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15 September 2000

Chemical Physics Letters 327 (2000) 253–262

**CHEMICAL
PHYSICS
LETTERS**

www.elsevier.nl/locate/cplett

Ultrafast competition between energy and charge transfer in a functionalized electron donor/fullerene derivative

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Received 13 June 2000; in final form 1 August 2000

Abstract

The fact that fullerenes are good electron acceptors has generated interest in covalently linked complexes between electron donors and fullerenes; photoinduced charge transfer in these dyads has great potential for use in photovoltaic devices. In this Letter, we investigate the excited-state properties of a perylene–fulleropyrrolidine dyad using steady-state and femtosecond time-resolved spectroscopies. Following photoexcitation, charge separation and energy transfer occur in nearly equal proportion; both processes take place on a sub-picosecond timescale. This suggests that competition between energy and charge transfer is common in these molecular systems, so that the best molecules for device applications are not necessarily those with the fastest electron transfer rates. © 2000 Published by Elsevier Science B.V.

1. Introduction

One of the remarkable features of the photosynthetic reaction center is that photoexcitation leads to charge separation with high efficiency. Synthetically mimicking this type of photoinduced electron transfer has become a goal for the production of efficient photovoltaic cells for solar energy conversion [1] as well as for other optoelectronic applications [2,3] and even for photography [4]. The challenge in designing molecular systems for photoinduced charge separa-

tion is to minimize undesirable side reactions that waste the energy of the absorbed photon: both back electron transfer from the charge-separated state and energy transfer from the donor to the acceptor are reactions to be avoided. With these considerations in mind, the fullerene C₆₀ is often selected as the electron acceptor moiety in molecular systems for photoinduced charge transfer [5]. Energetically, the electronic structure of C₆₀ is favorable to serve as a strong electron acceptor in both the ground and excited states. In addition, the reorganization energy associated with transferring an electron to C₆₀ is unusually small, a result that often places the back electron transfer reaction in the Marcus inverted regime, minimizing the rate of the back electron transfer reaction [5].

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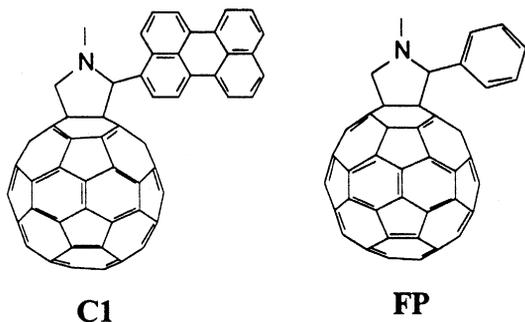
The potential for using fullerenes as electron acceptors in solar cells is highlighted by recent work showing ultrafast photoinduced charge separation in blends of C_{60} with semiconducting polymers such as poly(phenylene vinylene) (PPV) [6,7]. Production of devices based on molecular blends like this, however, is hampered by the poor solubility of C_{60} in common organic solvents and the problem of phase segregation in mixtures of C_{60} with other molecules. Overcoming these difficulties has motivated the synthesis of functionalized C_{60} s, such as the fulleropyrrolidines (FP; see below for the chemical structure of FP), which also offer the possibility to covalently link the donor and acceptor groups so that phase segregation is no longer an issue. For example, Hadziioannou and co-workers have reported the successful preparation of a photovoltaic cell based on a donor–acceptor dyad consisting of a semiconducting oligophenylenevinylene (OPV) unit linked to FP [8]. More recently, Armaroli et al. have synthesized a very similar FP derivative linked to two OPV groups [9]. Surprisingly, this dual-substituted fullerene derivative showed no signs of electron transfer or charge separation upon photoexcitation: only energy transfer from the OPV groups to the fullerene was observed [9]. This result was unexpected given that ultrafast electron transfer appears to be the dominant photophysical process in the mono-substituted OPV-FP complex [8] and in PPV/ C_{60} blends [6,7], both of which are chemically very similar to the di-substituted complex that shows only energy transfer.

