

Understanding Photoinduced Symmetry-Breaking Charge Separation

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Abstract: Symmetry-breaking charge separation (SB-CS) is a photoinduced electron transfer reaction in which the chromophore acts as both the acceptor and the donor. This reaction which is still poorly understood may enable long-lived charge separation interesting for many applications. Here we show that SB-CS can be realised bimolecularly with perylene and discuss the factors favouring it. Furthermore, using a pyrene bichromophoric system, we discuss the influence of interchromophore coupling and how the photophysics can be fine-tuned to yield SB-CS over other processes such as excimer formation.

Keywords: Electron transfer · Excimer · Interchromophore coupling · Photochemistry · Transient absorption spectroscopy



Johannes Wega earned his BSc in chemistry from the University of Göttingen in 2020, focusing on chiral molecular beam scattering experiments under the supervision of Dr. Tim Schäfer. He completed his MSc in physical chemistry at Uppsala University in 2022, researching the photochemistry of iron complexes with NHC ligands in Prof. Reiner Lomoth's group. Since November 2022, he has been pursuing

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1. Introduction

Photoinduced electron transfer (PET) is the key step in many light-based applications such as organic photovoltaics,^[1] OLEDs^[2] or photoredox catalysis.^[3] Distinct donor (D) and acceptor (A) molecules are often used in such systems. After absorption of a photon, one of them is promoted to an excited state and a subsequent charge separation (CS) step yields the desired charged species D^{+} and A^{-} . To harvest these charges, it is then necessary for the ion pair to separate. However, charge recombination (CR) frequently ensues immediately after CS, leaving no time for the ions to separate, thus rendering any applications inefficient (Fig. 1, left).

An interesting alternative is to employ a molecule M that itself can simultaneously act as both the D and A (Fig. 1, right). The resulting PET, $M^{*} + M \rightarrow M^{+} + M^{-}$, is typically termed photoinduced symmetry-breaking charge separation^[4,5] (SB-CS). Many molecules do not fit the energetic requirements for SB-CS to take place (see below). However, those which do^[4,6–9] often have a rather low driving force for CS. Although the rate of the electron transfer step is expected to be smaller in this case, most of the light energy is stored in the ion-pair state and not dissipated thermally. An additional benefit is that CR becomes more exergonic (Fig. 1). As CR is typically located in the Marcus-inverted region, this

means that its rate is expected to be slowed down compared to conventional PET, leaving more time for the charges to separate.

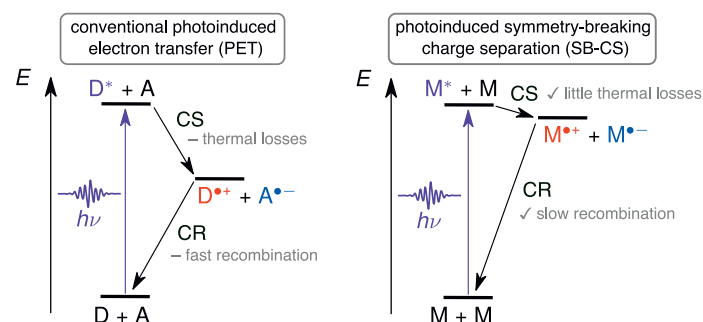


Fig. 1. Energetic schemes of conventional photoinduced electron transfer, shown exemplary for the donor being excited, (left) and symmetry-breaking charge separation (right).

However, SB-CS is not only interesting from an applications point-of-view but also from a fundamental one. At first glance, one might think that this reaction should not take place as it would have zero driving force when relating the oxidation/reduction potentials and excited state energy merely to the HOMO and LUMO energies.^[4] In reality, however, several molecules exhibit an intrinsic exergonicity for this reaction in polar media. This arises from an intricate balance between Coulomb and exchange contributions to the excited-state energy,^[10] as well as differences in solvation energy between the reactant and product states.^[11] It will thus be of interest to elucidate the electronic properties favoring SB-CS.

