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Symmetry-breaking intramolecular charge transfer in the excited state of *meso*-linked BODIPY dyads†

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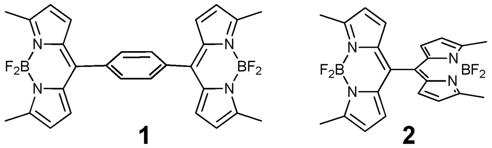
We report the synthesis and characterization of symmetric BODIPY dyads where the chromophores are attached at the *meso* position, using either a phenylene bridge or direct linkage. Both molecules undergo symmetry-breaking intramolecular charge transfer in the excited state, and the directly linked dyad serves as a visible-light-absorbing analogue of 9,9′-bianthryl.

Photoinduced electron transfer reactions are crucially important for energy storage processes in both biological and photovoltaic systems. In the photosynthetic reaction center, electron transfer from the "special pair" is preceded by ultrafast formation of an intradimer charge-transfer state *via* symmetry breaking.[1] However, model compounds capable of such symmetry-breaking intramolecular charge transfer (ICT) are largely confined to biacenes absorbing predominantly ultraviolet wavelengths.[2–4] The 9,9′-bianthryl molecule is the best studied system of this sort,[5] and the emissive nature of its excited state provides a useful probe to study the nature of symmetry-breaking ICT.

During the course of our recent studies on charge and energy transfer reactions in BODIPY–porphyrin hybrids,[6] we have prepared a series of molecules that allow the investigation of interactions between multiple covalently tethered BODIPY units. Reported here are the synthesis and unusual symmetry-breaking ICT properties of symmetrical BODIPY dyads in which the units are connected through the *meso* position either indirectly by an intervening phenylene or directly through a C–C bond. The directly linked dyad is particularly interesting as it has excited-state properties that mimic behaviour found in 9,9′-bianthryl.

The first compound investigated was a phenylene-bridged BODIPY dyad **1** (Fig. 1, synthesis is given in the ESI). A similar dyad was previously reported by Akkaya as a precursor to multichromophoric ion sensors.[7] Analysis of **1** by single-crystal X-ray diffraction reveals two coplanar BODIPY units rendered identical by a crystallographic center of symmetry (see ESI†).



1 **2**

Fig. 1 BODIPY dyads **1** and **2**.

The phenylene bridge is canted at an angle of 47° relative to the BODIPY planes, suggesting minimal steric encumbrance to partial rotation of the BODIPY units with respect to the linker. Thus, electronic superexchange, which requires interaction of the BODIPY and phenylene π-orbitals, should be possible across the phenylene bridge.

Absorption spectra of **1** in solvents of varying polarity are nearly identical to the model compound 3,5-Me$_2$BODIPY–Ph, indicating minimal ground-state interaction or excitonic coupling between the chromophores of **1** (Fig. 2). Emission spectra of **1** display small Stokes shifts that are nearly invariant in all solvents. However, the photoluminescence quantum efficiencies (Φ) vary between 0.05 and 0.1 and drop precipitously in the most polar solvents (Table 1). In contrast, for 3,5-Me$_2$BODIPY–Ph the value of Φ is 0.29 in cyclohexane, and declines to 0.17 in acetonitrile.[8] The lower values of Φ for **1** indicate the possible formation of a nonemissive charge-transfer state that entails some degree of symmetry breaking since the BODIPY units are identical. The similarity in both emission spectra (see ESI†) and Φ for a range of nonpolar and weakly polar solvents suggests that the rate of formation of the charge transfer state is not dependent on solvent polarity, up to a polarity index of 41 (Table 1).

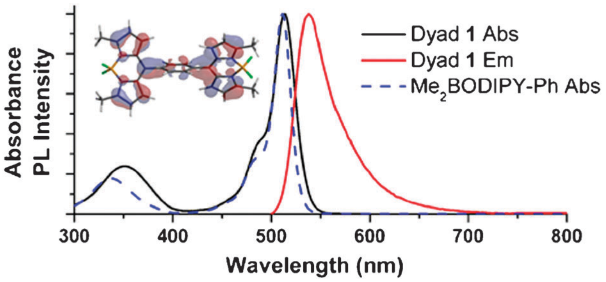


Fig. 2 Normalized absorption and emission spectra of dyad **1** and absorption spectrum of 3,5-Me$_2$BODIPY–Ph in CH$_2$Cl$_2$. The LUMO surface of **1** is also shown.

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Table 1 Photophysical properties of dyads **1** and **2** in various solvents

Solvent	$E_T(30)$[a] (kcal mol^{-1})	$\lambda_{max,abs}$ (nm)		$\lambda_{max,em}$ (nm)		Φ	
		1	**2**	**1**	**2**	**1**	**2**
Cyclohexane	30.9	513	523	538	564	0.052	0.78
Toluene	33.9	515	526	540	574	0.095	0.62
2-MeTHF	36.5	511	524	540	620	0.046	0.18
Chloroform	39.1	515	526	538	585	0.097	0.35
Dichloromethane	40.7	513	530	538	651	0.069	0.087
DMF	43.2	512	530	536	—[b]	<0.001	—[b]
Acetonitrile	45.6	508	526	531	—[b]	<0.001	—[b]

[a] Solvent polarity index.[10] [b] PL quantum yield could not be accurately determined due to overlap with BODIPY monomer impurity emission.