A partial resolution to this puzzle can be found in the recent work of Segura et al. who examined the photophysics of a soluble FP–oligonaphthalenevinylene dyad in a variety of solvents [10]. These workers found that both energy transfer and intramolecular electron transfer take place following photoexcitation; the two processes act in competition with each other on a timescale of tens of picoseconds. By varying the solvent polarity, the detrimental energy transfer step could be minimized with respect to charge separation, allowing some hope of using this dyad for energy conversion with high efficiency [10]. The question that remains is why, for a series of ostensibly similar chemical systems, does intramolecular charge transfer take place quantitatively in some cases while energy and charge transfer can compete effectively in other examples?

In this Letter, we address this question by exploring the competition between energy transfer and charge transfer in a related molecule: a dyad consisting of a perylene donor linked to an FP unit (see **C1** below for chemical structure). We find that, like Segura et al. [10], a combination of charge and energy transfer to the C_{60} moiety takes place upon excitation of the perylene chromophore. By comparing the results of both steady-state and femtosecond time-resolved measurements, we also find that the energy transfer and charge transfer processes compete on a sub-picosecond timescale in this molecule, resulting in a roughly equal branching ratio for the two processes. This result contrasts previous work on related systems in which the competition between the two processes takes place on a timescale nearly two orders of magnitude slower [10]. We speculate that the important factor in controlling the branching ratio is the specific geometry of the donor–fullerene complex, and that changes in geometry which improve the rate of charge transfer also tend to improve the prospects for energy transfer. In combination with previous work in the literature [5–10] the results suggest that competing energy and electron transfer is a universal phenomenon in donor–fullerene molecular complexes. This conclusion has two major ramifications for studies in this field. First, the presence of strong quenching of the donor fluorescence in a complex cannot be unambiguously assigned to charge transfer alone. Second, the best molecular complexes for photovoltaic device applications may not be those with the fastest charge transfer rate; instead, it is important to control the molecular geometry to minimize the energy transfer rate relative to the charge transfer rate to increase the quantum yield for charge separation.

2. Experimental

The C_{60} -perylene derivative (**C1**) and the control molecule (FP) were synthesized according to well-established reaction procedures (see, e.g., Ref. [11]). These compounds were fully characterized by NMR, mass spectroscopy, and cyclic voltammetry in *o*-dichlorobenzene (ODCB). Details on the synthesis procedure and characterization will be described elsewhere [12].



The laser system used for the time-resolved experiments is a regeneratively amplified Ti:Sapphire laser system (Spectra Physics) which produces ~ 150 fs pulses with ~ 1 mJ of energy at a 1 kHz repetition rate. The excitation (pump) light at 460 nm was produced by fourth harmonic generation of the 1840-nm idler beam from a dual-pass optical parametric amplifier (OPA) pumped by the 790-nm fundamental of the amplified laser. Probe pulses at 510 nm were produced by sum frequency mixing the 1400-nm signal beam from the OPA with the remaining 790-nm fundamental light; probe light at 700 nm was generated as the second harmonic of the 1400-nm signal beam. The probe beam is split into signal and reference components that are digitized on a shot-by-shot basis after being detected by matched Si photodiodes. Further details on the experimental

setup and data collection routines have been published elsewhere [13].

Solutions of the various molecules under study, perylene, FP, and **C1** in spectroscopic-grade ODCB were flowed through a 2-mm-length quartz cell. All the experiments that used the same combination of pump and probe wavelengths, even those on different molecules, were run back-to-back without moving the cell between different experiments. The intensity of the excitation beam was kept very low ($\leq 20 \mu\text{J}/\text{cm}^2$) to avoid photodegradation. At these low intensities, there was no detectable signal from the neat solvent and all the measured dynamics were intensity-independent. For the scans presented below, the relative polarizations of the pump and probe beams were chosen to be perpendicular to avoid contributions from a coherence artifact near time zero. We found no difference in any of the longer-time dynamics using parallel or magic angle relative pump and probe polarizations, a result consistent with the fact that rotational diffusion of these large molecules should be exceedingly slow.

