Charge-transfer in a π-stacked fullerene porphyrin dyad: evidence for back electron transfer in the 'Marcus-inverted' region

Dirk M. Guldi,*[a] Chuping Luo,[a] Maurizio Prato,*[b] Elke Dietel[c] and Andreas Hirsch*[c]

[a] *University of Notre Dame, Radiation Laboratory, Notre Dame, IN 46556, USA*
[b] *Dipartimento di Scienze Farmaceutiche, Università di Trieste, Piazzale Europa 1, 34127 Trieste, Italy*
[c] *Institut für Organische Chemie der Universität Erlangen-Nürnberg, Henkestrasse 42. D-91054 Erlangen, Germany. E-mail: hirsch@organik.uni-erlangen.de*

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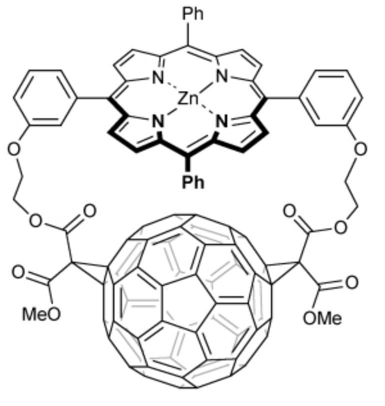
The 'Marcus-inverted' region for BET in a π–π stacked fullerene–porphyrin dyad was determined based on (i) the photoactivation of an intramolecular ET in a variety of solvents and (ii) the formation of a highly energetic charge-separated state

Photoinduced electron transfer (ET) to fullerenes is a subject of current interest.[1] Specifically, the moderate first reduction potentials of fullerenes[2] and their small reorganization energies in ET reactions[3] make them excellent building blocks for the design of novel donor–acceptor systems. According to the Marcus theory, electron transfer rates (k_{ET}) are expected to exhibit a parabolic dependence on the free energy gap of the electron transfer ($-\Delta G°_{ET}$).[4] In particular, k_{ET} decreases as the reaction becomes more exergonic, especially at large $-\Delta G°_{ET}$. The maximum of the theoretically expected bell-shaped energy gap dependence (*i.e.* $-\Delta G° \approx \lambda$, [$\lambda$ = reorganization energy (Marcus theory)]) is largely controlled by the nuclear reorganization energy including the solvent reorganization associated with the ET. Surprisingly, experimental support to ET kinetics clearly occurring in the inverted region, is limited to charge recombination processes in geminate radical pairs[5] and a few examples of non fullerene-containing donor–acceptor dyads.[6] In order to optimise the stability of a charge-separated state (*i.e.* retarding charge recombination) it is desirable to reach the thermodynamic maximum at small $-\Delta G°$ values and, thus, to push the exergonic back electron transfer (BET) into the 'Marcus-inverted' region. The small reorganization energy of the rigid C_{60} cage should be an ideal prerequisite to shift the maximum of the 'Marcus parabola' to smaller values and BET in fullerene-based donor–acceptor arrays is proposed to be decelerated compared with two-dimensional electron acceptors. Here, we present the first experimental evidence for an electron transfer within a C_{60} based compound in the 'Marcus-inverted' region.

The model compound that we used in this study is the π–π stacked C_{60}–ZnTPP dyad **1** involving a *trans*-2 addition pattern,[7] which we reported recently.[8] The fluorescence quantum yield of **1**, is strongly quenched ($\Phi = 1.26 \times 10^{-4}$) relative to a ZnTPP reference complex ($\Phi = 0.04$) even in a non-polar toluene solution. Similarly low fluorescence quantum yields were found in tetrahydrofuran ($\Phi = 1.16 \times 10^{-4}$), dichloroethane ($\Phi = 1.37 \times 10^{-4}$) and benzonitrile ($\Phi = 1.37 \times 10^{-4}$). This points to a very efficient electronic communication between the two moieties in the excited state. Significantly, the texture of the ZnTPP fluorescence is still preserved. Assuming that the lifetime of the ZnTPP singlet excited state is 2700 ps, the lifetime of the chromophore in dyad **1** can be estimated to be *ca.* 8.5 ps corresponding to an intramolecular rate constant of 1.18×10^{11} s^{-1}. The new emission band,[7] centered around 820 nm, was found exclusively in toluene solutions and is missing in the other solutions. To characterize this emission band, the phosphorescence of a ZnTPP reference compound was probed. The resemblance of the ZnTPP phosphorescence with the emission band of **1** in toluene suggests the spin-forbidden phosphorescence of the ZnTPP chromophore. The lifetime of the 820 nm emission band (τ = 2.84 ns)[7] matches nicely the proposed energy transfer rate measured by picosecond-resolved transient absorption spectroscopy (see below).



