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Electronic Communication in Closely-connected BODIPY-based Bichromophores

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ABSTRACT: A small series of closely-spaced, bichromophoric boron dipyrromethene (BODIPY) derivatives has been examined by optical spectroscopy and compared to the corresponding mononuclear dyes. The compounds vary according to the site of attachment and also by the nature of alkyl or aryl substituents incorporated into the dipyrryn backbone. Excitonic coupling splits the lowest-energy absorption transition in each case, but to highly variable degrees. There are also marked changes in the fluorescence quantum yields across the series, but much less variation in the excited state lifetimes. After comparing different models, it is concluded that the ideal dipole approximation gives a crude qualitative representation of the observed splitting of the absorption transition, but the extended dipole approach is not applicable to these systems. Agreement is substantially improved by employing a model that takes into account the dihedral angle between the planes of the two dipyrryn units. The large variation in radiative rate constants, and those for the accompanying non-radiative processes, are accountable in terms of electronic coupling and/or intensity borrowing between the two excitonic states. In all cases, the dihedral angle between the two BODIPY units plays a key role.

INTRODUCTION

The so-called “special pair” plays a critical role in natural photosynthesis,¹ being both the ultimate acceptor for photons absorbed by the light-harvesting machinery and the primary electron donor for subsequent charge separation.^{2,3} Strong coupling between the two chromophores, which are chemically identical but subjected to slightly disparate environments, favors exciton/charge delocalization around what is effectively a molecular dimer.^{4,5} Apart from experimental and theoretical studies aimed at better appreciating the nuances of the special pair, considerable attention has been given to the detailed spectroscopic examination of artificial molecular dimers.^{6–10} Notable among such studies have been dimers formed from porphyrins,¹¹ nucleobases,¹² aryl mono- and diimides,¹³ and aryl hydrocarbons.¹⁴ Many more studies have addressed the electronic properties of intermolecular¹⁵ and intramolecular excimers.¹⁶ It is recognized that the degree of electronic coupling between the two chromophores depends on the separation distance,¹⁷ their mutual orientation¹⁸ and the nature of the local environment.¹⁹ The same factors govern electrostatic interactions and are seen in the Förster theory²⁰ for electronic energy transfer. Kasha²¹ integrated these features into one of the first coherent discussions of excitonic interactions in molecular dimers and classified the orientations into several major groupings. Refinements to the general theory have been made by Gouterman,²² Davydov,²³ Katz,²⁴ and Shipman²⁵ and their coworkers, although the basic framework introduced by Kasha²¹ remains intact for dimers formed from relatively small molecules. It seems doubtful that the same approach can be applied to molecular interactions in conducting

polymers²⁶ or compact crystals,²⁷ where the nearest neighbor principle is often invoked.

Tremendous interest has been shown, over the past decade or so, in the photophysical properties of the boron dipyrromethene (BODIPY) family of dyes.²⁸ These highly fluorescent compounds have found important applications in many diverse fields and continue to attract attention.^{29–31} In certain circumstances, BODIPY dyes will aggregate in the form of either fluorescent or non-emissive entities as has been well demonstrated by Johansson et al.³² In addition, various covalently-linked BODIPY bichromophores have been reported. The latter include both face-to-face³³ and side-by-side analogues³⁴ wherein the photophysical properties are controlled by the molecular topology. Notable among these systems are the tilted molecular dimers described by Harriman et al.³⁵ and the adjacent dimers reported by Bröring et al.³⁶ We now expand the library of known BODIPY-based bichromophores to include a series of side-by-side derivatives. In most cases, the two BODIPY units are connected via a solitary C-C bond so that the mutual orientation is set by any peripheral groups and by the position of attachment. This strategy permits subtle structural effects to be examined in fluid solution using optical spectroscopy. Particular attention has been given to understanding excitonic coupling in those bichromophores where the individual transition dipole moment vectors are in-line but out-of-plane. This allows examination of how the molecular alignment, measured by way of the central dihedral angle, affects the degree of excitonic interaction along the molecular axis.