UV-visible absorption spectra were recorded on a Hewlett Packard 8453 spectrophotometer. Fluorescence emission and excitation spectra were measured on a Spex Fluorolog-3 spectrometer. The fluorescence spectra were excited at 460 nm and the excitation spectra were monitored at either 500 or 715 nm.

Table 1
Absorption and emission parameters for molecules studied in this work

Molecule	Fluorescence quantum yield	510-nm Excited state cross-section ($\text{M}^{-1} \text{cm}^{-1}$)	700-nm Excited state cross-section ($\text{M}^{-1} \text{cm}^{-1}$)	460-nm Ground state cross-section ($\text{M}^{-1} \text{cm}^{-1}$)
Perylene	0.94 ^{a,b}	-7500 ± 2500 ^c	53000 ± 6000 ^c	2000 ± 1000 ^c
C1	< 0.00012 ^a			35000 ± 5000
FP	0.009 ^d	7000 ± 3500 ^e	5000 ± 2500 ^e	3000 ± 1000 ^f
Per ⁺		25000 ± 8000 ^g	2000 ± 2000 ^g	

^a Fluorescence only of the perylene moiety of **C1** measured between 460 and 600 nm (i.e., the fullerene emission near 700-nm is excluded.)

^b In cyclohexane [14].

^c Ref. [17]. The negative value for the 510-nm cross-section indicates stimulated emission. Note that the cross-section for stimulated emission from the perylene chromophore in **C1** is much larger than for free perylene due to the red-shift of the emission in the dyad; see Fig. 1b.

^d Fluorescence of the fullerene group collected between 650 and 900 nm.

^e Refs. [18,19].

^f Ref. [15].

^g Ref. [20]; ground state absorptivity for the transiently produced radical cation.

The quantum yield Φ_F of the perylene moiety fluorescence from **C1**, in the 460–600 nm range, was determined to be $< 1.2 \times 10^{-4}$, using perylene as a standard ($\Phi_F = 0.94$ in hexane [14]) (Table 1).

3. Results and discussion

The steady-state photophysics of the molecules considered in this study are shown in Fig. 1. In Fig.

1a, the absorption spectrum of the FP molecule is shown as the dashed curve, while the solid line gives the absorption spectrum of the perylene–FP complex, **C1**. Within experimental error, the absorption spectrum of the **C1** complex is equal to the sum of the absorption spectra of the two individual moieties (FP and perylene) that constitute the dyad. This result is in agreement with previous studies on donor–acceptor dyads in solution [8–10] and sug-

