

Charge-Recombination Fluorescence from Push–Pull Electronic Systems Constructed around Amino-Substituted Styryl–BODIPY Dyes**

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Abstract: A small series of donor-acceptor molecular dyads has been synthesized and fully characterized. In each case, the acceptor is a dicyanovinyl unit and the donor is a boron dipyrromethene (BODIPY) dye equipped with a single styryl arm bearing a terminal amino group. In the absence of the acceptor, the BODIPY-based dyes are strongly fluorescent in the far-red region and the relaxed excited-singlet states possess significant charge-trans-

fer character. As such, the emission maxima depend on both the solvent polarity and temperature. With the corresponding push-pull molecules, there is a low-energy charge-transfer state that can be observed by both absorp-

Keywords: donor–acceptor systems • electrochemistry • electron transfer • fluorescence • photophysics tion and emission spectroscopy. Here, charge-recombination fluorescence is weak and decays over a few hundred picoseconds or so to recover the ground state. Overall, these results permit evaluation of the factors affecting the probability of charge-recombination fluorescence in push-pull dyes. The photophysical studies are supported by cyclic voltammetry and DFT calculations.

original series of D- π -A compounds were based on a 4-nitrophenyl moiety as the electron acceptor with an *N*,*N*-di-

methylanilino group as the complementary electron donor.^[8]

More recently, attention has turned to the use of stronger

organic donor and acceptor functions, including julolidine^[9]

derivatives, pyran-containing compounds such as 2-(2-*tert*-butyl-6-methyl-4*H*-pyran-4-ylidene)malonitrile,^[10] 4,5-dicya-

noimidazole derivatives,^[11] and the so-called "super-accept-

or" 7,7,8,8-tetracyanoquinodimethene.^[12] The nature of the

terminals affects the optical and electronic properties of the

resultant materials, but so does the composition and length

of the π -conjugated backbone. Various conjugated spacers,

such as fluorene, stilbene, thiophene, polyenes, polyynes,

porphyrins, phthalocyanines, and merocyanine dyes, have been incorporated into push-pull electronic systems.^[13,14]

Along somewhat related lines, it is recognized that photoinduced electron transfer remains one of the most intensively studied subjects in contemporary science and has particular relevance for understanding the workings of both natural and artificial photosynthesis.^[15] Innumerable studies have addressed the various factors that promote light-induced electron transfer in molecular dyads, triads, tetrads, and higher-order analogues. The information gathered from such studies, used in conjunction with our ever-growing aware-

ness of the natural process,^[16] has led to new ideas about

how to achieve sustainable solar-fuel production.^[17] It has

become clear that the efficacy of a light-induced electron-

transfer reaction depends critically on a range of parameters

that must be controlled to a supreme level of precision to

achieve the optimum output. The main variables include

both thermodynamic properties (excitation energy and elec-

trode potentials) and structural elements (separation dis-

tance, mutual orientation, and nature of the bridge).^[18] The

Introduction

Push-pull π -conjugated chromophores are of great topical interest because of their putative applications in optoelectronics,^[1] organic light-emitting diodes,^[2] and informationstorage devices.^[3] Such compounds comprise an electron donor (D) fitted with one or more electron-withdrawing (A) groups connected through a π -conjugated spacer so as to generate a substantive dipole moment across the molecule. In addition, push-pull D- π -A chromophores have been investigated extensively for their nonlinear optical properties^[4-6] and have proved to be useful materials for exploring the intricacies of electron-transfer processes.^[7] The field benefits from the almost limitless variety of D- π -A systems that can be isolated by combining different donor/acceptor modules with known π -bridging spacer units. Many of the

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[**] BODIPY: boron dipyrromethene (4,4-difluoro-8-(4-iodo)phenyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene).

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range of systems that has been developed to advance this subject is incredibly far-flung and includes covalently linked donor–acceptor pairs,^[17,19] supramolecular assemblies based on coordinative interactions^[20] or hydrogen-bonding strategies,^[21] and self-associated donor–acceptor systems.^[22] Along these lines, boron dipyrromethene (BODIPY) derivatives, featuring invaluable optical and electrochemical^[23] properties, have been less exploited as photoactive bridges in D– π –A scaffolds and photoinduced electron transfer involving BODIPY dyes is not so common.^[24] The most popular reactants for such materials are bioinspired, such as porphyrins, carotenes, and quinones.

Our current interest in this field includes developing new artificial systems for light-induced electron-transfer processes that incorporate BODIPY chromophores. Such dyes have been used successfully in photovoltaic devices,^[25] as ion sensors,^[26] and as fluorescent probes in biological analyses.^[27] Surprisingly, given the great popularity of these highly emissive dyes, there have been few attempts to incorporate BODIPY dyes into push-pull molecular architectures.^[28] Notably, D- π -A chromophores have been built from a BODIPY-based core with electron-donor and electron-acceptor units attached at the 2- and 6-positions.^[29] Such compounds, although enabling facile tuning of the optical properties, do not promote light-induced charge separation. In the present work, we report the synthesis of dipolar pushpull chromophores having unusually strong donating (i.e., julolidine or triazatruxene) and withdrawing (i.e., dicyanovinyl) substituents attached to the central π -conjugated backbone (Scheme 1). The photophysical properties of the target molecules become understandable by virtue of systematic examination of model compounds lacking the dicyanovinyl terminal.