2. Bimolecular SB-CS

Even though SB-CS has been observed intramolecularly in a variety of multi-chromophoric systems,^[5,12] reports of bimolecular SB-CS, where the resulting ion pairs have the chance to dissociate, have been scarce. One molecule which shows an intrinsic driving force for SB-CS according to the Weller equation^[4] is perylene (Pe, chemical structure shown in Fig. 2). Indeed, the great majority of systems in which SB-CS was observed intramolecularly are based on perylene-diimide chromophores.^[6,13–16]

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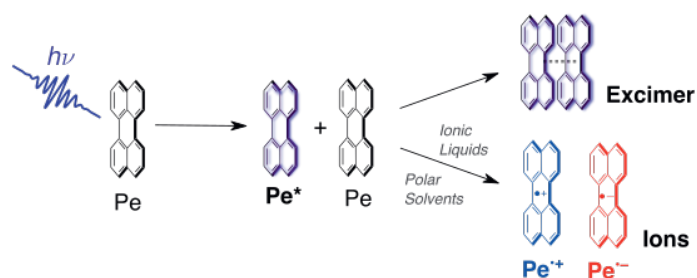


Fig. 2. Photochemistry of perylene in a concentrated solution, highlighting the competition of excimer formation and SB-CS in polar media. Fig. adapted from ref. [21].

Bimolecular SB-CS is challenging to study due to the high concentrations (mM – M) needed for M^* to diffusionally encounter a M molecule during its lifetime, which for typical organic chromophores lies in the lower nanosecond range. At such high concentrations, problems related to inner-filter effects or aggregation/solubility issues complicate spectroscopic investigations.

Nevertheless, reports of the occurrence of SB-CS in concentrated solutions of Pe in polar solvents range back to the 1970s–1980s.^[17–19] In these studies, the prompt appearance of the characteristic absorption bands^[20] of Pe^+ at 540 nm and Pe^- at 580 nm several microseconds after pulsed laser excitation of concentrated solutions of Pe in acetonitrile was observed. The formation mechanism of the ions from the excited singlet state Pe^* (lifetime ~ 5 ns) could, however, not be elucidated due to the lack of time resolution in the flash photolysis experiments at the time.

In a recent study,^[21] we reinvestigated bimolecular SB-CS with Pe using transient absorption (TA) spectroscopy with sub-nanosecond – microsecond time resolution.^[22] We utilized five solvents of increasing polarity and mM solutions of Pe. At these concentrations, no aggregation was evident in the absorption spectra. The TA spectra for the least polar solvent (toluene, TOL) and the most polar solvent (acetonitrile, ACN) are shown in Fig. 3. Initially, both spectra are dominated by the absorption of Pe^* at around 700 nm. Concurrent with its decay during the first few nanoseconds is the rise of a broad structureless absorption band at around 600 nm which persists for roughly 20 ns. This band could be attributed to the perylene excimer^[23] which can be described as a complex in the excited state in which the excitation is equally delocalized over both chromophoric units ($Pe \cdots Pe$)*. Additional to the excimer band, the characteristic bands of Pe^+ and Pe^- appear in ACN, which are absent in the TOL solution. These bands decay on the microsecond timescale and thus correspond to separated ions that recombine non-geminately.

Indeed, we only observed these ion features in the polar solvents, acetone, acetonitrile and dimethylsulfoxide. This highlights the importance of polar solvation of the ion-pair state to render SB-CS exergonic in this system. On the other hand, the estimated yield of free ions normalized to the quenching efficiency was rather low with values not exceeding 15 %.

Most interestingly, we observed a significant increase in the ion yield in room-temperature ionic liquids (RTIL). This observation might appear counterintuitive as these liquids are very viscous, thus making diffusion of Pe and Pe^* less efficient. However, during the lifetime of Pe^* the diffusion rate has not reached its stationary state, making quenching much faster^[24] than one might expect. Additionally, we observed a much less intense excimer peak in the TA spectra. To form the excimer, the two Pe molecules need to come into close contact and π -stack. Electron transfer on the contrary does not require a well-defined orientation and can happen over a variety of distances.^[25] We therefore propose a competition between excimer formation and SB-CS (Fig 2.). Moreover, one needs to consider that RTIL are essentially liquid

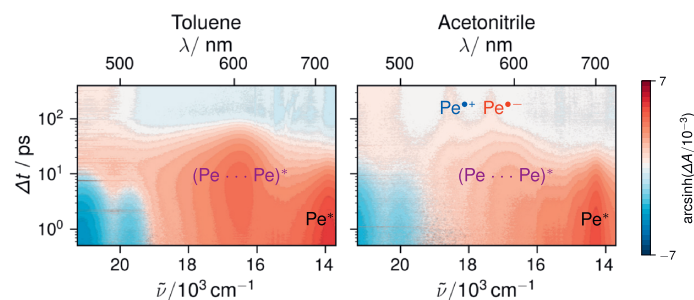


Fig. 3. Nanosecond transient absorption spectra of concentrated solutions of perylene in toluene (left) and acetonitrile (right). Data taken from ref. [21].