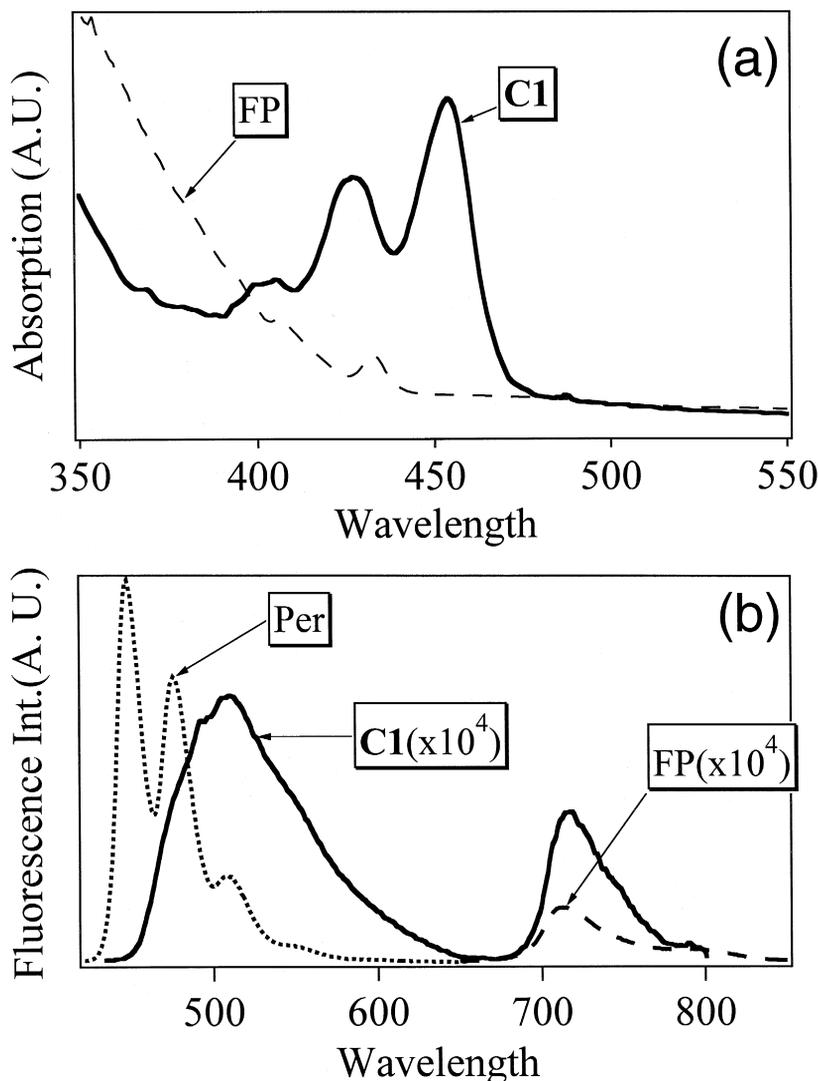


Fig. 1. (a) UV-visible absorption spectra of **C1** (solid curve) and FP (dashed curve) in ODCB. (b) Fluorescence spectra of equimolar solutions of perylene (dotted curve), **C1** (solid curve), and FP (dashed curve) exciting at 460 nm in ODCB. The absolute fluorescence intensities for FP and **C1** have been scaled by 10^4 in order to compare the data on the same intensity scale.

gests that there is no ground-state interaction between the two chromophores. When fullerenes do form ground-state charge transfer complexes with electron donors such as amines, a charge transfer band appears in the 450–650 nm region [15,16]. Excitation of the charge transfer band leads to charge separation on the picosecond timescale [15,16]. The absence of any characteristic charge transfer band in the absorption spectrum of **C1** implies that any charge separation occurs only after localized excitation on either the perylene or fullerene groups.

The emission spectra of perylene, FP, and the **C1** dyad following excitation at 460 nm are shown as the dotted, dashed, and solid curves, respectively in Fig. 1b. The fluorescence of the **C1** dyad can be qualitatively described as the sum of separate emissions from the perylene and fullerene portions of the complex. The emission from the perylene half of the **C1** complex near 500 nm is slightly red-shifted compared to the fluorescence of free perylene, consistent with the red-shifted absorption of the substituted chromophore in the **C1** dyad. More important than the slight red shift, the fluorescence of the perylene group in **C1** is quenched nearly completely: there is a more than four order-of-magnitude decrease in fluorescence intensity relative to free perylene (Table 1)². The fluorescence intensity of the fullerene moiety in the complex near 715 nm, on the other hand, is enhanced by nearly a factor of 4 relative to the free FP molecule at the same excitation wavelength and concentration. Since the absorption spectrum of the **C1** dyad is the sum of individual perylene and fullerene absorption bands, the enhanced fullerene emission from the complex must result from light absorbed by the perylene moiety of the dyad.

The only way that enhanced fullerene emission can result from excitation of the perylene portion of the **C1** complex is via energy transfer from the localized perylene excited state to the excited-state orbitals of the fullerene moiety. The presence of this energy transfer is quantified in Fig. 2, which shows

