Nonradiative Decay Channels for a Structurally-Distorted, Mono-Strapped BODIPY Derivative

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ABSTRACT: A boron dipyrromethene (BODIPY) derivative has been synthesized whereby a phenoxy ring attached at the 3-position is bound through the oxygen atom to the boron center. This compound is structurally distorted, with the molecular surface being curved, and undergoes further geometrical perturbation at the excited-singlet state level. Fluorescence is readily observed in solution at ambient temperature, with the quantum yield rising with increasing viscosity of the surrounding solvent. Dual-exponential decay kinetics are observed, corresponding to E-type delayed fluorescence. In solution, the emission yield falls with increasing temperature but the opposite situation is found for the same compound dispersed in an amorphous sugar. These results are considered in terms of two radiationless decay channels. A viscosity-dependent avenue allows the fluorophore to function as a conventional fluorescent rotor for tracking changes in local rheology. A temperature-dependent channel leads to trapping within a new conformation, which is weakly coupled to the ground state but is able to repopulate the emitting state on a relatively slow timescale. Analysis of the experimental data allows estimation of some of the key kinetic parameters as a function of temperature.

INTRODUCTION

The term “fluorescent rotor” refers to a fluorophore that undergoes an environmentally sensitive conformational exchange which permits the emission intensity to report on changes in the local conditions.¹⁻⁴ A popular fluorescent sensor is one where changes in rheology, most notably viscosity, can be assessed simply by monitoring the emission quantum yield. Many such molecular systems have been described in recent years,⁵⁻⁸ including those based on the well-known boron dipyrromethene (BODIPY) fluorophore.^{7,8} In this latter case, the normal conformational vector involves gyration of a *meso*-aryl ring around an unconstrained dipyrroin backbone.⁸ One way to rationalize the observed behavior is to invoke the concept that steric clashes between adjacent hydrogen atoms cause rupture of the potential energy surface for the excited-singlet state, introducing pinholes⁹ which facilitate rapid return to the ground state. Frictional forces between the rotating aryl ring and the surrounding medium serve to modulate the ease of gyration and provide the means by which to couple the emission quantum yield to changes in local viscosity. At a microscopic level, rotation of the *meso*-aryl ring causes slight buckling of the upper rim of the dipyrroin unit⁸ and it is this structural modification that underpins the sensory behavior. Alkyl substituents attached to appropriate sites on either the rotor or the dipyrroin upper rim dampen these structural oscillations and minimize the rotor effect.¹⁰

Surprisingly, attaching aryl groups to the lower rim of the dipyrroin unit also modulates the sensory properties but

in a most unexpected manner.¹¹ Thus, the 3,5-diaryl-BODIPY derivative is a poor rheology probe but the corresponding mono-functionalized 3-aryl derivative is the most effective BODIPY-based rotor identified to date! This finding poses a challenge to the conventional appreciation of the mechanics of the rotary behavior. In attempting to improve understanding of this situation, we note recent work¹² has established that the 3-aryl ring can be fixed in place by attaching it to the boron center via a C-O-B strap. In so doing, a new radiationless decay channel is opened that leads to delayed fluorescence from the BODIPY chromophore. The present report explores this deactivation process by recording the emission properties as a function of the fluidity of the surrounding medium. It is found that, relative to the corresponding rotors lacking the strap,¹¹ the photophysical properties are complicated by competing structural changes. These findings might be useful in terms of designing highly specific fluorescent rotors for monitoring environmental change.

RESULTS and DISCUSSION

Structural Details

The target compound, BDFO (Figure 1), was synthesized¹² and purified as reported previously. The computed (B3LYP/6-311G(d)/PCM/CHCl₃) geometry indicates that the dipyrroin unit is severely distorted, in good agreement¹² with the X-ray crystal structure (Supporting Information). In particular, the dipyrroin unit is curved and has the general appearance of a hemispherical dome since curvature is clearly apparent for both the dipyrroin and the strapped aryl ring (Figure 1). Distortion is also evident around the boron

Figure 1. Chemical formula for the target compound, BDFO, and examples of the computed (B₃LYP/6-311G(d)/PCM/CHCl₃) energy-minimized geometry.

center, with N-B-N (N-B = 1.535 Å and 1.539 Å) and O-B-F (B-O = 1.493 Å and B-F = 1.386 Å) angles of 108.2° and 102.5°, respectively. The *meso*-aryl ring is held at an average dihedral angle of 56° to the plane of the dipyrin unit, taking into account that the latter is asymmetric because of the strap, but can oscillate around the mean position. The dipyrin unit is not planar, as can be illustrated by the angle of 6.1° along the B-C(*meso*)-C(aryl) vector (Figure 1).

