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Small reorganisation energy and unique stabilisation of zwitterionic C_{60}–acceptor moieties†

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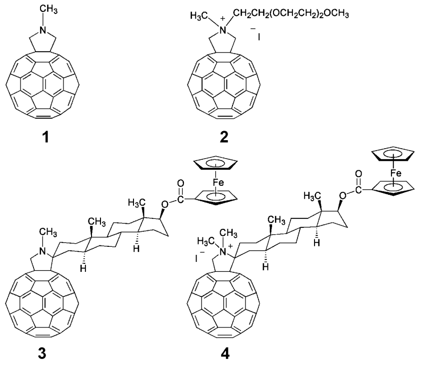
Fulleropyrrolidine- and fulleropyrrolidinium-based donor–acceptor ensembles, C_{60}–Fc, were tested in view of intrinsic reorganisation energies for light-induced electron transfer events; overall, the zwitterionic character of the reduced fulleropyrrolidinium acceptor plays a central role in accelerating charge separation and decelerating charge recombination.

A large body of work performed in recent years has demonstrated that C_{60} is a promising building block for applications in materials science, most eminently in the fields of photovoltaics and optoelectronics.[1] Implementation of C_{60} as a three-dimensional (3-D) electron acceptor holds great expectations in electron transfer on account of its small reorganisation energy in light-induced charge-separation processes.[2] The delocalisation of charges within the spherical carbon framework together with the rigid, confined structure of the aromatic π-sphere offers new opportunities to the stabilisation of charged entities.[3]

The function and benefits of different electron donors, covalently linked to the reactive framework of C_{60}, has been thoroughly probed *en route* to synthetic models of light harvesting arrays and reaction centers.[4] By contrast, only a few scattered reports can be found that focus on the modification of the acceptor properties of the fullerene derivative.[5–9] Among the relatively few examples, relevant contributions comprise the work on integrating C_{70} or, more recently, $C_{59}N$—both being slightly better electron acceptors than C_{60}—into photoactive charge-transfer materials.[6,7] However, a quantitative comparison of reorganisation energies for intramolecular electron transfer processes involving different 3-D acceptor units has yet to be reported, mainly due to synthetic challenges.

In this work we report on the effects stemming from changes of the C_{60} acceptor, that is, probing a fulleropyrrolidine *versus* fulleropyrrolidinium core, on charge-separation and -recombination in connection with a ferrocene donor. This allows for the first comprehensive assay of λ-values for intramolecular electron transfer involving different C_{60} acceptors.

In the two references, fulleropyrrolidine **1** and fulleropyrrolidinium salt **2** (Scheme 1), the photophysics of the fullerene singlet excited state are governed by slow (5×10^8 s^{-1}), but efficient intersystem-crossing dynamics to the triplet manifold. Spectroscopically, strong transitions in the near-IR (*i.e.*, singlet–singlet at 880 nm) and visible (*i.e.*, triplet–triplet at 700 nm) help to identify the two excited states.[10] The dynamics of the intersystem-crossing processes are nearly solvent independent.



Scheme 1

Upon photoexciting the C_{60} core in dyads **3** and **4** with short 355 nm laser pulses the same singlet excited state absorptions of $^{1*}C_{60}$ were found around 880 nm. In most cases the decays were notably faster than in the references, **1** and **2** (Fig S1†). Furthermore, characteristic bands in the near-IR, that are centered around 1000 nm and ascribed to the fullerene radical anion, $C_{60}^{\bullet-}$—similar to Fig. 1—appeared concomitantly with the $^{1*}C_{60}$ decay. We conclude that in the investigated donor–acceptor systems intramolecular electron transfer controls the transformation of the $^{1*}C_{60}$–Fc precursor into the $C_{60}^{\bullet-}$–Fc^+ product.