the fluorescence excitation spectrum of the **C1** dyad for fullerene emission collected at 715 nm (solid curve). Clearly, the resemblance of the excitation profile to the absorption spectrum of perylene confirms that some of the energy initially deposited into the perylene excited state migrates to the fullerene excited-state orbitals, resulting in fullerene emission. The excitation spectrum of **C1** shown in Fig. 2, however, does not perfectly match the absorption spectrum shown in Fig. 1 (particularly at $\lambda < 400$ nm), implying that the energy transfer from the perylene to the fullerene moiety is not quantitative. To determine the quantum yield for energy transfer, we fit a linear combination of the absorption spectra of FP (solid curve in Fig. 1) and perylene (weighted difference of the two curves in Fig. 1)³ to the 715-nm excitation spectrum of **C1**. The excitation spectrum of **C1** is well described as a sum of the individual perylene and FP components (Fig. 2 dashed curve) with a relative weight of 0.6 ± 0.1 for the FP component. Since we expect excitation on the fullerene end of the dyad to result in the same emission quantum yield as for the free fullerene, the fit implies that about 40% of the excitations on the perylene end of the dyad result in energy transfer to the fullerene group. Thus, the quantum yield for energy transfer is ~ 0.4 . In addition, given the relative absorption cross-sections of perylene and FP in the complex at the excitation wavelength (Table 1), the ~ 4 -fold increase in fullerene emission from **C1** relative to free FP implies a quantum yield for energy transfer ≥ 0.3 , consistent with the fit to the excitation spectrum.

Since less than half of the excitations on perylene transfer to the fullerene excited state, the next question to address is what is the fate of the rest of the excitations deposited into the perylene part of **C1**? We know that these excitations do not remain as perylene singlet excited states because the perylene fluorescence is quantitatively quenched. Thus, to directly monitor the fate of the perylene excited state, we have performed femtosecond transient ab-

² The apparent loss of vibronic structure in the emission spectrum of **C1** in Fig. 1 results from the decrease in resolution due to use of an especially wide collection slit on the fluorimeter to collect the small number of emitted photons.

³ Since the substituted perylene in **C1** has a red-shifted absorption relative to free perylene, we calculated the absorption of the perylene in **C1** as the difference between the absorption of the complex and the absorption of FP.

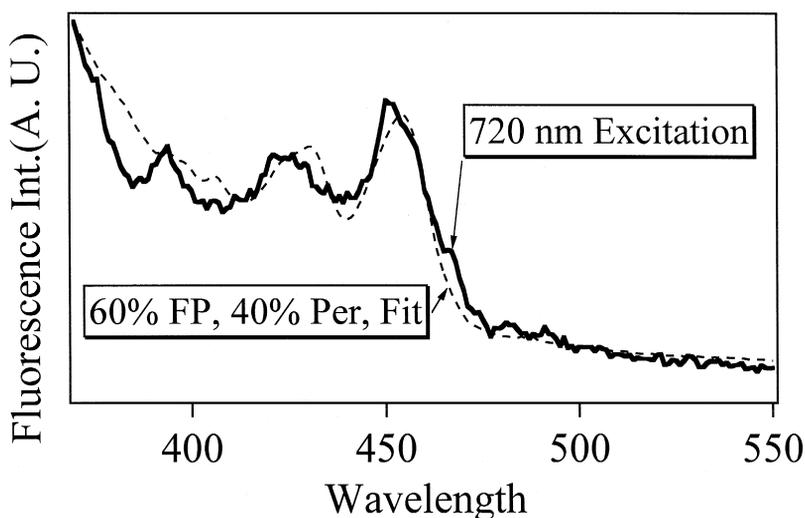


Fig. 2. Fluorescence excitation spectrum of **C1** for emission collected at the 720-nm peak of the fullerene fluorescence (cf. Fig. 1b) in ODCB (solid line). The dashed curve is a fit to a 40:60 superposition of the individual absorptions of perylene and FP, respectively. See text for details.

sorption experiments, the results of which are presented in Figs. 3 and 4. For all the pump–probe experiments presented here, we chose an excitation wavelength corresponding to the reddest absorption

peak of the perylene moiety, 460 nm. At this excitation wavelength, roughly 90% of the absorbed photons excite the perylene chromophore; the remainder directly excite the FP moiety (Table 1).