There is a small barrier of almost 1 kcal/mol for positioning the *meso*-aryl ring orthogonal to the dipyrin unit (Figure 2a). Full rotation about the connecting C-C (C₅-C₆-C₁₃-C₁₄) bond requires concerted motion of the *meso*-substituent away from the dipyrin and further bending of the pyrrole unit lacking the strapped aryl ring. This internal displacement provides a passage for rotation without contact between neighboring hydrogen atoms (see Supporting Information for details and examples of structures). The apparent energy barrier for full rotation of the *meso*-aryl ring (C₅-C₆-C₁₃-C₁₄) is ca. 7 kcal/mol (Figure 2a). Because of the collective distortions involving much of the molecular backbone, including atoms quite remote from the *meso*-position, the rotational energy profile is relatively broad. The dihedral angle for the *meso*-aryl ring is likely to fluctuate around the mean position, imposing structural perturbations over the rest of the molecule, with only occasional passage over the larger barrier in solution at ambient temperature. As such, the ground-state landscape is expected to comprise a wide distribution of geometries at any given instance.

At the excited-singlet state level (TD-B₃LYP/6-311G(d)/PCM(CHCl₃)), the dipyrin backbone is also distorted from planarity. The energy-minimized geometry (Figure S18) shows pronounced curvature for the dipyrin unit, with N-B-N (N-B = 1.523 Å and 1.551 Å) and O-B-F (B-O = 1.509 Å

Figure 2. Plots showing the effect of dihedral angle for the *meso*-aryl ring (C₅-C₆-C₁₃-C₁₄) on the total energy of the molecule as determined by the chain method (see Supporting Information for details) for (a) the ground state and (b) the first-excited singlet state in a solvent reservoir.

and B-F = 1.380 Å) angles of 107.7° and 101.5°, respectively. The C₅-C₆-C₁₃-C₁₄ dihedral angle is calculated to be 57° while the angle subtended by the B-C(*meso*)-C(aryl) axis is 11.4°. This latter angle, taken as a crude representative of structural distortion across the dipyrin unit, exceeds that found for the ground state. Again, full rotation of the *meso*-aryl ring requires collective motions of the ring and the non-strapped pyrrole unit but the energy barrier (E_B = 2 kcal/mol) is significantly smaller than for the ground state (Figure 2b) – see the Supporting Information for a listing of the coordinates. Again, we might expect that the *meso*-

aryl ring will oscillate around its mean position, with random passage over the modest barrier, giving rise to a wide variety of geometries.

These calculations are consistent with BDFO functioning as a molecular rotor¹⁻⁴ where friction provided by the surrounding solvent layer will impede gyration of the *meso*-aryl ring. Three internal structural changes are implicated in the overall process: these involve (i) displacement of the rotor out of the plane defined by the *meso*-C and B atoms, (ii) bending of the pyrrole unit away from the *meso*-aryl ring so as to minimize steric clashes, and (iii) oscillation of the *meso*-aryl ring (see Supporting Information for further details). Each structural change will encounter resistance from neighboring solvent molecules and is likely to be inhibited in the solid state. Key geometry differences (Figure 2) between energy-minimized ground- and excited-states mean that there could be a significant Stokes' shift. It is also clear that there will be a wide variety of interconverting conformers in solution at ambient temperature at both ground- and excited-state levels.

Photophysical and Electronic Properties

In 2-methyltetrahydrofuran (MTHF) solution, BDFO¹² exhibits a pronounced absorption maximum at 561 nm and a weak fluorescence maximum at 587 nm (Figures S1 and S2). The corresponding Stokes' shift is 790 cm⁻¹, which is quite large for a BODIPY-based dye,¹³ while the emission quantum yield (Φ_F) is determined to be 0.11 $\pm$ 0.01 at room temperature. Relative to conventional (i.e., non-rotor) BODIPY derivatives (0.6 < Φ_F < 1.0),¹⁴⁻¹⁶ the emission yield is low but, in comparison to the non-strapped, 3-aryl analogue (Φ_F = 0.013 $\pm$ 0.002),¹¹ the fluorescence yield is unexpectedly high. This situation could be rationalized in terms of the rotor effect where Φ_F is set by the ease of gyration of the *meso*-aryl ring. However, time-resolved emission studies indicate that, whereas fluorescence from the non-strapped derivative decays *via* first-order kinetics with a lifetime (τ_s) of 92 $\pm$ 8 ps, emission from BDFO decays by way of a dual-exponential process according to Equation 1. In MTHF at 20 °C, the two derived lifetimes are τ_1 = 350 $\pm$ 25 ps (A_1 = 84%) and τ_2 = 1.4 $\pm$ 0.1 ns (A_2 = 16%). Similar results, which remain independent of emission wavelength, were obtained under varying experimental conditions, including a few different excitation wavelengths, and for disparate samples of BDFO.

