of C_{60} -ZnTPP Dyad **1** and Dyad **2**

solvent	$\Phi_f(\tau)$ ZnTPP	Φ_f dyad 2	$k_{\text{ET}}[\text{s}^{-1}]^a$ dyad 1	$k_{\text{ET}}[\text{s}^{-1}]^a$ dyad 2	$k_{\text{ET}}[\text{s}^{-1}]^b$ dyad 2	$-\Delta G_{\text{BET}}^\circ [\text{eV}]^c$ dyad 2	$-\Delta G_{\text{ET}}^\circ [\text{eV}]^d$ dyad 2	$k_{\text{BET}}[\text{s}^{-1}]^e$ dyad 1	$k_{\text{BET}}[\text{s}^{-1}]^e$ dyad 2
toluene	0.04/3.47 ns		1.2×10^{11}	<i>f</i>	<i>f</i>				
THF	0.04/3.22 ns	12.0×10^{-4}	1.5×10^{11}	9.8×10^9	6.7×10^9	1.39	0.61	2.6×10^9	3.8×10^5
dichloromethane	0.04/3.4 ns	4.4×10^{-4}	1.3×10^{11g}	2.6×10^{10}	2.1×10^{10}			1.5×10^{10g}	
dichlorobenzene	0.039/3.48 ns	9.5×10^{-4}	1.4×10^{11}	1.1×10^{10}	8.9×10^9	1.33	0.67		5.4×10^5
benzonitrile	0.035/3.22 ns	5.6×10^{-4}	1.3×10^{11}	1.9×10^{10}	1.8×10^{10}	1.21	0.79	2.6×10^{10}	9.1×10^5
DMF	0.035/3.29 ns	4.3×10^{-4}		2.4×10^{10}	2.9×10^{10}	1.18	0.82		4.9×10^6

^a $k_{\text{ET}} = [\Phi(\text{ZnTPP}) - \Phi_f(\mathbf{1,2})]/[\tau(\text{ZnTPP}) \Phi_f(\mathbf{1,2})]$ where **1,2** refer to the two dyads. ^b Determined from the $^1*(\pi-\pi)\text{ZnTPP}$ lifetime. ^c Free energy changes for BET of the $\text{C}_{60}^{\bullet-}-\text{ZnTPP}^{\bullet+}$ radical pair: $-\Delta G_{\text{BET}}^\circ = E_{1/2}(\text{D}^{\bullet+}/\text{D}) - E_{1/2}(\text{A}/\text{A}^{\bullet-}) + \Delta G_{\text{S}}$; $\Delta G_{\text{S}} = (e^2/4\pi\epsilon_0)[(1/(2R_+) + 1/(2R_-) - 1/R_{\text{D-A}})(1/\epsilon_{\text{S}}) - (1/(2R_+) + 1/(2R_-))(1/\epsilon_{\text{R}})]$; $E_{1/2}(\text{D}^{\bullet+}/\text{D}) = 0.38 \text{ V}$ versus Fc/Fc^+ ; $E_{1/2}(\text{A}/\text{A}^{\bullet-}) = -1.13 \text{ V}$ vs Fc/Fc^+ ; $R_+ = 5 \text{ \AA}$; $R_- = 4.4 \text{ \AA}$; $R_{\text{D-A}} = 15.1 \text{ \AA}$. ^d Free energy changes for ET evolving from $\text{C}_{60}^{\bullet-}*\text{ZnTPP}$: $-\Delta G_{\text{ET}}^\circ = \Delta E_{0-0} - (-\Delta G_{\text{BET}})$. ^e Determined from the radical pair lifetime. ^f Energy transfer. ^g In dichloroethane.

The different donor–acceptor orientations (i.e., face-to-face versus face-to-edge) have a strong impact on the back electron transfer (BET) dynamics (Table 1). Previously, we reported that the lifetime of the $\text{C}_{60}^{\bullet-}-\text{ZnTPP}^{\bullet+}$ radical pair in the trans-2 dyad **1** is of the order of a few hundred picoseconds (and that BET is facilitated by the strong interaction between the fullerene and porphyrin π -systems).⁵ Analysis of the decay kinetics of the radical pair of **2** gives a lifetime of the order of microseconds. *Modification of the relative alignment between acceptor (C_{60}) and donor (ZnTPP), and its alteration of the π - π interactions, changes the lifetime of the charge-separated state by 4 orders of magnitude.* The dependence of k_{ET} versus free energy changes indicates stabilizing effects for the charge-separated state at higher $-\Delta G^\circ$ values (i.e., in solvents of lower polarity) in both systems. These are clear attributes describing the inverted region of the classical Marcus parabola, the highly exergonic region, where k_{ET} start to decrease with increasing exothermicity.¹⁰

Semiempirical molecular orbital calculations¹¹ in a scheme similar to what was used previously for electron transfer¹² were used to obtain $|V|$ for **1** and **2**. At the geometries obtained by the MD simulations, their ratio was ~ 7 (415 cm^{-1} vs. 59 cm^{-1}). In terms of rate constants, if the ET in the two systems has a similar reorganization energy, λ , the corresponding ratio is 49. Notice that as suggested by one referee, it is likely that $\lambda(\mathbf{2}) \geq \lambda(\mathbf{1})$ because the charges are more separated in **2** than in **1** and

solvation is therefore more efficient in the former than in the latter. In any event, the calculated $|V|$ prove the remarkably different aspects that the same process of ET takes in the two dyads which differ only by the relative orientation of their moieties. The simulations also show that in **1** the largest BET probability is calculated from the 1,1' positions of the pyrrole ring closest to C_{60} , whereas in **2** the electron “jumps” from the 2,2' sites. Super-exchange transfer through a solvent molecule (toluene or $\text{CH}_2\text{-Cl}_2$) was also considered for **2**. The largest $|V|$ value was found for the transfer of an electron from the porphyrin HOMO to the toluene HOMO with simultaneous transfer from the toluene HOMO to the C_{60} LUMO (13 cm^{-1}). This small $|V|$ value makes us conclude that the solvent's main role is not to act as a bridge as in Zimmt's systems.¹³ It should, however, be remarked that apart from super-exchange and modification of λ , the solvent can assist the transfer changing directly the value of $|V|$. This investigation is now in progress and will be reported in the future.

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Supporting Information Available: Details regarding spectroscopic characterization and conformational studies of dyad **2**, along with absorption data and calculation of electronic coupling (V) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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