RESULTS and DISCUSSION

MATERIALS

The compounds examined in this work are illustrated in Charts 1-3 and comprise a series of chromophores based on the BODIPY nucleus and their complementary bichromophores. It might be noted that most of the compounds lack a phenylene ring at the *meso*-position and, therefore, are not to be regarded as putative molecular-scale rotors.³⁷ In certain cases, the *meso*-position is without substitution but it should be realized that the substitution pattern differs throughout the series and this effect causes minor perturbation of the optical spectra. Two of the compounds possess an aryl group at each of the 3,5-positions which, at least in the case of B3, introduces severe steric hindrance for internal rotation occurring within the bichromophore. The corresponding single chromophoric analogues, M1-M3 (Chart 1) are required as spectroscopic reference compounds. A second set of bichromophores (Chart 3) involves more sterically encumbered derivatives that carry a tolyl group at the pseudo-*meso*-position and at the 3-position (compound P1). When both the 3- and 5-positions are blocked with an aryl substituent, the coupling reaction proceeds selectively at the 2-position, providing access to compound P2.

Chart 1. Molecular formulae of the relevant single chromophore analogues used as spectroscopic markers.

Chart 2. Molecular formulae of the bichromophores prepared via oxidative homo-coupling reactions.

Synthetic details³⁸⁻⁴⁰ for these compounds have been published previously and the compounds were further purified by TLC prior to measurement of their photophysical properties. Some of the bichromophores (Chart 2) have also been reported previously.⁴⁰ These compounds are reasonably soluble in common organic solvents and are not prone to aggregation under our experimental conditions. Crystal structures have been reported for B1, B3 and P1 while M1 is well known⁴¹ in the literature. Authenticity of the remaining bichromophores was established by high-resolution ¹H- and ¹³C-NMR spectroscopy before starting the experiment.

Chart 3. Molecular formulae for the two sterically-encumbered bichromophores prepared by oxidative homo-coupling. Note these compounds bear a tolyl group at the pseudo-*meso*-position.

REFERENCE COMPOUNDS

The photophysical properties of the isolated chromophores were measured in 2-methyltetrahydrofuran (MTHF) solution and the derived parameters are summarized in Table 1. The important terms relate to absorption (λ_{MAX}) and fluorescence (λ_{FLU}) maxima in solution, the Stokes' shift (Δss) derived after spectral deconstruction into Gaussian components, and the molar absorption coefficient (ϵ_{MAX}) for the lowest-energy absorption transition. Variations in ϵ_{MAX} are offset by comparison of the corresponding oscillator strengths (f), which take into account the relative width of the absorption bands. The derived values are quite similar across the series, although there are minor spectral variations. It might be noted that aryl substitution at the dipyrroin periphery leads to a markedly increased Δss while the substitution pattern perturbs the spectral properties, as can be seen by comparing data for M1 and M2.

Figure 1. Normalized absorption (black curve) and fluorescence (gray curve) spectra recorded for M2 in MTHF solution at ambient temperature. The inset gives the energy-minimized structure computed for the ground state.

Also compiled are the fluorescence quantum yields (Φ_F), excited-singlet state lifetimes (τ_S), and the corresponding radiative rate constants (k_{RAD}) calculated from the Strickler-Berg expression.⁴² Fluorescence decay profiles were mono-exponential in each case and excellent agreement was found between excitation and absorption spectra. Typical absorption and fluorescence profiles are shown in Figure 1 for reference purposes while all the spectra are collected in the Supporting Information. Peak maxima are dependent on the substitution pattern, especially if aryl groups are attached to the dipyrroin core, but the overall properties remain within reasonably close limits. Furthermore, the results tabulated here remain in good agreement with those reported²⁸⁻³¹ elsewhere in the literature for related conventional BODIPY dyes and it should be

stressed that, in the main, these dyes are highly fluorescent and free from problems of aggregation.

The emission properties hardly change on cooling to 77K, other than a slight spectral blue-shift and a narrowing of the optical bandwidth for the transition. At room temperature, the absorption and emission spectra could be well reproduced by summation of ca. five Gaussian-shaped components of common half-width (see Supporting Information). This allows calculation of the low-frequency vibronic mode ($h\omega$) that accompanies the optical transition (Table 1). This value ranges from 530 to 800 cm^{-1} and corresponds, in generic terms, to large-scale torsional motion of the dipyrin backbone. It is interesting to note that aryl substitution at the dipyrin core induces a significant increase in the mean value. There is also a marked variation in the Huang-Rhys factor (S) derived⁴³ by fitting the emission spectrum. This value falls markedly on aryl substitution due to increased π -conjugation between the dipyrin and the aryl substituent. Indeed, there is a clear correlation between S and both λ_{MAX} and λ_{FLU} . The same effect is not seen when the aryl group is placed at the *meso*-position.

Table 1. Summary of the photophysical properties of the control compounds measured in MTHF solution at room temperature.

