Inter *versus* intra-molecular photoinduced charge separation in solid films of donor–acceptor molecules†

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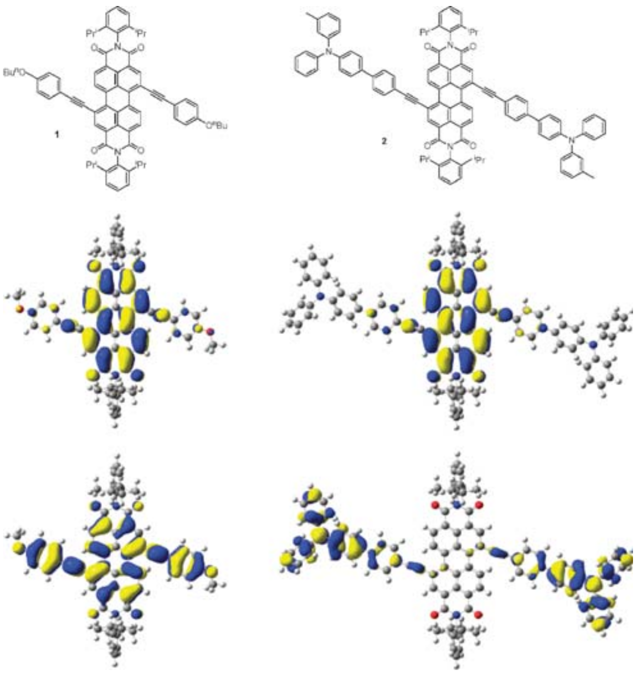
We report on photoinduced charge separation in solid films of two perylene diimides; intramolecular charge separation and recombination is correlated with a reduction in the yield of long-lived, intermolecular charge-separated species.

There is extensive interest in the synthesis and characterisation of molecular donor–acceptor structures, arising from the possibility of mimicking the photochemical processes in photosynthetic reaction centres and, in part, due to the potential use of such molecules in applications ranging from solar energy conversion to non-linear optical absorption.[1] The structure–function relationships which determine the solution photophysics and photochemistry of such molecules have now been elucidated in considerable detail.[2–5] However, relatively few studies have addressed the question of whether this understanding of solution photochemistry can be extended to the function of such donor–acceptor structures in solid films. This issue is of particular importance for technological applications, which will typically be based upon solid-state, rather than solution, materials.[6–8]

Here we report a study of the photoinduced electron-transfer processes occurring in films of a bis(4-(diarylamino)-biphenylethynyl)-substituted perylene diimide dyad (**2**), and compare these to films of a bis(4-alkoxyphenylethynyl)-substituted perylene diimide control (**1**), see Scheme 1. **1** and **2** were synthesized by Sonogashira coupling between the appropriate dibromoperylene diimide and terminal alkynes as described in the ESI.† The solution photochemistry of these molecules, including in particular ultrafast intramolecular charge separation in **2**, will be reported elsewhere.[10] In this contribution, we address the charge photogeneration properties of thin solid films of these molecules, focusing upon the generation of the long-lived charge-separated species which are essential for applications such as solar energy conversion. In particular, we consider whether the donor–acceptor structural motif that is found in solution to favour intramolecular charge separation in many donor–acceptor molecules such as dyad **2**, also results in enhanced intermolecular charge generation in solid films.

Solid films of both **1** and **2** were prepared by spin coating (500 rpm for 60 s) from 20 mg ml^{-1} solutions in chloroform. The resultant films were approximately 120 nm thick, with AFM data indicating rms roughness of 5.6 nm, and were optically nonscattering. UV/visible absorption spectra of the spin-coated films (see ESI†) were essentially indistinguishable from the corresponding solution spectra, indicating only modest intermolecular interactions. As will be discussed in more detail elsewhere,[10] whereas the lowest energy absorption of **1** has vibrational structure similar to that of unsubstituted perylene diimides (PDIs) and is only somewhat red-shifted, the low-energy absorption band for **2** is a considerably red-shifted, structureless band (with a structured PDI-like absorption at higher energy) suggesting considerable donor–acceptor charge-transfer character in the lowest excited state of **2**.



Scheme 1 Structures of the control **1** (left) and the donor substituted perylene diimide **2** (right) molecules used in this study (top). Also shown are the calculated LUMOs (middle) and HOMOs (bottom) for the two molecules.

