

Photoinduced Symmetry-Breaking Charge Separation

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Molecular systems where several apparently equivalent charge separation pathways exist upon photoexcitation are presented. They encompass MQ_n ($n \geq 2$) architectures, where M is a chromophore and Q an electron transfer quencher (either donor or acceptor), and M–M systems where M acts as both electron

donor and acceptor. In all cases, charge separation involves symmetry breaking. The conditions for such process to be operative as well as the origin of the symmetry breaking are discussed.

1. Introduction

When having to choose among several equivalent possibilities, one either tosses a coin or scrutinise each possibility until a difference appears. What happens at the molecular level? The topic of this Minireview is precisely to discuss cases where several apparently equivalent photoinduced charge separation (CS) pathways are possible, known as symmetry-breaking (SB) CS reactions.

The most known example of SB–CS is probably that occurring in the reaction centre (RC) of photosynthetic bacteria. In this type II RC, a pair of bacteriochlorophylls (P) is surrounded by two identical branches of protein-bound cofactors, A and B, as illustrated in Figure 1. The optical energy, initially captured by the light-harvesting complexes, is trapped by P, triggering a sequence of electron transfer (ET) processes occurring on time scales ranging from less than 1 ps to hundreds of μ s and resulting in the reduction of the B branch quinone.^[2,3] Although the RC is quasi-symmetric, it was found, mainly by EPR spectroscopy, that only the A branch is active.^[4] The origin of

this asymmetry has been the object of many discussions and studies.^[5] Although the arrangement of the cofactors in the RC does not have perfect C_2 symmetry, the structural differences between the two branches cannot account for the observed 200:1 ratio of the CS activity. The environment is known to greatly influence the dynamics of charge transfer processes. In the case of the bacterial RC, it consists of two homologous membrane proteins, L and M, which, although similar, do not have identical sequences, thus altering the symmetry of the A and B branches. Mutations of the residues close to cofactors were found to substantially affect the CS dynamics.^[6] In fact, the slightly asymmetric environment of P results in a net charge transfer character of its lowest singlet excited state,^[7] demonstrating the crucial role of the environment in SB–CS processes.

We do not further address natural photosynthetic systems, but concentrate on photoinduced SB–CS in chemistry. Two main classes of SB–CS processes are distinguished (Figure 2): 1) those occurring in $M-Q_n$ ($n > 1$) systems, where M is a chromophoric molecule and Q are identical quenchers, either electron donors (D) or acceptors (A), and where several equivalent CS pathways are present, like in the RC, and 2) those occurring between two identical molecules, M, and where two equivalent CS directions exist, that is, electron or hole transfer from

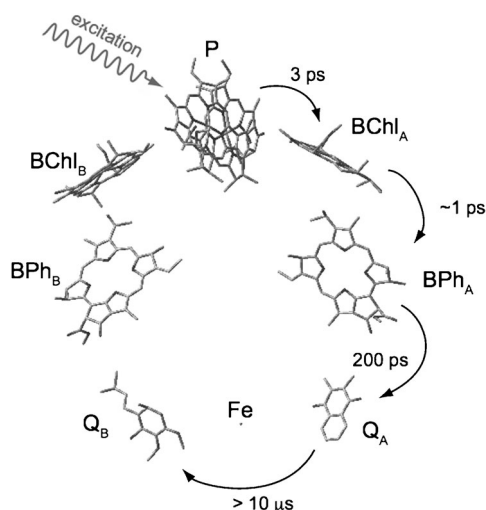


Figure 1. Reaction centre of *Rps. viridis*.^[1] P: special pair, BChl: bacteriochlorophyll, BPh: bacteriopheophytin, Q: quinone and typical time constant for CS in type II reaction centres (for clarity, only the cofactors without their bulky substituents are shown).

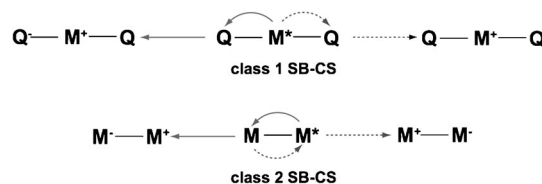


Figure 2. Two classes of photoinduced SB–CS processes (Q was arbitrarily chosen to be an electron acceptor).

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M* to M. We further distinguish between inter- and intramolecular cases. Before this, we briefly discuss the most important concepts underlying photoinduced ET processes. Some similarities could be found between class 2 SB-CS and charge transfer in mixed-valence systems, which generally consist of two identical chemical moieties at different oxidation states. There is, however, a fundamental difference: mixed-valence systems are charged and have a degenerate ground state, for example, M–M⁺ and M⁺–M, whereas the systems that are discussed herein have a non-degenerate neutral ground state but a degenerate CS state. There is also a class of excited mixed-valence systems with non-degenerate ground state and degenerate excited state, but, contrary to the molecules discussed here, they are ionic, and thus their excited states are not CS states.^[8] Mixed-valence systems have been discussed in several recent reviews,^[9–11] and will thus not be further considered hereafter.

2. Photoinduced Electron Transfer Basics

We will mostly discuss photoinduced CS processes, namely ET taking place between two neutral reactants, with one in an electronic excited state, and yielding a pair of radical ions. However, most ET processes obey the same general principles. The best criterion to estimate the feasibility of a photoinduced CS is to consider its free energy, using the Weller equation [Eq. (1)] (Figure 3).^[12]

$$\Delta G_{\text{CS}} = e[E_{\text{ox}}(D) - E_{\text{red}}(A)] - E^* - \frac{e^2}{4\pi\epsilon_0\epsilon_s d_{\text{DA}}} \quad (1)$$

where E_{ox} and E_{red} are the oxidation and reduction potentials of D, and A, respectively, and E^* is the energy of the excited state. The last term accounts for the Coulombic interactions between two ions produced at a distance d_{DA} and screened by the solvent with a static dielectric constant ϵ_s . Equation (1) is strictly valid in polar solvents. When going to a non-polar solvent, the driving force decreases by typically 0.3–0.4 eV.

