Ultrafast Dynamics

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Photoinduced Symmetry-Breaking Charge Separation: The Direction of the Charge Transfer**

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Photoinduced symmetry breaking (SB) charge separation (CS) occurs when an excited chromophore is surrounded by several identical electron donors or acceptors, but it can also happen between two identical molecular units when one of them is in an excited state. Such a process is observed in the reaction center of photosynthetic purple bacteria, where a bacteriochlorophyll dimer is surrounded by two almost identical branches of protein-bound cofactors.[1] Despite this symmetry, electron transfer takes place almost exclusively along one branch.[2] It has been shown that because the constituents of the dimer have slightly different geometries and local environments, CS along one branch is energetically more favorable and thus substantially faster than along the other.[3] Photoinduced SB-CS has also been observed in a few multichromophoric systems containing two or more identical molecular units, such as anthracene,[4] stilbene,[5] naphthalenediimides,[6] and perylenediimides.[7] Occurrence of SB-CS in these systems has been deduced from the transient absorption spectra recorded upon photoexcitation of one of the molecular units, M. However, the $M^{\bullet-}$ and $M^{\bullet+}$ ions could not be unambiguously recognized and distinguished, mainly because their absorption bands overlap or have too dissimilar intensities. Furthermore, the direction of the charge flow, that is, whether the electron is transferred from or toward the excited unit, could not be determined. The CS direction was supposed to be random and solely determined by solvent fluctuations, except in one case,[7a] where structural relaxation of the excited unit was proposed to be at the origin of SB.

Herein, we present investigations into the photoinduced SB-CS in 1,3-bis(3-perylenyl)propane (Pe-Pr-Pe), a bichromophoric dyad with which we could unambiguously determine the CS direction, that is, whether photoinduced electron or hole transfer is taking place. Perylene (Pe) was selected because this molecule has already been shown to undergo intermolecular photoinduced SB-CS,[8] and also becuase both $Pe^{\bullet+}$ and $Pe^{\bullet-}$ ions can be easily distinguished by their intense $D_5 \leftarrow D_0$ absorption band centered around 540 and 585 nm, respectively.[9] A propyl bridge was chosen to avoid too strong an electronic coupling between the two perylene units and to ensure that they are not parallel to each other. This lack of planarity was confirmed by conformational analysis, which also predicted the coexistence of compact and open conformers of Pe-Pr-Pe in acetonitrile at 300 K (Figure 1 and Supporting Information).

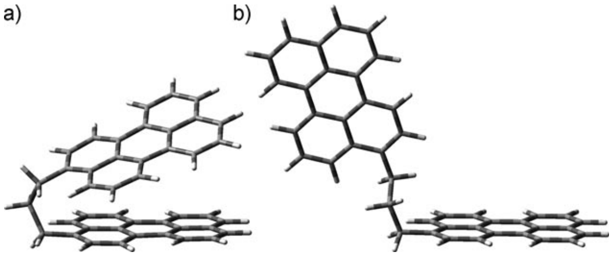

Figure 1. Structures of coexisting compact (a) and open (b) conformers of Pe-Pr-Pe in acetonitrile at 300 K. Structures were obtained from conformational analysis based on well-tempered metadynamics (WT-MTD) simulations on the isolated molecule and subsequent optimization in acetonitrile using the dispersion-corrected DFT-D3 method.

The dipole moment associated with the local $S_1 \leftarrow S_0$ transition of perylene, $\vec{\mu}_0$, and those related to the $D_5 \leftarrow D_0$ band of the ionic forms, $\vec{\mu}_+$ and $\vec{\mu}_-$, are all parallel to the perylene long axis.[10] Therefore, if the excited perylene unit always acts as electron donor, $\vec{\mu}_+$, but not $\vec{\mu}_-$, is parallel to $\vec{\mu}_0$ (Figure 2), and the polarization anisotropy of the cation band, r_+, is larger than that of the anion band, r_-. On the other hand, the contrary is true if the excited perylene acts as a hole donor only. Finally, $r_+ = r_-$ if CS is bidirectional.