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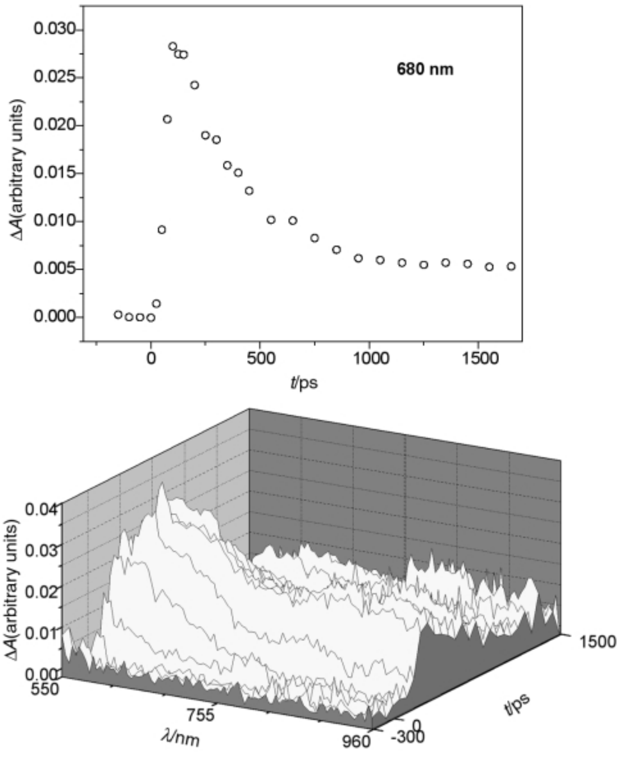

Fig. 1 (a) Differential absorption spectra obtained upon picosecond flash photolysis (532 nm) of *ca.* 10^{-5} M solutions of dyad **1** in nitrogen saturated toluene with time delays between −300 and 1500 ps. (b) Time-absorption profiles at 680 nm (*i.e.* maximum of the $ZnP^{\cdot+}$ absorption).

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Table 1 Photophysical properties of dyad **1** in various solvents

Solvent	ε^a	10^4 Φ (fluorescence)	τ (radical pair)/ps	$\Delta G_{CR}°$/eV	$\Delta G_{ET}°$/eV	Product
Toluene	2.38	1.26	619	1.536	0.524	Triplet excited state
Tetrahydrofuran	7.6	1.16	385	1.452	0.608	Singlet ground state
Dichloromethane	9.08		121	1.445	0.615	Singlet ground state
Dichloroethane	10.19	1.37	66	1.441	0.619	Singlet ground state
Benzonitrile	24.8	1.37	38	1.424	0.636	Singlet ground state

[a] Dielectric constant.

In order to measure the absolute quenching rate constants and to unravel the underlying mechanism, **1** was studied in various solvents by means of picosecond-resolved transient absorption spectroscopy. In all solvents used, **1** gives rise to the rapid formation of the ZnTPP π-radical cation absorption between 670 and 680 nm (Fig. 1). However the rise time, representing the actual forward ET process, is masked by the instrument response time. Thus, we can only provide an upper limit of the ZnTPP lifetime, for example, in a toluene solution of ~35 ps. Despite this inaccuracy, the estimate is in reasonably good agreement with the steady-state emission study.