$$I_F(t) = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} \quad (1)$$

Cyclic voltammetry carried out in deoxygenated CH₂Cl₂ containing background electrolyte indicates a *quasi*-reversible one-electron reduction step,¹⁷ with a half-wave potential of -1.11 V vs Ag/Ag⁺ and a peak separation of 75 mV at a scan rate of 60 mV/s. On oxidative scans, an irreversible wave is observed at a peak potential of 1.03 V vs Ag/Ag⁺. This latter process appears to be a two-electron electrochemical step. To help assign the electrochemical results, a series of DFT calculations was performed in order to identify the main frontier molecular orbitals. Now, the LUMO appears to be closely associated with the BODIPY core with only a small amount of electron density off-

loaded to either the *meso*-aryl ring, the strapped aryl ring or the bridging oxygen atom (Figure 3). In contrast, the HOMO involves both the dipyrroin unit and the strapped aryl ring, including the oxygen atom. This extended molecular orbital helps to reduce the band gap, thereby pushing the absorption maximum to lower energy, while the decreased overlap and increased spatial separation of HOMO and LUMO are likely to lower the excited singlet-triplet energy gap.^{18,19} At the HOMO(-1) level, the electron density distribution moves from the dipyrroin unit to the strapped aryl ring, with a minor contribution from the unstrapped pyrrole unit (Figure 3). The *meso*-aryl ring does not contribute to either HOMO or HOMO(-1).

Figure 3. Kohn-Sham electronic isodensity plots of the LUMO (upper panel), HOMO (center panel) and HOMO(-1) (lower panel) for BDFO as computed at the DFT-6311(G)/PCM/CHCl₃ level.

With this information, electrochemical reduction appears to be fully consistent with formation of the dipyrroin-based π -radical anion.¹⁷ The first oxidation process is assigned to removal of an electron from the HOMO, the electrochemical band gap of 2.14 eV (i.e., 580 nm) being close to the HOMO-LUMO energy gap of 2.18 eV (i.e., 570 nm). These values can be compared with the optical band gap of 2.21 eV (i.e., 561 nm) calculated for the energy-minimized geometry. The second oxidative process is possibly related with the need to relieve steric strain imposed at the π -dication level, which is most easily achieved by breaking the B-O bond and subsequent structural rearrangement. There is no obvious indication for the involvement of an intramolecular charge-transfer state (*vide infra*).

According to our computational studies, rotation around the connection between the dipyrroin unit and the *meso*-aryl ring has little effect on the energy of either the HOMO or HOMO(-1) (Figures S28 and S29). There is more effect

Table 1. Summary of the spectroscopic properties derived by Gaussian analysis of the spectroscopic and photophysical properties recorded for BDFO in n-alkanols at 20 °C.

Property	CH ₃ OH	C ₂ H ₅ OH	C ₄ H ₉ OH	C ₇ H ₁₅ OH	C ₁₀ H ₂₁ OH
η / cP	0.594	1.095	2.54	5.97	11.50
λ_{ABS} / nm	559	559	560	560	561
λ_{FLU} / nm	580	582	584	586	587
Φ_{F}	0.13	0.16	0.20	0.25	0.27
τ_1 (A ₁) / ps	75 (0.95)	110 (0.92)	140 (0.83)	170 (0.79)	230 (0.65)
τ_2 (A ₂) / ns	0.87 (0.05)	0.91 (0.08)	1.09 (0.17)	1.08 (0.21)	1.25 (0.35)
ν_{OO} / cm ⁻¹ (a)	17,275	17,210	17,175	17,140	17,135
FWHM / cm ⁻¹ (b)	915	870	865	855	830
k_{NR} / 10 ⁸ s ⁻¹	13.0	10.7	8.3	6.4	5.1

(a) Energy of the o,o transition derived from Gaussian fitting of the reduced emission band. (b) Full width at half-maximum of the individual Gaussian components used to indicate the relative broadness of the spectral band.

on the energy of the LUMO, especially as the two units become co-planar. In reality, however, the ground state is not expected to sample the structural regime where the HOMO-LUMO energy gap deviates far from the value computed for the energy-minimized geometry (Figure S29).

Viscosity Effect

In order to assess the significance of solvent viscosity on the emission properties of BDFO, a series of measurements was made in linear alcohol solvents at 20 °C. The nature of the solvent had a minor effect on the absorption (λ_{MAX}) and fluorescence (λ_{FLU}) maxima, leading to a slightly enlarged Stokes' shift as the viscosity decreases. There was, however, a more substantial perturbation of the fluorescence quantum yield, which became amplified with increasing solvent viscosity (η). Indeed, Φ_{F} swelled from 0.16 in ethanol to 0.27 in decan-1-ol. It was noticeable that the fluorescence spectra were broadened in the shorter alcohol solvents. This effect (Figures S6-S10) could be quantified by deconstructing the entire emission envelope into a set of five Gaussian components of common half-width (FWHM). On this basis, we see that the half-width falls steadily with increasing solvent viscosity (Table 1). Excitation spectra recorded under the same conditions do not show the same level of broadening as seen for emission (Figures S4 and S5, Table S2). The conclusion drawn from this work is that the excited-singlet state samples a wider conformational landscape than does the ground state and that the width of the distribution is dependent on solvent viscosity.