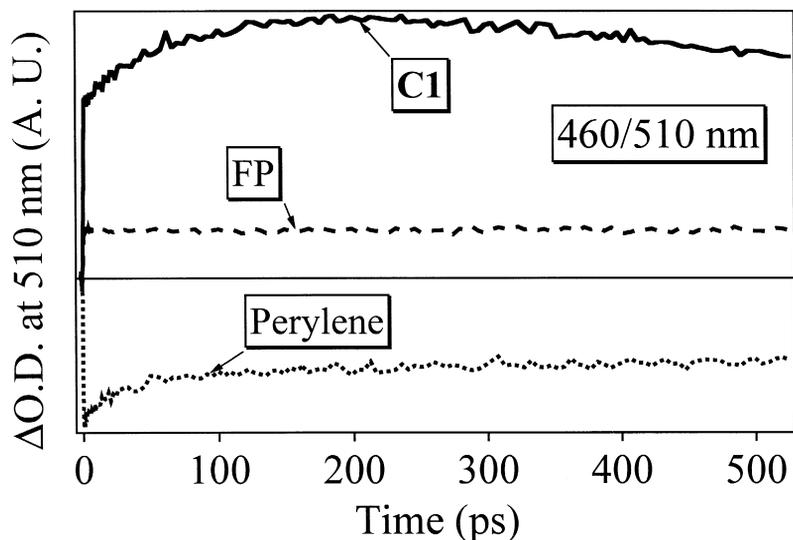


Fig. 3. Change in 510-nm absorbance following excitation at 460 nm on the hundreds of picoseconds timescale for the **C1** dyad (solid curve), FP (dashed curve) and perylene (dotted curve). The negative signal for perylene indicates an increase in transmittance through the sample due to stimulated emission.

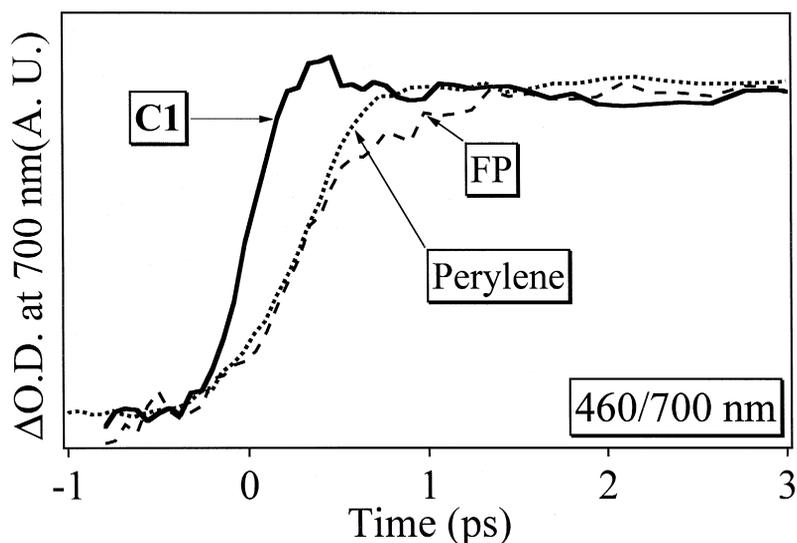


Fig. 4. Change in 700-nm absorbance following excitation at 460 nm on a few picosecond timescale for the **C1** complex (solid curve), FP (dashed curve) and perylene (dotted curve).

Fig. 3 shows the transient absorption dynamics for **C1** (solid curve), FP (dashed curve), and free perylene (dotted curve) exciting at 460 nm and probing at 510 nm. This probe wavelength corresponds to the emission maximum of the perylene chromophore (Fig. 1b), and indeed the free perylene shows stimulated emission dynamics (negative change in absorption) [17]. The initial rapid decay of the stimulated emission of excited perylene corresponds to vibrational cooling or solvation; the stimulated emission then persists for the ~ 5 -ns perylene excited-state lifetime [14]. The FP molecule shows a weak transient absorption at 510 nm with little transient dynamics; the excited fullerene is known to undergo intersystem crossing, but the excited singlet and triplet absorption cross-sections are roughly equal at this wavelength, leading to little change in the transient absorption with time (quasi-isosbestic wavelength) [18,19].