Taking into account the strong fluorescence quenching and the formation of $\mathrm{ZnTPP}^{\bullet+}$, we can conclude that electron transfer prevails in the deactivation of the ZnTPP singlet excited state, to yield the $C_{60}{}^{\bullet-}$–$\mathrm{ZnTPP}^{\bullet+}$ pair. In line with the spectral identification of the $C_{60}{}^{\bullet-}$–$\mathrm{ZnTPP}^{\bullet+}$ pair is the assumption, which is based on the thermodynamic driving force ($-\Delta G_{ET}°$) for an intramolecular electron transfer from the photoexcited ZnTPP. The $\Delta G_{ET}°$ values are approximated by:

$$\Delta G_{ET}° = -[E^*_{0-0} + \Delta G_{CR}°] \quad (\text{with } \Delta G_{CR}° = -[\Delta E° + e^2/d\varepsilon_S]) \qquad (1)$$

and summarized in Table 1.

The fact that ET rather than energy transfer events govern the fate of the photoexcited ZnTPP chromophore, can be rationalized by the close packing of the two moieties. This clearly reflects the higher efficiency of an electron exchange mechanism compared with a dipole–dipole energy transfer mechanism.

As determined by transient absorption spectroscopy the product of the charge-recombination is the singlet ground state in any solvent [eqn. 2(a)]. The only exception is toluene [eqn. 2(b)]: Nanosecond-resolved photolysis confirmed the

$$C_{60}{}^{\bullet-} - \mathrm{ZnTPP}^{\bullet+} \xrightarrow{\mathrm{BET}} C_{60} - \mathrm{ZnTPP} \qquad (2a)$$

$$C_{60}{}^{\bullet-} - \mathrm{ZnTPP}^{\bullet+} \xrightarrow{\mathrm{BET}} C_{60} - {}^{3}{*}\mathrm{ZnTPP} \xrightarrow{\mathrm{EnergyT}} {}^{3*}C_{60} - \mathrm{ZnTPP} \qquad (2b)$$

formation of the fullerene triplet excited state with an overall quantum efficiency of 0.196. To shed further light onto the exact formation mechanism, we reinvestigated the dynamics of **1** in toluene on the picosecond time scale. Here, the radical pair (1.54 eV) decays *via* a transient intermediate, before the fullerene triplet excited state evolves (τ = 3970 ps). Based on the close spectral reminiscence with the ZnTPP triplet excited state we propose the formation of the latter state as an intermediate step towards the fullerene triplet excited state. Its excited state energy (1.53 eV) is then a sufficient promoter to activate an intramolecular triplet–triplet energy transfer to the lower lying fullerene triplet (1.50 eV).

In more polar solvents the energy of the radical pair state is decreased (< 1.45 eV; see Table 1) and, as a consequence, charge recombination, yielding the porphyrin or fullerene triplet excited state is thermodynamically hindered. Instead, direct generation of the singlet ground state takes place [eqn. 2(a)].

The clean decay kinetics of the π-radical cation absorption allowed us to measure the lifetime of the radical pair as a function of solvent polarity. The lifetime is subject to an interesting trend: The lifetimes in tetrahydrofuran (τ = 385 ps) and dichloromethane (τ = 122 ps) are markedly increased relative to the more polar solvents dichloroethane (τ = 61 ps) and benzonitrile (τ = 38 ps) (Table 1). This dependency prompts to an important conclusion: The rates of the back electron transfer processes, from the $C_{60}{}^{\bullet-}$–$\mathrm{ZnTPP}^{\bullet+}$ state to the ground state, are clearly in the 'Marcus-inverted' region [*e.g.* a region in which larger free energy changes ($-\Delta G°_{ET}$) lead to slower electron transfer rates (k_{ET})].

Since the correct choice of intermolecular separation is essential to the efficiency of light-driven electron transfer, especially in light of guaranteeing $-\Delta G° > \lambda$, a comparison of **1** with non-fullerene systems, that have similar van der Waals contacts, was deemed necessary. In these systems,[6e,g] the inverted BET reactions are activated only at values exceeding 1.9 eV, while in **1** the 'Marcus-inverted' region was established even at values smaller than 1.5 eV. This underlines the unique role of [60]fullerene, possessing a smaller reorganization energy than two-dimensional acceptor moieties, as a novel electron acceptor.

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Note added in proof: similar investigations on a different dyad were recently reported by D. Schuster *et. al.*[9]

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