The potential for **1** to undergo symmetry-breaking ICT was examined by electrochemistry. Cyclic voltammetry of **1** revealed a reversible reduction ($E_{1/2}$ = −1.37 V) and an irreversible oxidation (E_{pa} = 0.94 V, both *vs.* Fc^+/Fc). The corresponding values for 3,5-Me_2BODIPY–Ph are E_{pc} = −1.5 V and E_{pa} = 0.90 V (both irreversible). The difference between oxidation and reduction values (2.31 V) of **1** indicates that the S_1 state (E_{00} = 2.38 eV in cyclohexane) should be energetic enough to undergo ICT, as previously discussed by Zander and Rettig.[9] DFT calculations (B3LYP/6-31g*) show both the HOMO (−5.68 eV) and LUMO energies (−2.88 eV) of **1** are stabilized relative to the respective values in 3,5-Me_2BODIPY–Ph (−5.51 eV and −2.56 eV). The increase in the electron affinity of **1** is likely due to delocalization across the phenylene bridge as shown in the surface contours of the LUMO (see Fig. 2 and ESI†).

Support for the formation of an ICT state in polar solvents was provided by femtosecond transient absorption measurements (Fig. 3). Excitation of **1** at 509 nm in acetonitrile populates the S_1 state, as reflected by the appearance of a stimulated emission band from 525–600 nm that matches the S_1 emission lineshape. Over the course of 10 ps, this band disappears concomitant with the rise of a weak induced absorption band peaked at 545 nm that matches absorption spectra reported for the BODIPY radical anion and cation.[11] A global fit to the data (Fig. 3b and ESI†) yields a rate of 4.8 ps for the formation of this ICT state. Subsequently, all transient spectral features decay with a rate constant of 34 ps, indicating a fast nonradiative return to the S_0 state, consistent with asymmetric dyads incorporating a BODIPY acceptor.[11] On the other hand, excitation of **1** in toluene leads to formation of an S_1 state that decays at a rate consistent with the lifetime determined from emission studies (τ = 860 ps).

The importance of twisting and other structural changes of ICT excited states in donor/acceptor molecules has been extensively explored.[3] Additionally, rotation of *meso*-aryl substituents relative to BODIPY chromophores has previously been invoked as a major pathway for nonradiative deactivation.[12] In the present case, facile rotation of the phenylene bridge in **1** is also what likely allows the ICT state to undergo ultrafast direct surface crossing to the ground state. Thus, we aimed to extend these studies using dyad **2** (synthesis is given in the ESI), with the two BODIPY units linked directly at the *meso* position, significantly restricting rotational freedom. We have been unable to obtain X-ray quality crystals of **2**, however, structure minimization using DFT (B3LYP/6-31g*) methods indicates that the planar BODIPY units of **2** have local geometries similar to those of **1**, with BODIPY units canted at a dihedral angle of 71°.

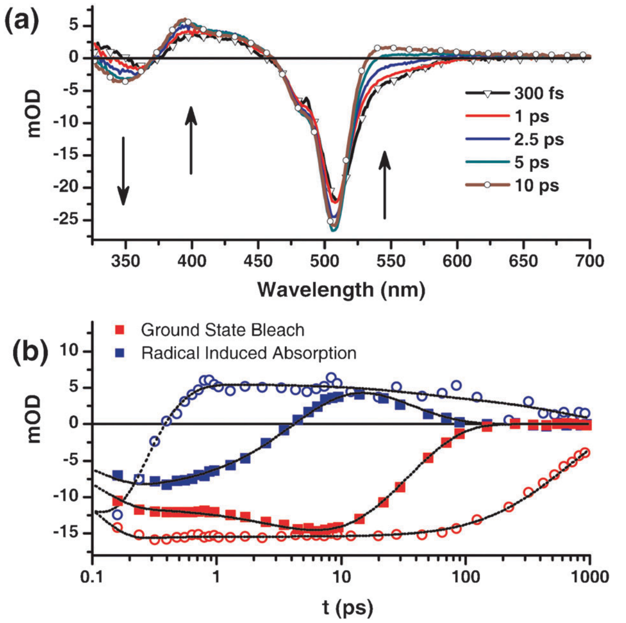

Fig. 3 (a) Ultrafast transient absorption spectra of **1** after excitation at 509 nm in acetonitrile. (b) Time domain slices of the ground state bleach (red) and BODIPY radical absorption (blue) for dyad **1** (filled squares; bleach: 507 nm x0.55, induced absorption: 550 nm x2.5) & **2** (open circles; bleach: 527 nm ×2.5, induced absorption: 590 nm) with predicted traces based on a kinetic model (dashed black).