For the **C1** dyad, even though the majority of the absorbed light excites the perylene moiety, the pump–probe experiments show the instrument-limited (≤ 300 fs) appearance of a transient absorption at 510 nm. Given that the excited-state cross-section of the FP group is slightly smaller than the stimulated emission cross-section of the perylene group (Table 1), the instrument-limited appearance

of an absorption in excited **C1** implies that emissive excitations on the perylene group live for a time less than or equal to our instrument response. Since energy transfer in **C1** produces excited FP, one might expect that the transient absorption dynamics of **C1** and FP should be the same if the energy transfer process were quantitative or if the product of any complementary photophysical process was dark at 510 nm. This is clearly not the case in Fig. 3; the dynamics of **C1** are very different from those of FP. The signal size from FP is quite a bit smaller than that from **C1** and the shapes of the transients are clearly different. The net absorption signal and the different dynamics from the pure FP molecule must arise from the presence of an extra reaction product that absorbs the 510-nm probe light.

What could this extra 510-nm absorbing species be? Literature reports show that the perylene radical cation ($\text{Per}^{\cdot+}$) has a strong absorption band centered at ~ 515 nm [20]. Thus, we expect that the absorption arises from an intramolecular charge transfer reaction in **C1** that creates a charge-separated state with a perylene radical cation on one side of the molecule and the fullerene radical anion on the other side. The transient absorption signal presented for the complex in Fig. 3 is assigned to a combination of the $\text{Per}^{\cdot+}$ absorption created by charge transfer and

of the FP excited-state (FP^{*}) absorption created by energy transfer. The relative magnitudes of the two transient absorptions in the signal are weighted by the quantum yields of the competing charge transfer and energy transfer reactions and by the cross-section of each absorbing species at 510 nm. The fact that the absorption dynamics of **C1** are different from those of FP suggests that the majority of the 510-nm absorption is due to the Per⁺. Based on the known absorption cross-sections of Per⁺ and FP^{*}, (Table 1) the observed signal is consistent with a situation where roughly 60% the excited-state species are Per⁺ and 40% are excited FP moieties. In combination with the nearly complete quenching of the perylene moiety fluorescence, the lack of stimulated emission from **C1** leads us to conclude that less than 10⁻² % of the excitations originally placed on the perylene group remain there on a timescale longer than our instrument response. The Per⁺ is produced on a sub-picosecond timescale, and lives for at least hundreds of picoseconds⁴, showing that the fraction of excitations that result in charge transfer lead to efficient charge separation. To confirm the ultrafast nature of the charge transfer process, experiments are presently underway to detect rapid appearance of the fullerene radical anion via its near-infrared absorption near 1080 nm [21]. Overall, the 510-nm transient signals show that a species like Per⁺ must be present on a sub-picosecond timescale; there is no way to describe the observed transients as a simple linear combination of the singlet excited perylene and singlet excited fullerene groups.

We can verify that the perylene excited singlet state in the dyad decays on a subpicosecond timescale by examining the dynamics of the perylene singlet excited-state absorption, which peaks near 700 nm [17]. Fig. 4 shows the first 3 ps of the transient absorption at 700 nm following 460-nm excitation of free perylene (dotted curve); the FP molecule (dashed curve) and the **C1** complex (solid curve). Both the perylene and the FP signals rise with the time resolu-

tion of our experimental setup in a few hundred femtoseconds. In contrast, the excited-state absorption of **C1** shows a much faster rise, strongly suggestive of a fast decay component hidden under the instrument convolution. The three transients were recorded one after the other without moving the cell or changing the overlap of the pump and probe beams, so that the position of time zero and the magnitude of any solvent-based coherence artifacts are identical for each of the three scans⁵. Thus, the rapid rise of the **C1** signal is indicative of a very fast process that takes place in the first few hundred femtoseconds following excitation. This is consistent with the formation of the perylene singlet excited state, which has a very large cross-section at 700 nm (Table 1) [17], and the subsequent decay of this state on a timescale faster than our ~ 300 fs instrumental resolution due to the competing energy transfer and charge transfer reactions. We are unable to directly determine the energy transfer or charge transfer rate constants from this data because both the Per⁺ and FP^{*} products have weak absorptions at 700 nm and because both reactions take place on timescales comparable to or faster than our instrument resolution. Given what is known about the 700-nm cross-sections of excited perylene, Per⁺ and FP^{*} (Table 1), we can at least argue that the 700-nm transient of **C1** shown in Fig. 4 is consistent with the ~ 40:60 energy transfer/charge transfer branching ratio determined by the fit to the fluorescence excitation data in Fig. 2.