The stationary absorption and emission spectra of Pe-Pr-Pe in cyclohexane (C_6H_{12}) and MeCN are very similar to those of perylene, except for a small red shift that can be accounted for by the presence of the propyl bridge (Supporting Information, Figure S2). This resemblance points to a weak electronic coupling between the perylene units and to a localization of the excitation entirely on one perylene. However, the fluorescence quantum yield is 0.45 in MeCN and 0.91 in C_6H_{12}, suggesting the existence of an additional non-radiative deactivation pathway in polar solvents, which is most probably SB-CS. This is corroborated by time-resolved

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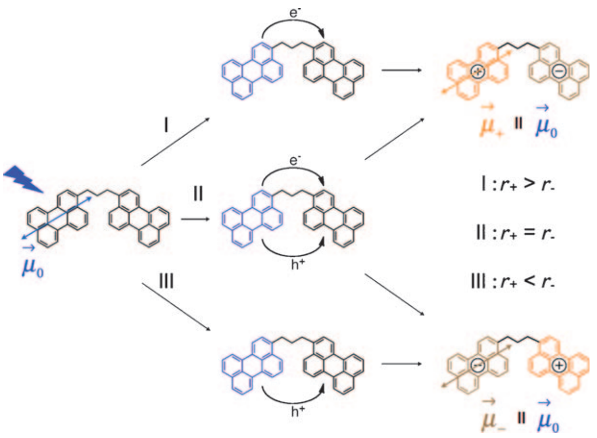

Figure 2. Relationship between the direction of the charge separation and the polarization anisotropy of the cation and anion absorption bands.

fluorescence, which reveals the presence of 10 and 105 ps decay components in MeCN, with 0.26 and 0.18 relative amplitudes, along with nanosecond components that are predominant in C$_6$H$_{12}$ (Supporting Information, Figure S4).

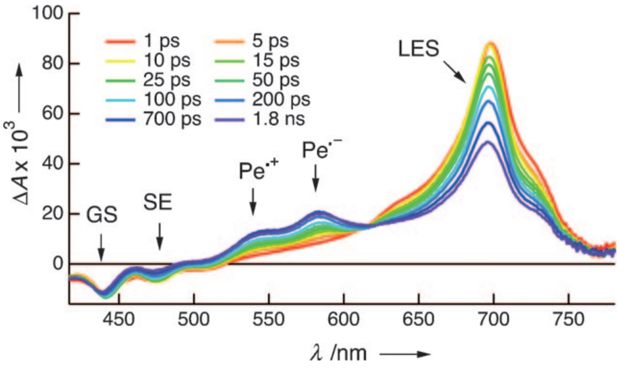

Figure 3. Transient absorption spectra recorded at different time delays after 400 nm excitation of Pe-Pr-Pe in acetonitrile (GS ground-state depletion, SE stimulated emission, LES local S$_1$-state absorption).

Insight into the origin of these decay components was obtained from transient absorption (TA) spectroscopy (Figure 3). The spectra recorded in MeCN immediately after 400 nm excitation are dominated by a band at 700 nm that can be ascribed to the absorption of the locally excited perylene unit. This band decreases with time, whereas two bands, centered at 540 and 585 nm, appear. These two spectral features, characteristic of the cationic and anionic forms of perylene, point unambiguously to the occurrence of SB-CS in Pe-Pr-Pe. The growth of both Pe$^{\bullet+}$ and Pe$^{\bullet-}$ bands can be reproduced with a biexponential function with 12 and 130 ps time constants, in agreement with the fluorescence lifetimes. This multiphasic CS dynamics can be explained by the coexistence of several Pe-Pr-Pe conformers with different mutual orientations and distances between the perylene units. These ion bands are not present in C$_6$H$_{12}$ (Supporting Information, Figure S5 A), indicating that polar solvation is required to stabilize of the charge-separated state relatively to the local excited state.

Although the propyl bridge should allow formation of an intramolecular perylene excimer,[11] neither excimer fluorescence in the 550–650 nm region[12] nor excimer transient absorption band at 600 nm[13] was identified in any solvent investigated. Moreover, the high, perylene-localized, fluorescence quantum yield of Pe-Pr-Pe in non polar solvents indicates that intramolecular perylene excimer is not formed in a significant amount. Thus, SB-CS in Pe-Pr-Pe does not occur upon dissociation of an intramolecular perylene excimer.