Across the series of linear alcohols, time-resolved emission profiles required analysis as the sum of two exponential components, according to Equation 1 (Figure 4). The derived lifetimes, τ_1 and τ_2 , were sufficiently distinct for meaningful analysis^{20,21} and, in each case, consisted of a short-lived species with a lifetime around 0.2 ns and a longer-lived species having a lifetime around 1 ns. The faster decaying component makes the major contribution

toward the total signal in each solvent. The shorter lifetime, τ_1 , was found to increase progressively with increasing solvent viscosity whereas the longer lifetime, τ_2 , showed somewhat less sensitivity toward solvent viscosity. There was, however, a sharp rise in the contribution of the longer-lived component, A₂, with increasing viscosity. In fact, it is this higher fractional contribution of the second component that causes the quantum yield to increase at higher viscosity.

With conventional BODIPY-based rotors,^{6,7,11} time-resolved emission decay profiles could be well described in terms of single-exponential fits – leading to the conclusion that the longer lifetime is somehow related to the presence of the C-O-B strap. On making a crude approximation of the combined rate constant for nonradiative decay, k_{NR} , by Equation 2,²² it is seen that the effect of viscosity is explained²³ reasonably well in terms of Equation 3 (Figure S3). Here, ν refers to the pressure exerted by the rotor as it twists through the medium and α is a coefficient that effectively relates to micro-viscosity.²⁴ The activation barrier, E_{A} , can be considered to contain contributions from the structural change and from the temperature effect on the solvent viscosity. The value of α determined from a log-log plot is 0.44 (Figure S3), which is close to that found earlier for the unsubstituted BODIPY-based rotor ($\alpha = 0.41$)²⁵ but significantly less than that found for the non-strapped 3-aryl derivative ($\alpha = 0.61$).¹¹ It might be noted that other expressions^{26,27} are available by which to correlate k_{NR} with η , including the model developed by Kramers,²⁸ which might be more suitable than the empirical formulation set by Equation 3. However, the scarcity of experimental data, together with the complexity of the system under study, precludes more elaborate analysis.

$$A_1 = \frac{k_{\text{RAD}} + k_{\text{NR}} - (1/\tau_2)}{(\frac{1}{\tau_1}) - (\frac{1}{\tau_2})} \quad (2)$$

$$k_{\text{NR}} = \frac{\nu}{\eta^\alpha} e^{-\frac{E_{\text{A}}}{RT}} \quad (3)$$

Figure 4. Examples of time-resolved fluorescence decay traces recorded for BDFO in alcohol solvents at room temperature. The excitation wavelength was 525 nm. The instrument response function (irf) is shown in grey with the calculated fits appearing as red lines superimposed over the experimental data.

Temperature Dependence in Fluid Solution

Except for the dual-exponential decay profiles and viscosity-induced broadening of the fluorescence profiles, BDFO appears to function as a moderately effective molecular rotor. This belief was strengthened by the observation that Φ_F increased steadily with decreasing temperature in MTHF (Figure 5). Indeed, in the rigid glass²⁹ that forms at temperatures below ca. 100K, Φ_F is close to unity. In the amorphous glassy region that persists between 100 and 140K, Φ_F remains rather high but starts to decrease as the glass melts (mp = 137K). The quantum yield continues to fall with increasing temperature and reaches a value of 0.11 at 20 °C. The profile for this temperature dependence cannot be explained in terms of the relaxation time of the solvent³⁰ or simply by changes in viscosity³¹ (Figure 5). Instead, the evolution of Φ_F with temperature shows a more complex behavior, even when compared to related BODIPY-based molecular rotors in the same solvent.

The energy of the emission maximum is at its highest in the rigid glass, formed at temperatures below ca. 100K, and falls sharply as the solvent enters the amorphous glassy phase. The solvent melts at 137K, thereafter the emission maximum increases gently with rising temperature, although this effect is modest. These changes are possibly associated with variations in solvent polarizability or polarity (Figures S14 and S15, Tables S4 and S5).³²

According to our Gaussian analysis, the band half-width exhibits a pronounced temperature dependence in fluid solution. In fact, the FWHM is small in the rigid glass but increases across the amorphous region. Once the solvent melts at 137K, the individual bands begin to broaden with increasing temperature. This latter effect is illustrated by the inset to the upper panel in Figure 5 and is emphasized in Figure 6. In fluid solution, the FWHM is significantly larger than found for conventional BODIPY-based dyes and is explained in terms of the molecule adopting an unusually wide distribution of geometries that interconvert

slowly on the timescale for emission. This structural heterogeneity increases with increasing temperature and/or decreasing viscosity; the same effect is apparent for the linear alcohols at room temperature.

Figure 5. Fluorescence spectral evolution as a function of temperature for BDFO in MTHF (upper panel) and the effect of temperature on the fluorescence quantum yield (red points) for the same experiment (lower panel). The inset compares spectra recorded at low (red curve) and high (blue curve) temperatures. Also given on the lower panel are the temperature dependences for the solvent viscosity (in units of cP, grey points) and the emission maximum (in units of cm^{-1}) for Oxazine-4 in MTHF (a dye reported³⁰ to respond exclusively to changes in solvent relaxation time) (open circles). These latter values have been normalized for convenient display and the actual values are given in Tables S4 and S5.