Property	M1	M2	M3
$\lambda_{\text{MAX}} / \text{nm}$	495	534	549
$\epsilon_{\text{MAX}} / \text{M}^{-1}\text{cm}^{-1}$	93,470	75,830	62,090
$f^{(a)}$	0.50	0.45	0.50
$\lambda_{\text{FLU}} / \text{nm}$	508	549	591
$\Delta_{\text{SS}} / \text{cm}^{-1}$	510	505	1,275
Φ_{F}	0.94	0.91	0.87
$\tau_{\text{S}} / \text{ns}$	5.6	5.5	6.4
$k_{\text{RAD}} / 10^8 \text{ s}^{-1} \text{ (b)}$	1.70	1.65	1.35
$h\omega / \text{cm}^{-1} \text{ (c)}$	580	530	800
S	0.58	0.42	0.23

(a) Oscillator strength calculated for the lowest-energy transition. (b) Radiative rate constant calculated from the Strickler-Berg expression. (c) Low-frequency vibronic mode coupled to nonradiative decay as derived from spectral deconstruction.

Quantum chemical calculations (DFT/B3LYP-6-31G(d)) carried out for the various control compounds indicate that, as might be expected, both HOMO and LUMO are distributed around the dipyrin core; Figure 2 gives a typical example while distribution patterns for all the control compounds are provided as part of the Supporting Information. It is apparent that the BF_2 unit plays no significant role in determining the electronic properties of either HOMO or LUMO. Interestingly, the *meso*-carbon atom has an important function for the LUMO but is much less significant for the HOMO. These computational studies show that the dipyrin core is planar in each case (See Table S1) and that the compounds are highly symmetrical. Computed oscillator strengths and transition dipole moments are sensitive to the nature of the substituents while the calculated wavelengths for the first-allowed absorption transitions are reasonably close to the experimental values (see Table S2). The phenyl rings are held at an average dihedral angle of ca. 50° to the plane of the dipyrin nucleus for the ground-state structures but these appended groups are free to rotate over a wide range (see Supporting Information). The ability of the HOMO/LUMO to off-load electron density to the aryl substituent depends on the relevant

dihedral angle,⁴⁴ as might be expected (See Supporting Information).

Figure 2. Kohn-Sham representations of the HOMO (upper panel) and LUMO (lower panel) computed for M2 in a solvent reservoir corresponding to a dielectric constant of 10.

ROTATION AROUND THE CONNECTING BOND

In order to obtain information about the likely molecular conformations of the bichromophores in solution, a series of DFT calculations (B3LYP-aug-cc-pVTZ) was made for the ground-state molecules; the results are provided as part of the Supporting Information. For B1, the two BODIPY units are held at an average dihedral angle of 72° but gyration about this position is essentially unhindered over a wide variance. Full rotation about the connecting C-C bond is unlikely, however, since the methyl groups impose severe steric crowding at 0° and 180° . Instead, the dihedral angle can vary between 40° and 140° with little resistance, although there is a slight barrier to attaining the mutually orthogonal geometry (Figure 3). Similar conclusions are drawn for B2A, where the average dihedral angle between the two BODIPY residues is reduced to 57° at the ground-state level. Again, steric crowding between the substituents hinders attainment of planar geometries, for 180° the problem is caused by the *meso*-hydrogen atoms, but there is a much reduced barrier for rotation around 0° . For this derivative, the mean dihedral angle lies within the range 30° to 90° .

The indirectly linked bichromophore B2B has more internal flexibility and the mean dihedral angle between the two BODIPY units is 50° at the ground state. Steric clashes between the methyl group and the second BODIPY unit introduce a substantial barrier for full rotation, while again there is a minor obstacle to attaining the orthogonal geometry. Nonetheless, the dihedral angle can vary widely and is expected to cover the range 40° to 140° at ambient temperature. Molecular dynamics simulations (MDS) carried out in a reservoir of water molecules are consistent with the above results but indicate a much narrower distribution of accessible geometries, with typical variance of 11° around the energy-minimized structure.

Figure 3. Effect of dihedral angle between the two BODIPY units on the total energy of the molecule calculated for B1 in a solvent reservoir. The inset gives an expansion of the region where the BODIPY units approach an orthogonal geometry.