salts with molar ionic strengths. Indeed, simulations suggest that high ionic strengths increase the ion separation yield. This occurs first due to charge screening, which reduces Coulombic attraction between Pe^+ and Pe^- , facilitating their escape from the solvent cage into free ions. Second, a high ionic strength destabilizes the ion pair state, slowing down the CR rate by making CR more exergonic.

3. Fine-Tuning SB-CS

As seen for the Pe system, SB-CS is not the only photoinduced reaction that might take place upon the encounter of M^* and M. Other processes^[5,26] such as excimer formation (see previously) or singlet fission ($^1M^* + ^1M \rightarrow ^3M^* + ^3M^*$) might occur, reducing the efficiency of SB-CS. The question that arises is whether one would be able to finetune the interaction of M^* and M to favor SB-CS over one of these other processes.

To investigate this question in more detail, we studied a bichromophoric system where two pyrene (Py) molecules are attached to a crown-ether backbone.^[27] Upon binding cations of different sizes into the crown, the average distance between the two Py moieties is altered. Molecular dynamics (MD) simulations indicate that when no cation is bound, the two Pys are close to one another and preferentially π -stacked (see Fig. 4). On the other hand, when the relatively large Ba^{2+} is bound, π -stacking is disrupted and the average distance between the two Pys is increased substantially. The middle ground can be achieved when binding the smaller Mg^{2+} , resulting in Py-Py distances between these two extremes.

This has profound consequences for the photophysics of these complexes. Already the stationary absorption and emission spectra show significant differences. In Py_2 , the emission spectrum is dominated by the characteristic excimer emission band of Py. On the other hand, for $Py_2 \subset Ba^{2+}$ the emission spectrum is governed by a band that resembles the emission from a single Py

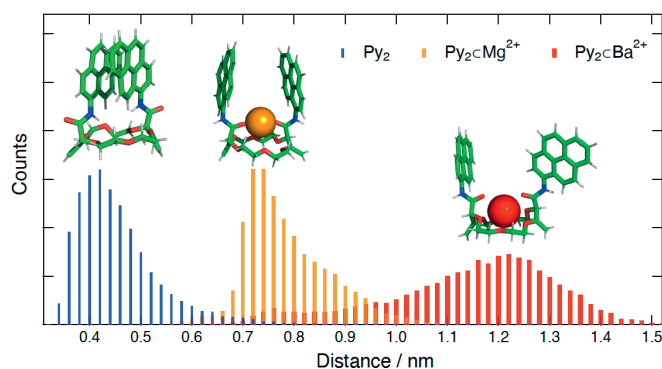


Fig. 4. Classical molecular dynamic simulations of the center-of-mass Pyrene-Pyrene distance in a crown ether bichromophore with different or no cations bound in the crown. Reprinted (adapted) with permission from ref. [27]. Copyright 2024 American Chemical Society.

monomer. For $\text{Py}_2 \subset \text{Mg}^{2+}$, both excimer and monomer emission bands are observed, highlighting the distribution of possible structures (Fig. 5).