The CS rate constant can be estimated using Marcus theory,^[13–15] which, in its classical formalism, considers CS as a thermally activated process [Eq. (2)]:

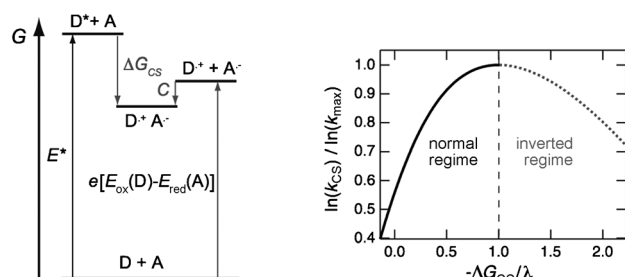


Figure 3. Left: Energy level scheme pertaining to a photoinduced CS. Right: Free energy dependence of the CS rate constant calculated using Equation (3) [Eq. (2) predicts the same behaviour in the normal regime].

$$k_{\text{CS}} = \frac{2\pi}{h} V^2 (4\pi\lambda k_B T)^{-1/2} \exp\left(-\frac{(\Delta G_{\text{CS}} + \lambda)^2}{4\lambda k_B T}\right) \text{ only if } -\Delta G_{\text{CS}} \leq \lambda \quad (2)$$

where k_B is the Boltzmann constant, V the electronic coupling between the initial and final states, and λ the reorganisation energy. The latter is usually partitioned in two parts, that is, $\lambda = \lambda_s + \lambda_i$, which depend on the differences in the solvent and intramolecular equilibrium coordinates of the reactant and product states.^[13] For typical organic reactants in polar solvents, λ_s and λ_i are of the order of 1 and 0.4 eV, respectively. When $-\Delta G_{\text{CS}} < \lambda$, the argument in the exponential function, which represents the barrier height, decreases as $-\Delta G_{\text{CS}}$ approaches λ . As a consequence, the CS rate constant increases (Figure 3); this is the *normal* regime. When $-\Delta G_{\text{CS}} = \lambda$, the barrier vanishes and k_{CS} has its maximum value. A further increase in the driving force leads to the reappearance of an activation barrier and to a decrease of k_{CS} . This is known as the *inverted* regime. However, this classical equation is no longer valid when $-\Delta G_{\text{CS}} > \lambda$, because it totally neglects nuclear tunnelling, which plays a predominant role in this regime. In this case, CS is no longer thermally activated but should rather be viewed as a non-radiative transition between two electronic states. As a consequence, the CS rate constant can be expressed in a Fermi Golden Rule form [Eq. (3)].^[16]

$$k_{\text{CS}} = \frac{2\pi}{h} V^2 FCWD \quad (3)$$

where $FCWD$ is the Franck–Condon weighted density of states.^[13,16,17] According to Equation (3), the inverted regime is equivalent to the free energy gap law observed for non-radiative transitions and is fundamentally different from that predicted from Equation (2), where CS remains thermally activated, except at $-\Delta G_{\text{CS}} = \lambda$. A practical difference is that the inverted regime is less pronounced than that predicted by Equation (2) (Figure 3).

Experimentally, most photoinduced CS processes take place in the normal regime where Equation (2) can be applied. The inverted regime has been observed for intramolecular photoinduced CS,^[18] but not for intermolecular CS. In the latter case, the observed quenching rate constant increases with increasing driving force until it becomes diffusion-limited and remains constant even at high exergonicity.^[19] The origin of this behaviour is still debated.^[20] The inverted regime is mostly observed with charge recombination (CR) processes,^[21,22] because the free energy gap between the charge-separated state and the neutral ground state is usually quite large, that is > 1.5 –2 eV.

As solvent stabilisation of the CS product is often required to make the process energetically favourable, CS can in principle not be faster than solvation. In order to take into account the finite response of the solvent that limits the CS dynamics, Equation (2) should be multiplied by Equation (4).^[15]

$$A_s = \left(1 + \frac{4\pi V^2}{h\lambda_s} \tau_s\right)^{-1} \quad (4)$$

where τ_s is the dielectric relaxation time of the solvent. The response of most solvents is biphasic, with an ultrafast component of the order of 100 fs due to the inertial motion of the solvent molecules and a component associated with diffusional motion that slows down with increasing solvent viscosity.^[23] For a "fast" solvent such as acetonitrile, the average response time is around 250 fs and, thus, unless the electronic coupling is high, that is, $V > 100 \text{ cm}^{-1}$, the solvent response can be neglected. The average response time of more viscous solvents can be as large as several tens of picoseconds and, in this case, the CS dynamics may become solvent controlled even at moderate electronic coupling. Practically, this means that the measured ET rate constant is essentially equal to the inverse of the solvation time.

3. SB-CS in M-Q_n ($n > 1$) systems

We characterise the systems according to the electronic coupling, V , between M and Q, where M and Q are acting either as D or A. The coupling depends on the DA distance, and for linked systems, on the nature of the bridge. At large distances and/or with saturated bridging units, the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) are almost entirely localised on D and A, respectively, and V is small. As the DA distance is reduced and/or with a conjugated bridge, both HOMO and LUMO "spill" onto the A and D fragments, respectively, and V increases.

An overlap of the frontier MOs results in a non-vanishing dipole moment for the optical transition from the ground state to the CS state, thus to the existence of a distinct charge-transfer (CT) absorption. The CT state can thus be directly populated by optical excitation and can relax radiatively to the ground state. As coupling decreases, the oscillator strength of the CT band as well as the radiative rate constant for CT emission decrease and tend to zero. Full CS is only possible when the orbital overlap is small and thus in the weak coupling limit. When CS is not complete, one usually refers to a CT state rather than to a CS state.

3.1. Strongly Coupled Systems

Over the past few years, a substantial number of molecules containing one electron-donating (or accepting) and several accepting (or donating) moieties have been synthesised, mostly toward the development of efficient two-photon absorbers. It is now well-established that molecules undergoing a large change of quadrupolar or octupolar moment upon photoexcitation, such as systems with a D-A_n or A-D_n ($n = 2$ or 3) motif, exhibit a large cross section for two-photon absorption.^[24] In principle, such changes in the electronic distribution imply an equal CT in the two or three arms of the molecule and thus a delocalisation of the CT excitation over the whole molecule. The nature of the excited state of these multi-branched push-pull systems has been the object of several investigations.^[25–27] For example, the solvatochromism of donor-substituted triarylboranes of the A-D₃ type (**1**, Figure 4) has been found to be similar to that of a triarylborane with

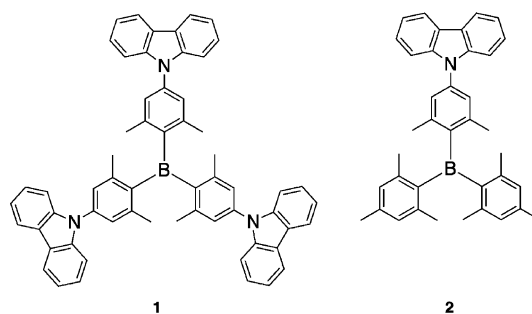


Figure 4. A-D₃ (**1**) and A-D (**2**) arylboranes.^[29]