All indications suggest that this broadening is inhomogeneous in nature.³³⁻³⁶ Certainly, the spectral band-shape is well represented by Gaussian profiles but cannot be analyzed as Lorentzian (Figure S12). The broadening is not apparent in the rigid glass but increases progressively with increasing temperature in fluid solution, especially towards higher temperatures. A small increase in ν_{O_2} accompanies the spectral broadening (Table S3). The broadening does not depend on excitation wavelength but, at a given temperature, is restricted by increased viscosity. This points towards some type of structural perturbation as playing a key role. This geometry change could be related to nuclear displacements around the dye molecule and its interaction with the solvent.^{37,38} While the major contributor to the observed spectral broadening most likely stems from the distribution of molecular geometries at ground and excited state levels,^{39,40} it should be stressed that linear

spectroscopy of the type applied here does not allow meaningful discrimination between homogeneous and inhomogeneous broadening.

Figure 6. Effect of temperature on the fluorescence spectroscopic properties observed for BDFO in MTHF. Individual panels refer to (a) the emission maximum, (b) the band half-width for deconstructed Gaussian-shaped components.

Temperature Dependence in the Glassy State

In an effort to isolate structural changes from possible temperature effects, samples of BDFO were dispersed in sucrose octaacetate (SOA) and cast into a transparent block. At room temperature, very strong fluorescence was recorded with a quantum yield of 0.94 ± 0.04 , as measured with an integrating sphere and excitation at 525 nm. Time-resolved fluorescence studies indicated that the decay profiles for BDFO in SOA at room temperature could be analyzed satisfactorily in terms of a dual-exponential process with lifetimes of 0.35 ± 0.05 ns ($A_1 = 31\%$) and 9.1 ± 0.3 ns ($A_2 = 69\%$). A fluorescence lifetime of 9 ns is too high for a BODIPY-based dye since the radiative lifetime is usually on the order of ca. 5 ns or less.⁴¹ It might be noted that Rhodamine 6G dispersed in SOA is strongly fluorescent ($\Phi_F = 0.95 \pm 0.4$) and shows a single exponential decay profile with a lifetime of 4.3 ± 0.1 ns.

Fluorescence studies were carried out as a function of temperature for BDFO in the SOA matrix. The emission intensity increased progressively as the temperature was raised from 80 to 340 K (Figure 7). This behavior is in marked contrast to that reported above for MTHF solution. The emission maximum ($\nu_{00} = 17,100$ cm⁻¹) remained approximately constant across this temperature range. The corresponding band half-width, FWHM, increased slightly with temperature but this effect is nowhere near as pronounced as that observed in fluid MTHF.

For fluorophores embedded in a soft matrix, phonon interactions are to be expected and this situation will broaden the natural linewidth according to a temperature dependent dephasing term. The significance of this latter term will differ according to the environment surrounding the emitter. Dye molecules within the matrix will experience local perturbations due to the different locations, which can cause disparate electric fields. This field might disturb the electronic levels (i.e., the Stark effect) and

thereby modify the transition energy. This is insignificant for BDFO in SOA. The overall effect, however, is that the spectral profile deviates from Lorentzian (Figure S12). In fact, the temperature dependence recorded for the band half-width follows a power law dependence, indicating that the inhomogeneous broadening arises from sampling different environments.⁴²

Figure 7. Effect of temperature on the fluorescence spectral profile recorded for BDFO in an amorphous SOA gel. The inset shows the sample (half-filling an inverted glass tube) in the dark and under UV excitation while the arrow indicates the direction of increasing temperature.

$$\tilde{n} = \frac{\Phi_F}{\Phi_{PF}} - 1 = \frac{\Phi_T \times \Phi_S}{1 - \Phi_S \Phi_T} \quad (4)$$

$$\Phi_{PF} = \frac{k_{RAD}}{k_{RAD} + k_{NR}} = k_{RAD} \times \tau_F \quad (5)$$

$$\Phi_T = \frac{k_{NR}}{k_{RAD} + k_{NR}} \quad (6)$$

$$\Phi_S = \frac{k_{DS} \exp^{-\Delta E/RT}}{k_{DS} \exp^{-\Delta E/RT} + k_G} \quad (7)$$

$$\Phi_F = \Phi_{PF} (1 + \Phi_S \Phi_T + (\Phi_S \Phi_T)^2 + \dots) \quad (8)$$

The increasing Φ_F with rising temperature found in glassy SOA is reminiscent of the delayed luminescence⁴³ observed in certain conducting polymers,^{44,45} fullerenes⁴⁶ and organic dyes.^{47,48} A similar effect was reported⁴⁹ recently for a BODIPY dye equipped with a redox-active strap attached to the boron center. In fact, the temperature dependence can be fully explained by slight adaptation of the model for thermally-activated, delayed fluorescence developed by Baleizão and Berberan-Santos⁵⁰ and by Dias *et al.*⁵¹ In our version, part of the initial population of the emitting state, S_i , decays via prompt fluorescence with a rate constant of k_{RAD} . Nonradiative decay, occurring with a global rate constant of k_{NR} , accounts for decay of the remainder of the emitting state. This latter radiationless pathway leads to formation of a molecular conformation distinct from those of either the ground state or the emitting state. Deactivation of this new state can lead to repopulation of the emitting S_i state, with a rate constant k_{DS} , or formation of the ground state, with a rate constant k_G .⁵²