The bichromophore possessing aryl substituents at the lower rim of the dipyrin unit is more prone to steric inhibition for rotation around the C-C connection. This situation serves to restrict the range over which the dihedral angle is likely to oscillate at room temperature. Thus, for B3 the preferred dihedral angle is ca. 76° but mutual gyration covers a fairly wide variance. The main steric problems are caused by clashes between the ancillary phenyl rings on the one hand and clashes between a phenyl ring and the 5-methyl group on the other. As above, the general findings were confirmed by MDS studies using periodic boundary conditions ($50 \times 50 \times 50 \text{ \AA}^3$) with a water reservoir. Here, the variation around the starting geometry was less than 10° .

The two analogues bearing *meso*-tolyl groups prefer to maintain the dipyrin units in an almost perpendicular geometry, dihedral angles being 66° and 64° respectively for P1 and P2. Both structures show slight curvature in line with the X-ray data.⁴¹ Full rotation around the connecting linkage is blocked by steric clashes between the fluorine atoms for P1 and by fluorine-tolyl interactions for P2. In the main, the structural data agree well with that derived from the crystal structures while MDS studies indicate highly restricted rotation around the connecting bonds. Further details are provided in the Supporting Information.

PHOTOPHYSICS OF THE BICHROMOPHORES

Absorption and fluorescence spectra were recorded for the bichromophores in MTHF at room temperature and the main findings are summarized in Table 2. Examples of the spectra are provided as Figure 4. In each case, absorption and emission spectra are red shifted with respect to the corresponding control compound while the fluorescence quantum yields are lowered by a significant factor. The excited-singlet state lifetimes are shortened relative to the control compounds but to a less extent than noted for the quantum yields. As a consequence there is a marked variation in the corresponding radiative rate constants. These are reduced relative to the control compounds but are now surprisingly sensitive to the structure of the bichromophore. In particular, compounds B1 and B3 remain reasonably emissive but the other compounds in the series are weakly fluorescent. As before, there is good agreement between absorption and excitation spectra and, throughout the series, the fluorescence decay profiles were well represented by single-exponential fits. The fluorescence spectra sharpen and undergo a slight blue shift on cooling to 77K but there are no major spectral changes.

Figure 4. Comparison of absorption (black curve) and fluorescence (gray curve) spectra recorded for (a) B1 and (b) B2B in MTHF solution at ambient temperature.

At room temperature, a low-frequency vibronic mode ($h\nu_L$) of around 700 cm^{-1} promotes nonradiative deactivation of the excited-singlet state (Table 2). The magnitude of this vibronic mode remains comparable to that derived for the relevant control compound. Except for B2B, the bichromophores exhibit a smaller Huang-Rhys (S) factor⁴³ than found for the control compound (Table 2). This is taken as being indicative of increased π -conjugation at the excited-state level for the bichromophoric derivatives. This is not the case for B2B, where the conjugation is broken by the sp^3 -connecting carbon atom and the derived S value is close to what might be anticipated for the corresponding control compound.

Absorption spectra recorded for the bichromophoric compounds in MTHF display increased oscillator strengths, as might be expected, and are red-shifted compared to spectra recorded for the control compounds. In fact, the oscillator strengths are roughly twice that of the control compound. Most notably for B2B, the absorption spectra display the characteristic features of excitonic splitting due to close electronic interaction between the two dipyrin units.²¹⁻²⁵ A comprehensive curve-fitting analysis based on the assumption of Gaussian-shaped components allows estimation of the splitting energy by assigning 0,0 transition energies for the lower (E_{10}) and upper (E_{20}) transitions (Table 3). The magnitude of the splitting ($\Delta\epsilon$) varies from 530 cm^{-1} for B1 to $1,630 \text{ cm}^{-1}$ for B2B. It is also evident that the relative intensities of these two transitions (A_{10} and A_{20}) vary across the series,⁴⁵ this point is exemplified by the ratio (N) of integrated absorption intensities for the two transitions; note, these intensities take into account any vibronic bands associated with the 0,0 transition. The spectra are complicated by the appearance of strong vibrational satellites accompanying the main transitions and the corresponding low-frequency modes associated with upper- ($h\nu_1$) and lower-energy ($h\nu_2$) transitions are collected in Table 3. These latter values are somewhat sensitive to the nature of the bichromophore and tend to increase for the lower transition. Figure 5 illustrates the scope of this spectral analysis, while fitted spectra for all the bichromophores are included in the Supporting Information.

Table 2. Summary of spectroscopic properties determined for the bichromophores in MTHF solution at room temperature.