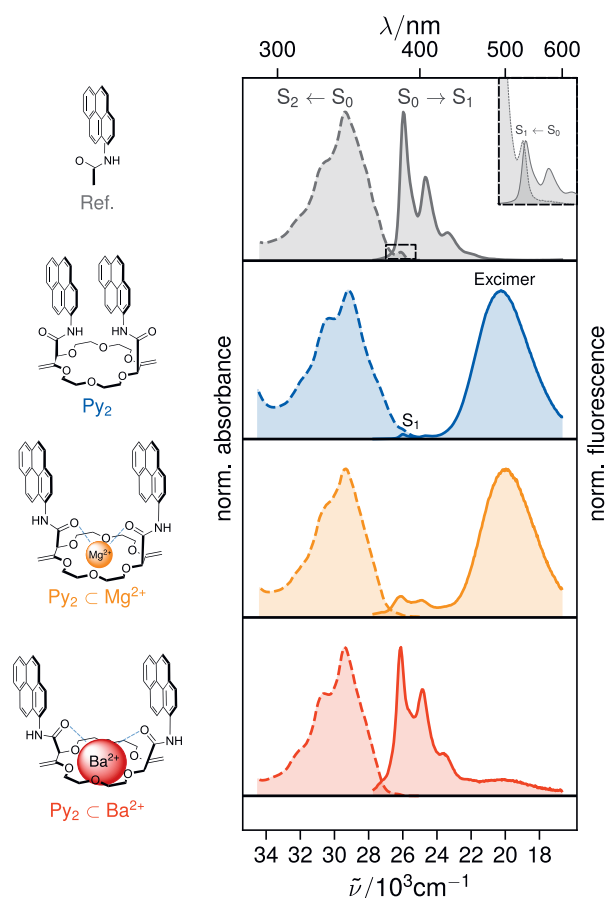


Fig. 5. UV-vis absorption and emission spectra of the different pyrene chromophores. Reprinted (adapted) with permission from ref. [27]. Copyright 2024 American Chemical Society.

To investigate the photophysics in more detail, we measured the TA spectra of these complexes from the femto- to microsecond timescales. Upon excitation of the first allowed transition which for Py is the $S_2 \leftarrow S_0$ transition, internal conversion to the S_1 state is observed on the sub-picosecond timescale^[28] for all systems (see Fig. 6). For $\text{Py}_2 \subset \text{Ba}^{2+}$, the two Pys do not communicate with each other and the excitation remains on a single Py. On the other hand, for the π -stacked Py_2 , the excitation which is initially localized on one Py quickly delocalizes over both Pys in less than 10 ps yielding the Py excimer. For $\text{Py}_2 \subset \text{Mg}^{2+}$, the characteristic bands of the Py radical ions start to appear after roughly 1 ns. As expected for SB-CS, the resulting ion-pair state is relatively long-lived at ~ 43 ns even in this intramolecular system.

These results were surprising, as Py is the hallmark example^[29] of excimer formation and in many multichromophoric Py systems the photophysics is solely governed by its excimer.^[30,31] Here, on the contrary, the interchromophore coupling could be fine-tuned in such a way that, for $\text{Py}_2 \subset \text{Mg}^{2+}$, the average geometry still allows for communication between the two Pys and subsequent electron transfer. However, the Py-Py distance was not sufficient for effective excimer formation.

4. Conclusions

SB-CS is an interesting reaction from both a fundamental as well as from an applications point-of-view with advantages over traditional PET. We could show that SB-CS can be realized in a

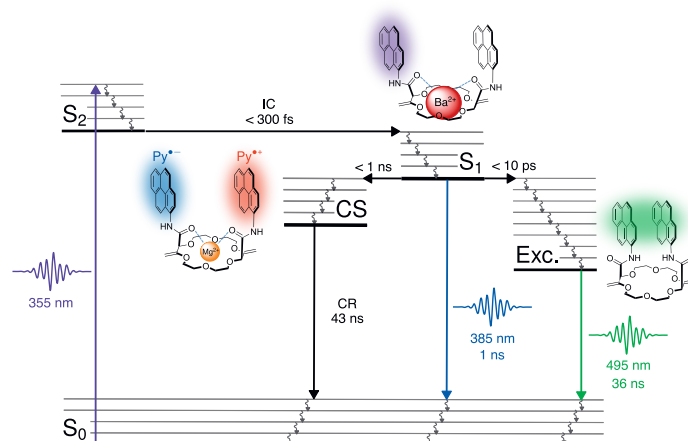


Fig. 6. Jablonski diagram summarizing the distinct photophysical pathways in the pyrene bichromophore due to the different magnitude of the interchromophore coupling for each system. Reprinted (adapted) with permission from ref. [27]. Copyright 2024 American Chemical Society.

bimolecular fashion with Pe in which the resulting radical ions can separate. A polar environment and a high ionic strength were shown to favor SB-CS. Excimer formation, on the other hand, reduces the efficiency of SB-CS.

To enhance the efficiency of SB-CS it is thus of interest to block excimer formation. Using a bichromophoric system with structural control based on Py, we showed that excimer formation can be blocked and the photophysics guided towards SB-CS. This was achieved by fine-tuning the interchromophore distance to find a geometry for which electron transfer is possible, but excimer formation is not.

Future systematic investigations are needed to elucidate the electronic and structural factors leading to SB-CS.

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