Table 2. Compilation of the parameters relating to the temperature-dependent fluorescence quantum yield derived for BDFO in the SOA glass^a and in MTHF solution.^b

Medium	$k_{\text{RAD}} / 10^7 \text{ s}^{-1}$	$k_{\text{DS}} / 10^9 \text{ s}^{-1}$	$k_{\text{NR}} / 10^7 \text{ s}^{-1}$	$k_{\text{G}} / 10^7 \text{ s}^{-1}$	$k_{\text{PH}} / 10^9 \text{ s}^{-1}$	$\Delta E / \text{kJ mol}^{-1}$	$E_{\text{P}} / \text{kJ mol}^{-1}$
SOA	13	63	14.5	52	NA	7.5	NA
MTHF	13	19	0.35	22	28	8.1	6.0

(a) Values derived by iterative fitting across the full temperature range to Equations 4-10. (b) See supporting Information.

Table 3. Comparison of calculated and observed fluorescence lifetimes for BDFO in the SOA glass at selected temperatures.

Temperature / K	Φ_{F}	$\tilde{n}$	$\tau_{\text{PF}} / \text{ns}$ (a)	$\tau_{\text{DF}} / \text{ns}$ (b)	$\tau_1 (A_1) / \text{ns}$ (c)	$\tau_2 (A_2) / \text{ns}$ (d)
150	0.475	0.06	2.4	22.6	2.60 (94%)	19.8 (6%)
170	0.655	0.20	1.7	15.3	1.65 (83%)	14.7 (17%)
210	0.825	0.8	0.90	10.8	1.00 (55%)	11.2 (45%)
240	0.900	1.6	0.55	9.7	0.65 (39%)	10.1 (61%)
290	0.910	2.2	0.33	9.0	0.35 (31%)	9.1 (69%)

(a) Fast decaying component calculated from Equation 9. (b) Slow decaying component calculated from Equation 10. (c) Shorter lifetime (and its fractional contribution) observed in the time-resolved emission studies. (d) Longer lifetime (and its fractional contribution) observed experimentally.

To account for the temperature dependence noted for Φ_{F} , it is necessary to propose that k_{DS} involves crossing a modest energy barrier, ΔE , and that k_{G} is relatively slow. We can impose a few additional restrictions on the model that allow refinement of the numerical values for the various rate constants. These include the mean number ($\tilde{n}$) of cycles from the conformer back to S_1 (Equation 4) and definition of the quantum yields for prompt fluorescence (Φ_{PF}) and for formation of the conformer (Φ_{T}) in terms of k_{RAD} and k_{NR} (Equations 5 and 6). The probability for re-population of S_1 from the conformer (Φ_{S}) is expressed in Equation 7, where allowance is made for the thermally activated step. Now, the overall fluorescence quantum yield, Φ_{F} , at any temperature is given by Equation 8. To aid analysis of the temperature dependent Φ_{F} values, we have fixed k_{RAD} at $1.3 \times 10^8 \text{ s}^{-1}$, as indicated by application of the Strickler-Berg expression,⁵³ and we note that $\tilde{n}$ can be used to refine the product of Φ_{T} and Φ_{S} according to Equation 4.

Within the model,^{50,51} the various rate constants can be used to estimate the lifetimes for prompt (τ_{PF}) and delayed (τ_{DF}) fluorescence at any given temperature, according to Equations 9 and 10, where τ_{F} is defined in Equation 5. These calculated values can be compared to experimental lifetimes measured at selected temperatures and used to further refine the rate constants extracted from the global fits. The final values are collected in Table 2 while the fit to the temperature dependent Φ_{F} values is shown as Figure 8, together with an illustration of the model.