Property	B1	B2A	B2B	B3	P1	P2
$\lambda_{\text{ABS}} / \text{nm}$	526	558	557	584	691	634
$\epsilon_{\text{MAX}} / \text{M}^{-1}\text{cm}^{-1}$	154,955	79,700	139,105	157,615	67,500	92,250
f	0.91	0.94	0.94	0.93	0.85	1.00
$\lambda_{\text{FLU}} / \text{nm}$	563	600	565	628	770	712
Φ_{F}	0.40	0.090	0.072	0.40	0.13	0.15
$\tau_{\text{S}} / \text{ns}$	3.8	1.9	1.8	4.0	3.4	2.1
$\Delta_{\text{SS}} / \text{cm}^{-1}$	825	1,085	365	890	690	935
$k_{\text{RAD}} / 10^8 \text{ s}^{-1}$	1.05	0.47	0.40	1.0	0.38	0.71
$k_{\text{NR}} / 10^8 \text{ s}^{-1}$	1.6	4.8	5.4	1.5	2.6	4.1
S	0.35	0.31	0.61	0.24	0.16	0.26
$h\omega_{\text{L}} / \text{cm}^{-1} \text{ (a)}$	740	735	540	725	480	425
$v_{\text{FLU}} / \text{cm}^{-1} \text{ (b)}$	17,690	16,925	17,825	16,010	13,005	13,900

(a) Low-frequency vibronic mode accompanying nonradiative decay of the excited-singlet state as derived from spectral curve fitting. (b) Maxima derived for the emission spectral profiles on the basis of spectral curve fitting.

Table 3. Parameters derived by spectral curve fitting of the absorption spectra recorded for the bichromophores in MTHF solution at room temperature.

Property	B1	B2A	B2B	B3	P1	P2
$E_{1,0} / \text{cm}^{-1}$	19,040	19,035	19,820	17,795	14,290	15,695
$E_{2,0} / \text{cm}^{-1}$	18,515	18,010	18,190	16,900	13,695	14,835
$\Delta\epsilon / \text{cm}^{-1}$	525	1,025	1,630	895	1,485	860
$A_{1,0} / \%$	73.0	56.8	44.8	78.6	70.1	70.7
$A_{2,0} / \%$	27.0	43.2	55.2	21.4	29.9	29.3
$N_{\text{EXPT}} \text{ (a)}$	2.71	1.32	0.81	3.68	2.34	2.41
$N_{(1)} \text{ (b)}$	0.04	1.83	2.36	0.02	1.24	0.06
$N_{(2)} \text{ (c)}$	2.97	1.55	1.02	3.98	2.25	2.06
$h\omega_1 / \text{cm}^{-1} \text{ (d)}$	640	550	590	705	595	660
$h\omega_2 / \text{cm}^{-1} \text{ (e)}$	720	695	500	900	705	770
$\Phi / ^\circ$	71.4	57.1	72.0	75.9	66.0	64.1
$\theta / ^\circ$	1.8	60.2	52.8	1.0	52.2	5.9
$V_{\text{OB}} / \text{cm}^{-1}$	800	500	855	930	800	975
$V_{\text{XTD}} / \text{cm}^{-1}$	8,700	2,300	1,100	6,650	3,150	10,250
$V_{\text{IN}} / \text{cm}^{-1}$	400	105	55	465	60	485
$V_{\text{NP}} / \text{cm}^{-1}$	535	55	420	640	3.5	620
$V_{\text{ANG}} / \text{cm}^{-1}$	580	1,105	1,670	685	1,285	690

(a) Ratio of integrated absorption transition intensities for direct absorption to the upper and lower excitonic bands as derived by experiment. (b) The above ratio calculated on the basis of Equation 1. (c) The above ratio calculated from Equation 1 but with the dihedral angle, Φ , replacing the angle between the transition dipole moment vectors and the corresponding distance vectors. (d) Low-frequency vibronic mode associated with direct absorption to the upper-lying excitonic state. (e) Low-frequency vibronic mode associated with direct absorption to the lower-lying excitonic state.