a single donor (**2**).^[25] It was thus concluded that the CT state is mainly localised on one arm. A similar conclusion was drawn with subporphyrins having three D or A substituents.^[28] This localisation of the CT excited state was comforted by ultrafast transient absorption measurements of **1** and **2**.^[29] Comparison of the dynamic Stokes shift of the stimulated emission spectrum pointed to a substantially faster solvation of **1** compared to **2**.^[29] This difference was ascribed to a fast hopping of the excitation energy from one branch to another on a time scale faster than solvent relaxation. On the other hand, solvent relaxation leads to a localisation of the CT state on one branch, hence to SB. The stationary fluorescence anisotropy of **1** and other D-A₃ molecules in rigid polar glasses was found to depend on the excitation wavelength and to increase from about 0.1 to almost 0.4 by going from the blue to the red edge of the S₁←S₀ absorption band.^[25,30] Whereas a 0.1 value is consistent with a planar octupolar chromophore or with a very fast excitation energy hopping over the three coplanar arms, a 0.4 value indicates that emission only occurs from the initially excited branch. The red-edge effect has been invoked to explain this dependence of the anisotropy, with the low-energy side of the S₁←S₀ absorption band stemming from molecules already distorted in the ground state.^[30] Thus the transition energies of the three branches of these distorted molecules are no longer identical. Therefore, the SB mechanism that leads to a localisation of the CT state in these systems, that is, solvation of the excited state or distortion of the ground state, depends mainly on the rigidity of the molecule. However, it is rather clear that further spectroscopic investigations, for example time-resolved fluorescence anisotropy, are needed before a complete understanding of the nature of the excited state of these molecules is obtained.

Transition metal complexes like Ru(bpy)₃²⁺ can also be considered as D-A₃ systems, especially when photoexcitation in the metal-to-ligand charge transfer (MLCT) band is concerned. The location of the MLCT excitation in such complexes is highly debated: is the excited electron distributed equally over the three ligands or is it localised on a single one? According to Stark effect measurements of the MLCT band, the initially populated excited state of Ru(bpy)₃²⁺ is highly dipolar,^[31] pointing to a localisation of the excited electron on a single ligand immediately upon photoexcitation. A similar conclusion was obtained from the depolarisation ratio of resonance Raman bands.^[32] However, polarised transient absorption re-

vealed an anisotropy decay from ~ 0.55 to 0.4 with a time constant ranging from 60 to 170 fs depending on the solvent.^[33] From this, it was concluded that the excited state is initially fully delocalised over the whole molecule, and that the anisotropy decay reflects its localisation on a single ligand assisted by inertial solvent motion. Recent hybrid DFT/classical molecular dynamics simulations revealed that, in the gas phase, the excited electron is delocalised over the three ligands of $\text{Ru}(\text{bpy})_3^{2+}$.^[34] However, directly after excitation in aqueous solutions, the electron is either localised on a single ligand or equally shared by two ligands, the hopping time between these two states being of the order of 500 fs. These contradictory conclusions clearly call for further investigations of the nature of the $\text{Ru}(\text{bpy})_3^{2+}$ excited state.

The question of localisation has also been addressed with other transition metal complexes.^[35,36] For example, the lowest electronic excited state of the titanium metallocene $(\text{Cp})_2\text{Ti}^{\text{IV}}(\text{NCS})_2$ is a triplet ligand to metal CT state, $^3\text{LMCT}$. Excitation of this band involves a transfer of electronic density from the NCS^- ligands to the metal atom. Time-resolved IR measurements indicate that both NCS^- contribute equally to the CT.^[35] Thus in this case, the $^3\text{LMCT}$ state is delocalised on both ligands and symmetry is preserved upon excitation. Whether such delocalisation is general for $^3\text{LMCT}$ states is still an open question.

3.2. Weakly Coupled Systems

Over the past years, investigations of bimolecular photoinduced ET have been conducted in reacting solvents in order to eliminate the diffusion of the reactants that masks the intrinsic CS dynamics. In this case, the excited chromophore is surrounded by many quenchers, in principle giving rise to several equivalent CS pathways (Figure 5). The first measurements performed with Nile Blue in an electron-donating solvent, *N,N*-dimethylaniline (DMA), showed non-exponential fluorescence quenching dynamics dominated by a ~ 100 fs lifetime.^[37] Ultrafast fluorescence decays in anilines were found with other chromophores, such as oxazine, rhodamine and coumarins.^[38,39] The CS rate constant was assumed to be equal to the decay rate constant, that is, $k_{\text{CS}} = k_{\text{d}}$, and was typically of the order of $(0.1\text{--}1\text{ ps})^{-1}$. This $k_{\text{CS}} = k_{\text{d}}$ assumption implies that only one of the surrounding anilines can act as quencher, the others serving merely as solvent. This is equivalent to assume

an absence of symmetry in the reactant state that consists of the excited chromophore surrounded by anilines (Figure 5).

An alternative interpretation of the ultrafast fluorescence decay is to assume that the reactant state is fully symmetric and that each surrounding aniline has the same probability to quench the excited molecule. In this case, the fluorescence decay rate constant is $k_{\text{d}} = N_{\text{D}}k_{\text{CS}}$, where N_{D} is the number of surrounding donors. As N_{D} is typically between $12\text{--}17$, this implies that the CS rate constant is smaller by at least one order of magnitude than the fluorescence decay rate constant. Molecular dynamics simulations showed that among the $13\text{--}16$ DMA molecules surrounding a coumarin, around $3\text{--}4$ have, at any moment, a distance and orientation relative to the coumarin that yields a sufficiently large electronic coupling for ultrafast CS.^[40] The faster fluorescence dynamics recorded with cyanoperylene than with perylene in DMA could be explained by a larger number of reactive DMA with cyanoperylene ($\sim 3\text{--}4$) than perylene (~ 1) because of dipole–dipole interactions.^[41] As a consequence CS in electron donating solvents or at high quencher concentration (≥ 1 M) can also be considered as a SB process. However, the structure of the reactant state and thus the number of efficient quencher molecules are changing constantly. As a consequence, a precise determination of the CS rate constant in such systems is not really feasible.

This difficulty can be overcome by covalently binding several quenchers to a chromophore, so that the number of CS pathways is better defined. One such system (**3**, Figure 6) consists of an oligophenylethynyl (OPE) rod decorated with ten core-substituted naphthalenediimides (cNDIs).^[42] The visible absorption spectrum of **3** contains bands around 540 nm and 405 nm due to electronic transitions localised on the cNDI and OPE units, respectively (Figure 6). Femtosecond transient absorption measurements in polar solvents have shown that the same CS state, with the electron on a cNDI and the hole on the OPE, is populated independently on whether a cNDI or the OPE core is initially excited.^[42] However, whereas the CS dynamics upon cNDI excitation is biphasic with an average time constant of 4.5 ps, it proceeds with a 100 fs time constant upon OPE excitation (Figure 6). The biphasic nature of CS upon cNDI excitation was ascribed to the flexibility of the molecule, which allows for a distribution of relative DA orientations. Although the faster CS upon OPE excitation could be partially explained by a driving force larger by ~ 0.5 eV, the SB nature of CS, with the excited donor surrounded by ten identical acceptors, was invoked as the major factor.^[42] Thus, increasing the number of accepting or donating groups around a chromophore is an efficient approach to accelerate the CS dynamics without affecting the lifetime of the CS state.