4. Conclusions

In summary, we have investigated the excited-state photophysics of the perylene-FP dyad **C1**, and found that both energy transfer and charge transfer compete on an ultrafast timescale. The pump–probe data in

⁴ Because the 510-nm signal has components from both Per⁺ and FP^{*}, we cannot unambiguously assign a time for the back electron transfer. The fact that the long-lived 510-nm signal results predominantly from the cation suggests that the back electron transfer is relatively slow (hundreds of ps).

⁵ The data in Fig. 4 were taken with a perpendicular relative polarization of the pump and probe beams to minimize contributions from a coherence artifact due to the solvent: use of parallel-polarized pump and probe pulses on the pure solvent gave a rapid, apparently negative-absorbing coherence signal near time zero. This solvent signal is effectively eliminated by using perpendicular polarizations.

Figs. 3 and 4 place an upper limit for the time of each of the two reactions at ~ 300 fs, consistent with the nearly complete quenching of the fluorescence of the perylene moiety in the complex. The fit to the excitation spectra in Fig. 2 provides an estimate of a $\sim 40:60$ branching ratio between energy and electron transfer. The $\sim 40\%$ quantum yield for energy transfer is consistent with the facts that the fullerene emission from the **C1** dyad is ~ 4 times greater than that from the FP molecule, and that 460-nm light excites ~ 10 times as many perylene moieties as FP moieties in the complex. The $\sim 60\%$ quantum yield for charge transfer is also consistent with the pump–probe transients given the known cross-sections of the perylene radical cation and FP*. The idea of competing energy and charge transfer reactions in this class of molecules is similar to the work of Segura et al. [10] who obtained qualitatively similar results on a comparable dyad. The primary difference between our system and that studied by Segura et al. is that the energy and charge transfer reactions in the **C1** complex take place on a timescale nearly two orders of magnitude faster than seen in their work. It is important to notice that the energetics of these two systems are strikingly similar, with driving forces for both processes at ca. 1 eV [10,22].

All of this leads to the question of what controls the relative rates of energy and charge transfer in covalently linked donor–fullerene dyads? The Förster theory tells us that the rate of energy transfer depends on the overlap of the transition dipoles of the donor and acceptor, and that the rate scales as an inverse power of the distance between them [23]. There are many possible mechanisms to describe charge transfer [24], but all of them also depend sensitively on geometric factors like the orientation and distance between the orbitals of the donor and acceptor in the complex. Intuitively, it makes sense that the molecular geometries that produce the best overlap of the cation and anion wavefunctions to promote charge transfer also tend to lead to good overlap of the neutral wavefunctions, so that energy transfer is also enhanced. Thus, it is very difficult to increase the rate of charge transfer without also increasing the rate of energy transfer, leading to a trade-off when designing photovoltaic devices based on these materials. In general, increasing the rate of

charge transfer is important to maintain charge separation before the back charge transfer reaction can occur, but not if the increased charge transfer rate leads to a lower quantum yield for charge separation because of a competing energy transfer channel. In solution environments, the two rates can be tuned quasi-independently by changing the polarity of the solvent [10], but this is a difficult adjustment to make in the film environment of a device (our own attempts to vary the charge transfer rate by changing solvents were hampered by the poor solubility of **C1** in solvents other than ODCB). The dyad studied here has one of the highest charge transfer rates seen in molecules of this class, yet it is not an optimal choice for photovoltaic applications because of the accompanying high rate of energy transfer. Clearly, the competition between energy and charge transfer in donor–fullerene systems is a universal phenomenon, and needs to be carefully considered when designing new systems for optoelectronic applications.

Acknowledgements

B.J.S. gratefully acknowledges the support of a CAREER award from the National Science Foundation (CHE-9733218). B.J.S. is a Cottrell Scholar of Research Corporation and an Alfred P. Sloan Foundation Fellow. F. W. thanks the National Science Foundation for support of this work (DMR-9812046).

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