EXCITONIC COUPLING WITH THE BICHROMOPHORES

According to the excitonic coupling theory developed first by Kasha²¹ but extended by many others,²²⁻²⁵ interaction between the transition dipole moment vectors associated with the two dipyrin units causes a two-fold splitting of the excited-singlet state. The ratio of the relative intensities,⁴⁵ N , of the two absorption transi-

tions is expected to depend on the mutual alignment of the respective transition dipole moment vectors. In the case of perfectly aligned chromophores, one or other of these transitions is forbidden due to accidental cancellation of the transition dipole moments. Furthermore, fluorescence should occur exclusively from the lower-energy state since rapid internal conversion will be promoted by the small energy gap⁴⁶ between the two states. The vectors run down the long molecular axis of the dipyrin backbone and, in most

Figure 5. Examples of excitonic splitting of the lowest-energy absorption transition for the bichromophores in MTHF solution. The upper panel illustrates the model used for the spectral analysis while the experimental (black curve) and constructed (red curve) spectra are shown for P1 (central panel) and P2 (lower panel). Each spectrum is deconstructed into a series of Gaussian-shaped components corresponding to absorption to the higher-energy state (blue curves) and the lower-energy state (gray curves). The peak splitting ($\Delta\epsilon$) is taken as the energy gap between adjacent gray and blue curves.

cases, the two vectors run parallel to the distance vector connecting the centers of the chromophores (Figure 6). Because of steric constraints, however, the in-line transition dipole moment vectors lie out-of-plane. As such, it is instructive to enquire if the level of excitonic interaction is sensitive to the dihedral angle between the dipyrin units for these particular geometries. To do so, we first employ Equation 1, where μ_M refers to the transition dipole moment of the corresponding monochromic dye, to calculate the relative strengths (N) of the two absorption transitions. The geometry parameter, θ , refers to the mean angle between the transition dipole moment vectors and the distance vector connecting the centers of the chromophores (Figure 6).

$$N = \frac{\mu_1}{\mu_2} = \frac{\sqrt{2}\mu_M \sin\theta}{\sqrt{2}\mu_M \cos\theta} \quad (1)$$

This equation is intended for use with oblique geometries, but for B1, B3 and P2 the transition dipole moment vectors are essentially parallel. These compounds, therefore, are predicted to exhibit a value for N that is significantly less than unity (Table 3); in other words, absorption to the lower-energy transition (A_1) is strongly favored relative to direct absorption to the higher-energy state (A_2). This situation is at odds with the experimental data (N_{EXPT}) and, in fact, there is poor agreement between calculated and observed N values (Table 3). The vectors are almost orthogonal for B2B such that absorption should be primarily to the lower-energy state but, as above, this expectation does not give a proper representation of the experiment. Compounds B2A and P1 adopt an oblique geometry and agreement between calculated and observed N values is somewhat improved, but still poor (Table 3).

Notably, replacing θ in Equation 1 with the corresponding dihedral angle (Φ) between the respective dipyrin units leads to vastly improved agreement for the in-line bichromophores (Table 3 and Figure 6). This points towards a strong angular dependence for N . Indeed, the revised expression accurately predicts the ratio of the transition moments for each of the in-line compounds, although it should be stressed that the dihedral angle is subject to a variance of around $\pm 10^\circ$ in fluid solution at ambient temperature, according to the MDS studies. Even for the two oblique geometries, the insistence on a strong angular dependence leads to a better correlation between calculated and observed N values. This is not to say, however, that there is an important contribution from through-bond excitonic coupling.⁴⁶⁻⁴⁸

Figure 6. Comparison between the experimentally determined ratio of integrated absorption intensities for upper- and lower-energy transitions and the value calculated from Equation 1 with the dihedral angle replacing the angle between the transition dipole moment vectors and the distance vector. The inset illustrates the dihedral angle using red dots to signify the four carbon atoms.

It might be noted that the DFT calculations support the idea of weak interactions between the two BODIPY-based units in these bichromophores. This is evidenced by the observation that the molecular orbitals are clearly associated with each chromophore, rather than being delocalized over the entire super-molecule. There is little, if any, coupling at the ground-state level, despite the close proximity of the two units. Coupling occurs at the excited-state level to give the observed excitonic splitting.

Excitonic coupling theory²¹ predicts that the extent of the splitting of the lowest-energy absorption band ($\Delta\epsilon$) depends on the magnitude of the transition dipole moment (μ_M) of the mononuclear dye and the average distance (R_{CC}) between the centers of the respective transition dipole moment vectors (Equation 2).⁴⁹ Here, κ refers to the orientation factor representing the mutual alignment of the two vectors. In his original study, Kasha²¹ identified three key orientations in addition to the aligned geometry. Within the confines of the ideal dipole approximation,⁵⁰ these relate to oblique, inclined and non-planar arrangements of the transition dipole moment vectors (see Supporting Information for a full description of the methodology, including tabulation of the structural parameters). For an oblique geometry, the orientation factor (κ_{OB}) depends on the angle (α_{DD}) between the two dipole moment vectors and on the mean angle (θ) between each vector and the distance vector connecting the two dipole centers according to Equation 3. A similar relationship²¹ holds for the inclined geometry, where κ_{IN} is obtained from Equation 4. Exciton splitting for the non-planar geometry makes use of an orientation factor (κ_{NP}) based on the angle between the two molecular planes as illustrated by way of Equation 5. We can now calculate splitting energies for each of the three projected orientations and compare the results with the experimental data (Table 3).