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These experimental data were complemented by DFT and TD-DFT calculations, described in the ESI.† The calculated HOMOs and LUMOs of the geometry optimized structures are shown in Scheme 1 and indicate qualitatively different electronic structures for the two compounds. In contrast to molecule **1**, molecule **2** shows a clear spatial separation of its HOMO and LUMO, consistent with optical excitation resulting in the formation of an intramolecular charge separated state.

Fig. 1 shows time-resolved fluorescence decays for the two molecular films. The control film of **1** shows a monoexponential, 4.1 ns decay, indicative of formation of a long-lived singlet excited state. In contrast, the fluorescence for the film of **2** is strongly quenched, showing only an instrument-response limited, low-amplitude transient indicative of a singlet excited-state decay time of < 50 ps. These emission dynamics are similar to those observed in solution. The fluorescence quenching for the film of **2** is consistent with the observation of ultrafast (~ 10 ps) intramolecular charge separation for this molecule in dilute solution;[10] this emission quenching can, therefore, be attributed to intramolecular photoinduced charge separation in the film.

These emission data were complemented by transient absorption studies of photo-induced charge generation, as shown in Fig. 2. Solution transient absorption studies have revealed that the intramolecular charge separated state formed in **2** exhibits a decay time of 750 ps, which is assigned to intramolecular charge recombination.[10] Herein, however, we focus on the possibility of molecular films of this species generating long-lived, intermolecular charge separated species observable on the microsecond timescale. Control data in dilute solution showed no measurable signals on this timescale, consistent with ultrafast intramolecular charge recombination to the ground state. In contrast, solid films of **2** show clear transient absorption signals, as illustrated in Fig. 2. The absorption difference spectrum (Fig. 2a) shows a photoinduced absorption maximum at 740 nm, consistent with previous reports of the absorption of radical anions of PDI derivatives[9] and distinguishable from the PDI triplet absorption at 480 nm. This transient spectrum is, therefore, assigned to a charge-separated state in which the hole and electron are localised on triarylamine and PDI moieties, respectively. Fig. 2b shows the corresponding decay dynamics of this transient absorbance signal, monitored under low excitation densities (20 μJ cm^{-2} at 4 Hz). It is apparent that this absorbance is long-lived, exhibiting dispersive (approximately power law) decay dynamics on the microsecond timescale, with a decay halftime, $t_{50\%}$, of ~ 20 μs. These decay dynamics were observed to be independent of the presence of oxygen, confirming they cannot be assigned to triplet states (in agreement with the transient spectrum discussed above). Moreover, this decay halftime is four orders of magnitude longer than the intramolecular charge recombination timescale observed in solution, and therefore, cannot be assigned to the same intramolecular charge-separated species. Rather, this long-lived transient signal is assignable to the formation of dissociated, intermolecular charge-separated states, *i.e.* $\mathbf{2}^{\bullet +}/\mathbf{2}^{\bullet -}$. The observed recombination halftime, and dispersive, power law, behaviour of the recombination dynamics, are typical of those we have reported previously for intermolecular bimolecular recombination of dissociated charges in polymer–fullerene blend films.[11]

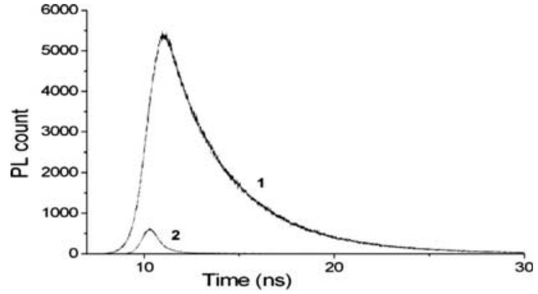

Fig. 1 Time-resolved single-photon-counting data for films of **1** and **2**. Data were collected using 467 nm excitation and 670 nm detection, with a 250 ps instrument response and data collection times corresponding to matched densities of absorbed photons.