Similar effect is also expected in other systems with a chromophores linked to several quenching units, like for example D–A–D triads consisting of a perylenediimide (PDI) with two covalently or hydrogen-bonded oligo(*p*-phenylene vinylene) (OPV) units, and developed for the elaboration of supramolecular n/p-heterojunctions.^[43] Unfortunately, the CS dynamics was only measured upon excitation of one OPV unit, where the CS time constant was of the order of 500 fs, but not of the

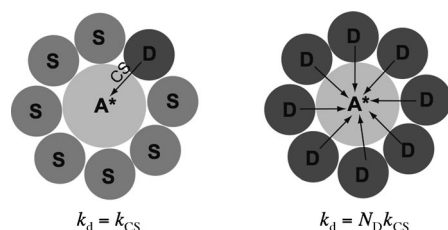


Figure 5. Two limiting interpretations of the fluorescence decay of an excited acceptor in an electron donating solvent: only one (left) or all (right) surrounding molecules are active.

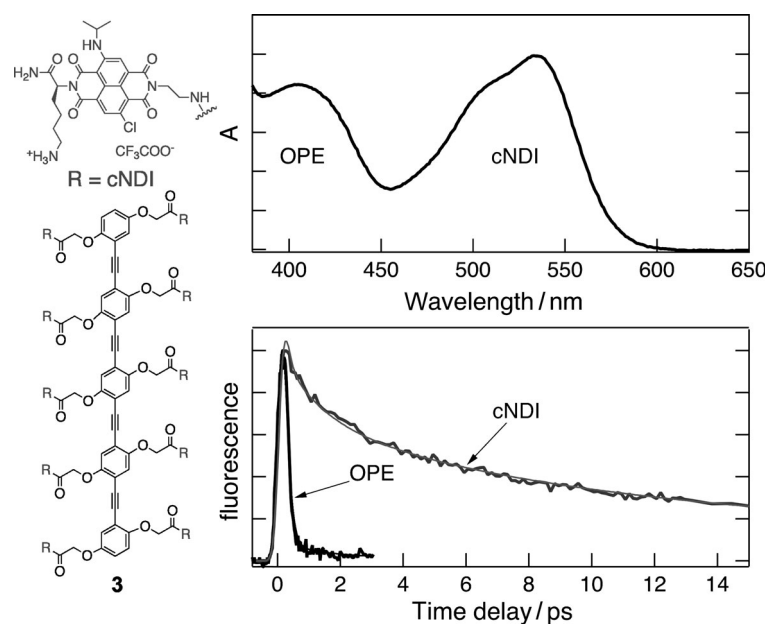


Figure 6. Absorption spectrum the OPE-cNDI multichromophoric system **3** (top) and fluorescence dynamics of the OPE and cNDI units (bottom).^[42]

central PDI, where even faster CS could be anticipated. More recently, photoinduced CS in a D''-D'-A-D'-D'' pentad has been compared to that in A-D'-D'', where A is the chromophore and D' and D'' are primary and secondary acceptors.^[44] The time constant for CS to D''-D'-A⁻-D''⁺-D'' (or D''-D''⁺-A⁻-D'-D'') was found to amount to 3.2 ps, that is, about twice as small as the CS time constant in the A-D'-D'' triad, in agreement with the SB nature of this process in the pentad, with two equivalent CS pathways. Along the same line, the initial CS in a (A)₂-D'-D'' system, where D' is the chromophoric unit, a ruthenium complex, and D'' is a Mn₂ complex, was found to take place from D' to one A, a NDI unit, with 10 and 30 ns time constants.^[45] This process was then followed by an ultrafast ET from D'' to the oxidised Ru complex, to give a long-lived CS state. No comparison with an A-D'-D'' system was performed to evaluate the effect of the presence of two A on the CS dynamics.

4. SB-CS between Identical Molecules

4.1. When is CS between Two Identical Molecules Possible?

Photoinduced SB-CS between two identical molecules M is usually considered as uncommon. In fact, the condition for this process to be possible is that ΔG_{CS} is negative. Table 1 shows a list of calculated values for several commonly used organic chromophores. In general, ΔG_{CS} does not depart strongly from zero, and is slightly negative in many cases. This should not be surprising, considering that E_{ox} and E_{red} are closely connected to the HOMO and LUMO energies, respectively, and that their sum should reflect the HOMO-LUMO gap (Figure 7A). Thus, if the excited state involved in the SB-CS is due to a one-electron HOMO-LUMO transition, E^* should not be far from

$e(E_{ox} - E_{red})$. Therefore, the energy of the $M + M^*$ and $M^+ + M^-$ states should be essentially the same (Figure 7B). This is however a very crude approximation, which neglects the differences in solvation energy and in electrostatic energy associated with the Coulombic and exchange integrals. As a consequence, photoinduced SB-CS between two identical molecules should not be considered as an uncommon reaction in polar solvents. On the other hand, this process is not expected in a non-polar environment.

4.2. Intermolecular SB-CS

Two types of intermolecular SB-CS can be distinguished:

- 1) Those where both reactants are excited:
 $M^* + M^* \rightarrow M^{*+} + M^{*-}$;
- 2) Those where only one of them is excited:
 $M^* + M \rightarrow M^{*+} + M^-$.

The first intermolecular SB-CS reported was of the first type and was observed in an anthracene crystal.^[46] Upon irradiation in the 415–455 nm region,

Table 1. Energetic parameters for photoinduced SB-CS between two identical molecules. The term C in Equation (1) has been neglected for the calculation of the driving force.

M	$E_{red}^{[a]}$	$E_{ox}^{[a]}$	E^* [eV]	ΔG_{CS} [eV]
	-2.55	1.91	4.5	-0.04
	-2.5	1.8	3.97	0.33
	R=H: -1.97 R=phenyl: -1.94 R=CN: -0.98	1.09 1.22 1.89	3.3 3.2 2.9	-0.24 -0.04 -0.03
	-2.09	1.16	3.33	-0.08
	-1.66	0.98	2.83	-0.19
	x = NHCH(CH ₃) ₂ : -0.81 x ₁ = NHCH(CH ₃) ₂ , x ₂ = Cl: -0.72	1.14 1.53	2.0 2.33	-0.05 -0.08
	M=2H: -1.21 M=Zn: -1.42	2.0 0.82	1.94 2.1	0.35 0.14

[a] in V vs SCE from refs. [50–52].