The weak absorption of Fc^+ with an extinction coefficient of ~500 M^{-1} cm^{-1} at 625 nm is masked by the much stronger absorption (>5000 M^{-1} cm^{-1}) of $C_{60}^{\bullet-}$ in this region.[10] By fitting the rise and decay of the fingerprint absorption to a first-order rate law, the charge separation rates (k_{CS}) evolving from $^{1*}C_{60}$ and the charge recombination rates (k_{CR}) within the $C_{60}^{\bullet-}$–Fc^+ pair were determined with best accuracy.‡

In the case of the fulleropyrrolidine-based dyad (**3**) transient absorption spectroscopy, carried out in toluene, *o*-dichlorobenzene, benzonitrile and DMF, led to a wide range of deactivation kinetics extending from 6.8×10^8 s^{-1} to 1.4×10^9 s^{-1}. The overall acceleration is well in accord with a progressively larger $^{1*}C_{60}$–Fc/$C_{60}^{\bullet-}$–Fc^+ energy gap, $-\Delta G_{CS}°$, when going from non-polar to polar environments. In **3**, $C_{60}^{\bullet-}$–Fc^+ is metastable and decays quantitatively to the ground state with rates of 9.3×10^5 s^{-1}, 1.2×10^6 s^{-1} and 2.8×10^6 s^{-1} in *o*-dichlorobenzene, benzonitrile and DMF, respectively.§

For dyad **4**, the charge-separation kinetics are all nearly the same. What is important to note is that the decay kinetics (~1×10^9 s^{-1}) are, at least, faster by a factor of 2 than the intersystem crossing rates (5×10^8 s^{-1}) found in the reference (**2**). The charge-recombination kinetics, on the other hand, in *o*-

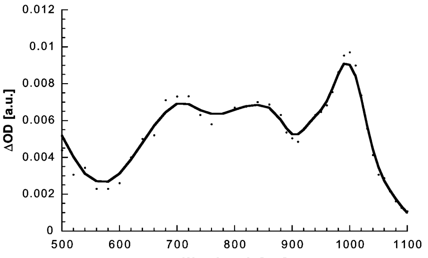


Fig. 1 Differential absorption spectrum obtained upon nanosecond flash photolysis (337 nm, InGaAs detector, 800 nm cut-off filter) of ~1.0×10^{-5} M solutions of dyad **4** in nitrogen saturated *o*-dichlorobenzene.

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† Electronic supplementary information (ESI) available: supplementary figures S1–S3. See http://www.rsc.org/suppdata/cc/b2/b206930j/

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Table 1 Charge separation and recombination kinetics in **3** and **4**

Dyad	Solvent	k_{CS}/s^{-1}	k_{CR}/s^{-1}	k_{CS}/k_{CR}
3	*o*-Dichlorobenzene	8.9×10^8	9.3×10^5	960
	Bezonitrile	1.0×10^9	1.2×10^6	835
	DMF	1.4×10^9	2.8×10^6	500
4	*o*-Dichlorobenzene	1.5×10^9	6.2×10^5	2420
	Bezonitrile	1.4×10^9	1.0×10^6	1400
	DMF	1.5×10^9	2.0×10^6	750

dichlorobenzene (6.2×10^5 s^{-1}), benzonitrile (1.0×10^6 s^{-1}) and DMF (2.0×10^6 s^{-1}) indicate an appreciable acceleration and correlate well with the solvent polarity.

To follow-up on this observation fluorescence assays were performed with dyads **3** and **4**. An illustration is given in Figs. S2 and S3,† which compare the fullerene steady-state fluorescence spectra. In principle the following tendency emerges: A solvent progression is only seen for dyad **3**, starting with toluene (*i.e.*, strongest fluorescence) and ending with DMF (*i.e.*, weakest fluorescence), while the quantum yields for dyad **4** in the same solvents are nearly indistinguishable. Also, the C_{60} fluorescence lifetimes in dyad **4**, as determined by the decay of the 720 nm emission, afforded rates on the order of $\sim 1 \times 10^9$ s^{-1}.