$$V_{IDA} = \frac{\mu_M^2 \kappa}{4\pi\epsilon_0 R_{CC}^3} = \beta \kappa \quad (2)$$

$$\kappa_{OB} = \cos\alpha_{DD} + 3\cos^2\theta \quad (3)$$

$$\kappa_{IN} = 1 - 3\cos^2\theta \quad (4)$$

$$\kappa_{NP} = \cos\alpha_{DD} - 3\cos^2\Phi \quad (5)$$

Figure 7. Correlation between the experimentally derived peak splitting, $\Delta\epsilon$, and that calculated for a strong angular effect according to Equation 6. The upper panel shows the same correlation for the peak splitting according to the ideal dipole approximation (Equations 2-5).

None of the above orientations accurately describes the molecular geometries of the target bichromophores and the various equations fail to reproduce the experimental splitting energies. No single orientation works for all the compounds and even taking the best agreement for each individual compound does not give a reasonable qualitative trend. Replacing the point sources with extended dipoles running the length of the transition dipole moment vector⁵¹ gives rise to splitting energies (V_{XTD}) much higher than the experimental results (Table 3). Here, the problem is caused by the unusually close proximity of one pair of coordinates. Although useful in many intermolecular dimers,⁵² the extended dipole method seems inappropriate for the bichromophores studied here.

Also collected in Table 3 are the peak separations (V_{ANG}) calculated from the respective dihedral angles (Φ) between the two dipyrin planes (Equation 6). This approach leads to excellent quantitative agreement between calculated and observed splitting energies (Figure 7). In turn, this points to a strong angular dependence for excitonic coupling in these systems and it might be argued that through-bond interactions could play an important role. The results obtained with B2B, however, appear to be inconsistent with this notion. This is because the sp^3 -hybridized carbon atom present in the connecting unit will restrict through-bond interactions by imposing an additional resistance.⁵³ In fact, B2B shows the largest splitting energy and the shortest center-to-center separation distance. Nonetheless, inclusion of an angular dependence dramatically improves the agreement between experiment and calculation for these particular compounds.

$$V_{ANG} = \beta(3 - \cos^2\Phi) \quad (6)$$

It seems appropriate to enquire if the same treatment could be applied to quantify the splitting of the oxidation and reduction peaks observed in the cyclic voltammograms recorded for these bichromophores. Unfortunately, some of these processes are electrochemically irreversible and therefore it is questionable if meaningful calculations can be attempted. For the successive one-electron reduction steps, which are split in each case because of electrostatic repulsion, there is reasonable qualitative agreement between the peak splitting and the size of the excitonic splitting found for the absorption spectra. This finding suggests that there is a similar angular dependence for the Coulombic effects associated with the electrochemistry.

One remaining issue relates to the large variation in the κ_{RAD} values found for the various bichromophores in fluid solution. For mononuclear BODIPY-based dyes, κ_{RAD} depends on the magnitude of the vibronic transition moment density and the average energy of the excited singlet state,^{42,54} usually denoted by the emission maximum (ν_{FLU}). For the bichromophoric dyes, the expression needs to be modified to allow for the fact that only the lower-energy excitonic state emits. As such, we might expect the following relationship to hold for the bichromophores (Equation 7):

$$k_{RAD} = \frac{32\pi^3 n^3}{3h} \nu_{FLU}^3 |\mu_L|^2 \quad (7)$$

Here, n is the refractive index of the solvent and μ_L is the transition dipole moment for direct absorption to the lowest-energy exciton state. The experimental κ_{RAD} values do not correlate with Equation 7 and, if anything, the trend is opposite to the predicted fit (Figure 8). Replacing μ_L with the overall transition dipole moment ($\mu_T = \mu_L + \mu_U$) does not improve the quality of the fit. Somewhat unexpectedly, it was noted that κ_{RAD} increases progressively with decreasing energy gap, $\Delta\epsilon$, between the two excitonic states. This situation might be indicative of coupling between the two states and is reminiscent of earlier work by Verhoeven et al.⁵⁵ where it was reported that certain compounds displaying charge-recombination fluorescence were prone to intensity borrowing from an upper-lying excited state. Indeed, by modifying the expression for the radiative rate constant derived by Verhoeven et al.⁵⁵ for