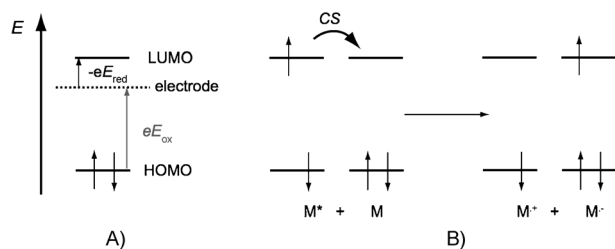
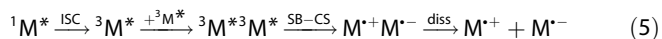


Figure 7. A) Relationship between the redox potentials and the HOMO–LUMO gap and B) MO level scheme illustrating CS between M^* and M .

a transient photocurrent whose intensity scaled with the illumination intensity was measured. This process, subsequently observed in other polyaromatic hydrocarbon (PAH) crystals, was explained in terms of singlet–singlet exciton annihilation, that is, as resulting from the encounter of two excitons diffusing in the crystal.^[47]

Later on, photocurrents were reported in polar solvents with PAHs, such as anthracene, pyrene and phenanthrene.^[48] The relatively slow rise of the photocurrent, the small concentration of excited PAHs and their short S_1 state lifetimes were incompatible with the singlet–singlet annihilation (SSA) mechanism observed in crystals. Instead, a triplet–triplet annihilation (TTA) process was proposed, the triplet state lifetime of PAHs in solution being long enough to allow a significant probability for the encounter of two excited molecules [Eq. (5)]:



The quantum yield of free ion formation per triplet–triplet encounter was generally small, typically of the order of 10^{-3} – 10^{-2} in THF.^[49] It is however not clear whether these yields are due to the inefficiency of the SB–CS process or of the ion-pair dissociation. Moreover, the intrinsic rate constant of the CS step could not be established because the rate-determining step of the whole process is the diffusional encounter of the excited molecules. Therefore, no dynamic information on the SB–CS is available.

The exact mechanism of the SB–CS upon TTA has not been discussed in detail in these studies. TTA proceeds generally through energy transfer between two molecules in the T_1 state, producing eventually one molecule in the S_1 state and the other in the ground state. For molecules that have a S_1 lifetime shorter than about 10 ns, TTA is the only efficient way to generate a $^1M^*M$ encounter complex at small to moderate concentrations. Depending on the driving force, SB–CS could then take place between $^1M^*$ and M . Alternately, the interaction of $^1M^*$ with M can lead, in some cases, to the formation of an excimer (MM^*). Excimers can be described by a linear combination of excitonic states, that is, MM^* and M^*M , and charge-transfer states, M^+M^- and M^-M^+ . Therefore, the dissociation of the excimers into M^+ and M^- could also be a possible mechanism.

Figure 8 compares the conventional TTA that eventually results in $^1M^*M$ with SB–CS TTA, directly yielding M^+M^- with a simple MO level picture. Both processes are closely related,

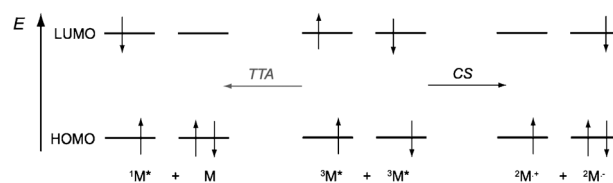


Figure 8. MO level schemes illustrating conventional triplet–triplet annihilation (TTA) and SB–CS between two molecules in the triplet state.

the first involving an electron exchange and the second an electron transfer. The driving force for CS upon TTA can be calculated using Equation (1) with E^* equal to twice the T_1 energy. Apart from a very few exceptions, the S_1 energy is substantially smaller than twice the T_1 energy, and consequently the driving force for CS upon TTA is considerably larger than that for CS between $^1M^*$ and M . Thus SB–CS between two identical molecules in the triplet state should be quite common, at least in polar solvents.

This has been confirmed with a series of ketones, including benzophenone, quinones and thioxanthone, in acetonitrile.^[53] The photocurrent was found to rise on the $\sim 1 \mu s$ time scale upon excitation within the $S_1 \leftarrow S_0$ absorption band. The rise time was measured to shorten with increasing either excitation intensity at constant ketone concentration, or ketone concentration at fixed excitation intensity, in agreement with SB–CS upon TTA. In this case, a SB–CS mechanism in $^1M^*M$ can be reasonably excluded because of the short S_1 lifetime of the ketones, typically a few ps. The origin of the small free-ion yield, $\sim 2\%$, could be either due to a slow CS compared to energy transfer in the $^3M^*^3M^*$ pair, or a fast CR of the $M^+M^{\cdot-}$ pair relative to its dissociation into free ions. Unfortunately, direct access to the dynamics of the processes occurring in the $^3M^*^3M^*$ pair is not possible because of the slow production of these pairs by the diffusional encounter of weakly concentrated molecules in the T_1 state.

Intermolecular SB–CS with only one excited reactant is much scarcer. To our knowledge, the only case reported so far is for perylene (Pe) in polar solvents. Although the exact mechanism responsible for the formation of Pe^+ and Pe^- has been debated somewhat,^[54–57] it is now accepted that these two ions are generated by SB–CS between one Pe in the S_1 state and the other in the ground state and that direct photoionisation of Pe can additionally produce Pe^+ . The efficiency of latter process is of the order of 5% whereas that of SB–CS is only around 2%.^[57] This small value can be due to the low probability of encounter between $^1Pe^*$ and Pe within the ~ 5 ns lifetime of $^1Pe^*$. Such SB–CS is not observed with others PAHs like anthracene or pyrene, for which encounter between $^1M^*$ and M results in dimerisation or excimer formation, respectively.

4.3. Intramolecular SB–CS

We now consider intramolecular SB–CS between two identical moieties of a molecule starting with the strongly coupled systems, where CS is only partial and results in a CT state, and fin-

ishing with weakly coupled systems, where the ensuing CS is mostly complete.

According to theory,^[58] the *trans*-to-*cis* photoisomerisation of an olefinic double bond requires first a partial SB–CS, a “sudden polarisation”, to reach the intermediate state upon $\sim 90^\circ$ rotation around the C–C bond. Time-resolved microwave conductivity measurements on tetraphenylethylene have evidenced a transient dipole moment as large as 7.5 D in non-polar solvents, inverting its direction every few picoseconds.^[59] This inversion corresponds to the transition between the two degenerate zwitterionic states. Subsequent femtosecond pump–probe experiments indicate that in polar solvents the zwitterionic state is stabilised by solvation.^[60]

Tetraphenylpentatetraene (**4**, Figure 9) can be viewed as a bichromophoric molecule with two equivalent and mutually orthogonal π systems. Although **4** is symmetric, electrooptical absorption measurements have revealed that, in non-polar solvents, the Franck–Condon S_1 state has a permanent electric dipole moment of 1.6 D.^[61] SB was proposed to be associated with different configurations of the phenyl groups at both ends of the cumulene chain making the two π systems inequivalent. However, the amount of CT in the excited state is relatively modest as a full CS on the distance of one cumulenenic double bond (~ 1.3 Å) would yield a dipole moment of about 5.5 D.