We conclude that in dyads **3** and **4** a highly exergonic charge-separation prevails with $-\Delta G_{CS}°$ close to the top of the Marcus parabola followed by charge-recombination, which is clearly in the inverted region of the Marcus parabola—the highly exergonic region ($-\Delta G° > \lambda$) where the electron transfer rates start to decrease with increasing free energy changes. Despite the fact that k_{CR} in both dyads is pushed into the inverted region of the Marcus parabola, it is remarkable that dyad **4**, for which smaller $-\Delta G_{CR}°$ values were determined, reveals definitively slower k_{CR}. This points unequivocally to the unique structure of the zwitterionic $C_{60}{}^{\cdot-}$ acceptor, which provides the means for stabilising the charge-separated $C_{60}{}^{\cdot-}$–Fc^+ pair.

In the next step we analysed the driving force dependence on the rate constants, by applying a linear expression of the Marcus equation [*i.e.*, eqn. (1)], in which V represents the electronic

$$k_B T \ln K_{ET} + \frac{\Delta G^0{}_{ET}}{2} = k_B T \ln\left[\left(\frac{4\pi^3}{h^2 \lambda k_B T}\right)^{1/2} V^2\right] - \frac{\lambda}{4} - \frac{(\Delta G^0{}_{ET})^2}{4\lambda} \quad (1)$$

coupling matrix element. The driving forces ($-\Delta G_{ET}°$) were determined, based on the oxidation potential of the ferrocene donor and the reduction potential of the fulleropyrrolidine and fulleropyrrolidinium acceptors, together with the energy level of the fullerene singlet excited state. In line with eqn. (1), plots of [$k_B T \ln k_{ET} + (\Delta G_{ET}°/2)$] *vs.* $(\Delta G_{ET}°)^2$ give for both dyads a linear correlation—see Fig. 2.¶ The reorganisation energies (λ) and electronic coupling (V) values are obtained for dyad **4** as 0.6 eV and 0.26 cm^{-1}, respectively. The linear correlation for **3** afforded a larger λ-value (0.77 eV) together with a similar V-value (0.3 cm^{-1}). Such a variance in λ between dyads **3** and **4** is the reason why the ratio of k_{CS} to k_{CR} is different in the two donor–acceptor systems. This is the first quantitative manifestation, which shows that chemical functionalization allows the control over λ-values of a C_{60} electron acceptor.

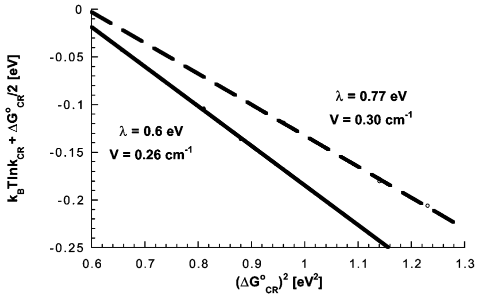

Fig. 2 Plot of [$k_B T \ln k_{ET} + (\Delta G_{ET}°/2)$] *vs.* $(\Delta G_{ET}°)^2$ for dyad **3** (dashed line) and dyad **4** (solid line).

In conclusion, we have demonstrated the beneficial role of a zwitterionic intermediate in a donor–acceptor dyad. Central to the stabilisation is the small reorganisation energy of the fulleropyrrolidinium acceptor, being 0.17 eV smaller than that found for the analogous fulleropyrrolidine. The favourable electron transfer properties of dyad **4**, that is, a ratio of ~ 2500 between charge-separation and charge-recombination is encouraging to pursue incorporation of **4** into a photovoltaic device *via* nanoscale organisation of photoactive thin films.

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Notes and references

‡ No evidence was found for the population of the ferrocene triplet excited state. Probing a toluene solution of the Fc model under similar conditions with a 18 ps laser pulse led to very weak absorption changes in the 500–760 nm range—an extinction coefficient of less than 500 M^{-1} cm^{-1} was estimated for the triplet–triplet absorption.

§ In toluene, the only product is the long-lived fullerene triplet.

¶ The delocalization of charges within C_{60} suggests that the reorganization energy in the present systems is not susceptible to changes in the solvent polarity.

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