Cyclic voltammograms of **2** in CH_2Cl_2 display two well resolved reversible reduction peaks ($E_{1/2}$ = −1.38 V, −1.19 V *vs.* Fc^+/Fc) and an irreversible oxidation peak (E_{pa} = 0.965 V *vs.* Fc^+/Fc). DFT calculations show that the HOMO energy of **2** (−5.61 eV) is similar to **1** but the LUMO (−2.97 eV) is stabilized due to conjugation across the *meso* linkage (see Fig. 4 and ESI†). The electrochemical gap of **2** ($E_{pa} - E_{1/2}$ = 2.15 V) is 100 mV less than the E_{00} energy of the S_1 state (E_{00} = 2.25 eV in cyclohexane), suggesting that the energetics are more favourable for ICT formation in **2** than for dyad **1**.

Absorption spectra of **2** are nearly invariant across several solvents and are similar to that of **1** and other BODIPY chromophores.[13] Slight splitting of the primary ($S_0 \rightarrow S_1$) absorption band at 530 nm indicates a modest degree of exciton coupling between the BODIPY units.[14] Fluorescence spectra, on the other hand, are dramatically affected by solvent. A progressive red-shift in the emission wavelength is observed with increasing solvent polarity, accompanied by a concomitant

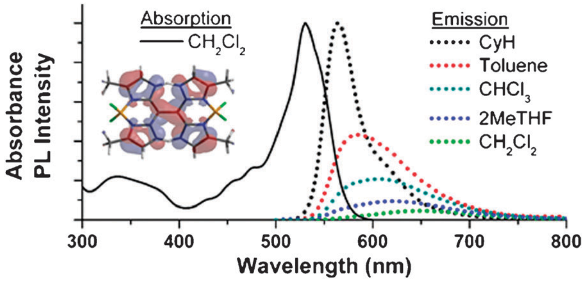

Fig. 4 Absorption spectrum of **2** in CH_2Cl_2 and emission spectra of **2** in solvents of varying polarity. The LUMO surface of **2** is also shown.

broadening and decrease in Φ (Fig. 4 and Table 1). The spectra indicate that **2** has a nonpolar ground state and a significantly higher dipole moment in the excited state, even though the two constituent chromophores are identical. Similar behaviour is observed for the 9,9′-bianthryl molecule.[5,15]

In cyclohexane, dyad **2** exhibits a simple first-order luminescence decay ($\tau = 9.3$ ns). In contrast, a biexponential decay is observed in CH_2Cl_2, comprised of a fast component (< 200 ps) accompanied by a longer-lived (*ca.* 7 ns) decay. Thus, excitation of the S_1 state in **2** leads to the population of a new emissive state. In acetonitrile, we find that the nonradiative decay rate of this new state ($k_{nr} = 1.5 \times 10^9\ s^{-1}$) is 20 times slower than that of **1** in the same solvent (see ESI). Given how the emission of **2** depends on solvent polarity, this new state likely corresponds to an emissive ICT state populated by solvent-induced symmetry breaking.[5]

Femtosecond transient absorption spectroscopy in acetonitrile was used to further illuminate the charge-transfer behaviour of **2** in polar media. The S_1 state observed upon excitation at 509 nm evolves within our experimental time resolution ($k_{IC}{}^{-1} \leq 170$ fs) to produce an excited state that absorbs at 590 nm, consistent with the formation of a BODIPY radical anion.[11] However, the spectral features associated with the ICT state of **2** persist an order of magnitude longer ($k_r{}^{-1} = 650$ ps, Fig. 3b) than those of **1**, relaxing with a rate that matches the emissive lifetime of **2** in acetonitrile (see ESI). We propose that steric congestion in dyad **2** hinders rotation to a surface crossing region, thus inhibiting nonradiative charge recombination.

Although several biacenes display similar luminescent properties,[2] to the best of our knowledge **2** represents the first example of a dyad that combines symmetry-breaking formation of an emissive ICT state with intense absorption in the visible region of the spectrum. While porphyrins are in many respects related to dipyrrins, the *meso*-linked porphyrin analogues of **2** do not undergo symmetry-breaking ICT because formation of such an excited state is endothermic with respect to the S_1 state.[16] BODIPY dyads directly linked at the α- or *β* positions also do not exhibit this sort of emissive behaviour.[17] However, Benniston *et al.* have reported a hybrid of **2** and 9,9′-bianthryl, a *meso*-linked 9-anthracenyl–BODIPY compound, that readily forms an emissive ICT state in polar solvents.[18]

In conclusion, excitation of BODIPY dyads **1** and **2** leads to formation of ICT states in polar media by solvent-induced symmetry breaking. The further presence of strong absorption at visible wavelengths enables these molecules to mimic features seen in the photosynthetic reaction center. Model systems that possess both these characteristics are rare.[4] Differing degrees of rotational freedom in the dyads significantly alter the behavior of the ICT state. Whereas dyad **1** undergoes rapid nonradiative decay to the ground state, the more hindered dyad **2** has a long-lived ICT state with moderate-to-high fluorescence quantum efficiency. The excited state properties of the dyads reported here could prove useful in facilitating charge separation in photovoltaic devices; studies that exploit these properties are currently underway in our laboratories.

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