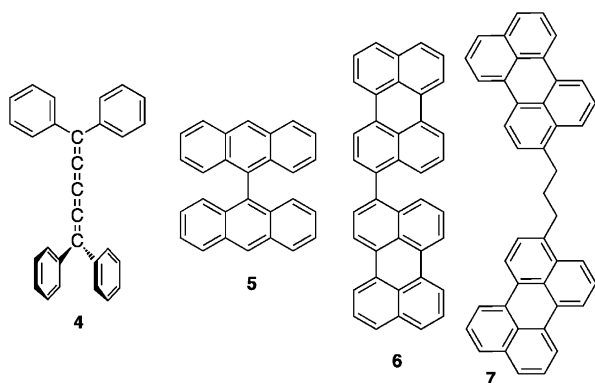


Figure 9. Examples of simple model systems undergoing intramolecular SB–CS.

Bianthryl, BA (**5**, Figure 9) is most certainly the most studied bichromophoric molecule with SB–CS properties.^[62] SB–CS in BA was first deduced from the substantial solvent dependence of the shape and position of the fluorescence band,^[63] and of the fluorescence quantum yield (0.94 in hexane and 0.22 in acetonitrile) and lifetime (7.3 in hexane and 25.8 ns in acetonitrile).^[64] These effects point to different emitting states: locally excited (LE) state in non polar solvents, where excitation is mostly on a single anthracene, and CT state in polar solvents. This was confirmed by transient absorption measurements that showed that the transient spectrum of BA in non-polar solvents is essentially the same as that of anthracene, whereas in polar solvents it is a combination of the spectra of anthracene radical cation and anion and of the LE state.^[65] However,

the two ions could not be really distinguished because of their similar spectra. These studies also showed that, in polar solvents, the CT is populated from LE state on a time scale that is close to that of solvent relaxation. Time-resolved microwave conductivity indicated that, even in a non-polar solvent, the relaxed S_1 state of BA has a dipole moment of about 5 D, much smaller than that of the CT state estimated to be around 20 D.^[64] This electric dipole flips with a ~ 2 ps period. This inversion is associated with solvent density fluctuations that lift the degeneracy of the M^+-M^- and M^--M^+ states and induce SB. In polar solvents, SB is also thought to stem from solvent fluctuations, that, at a given time, make CS in one direction more favourable than in the opposite direction. Once CS has taken place, solvent relaxation stabilises further the CT state. Investigations in molecular jets have revealed that the presence of a single acetonitrile molecule around BA suffices to break symmetry and to bring the CT state below the LE state.^[66] BA also undergoes ultrafast SB–CS when adsorbed on porous glass. In this case, the adsorption itself has been proposed to induce SB in the ground state.^[67]

SB–CS also takes place when the two anthracenes are separated by a larger distance, that is, in bianthryl–methane and –ethane. In the first case, however, the intensity of the CT state signal was found to increase quadratically with the excitation intensity and thus, the authors proposed a mechanism where both anthracenes are in their local S_1 state, undergo ISC and conformational changes to form a so-called “bicimer” in which SB–CS takes place.^[68] This hypothesis, mainly based on transient spectra recorded 20 μ s after 308 nm excitation, contradicts the observation of ultrafast SB–CS in BA. It is also at odds with a subsequent study with bianthrylethane in polar solvents where SB–CS was found to be ultrafast as well.^[69] The decay of the CS state was also observed to be very fast and to lead to the population of an excimer and not of the ground state. This new channel probably arises from the ethyl bridge, that is flexible enough for the anthracene moieties to adopt an appropriate mutual orientation.

As intermolecular SB–CS between one perylene (Pe) in the S_1 state and the other in the ground state is operative, the same can be expected between two covalently-linked Pe. Like bianthryl, the shape of the fluorescence spectrum of biperylenyl (**6**, Figure 9) depends substantially on the solvent, pointing to a LE or CT nature of the S_1 state in non-polar and polar solvents respectively.^[71] Increasing the length of the spacer leads to a decreased coupling between the Pe units and allows full CS. Recent ultrafast measurements on biperylenylpropane (**7**, Figure 9) revealed that SB–CS in acetonitrile follows a biphasic dynamics with ~ 10 and ~ 100 ps components, in agreement with the flexibility of the propyl bridge that allows the Pe units to adopt several mutual orientations and distances.^[70] Contrary to all intramolecular cases discussed so far, SB–CS was absolutely unambiguous because of the presence in the transient absorption spectra of the sharp and intense Pe cation and anion bands around 540 and 580 nm (Figure 10). Polarised transient absorption revealed that the polarisation anisotropy of both Pe cation and anion bands is the same within the limit of error, indicating that CS from the excited Pe moiety, that is,

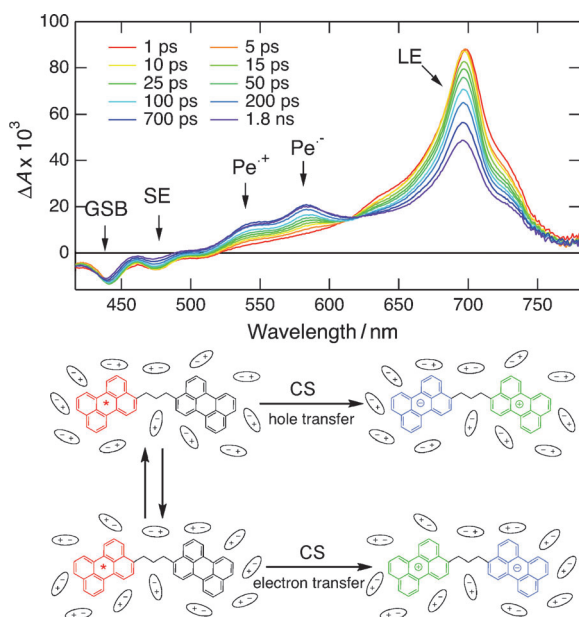


Figure 10. Top: Transient absorption spectra recorded with biperylenylpropane in acetonitrile at various time delays after 400 nm excitation (GSB: ground-state bleach, SE: stimulated emission; LE: local excited state). Bottom: The role of solvent fluctuations on the CS direction.^[70]

electron transfer, occurs with the same probability as CS in the other direction, that is, hole transfer. This is a clear demonstration that the origin of SB is not the excitation but rather the solvent configuration that, on a time scale longer than solvent motion, is mostly the same around both Pe units, but is different when considered on a shorter time scale. Thus, at a given instant, CS in one direction is more favoured than in the opposite direction (Figure 10).