It can be seen that k_{G} , the rate constant for escape from the trap to the ground state, is low relative to the rate constant, k_{DS} , for reverse population of the emitting state. The energy barrier separating the trap from the emitting species is small, being around $3RT$ at room temperature, and

this emphasizes the importance of the delayed fluorescence pathway for the SOA glass. The derived parameters give a very good representation of the emission lifetimes

Figure 8. The upper panel shows the effect of temperature on the fluorescence quantum yield, the solid line refers to a fit to Equation 9. Shown below is a potential energy diagram intended to illustrate the model used to explain the temperature dependence in the soft SOA gel. Note the inclusion of direct absorption to the conformational trap.

measured over the respective temperature range (Table 3). From the fractional amplitudes of the shorter- and longer-lived components seen in the time-resolved emission decay curves at room temperature, we can estimate⁵² the number of mean cycles ($\bar{n}$) as being slightly more than 2.

$$\tau_{PF}^{-1} = k_{RAD} + k_{NR} + k_{DS} \exp^{-\Delta E/RT} \quad (9)$$

$$\tau_{DF}^{-1} = \frac{k_G + k_{DS} \exp^{-\Delta E/RT} (1 - \Phi_F)}{1 + \tau_F (k_{DS} \exp^{-\Delta E/RT})} \quad (10)$$

Radiationless Decay in Fluid Solution

Complete rotation of the *meso*-aryl ring will be curtailed in the SOA glass but, according to our model, certain structural changes are facilitated in this soft gel. Internal distortions are less likely in the rigid MTHF glass that forms below about 100K and, as a consequence, Φ_F approaches unity under such conditions. This situation contrasts with that for SOA where $\Phi_F = 0.38$ at 80K. We can rationalize this disparity on the basis that slow cooling of the sample in MTHF achieves the lowest-energy conformation at 80K whereas the SOA sample is prepared by heating the mixture to 100 °C before cooling rapidly. This latter protocol is likely to create a distribution of higher energy geometries. Thus, the starting structures are different, with SOA favoring increased levels of structural distortion that do not relax to the energy-minimized geometry on solidification. For this reason, direct excitation to the trap has been included as a possibility on Figure 8 for SOA. In fluid solution, we anticipate that both gyration of the *meso*-aryl ring and distortion of the dipyrin backbone become more favorable with increasing temperature. These internal motions are considered to be concerted, on the basis of the structural calculations reported earlier. To explain the situation expressed in Figure 5, it is necessary to impose the condition that rotation of the *meso*-aryl ring promotes fast nonradiative return of the emitting state to the ground state.⁵⁴

We had previously proposed that this rotation ruptures the potential energy surface of the S_1 state so as to cause the appearance of pinholes through which the exciton can escape.^{55,56} It is now possible to combine these two events into a model relevant to BDFO in fluid solution. Here, the situation illustrated in Figure 8 to account for BDFO in a soft glass is modified by the inclusion of a pinhole⁵⁵ on the S_1 potential surface that acts as an escape route for irreversible return to the ground state. This pinhole is accessed as the *meso*-aryl ring twists about the connecting axis (Figure 9). It is the equivalent of a conical intersection between the two potential energy surfaces but it might not be so well defined. It might be argued that several such pinholes might appear on the surface as the structural changes take place at the excited state level. Conical intersections might be construed as having a specific geometry so the term pinhole, intended to be much looser, appears more suitable for the present case.

The so-called pinhole (or conical intersection) could be associated with either (or both) the excited-state surface or with the conformational trap (S_T). In fact, it proved impossible to obtain a meaningful fit to the quantum yields and

Figure 9. Illustration of the potential energy surfaces proposed for the target compound in a fluid solvent. Fast transformation to the ground state accompanies entry of the pinhole sink (PH), which is populated in competition with access to the conformational trap. The model allows for slow relaxation to the ground state via the trap. Note the alternative arrangement associates the pinhole sink with the conformational trap so that the two nonradiative channels act in tandem.

Figure 10. Effect of temperature on the fluorescence quantum yield recorded for BDFO in MTHF. The solid line drawn through the data points corresponds to a fit to a modified version of Equation 9 where an activated rate constant has been added to account for the rotary action of the *meso*-tolyl ring.

lifetimes using a model where the pinhole appeared on the S_T surface (Figure S16). Using reasonable parameters, the temperature dependence for Φ_F could be reproduced but the same parameters did not allow simulation of the excited-state lifetimes. Simulating the lifetimes resulted in a separate set of parameters, which looked reasonable, but could not reproduce the quantum yields. This dilemma was solved by separating the pinhole sink from the conformational trap (Figure 9). Now, a single set of parameters could be found by iteration that reproduced both lifetimes and quantum yields as a function of temperature. The resultant fit of the Φ_F values is shown as Figure 10. It might be noted that the fit is far from perfect in the region where the amorphous glass melts to a fluid solution. This indicates that further subtleties involving interactions between

solvent and solute contribute to the conformational mobility.

The model used to derive the parameters appropriate for fluid solution is provided as part of the Supporting Information. Also given is a collection of the experimental and simulated fluorescence lifetimes obtained using these parameters. The actual parameters are included as part of Table 2, where comparison can be made with the analysis for SOA. The most significant change between SOA and MTHF relates to k_{NR} , which is greatly increased in the amorphous sugar matrix. This is surely a consequence of disparate geometries established for the two cases. In fact, k_{NR} is important only at lower temperatures for MTHF. The viscosity dependence is associated with accessing the pinhole sink and it is likely that the associated activation energy⁵⁷ E_{P} is sensitive to the viscosity of the solvent.