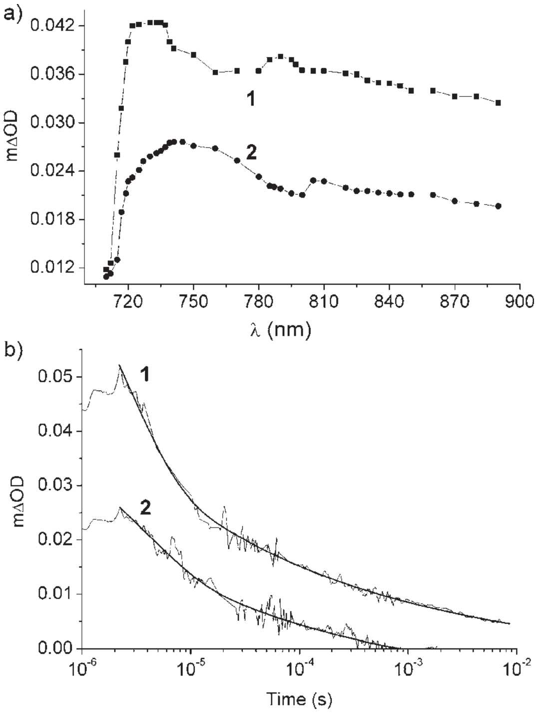

Fig. 2 (a) Transient absorption data for films of **1** and **2**, following excitation at 540 nm. The corresponding transient absorption spectra measured 1 μs after excitation. (b) The figure shows decay dynamics monitored at 740 nm.

We now turn to our control molecule, **1**. Studies in solution did not reveal any significant charge photogeneration, even on ultrafast timescales, consistent with the absence of a charge-transfer type feature in the absorption spectrum and with the weaker electron-donor properties of the alkoxyphenyl moiety.[10] However, it is apparent from Fig. 2 that solid films of **1** yield a transient absorption signal that is both larger and longer lived than that observed for **2**. The transient spectrum for film **1** again exhibited an absorption maximum at ~ 740 nm indicative of the formation of PDI anions and exhibited oxygen-independent, dispersive decay dynamics. This transient signal is, therefore, also assigned to intermolecular charge-separated states, in this case corresponding to the formation of $1^{\bullet+}$ and $1^{\bullet-}$. The transient signal for the film of **1** is larger than for the **2** film (normalised to equal densities of absorbed photons) for all probe wavelengths measured. As PDI radical cations are reported to show a sharp absorption maximum at longer wavelengths (900 nm for isolated PDIs[12] and presumably expected at still longer wavelengths for extended species such as $1^{\bullet+}$) the larger amplitude signal for the film of **1** is unlikely to be due to contributions from PDI^+ absorption alone, but rather to an approximately two fold increase in the yield of charge-separated species. We, thus, conclude that the film of **1** exhibits an approximately two fold enhancement of long-lived charge photogeneration relative to the **2** film.

It is clear from the above data that, at least for the molecules studied here, the ability of a molecule to achieve efficient intramolecular charge separation in solution is not in itself an indicator of the ability of that molecule to achieve efficient intermolecular charge separation in solid films. Clearly this is only a limited study covering two such molecules, and further studies are required to confirm its general applicability. Notwithstanding this caveat, this conclusion may have important implications for the relevance of solution studies of intramolecular electron transfer to the application of molecular donor–acceptor systems to solid-state solar energy conversion systems.

In general, it might be expected that the ability of a molecular structure to achieve an intramolecular charge-separated state should favour intermolecular charge separation in the solid state. This intramolecular charge separation should reduce the coulombic attraction (or 'binding energy') of the electron and hole, thereby facilitating subsequent intermolecular charge dissociation. Indeed charge-transfer molecules are employed to achieve efficient charge separation in both dye-sensitised and polymer–fullerene solar cells.[13,14] It is, therefore, striking that, for the molecules studied in this communication, intramolecular charge separation appears to correlate with a reduction in the yield of long-lived, intermolecular charge dissociation. The origin of this reduction in yield can be understood in terms of the relative lifetimes of the intramolecular photogenerated states for the two molecules studied. The lifetime of the intramolecular charge-separated state for the **2** dyad in solution, 750 ps, is, in fact, shorter than the lifetime of the singlet excited state of the control **1** (4.5 ns). In this context, the addition of the triarylamine moiety, enabling intramolecular charge separation, can be regarded as accelerating the decay of photogenerated states to the ground state. This acceleration can be understood in terms of an increase in vibronic coupling resulting from the generation of charged species. This accelerated decay to the ground state can be expected to compete with intermolecular charge dissociation, consistent with the observed lower charge generation yield. It is also possible that this reduction in yield may be associated with a reduction in intermolecular electronic coupling for the film of **2**, resulting perhaps from the triarylamine substituent disrupting the molecular packing. This will act in favour of an intramolecular charge recombination as opposed to charge dissociation. Indeed, we have previously reported an enhanced yield of intermolecular charge separation in solid films of planar TTF : fullerene dyads relative to their twisted analogues, and have attributed this to enhanced intermolecular coupling for the planar molecule.[15] In either case, it is apparent that whilst solution studies are essential for our understanding of the intramolecular photochemistry of molecular donor–acceptor systems, the application of such structures to solid-state solar energy conversion requires careful consideration of the film rather than solution photochemistry.

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