Such intramolecular SB–CS is not limited to PAHs and has also been reported in directly linked perylenemonoimide (PMI),^[60] and perylenediimide (PDI) dimers in polar solvents (**8–9**, Figure 11).^[72,73] SB–CS was mainly deduced from the strong decrease of the fluorescence quantum yield of the dimers with increasing solvent polarity and from transient absorption measurements. However contrary to biperylenylpropane, the radical cation and anion could not really be distinguished in the transient spectra, but the increase of the ground-state bleach and the parallel disappearance of the stimulated emission band were convincing evidences of SB–CS. SB–CS in the PDI dimers **8** was found to take place on the 50–100 ps time scale, whereas it was substantially faster in **9** with a 4.5 ps time constant.^[74] The main difference between the **8** and **9** is the push–pull character of the latter, for which torsion of the pyrrolidiny *R'* group in the LE state could lead to SB. This could also result in different solvent orientations around the two PMI units and thus further favour CS. Smaller structural changes are expected in the PDI dimers **8** where SB should be mostly due to solvent fluctuations. This difference could explain the faster CS in **9**. Unexpectedly, in cofacially arranged PDI and PMI dimers (**10** and **11**), SB–CS occurs even in toluene.^[72,74] Such SB–CS between face-to-face PDIs has been subsequently exploited to realise a small artificial photosynthetic system com-

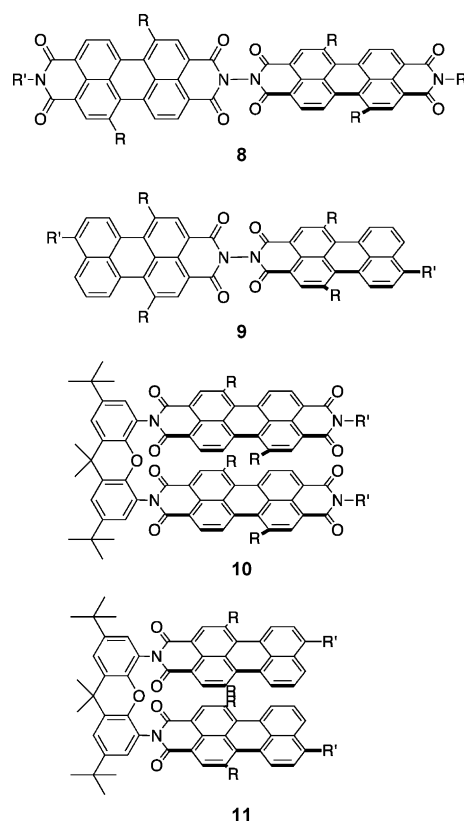


Figure 11. Dyads based on imide chromophores undergoing intermolecular SB–CS.

posed of two aggregated pentads consisting of one green PDI (with *R* = pyrrolidiny) that absorbs around 700 nm decorated with four peripheral PDIs differently substituted and absorbing around 500–570 nm.^[75]

More recently, SB–CS has also been observed between two core-substituted naphthalenediimides (cNDI) attached to a biphenyl spacer (**12**, Figure 12).^[51] In this case again, SB–CS was evidenced by a substantial shortening of the fluorescence lifetime compared to the monomeric cNDI and by the appearance of the cNDI^{•−} band around 500 nm in the transient absorption spectrum (Figure 12). The CS dynamics was strongly multiphasic because of the flexibility of the linker, and was dominated by 6 and 60 ps components. On the other hand, CR was found to occur on the 20 ps time scale (Figure 12 inset).

In all the above examples, the chromophoric units were either linked directly or with an inert bridge. However, bridge-mediated SB–CS has been observed in DNA dumbbells consisting of two stilbenediamide (Sa) chromophores separated by a double-bridge composed of adenine–thymine base pair sequences of varying length.^[76] Optical excitation of one Sa was found to result in the population of a CS state with one Sa oxidised and the other reduced. However, CS does not occur directly between the two Sa units but first takes place between the excited Sa and an adenine base that acts as a primary electron donor. The hole then hops from one adenine to another before either recombining with the electron on the initially excited Sa or being trapped by the other, unexcited, Sa. However,

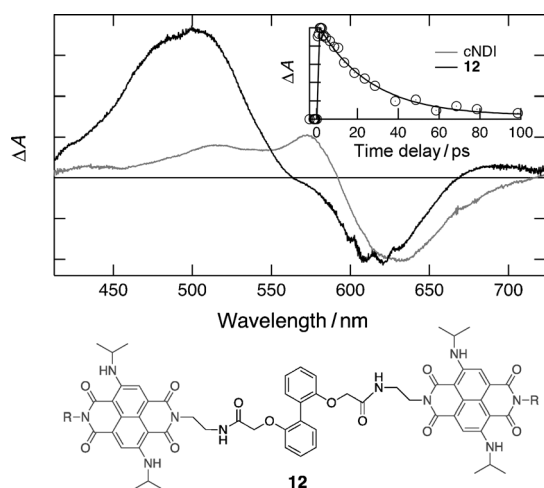


Figure 12. Comparison of the transient absorption spectra recorded a few ps after excitation of the dyad **12** and of the cNDI monomer in methanol and (inset) decay of the dyad signal at 500 nm due to the recombination of the CS state.^[51]

because of the active role of the bridge, such process cannot really be considered as a SB–CS process.

4.4. SB–CS in Large Multichromophoric Systems

SB–CS also occurs in systems containing more than two identical units. This idea can be exploited to realise artificial photosynthetic systems where the chromophores not only act as absorbers to collect light but also directly participate to the CS process. This differs considerably from natural photosynthetic apparatuses where light collection and CS take place in distinct multichromophoric assemblies, namely the light-harvesting complexes and the reaction centres. Figure 13A shows such an artificial transmembrane photosynthetic architecture resulting from the self-assembly of four multichromophoric molecules made of a paraoctiphenyl (POP) rod decorated with eight identical blue cNDIs.^[77] Excitation with red light is followed by an ultrafast SB–CS between two cNDIs.^[51] The resulting charges can either recombine on the 5 ps time scale or diffuse apart by hopping to nearby cNDIs and survive for a few hundreds of picoseconds. Instead of recombining, the cNDI^{•+} and cNDI^{•-} can be neutralised by secondary electron donors and acceptors located at both sides of the membrane.

This has been demonstrated with large unilamellar vesicles containing a quinone, the acceptor, at the interior and with EDTA, the donor, outside. Optical excitation of the tetrameric architecture located in the membrane, finally resulted in the creation of a transmembrane pH gradient upon subsequent proton transfer from water to the quinone anion.^[77]

Zipper-type self-assembly of cNDI-based multichromophoric systems with POP or oligophenylethynyl (OPE) rods on gold surfaces has been used to realise photovoltaic devices (Figure 13B).^[78,79] The characteristics of the resulting photoelectrodes were found to depend markedly on the sequence with which cNDIs of different colours (and redox potentials) were layered. From investigations of the excited-state dynamics of the multichromophoric systems in solution, it was concluded that the primary step upon optical excitation of these electrodes is SB–CS between two cNDIs. However, the electron donating ability of cNDIs decreases monotonically with increasing the energy of the first electronic transition and, for cNDIs with the first absorption band below ~550 nm, the hole, initially located on a cNDI is eventually trapped by the POP or OPE rod.^[42] Such confinement of the electric charges on distinct locations is extremely favourable for the realisation of supramolecular n/p-heterojunctions, with well-defined conduction channels for electrons and holes.