Occurrence of excitation energy hopping (EH) between the two perylene units was examined by measuring the polarization anisotropy in the 400–440 nm region that corresponds to the bleach of the local S$_1$←S$_0$ absorption band. The anisotropy first decreases from 0.36–0.4 with a 4–4.5 ps time constant and then decays to zero with a 75 ps lifetime (Supporting Information, Figure S5B). The slow component can be ascribed to the reorientational motion of Pe-Pr-Pe, and the fast one to EH. As EH is fully reversible, its time constant is twice the anisotropy decay time, that is, 8–9 ps (Supporting Information, Eq. S8).[14] The initial anisotropy value close to the maximum of 0.4 precludes the existence of any significant EH component faster than the time resolution of the experiment.

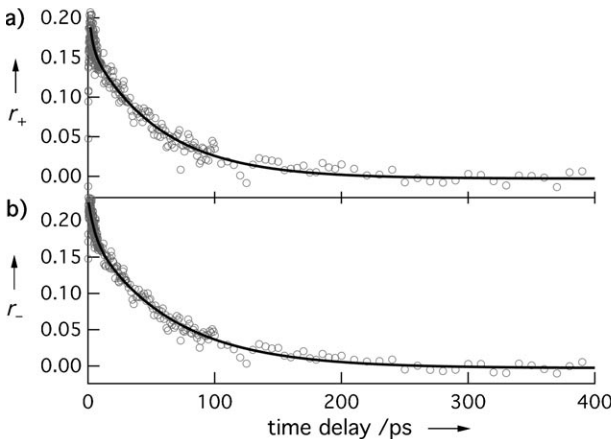

Figure 4. Decays of the polarization anisotropy measured with Pe-Pr-Pe in acetonitrile at a) 540 nm (Pe$^{\bullet+}$ cation) and b) 585 nm (Pe$^{\bullet-}$ anion). Best biexponential fits are also shown.

Information on the CS direction was obtained by comparing the polarization anisotropy of the cation and anion TA bands (Figure 4). Both $r_+(t)$ and $r_-(t)$ profiles are very similar and can be analyzed using a biexponential function with 4 and 60 ps time constants. The amplitude of the first component is slightly smaller at 540 than at 585 nm and can be ascribed to the localized excited state that contributes differently at these two wavelengths. On the other hand, the amplitudes of the slow component, that can be assigned to the ions, are the same within the limit of error at both wavelengths (540 nm: 0.17 ± 0.01, 585 nm: 0.18 ± 0.01). The two time constants are close to those measured in the 400–440 nm region and can be

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interpreted likewise, namely EH/CS and reorientational motion.

The very similar $r_+(0)$ and $r_-(0)$ values indicate that the initially excited perylene unit has the same probability to be oxidized as to be reduced. However, this does not necessary means that CS is bidirectional. Indeed, if EH were much faster than CS, the initial anisotropy of both ions bands would also be the same even if CS were unidirectional. However, our results shows that the EH time constant is around 8–9 ps, whereas a large fraction of the excited-state population undergoes CS with a 10–12 ps time constant. Numerical simulations described in the Supporting Information reveal that if CS were unidirectional, $r_+(0)$ and $r_-(0)$ would differ sufficiently to be distinguished even with EH five times as fast as CS. Consequently, both directions are operative, that is, both electron and hole transfer take place in Pe-Pr-Pe.

The break of symmetry introduced by optical excitation of Pe-Pr-Pe is not enough to favor a unique CS direction. This can be explained by the absence of dipolar interaction between the solvent and perylene in both ground and excited states. Thus, the time-averaged orientations of the solvent around Pe*-Pr-Pe and Pe-Pr-Pe* are the same. However, the instantaneous solvent orientation around Pe-Pr-Pe is not symmetrical and therefore CS is energetically more favorable in one direction than in the other. As the solvent orientation fluctuates, the preferred CS direction changes accordingly. Although solvent fluctuations have already been invoked as being at the origin of SB-CS, the present study represents a straightforward evidence of this effect.

This result should also hold for SB-CS in any multichromophoric systems with apolar units in a homogenous environment. Similarly, solvent fluctuations most probably govern the direction of CS in systems with a chromophore symmetrically surrounded by several electron donors or acceptors. On the other hand, the situation could differ with systems composed of chromophores experiencing a substantial change of electric dipole moment upon excitation. If the electronic structures of the ground and excited states are sufficiently dissimilar to polarize the solvent differently, CS should be energetically more favored in one direction.[7a] In such a case, the break of the symmetry originates from the optical excitation of one of the chromophoric units.

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