It should be mentioned that no long-lived (i.e., >10 ns) intermediate species could be detected following pulsed laser excitation of BDFO in fluid solution. In particular, the triplet-excited state was not evident under these experimental conditions. Also significant is the observation that the presence of molecular oxygen had no effect on the dynamics of the various processes discussed above. It might be mentioned here that an earlier report has suggested a link between the circularly polarized luminescence from a doubly-strapped BODIPY analogue and an intramolecular charge-transfer state.⁵⁸ Our spectroscopic studies do not indicate direct involvement of charge-transfer character for BDFO. Rotation around the connection between the dipyrroin unit and the *meso*-aryl ring does affect the HOMO-LUMO energy gap, most notably by perturbing the LUMO (Figures S28 and 29).

Natural transition orbitals^{59,60} have been computed for the first three optical transitions (Figure S30). For the first such transition, essentially HOMO-LUMO, the hole is spread over the strapped aryl ring, including the O atom, and the attached pyrrole unit. There is no involvement of either the *meso*-C atom or the *meso*-aryl ring. In contrast, the electron is more narrowly distributed over the dipyrroin unit, including the *meso*-C atom, with minor contributions from the *meso*-aryl ring. This situation confers a small dipolar polarization, giving rise to a small but definite intramolecular charge-transfer character. The second transition, nominally HOMO(-1)-LUMO, shows similar natural transition orbitals (Figure S30), with the hole being located further from the dipyrroin unit and nicely spread over the strapped aryl ring. This situation should augment the charge-transfer character because of increased spatial isolation. The band gap for the second transition, however, is far removed from that for the first transition. Thus, on the basis of charge-transfer excitations⁶¹ for BDFO, we can expect weak push-pull electronic properties that will be sensitive to the mutual geometry of the respective subunits. It should be stressed that the computational methodology used here is not ideal for resolving charge-transfer character.⁶²

CONCLUSIONS

The mono-strapped BODIPY derivative studied¹² here displays complex photophysical behavior, especially in solution, in marked contrast to the non-strapped analogue. The strap imposes structural distortion, forcing the dipyrroin unit to adopt a hemispherical dome-shaped structure, and introduces significant asymmetry for both ground- and excited-state geometries. An interesting consequence of such distortion is the appearance of E-type delayed fluorescence.^{63,64} Our interpretation of this behavior is that a *meta*-stable structure is reached at elevated temperatures, at least for the excited-singlet state. Exit from this trapped state can lead to either the ground state, aided by gyration of the *meso*-aryl ring, or to the emitting singlet-excited state. The interplay between these two avenues is sensitive to the environment but the complexity of the overall system does not make for a viable fluorescent rotor. Measuring viscosity by way of delayed fluorescence might be an interesting concept but requires specialized instrumentation and is fairly slow.

In conventional terms, E-type delayed fluorescence is associated with reversible population of triplet-excited states,⁶⁵⁻⁶⁹ excimers,⁷⁰ exciplexes⁷¹ or intramolecular charge-transfer states.⁷²⁻⁷³ The respective energy gaps between emitter and trap are of critical importance but often can be modulated by conformational changes.^{74,75} Thus, the importance of molecular topology in controlling the yield and lifetime of any delayed fluorescence has already been recognized.^{76,77} Likewise, the fluorescence blinking seen during super-resolution microscopy, and often attributed to reactions between the triplet-excited state and redox-active buffer,⁷⁸⁻⁸⁰ could easily be related to light-induced isomerization.⁸¹ Again, this is a reversible conformational change leading to formation of a *meta*-stable species.^{82,83} Our understanding of the photophysics of BDFO is that the emitting state is (re-)populated from a geometrically distorted trap that is not a triplet-excited state. It is not possible to rule out the involvement of intramolecular charge-transfer interactions but all indications point to internal structural changes playing an important role.

We do not possess any real information about the nature of the trap proposed for the strapped BODIPY derivatives. It represents a dark state but is raised from obscurity by the observation of thermally-activated, delayed fluorescence from the BODIPY unit. The lifetime for this delayed fluorescence at room temperature is reasonably long, provided access to the pinhole is blocked, but much shorter than that associated with excited-triplet state traps. The pinhole is common to all BODIPY-based molecular rotors and involves concerted translation of both rotor and the upper rim of the dipyrroin unit. More information about the trap might be gleaned from studies made with the corresponding strapped BODIPY dyes that lack the rotor at the *meso*-site. We should be able to comment on this situation in the near future.

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ABBREVIATIONS

MTHF, 2-methyltetrahydrofuran; SOA, sucrose octaacetate; BODIPY, boron dipyrromethene dye.

ASSOCIATED CONTENT

Supporting Information. Provided are experimental details, examples and procedures for Gaussian analysis of spectra, details for solvent and temperature effects, model for decay in fluid solution, computational details and temperature dependence for MTHF properties. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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