Self-organising surface-initiated polymerisation (SOSIP) has been recently used to build well-ordered architectures of π -stacked cNDIs on a transparent oxide surface.^[80,81] In the example shown in Figure 14, parallel π stacks of about 750 yellow cNDIs could be realised. The photocurrent obtained with this architecture on ITO-covered glass was much larger than with bulk polymerisation and random adsorption on the ITO sur-

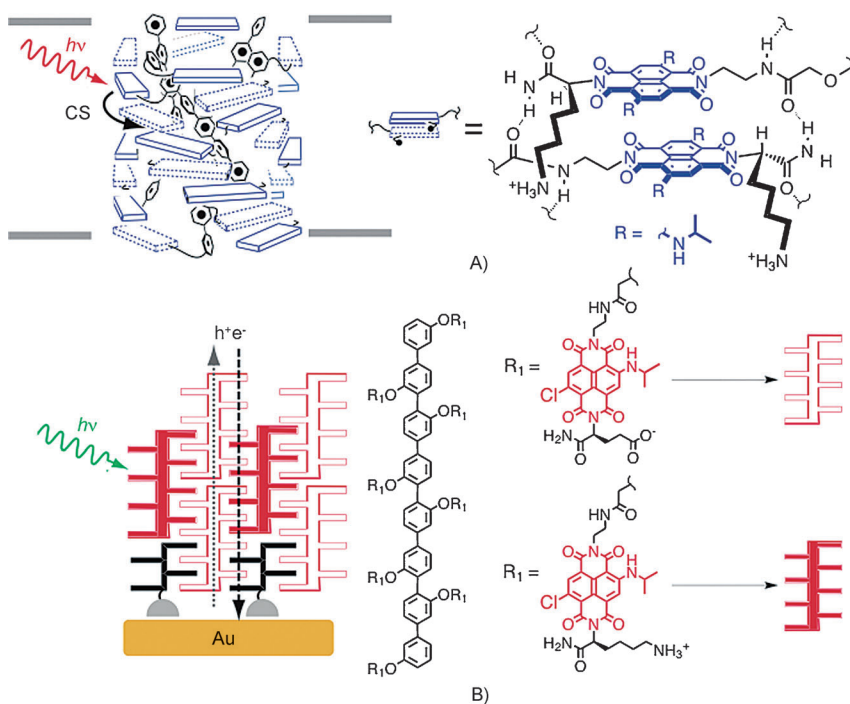


Figure 13. Self-assembled cNDI-based multichromophoric systems undergoing SB–CS for A) artificial photosynthesis^[77] and B) photovoltaics.^[78]

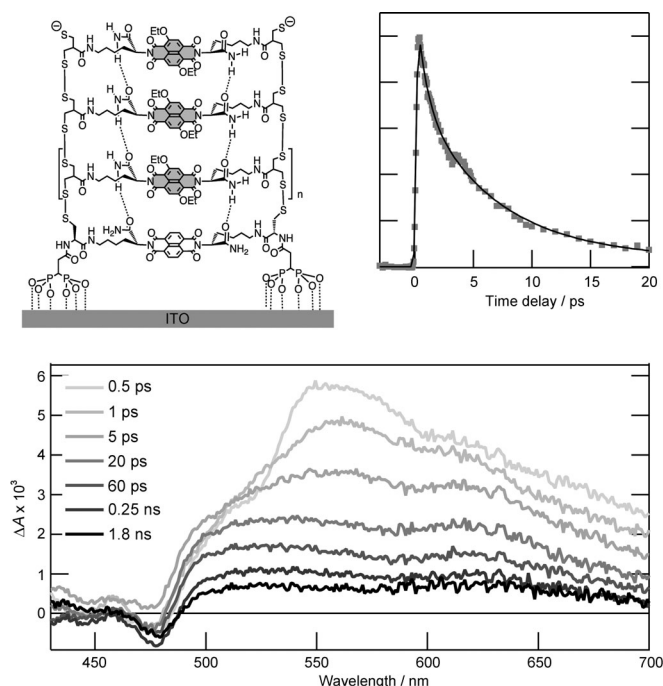


Figure 14. Fluorescence decay (top right) and transient absorption spectra (bottom) recorded upon excitation of the SOSIP architecture (top left) at 400 nm.^[80]

face. Ultrafast spectroscopy revealed the occurrence of SB-CS between two yellow cNDs following a biphasic dynamics with 0.9 and 7.8 ps time constants (Figure 14).^[80] The transient absorption spectra recorded a few ps after excitation consisted of a positive band with two maxima that could be quite well reproduced by the addition of the cNDI cation and anion spectra. The decay of these feature by CR was also biphasic with 74 ps and >2 ns time constants. SOSIP-based architectures with adjacent stacks of cNDIs of different colours have also been demonstrated.^[81] However, the excited-state dynamics in these systems, where SB-CS most probably also play a predominant role, has not been investigated so far.

5. Outlook

From the examples discussed above, one could conclude that symmetry-breaking CS is quite a misnomer. Indeed in most cases, symmetry is broken before CS itself takes place. The level at which this occurs depends on the system. In some cases, symmetry only exists on paper, but not in reality, because of the flexibility of the molecule. Therefore, the driving force and/or the reorganisation energy and, as a consequence, the barriers for the apparently equivalent CS pathways are different. Structural changes of the excited moiety have been suggested as a possible origin of SB in M–M systems. However, this aspect has still not been investigated in detail. Even if the molecule itself is symmetric, this is no longer the case when its environment is considered. A heterogenous environment, such as a protein or a surface, is an evident source of SB. However, a homogenous environment does not prevent SB. If, for example, the permanent electric dipole moment of M changes sig-

nificantly upon excitation, the solvent polarisation around the two M units is different, leading a break of symmetry that lasts as long as the excited state lifetime. Such mechanism is however not operative if M is centrosymmetric and the time-averaged orientation of the solvent molecules is mostly the same around the excited and non-excited units. However, the instantaneous orientations of the solvent around the two M are not the same and, therefore, at a given time, CS in one direction is more favourable than in the opposite direction, as demonstrated with biperylenylpropane. In this case, the CS direction alternates on the time scale of solvent fluctuations. Solvent fluctuations are also at the origin of SB–CS in “undistorted” M–Q_n systems.

Clearly more detailed investigations are needed before a comprehensive picture of photoinduced SB–CS is realised. Although the number of reports of such processes in M–M systems is still scarce, there is no fundamental reason why such process could not happen with many more molecules.

One can anticipate that, with the increasing number of new supramolecular architectures developed for various applications such as artificial photosynthesis, photovoltaics or photonics, SB–CS will be more and more advantageously exploited.

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Keywords: excitation energy hopping • multichromophoric systems • photoinduced electron transfer • photochemistry • ultrafast spectroscopy

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