the specific case of interest (Equation 8), it becomes possible to greatly improve the correlation between k_{RAD} and the energy gap parameter, γ (Figure 8a). Here, V^* refers to the electronic matrix element for coupling between the two excitonic states. This situation is consistent with intensity borrowing from the upper-lying excitonic state by the emissive state. To the best of our knowledge, this consideration has not been raised previously, although the situation is familiar for intramolecular charge-recombination fluorescence.⁵⁶

$$k_{\text{RAD}} = \frac{32\pi^3 n^3}{3\hbar} \frac{(V^* \mu_u)^2 v_{\text{FLU}}^3}{(\Delta\epsilon - v_{\text{FLU}})^2} = \frac{32\pi^3 n^3}{3\hbar} \gamma \quad (8)$$

Along similar lines, the corresponding rate constant for nonradiative decay (k_{NR}) does not exhibit the anticipated exponential dependence⁵⁷ on the amount of energy to be dissipated during the process. We have taken v_{FLU} as being representative of this latter term. Instead, it is found that k_{NR} shows a crude exponential dependence on the energy gap between the two excitonic states, $\Delta\epsilon$ (Figure 8b). The rate of radiationless decay tends to increase as this energy gap increases. This is the opposite of the situation found for k_{RAD} and, as a consequence, the fluorescence quantum yield shows a strong dependence on the extent of splitting between the two excitonic states. The effect observed for k_{NR} implies some mild stabilization of radiationless deactivation by way of mixing with the upper-lying excitonic state. Most likely, this overall behavior involves weak charge-transfer interactions such that state mixing introduces some degree of polarity into the lower-lying excitonic state. Indeed, in other BODIPY-based bichromophores, symmetry breaking has been observed under illumination.⁵⁸ We have not been able to detect long-lived charge-separated states in our systems but the involvement of mild charge-transfer interactions is a strong possibility.

Figure 8. (a) The upper panel shows a plot of the rate constant for radiative decay of the excited-singlet state vs the energy gap factor γ as described in Equation 8 (see Supporting Information for details). The inset shows the corresponding relationship between k_{RAD} and the energy factor in the absence of coupling to the upper-lying

excitonic state. (b) The lower panel shows a plot of the rate constant for nonradiative decay of the excited-singlet state vs the energy gap between the two excitonic states.

CONCLUDING REMARKS

Numerous studies have addressed important issues relating to excitonic coupling in bichromophoric molecules, many of which have been built around the BODIPY nucleus.^{32–36,58} Such compounds are important as simple models for the photosynthetic special pair^{1–3} but more significantly as a means by which to extend the opto-electronic properties of emissive dyes. The bichromophore might be considered to provide a facile way to increase the Stokes shift,³⁶ for subsequent applications in cytometry, microscopy and photon concentrators. Related compounds have been proposed for electro-generated chemiluminescent probes.^{40,59,60} In this contribution we have examined the optical properties of bichromophores that do not fall naturally into the categories identified by Kasha²¹ during his pioneering work on excitonic coupling. In certain cases, the transition dipole moment vectors appear to be aligned in a parallel manner and this should eliminate direct absorption to one or other of the two excitonic states. This is not seen experimentally because, in our case, the dihedral angle between the planes extended by the chromophores is not close to zero. This introduces a strong angular dependence for the optical properties that might be further exploited to optimize the molecular electronic properties. An interesting observation to emerge from this work is that the fluorescence quantum yield is sensitive to the extent of splitting of the excitonic bands. Again, this effect might be manipulated to obtain new dyes with advanced optical properties.

ASSOCIATED CONTENT

Supporting Information. Contains experimental details and information about the computed geometries for all compounds, Kohn-Sham orbital representations, absorption and emission spectra for the dyes, tabulated output from the DFT calculations, plots of how the dihedral angle affects the total energy of the system, deconstructed spectra showing the underlying Gaussian components, explanations of the alignment of the transition dipole moment vectors and plots for k_{NR} vs energy gap. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ABBREVIATIONS

DFT, density functional theory; NMR, nuclear magnetic resonance spectroscopy; TLC, thin-layer chromatography.

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