D-moieties

Scheme 1. Schematic representation of putative dipolar push-pull chromophores built around a central BODIPY unit.

Results and Discussion

Synthetic strategy: The prototypic push-pull chromophore **JLCV** (compound **5** in the synthetic schemes) was prepared in three steps from the tetramethyl-BODIPY derivative **1** as depicted in Scheme 2. Condensation of **1** with 9-formyl-10-butoxy-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1*H*,5*H*-pyrido-[3,2,1-*ij*]quinoline^[30] gave rise to the monostyryl derivative **JL** (compound **3** in the synthetic schemes) despite the pres-

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Scheme 2. Synthesis of compound **5** and its precursors: i) *p*-TsOH cat., piperidine, toluene, 140 °C; ii) [Pd(PPh₃)₂Cl₂] (10 mol%), HCOONa, DMF under a flow of CO, 100 °C; iii) AcOH/piperidine cat., methanol, 85 °C, 1 h.

ence of an excess amount of aldehyde. Formation of the mono-functionalized analogue might be explained in terms of julolidine being a strong electron donor that influences the acidity of the methyl group located at the 5-position on the BODIPY core. In any event, the result is the second known example of selective mono-condensation of a BODIPY dye with an electrophilic aldehyde.^[31] Transformation of JL into the carbaldehyde derivative 4 was realized using a carboformylation reaction catalyzed by a palladium(II) precursor and with sodium formate as the reducing reagent under a flow of CO at atmospheric pressure. The target compound JLCV was synthesized in 50% yield by condensation of 4 with malonitrile, using a Knoevenageltype reaction carried out according to a literature procedure.^[32,33] All compounds were fully characterized by modern spectroscopic protocols, as outlined in the Experimental Section and Supporting Information.

By way of analogy with the juloidine-based system, related dyes were synthesized from the triazatruxene platform as sketched in Scheme 3. This slightly ruffled scaffold has three interconnecting amino groups and an anchor by which to append secondary units. The iodo group on **TX** (compound **6** in the synthetic schemes) was converted to the corresponding formyl derivative using a carboformylation reaction, before the latter was transformed to the dicyanovinyl derivative **TXCV** (compound **8** in the synthetic schemes) using malonitrile as the reagent. It might be stressed that some of these dipolar BODIPY-based chromophores are difficult to isolate in high yield owing to their inherent instability during the purification procedures.

Electrochemistry: The redox behavior of the new BODIPY dyes was investigated by cyclic voltammetry in CH_2Cl_2 containing 0.1 M tetra-N-butylammonium hexafluorophosphate

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Scheme 3. i) [Pd(PPh_3)₂Cl₂] (10 mol %), HCOONa, DMF under a flow of CO, 100 °C; ii) AcOH/piperidine cat., THF, 95 °C, 20–30 min.

(TBAPF₆) as supporting electrolyte and the results are gathered in Table 1. The starting material lacking the styryl arm, **1**, displays a single reversible wave on both oxidative and reductive scans owing to the formation of the π -radical cation and π -radical anion, respectively, as has been observed previously for related compounds.^[34] These waves are highly reversible $(i_{pa}/i_{pc} \approx 1)$ and exhibit the characteristic shape $(\Delta E_p = 60-70 \text{ mV})$ of a Nernstian, one-electron process. The monostyryl BODIPY dyes **JL** and **4** display two distinct waves under oxidative scans, each of which is fully reversible and corresponds to transfer of a single electron. The first wave occurs with a half-wave potential of 0.38 V versus SCE and this oxidation is considerably easier (about 480 mV)

Table 1. Electrochemical data for the BODIPY, judolidine, and triazatruxene derivatives and relevant control compounds^[a]

Compound	$E^{0}(\text{ox, soln}) [V] (\Delta E [mV])$	E^{0} (red, soln) [V] (ΔE [mV])
1	+1.15 (70)	-1.24 (60)
2	+0.86(60)	-
JL (3)	+0.38(70), +0.79(60)	-1.17 (70)
4	+0.38(60), +0.81(60)	-1.16(70)
JLCV (5)	+0.38(70), +0.80(60)	-1.04 (irr.), -1.24 (70)
TX (6)	+0.67(70), +0.90(70)	-1.09(70)
7	+0.66(70), +0.92(70)	-1.06(70)
TXCV (8)	+0.72(60), +0.97(60)	-0.98 (irr.), -1.10 (60)
9	+0.86(70), +1.45(70)	_

[a] Potentials determined by cyclic voltammetry in deoxygenated dichloromethane, containing 0.1 M TBAPF₆ [electrochemical window from +1.6 to -2.2 V], at a solute concentration of approximately 1.5 mM and at RT. Potentials were standardized versus ferrocene (Fc) as internal reference and converted to the SCE scale assuming that $E_{1/2}$ (Fc/Fc⁺) = +0.38 V (ΔE_p =60 mV) versus SCE. The error in half-wave potentials is ±10 mV. For irreversible processes the peak potentials (E_{ap}) are quoted. All reversible redox steps result from one-electron processes. than for the isolated fragments. These potential shifts are a clear consequence of the increased conjugation provided by the connecting styryl linkage and to the occurrence of electronic coupling between the two units.

Turning attention to the triazatruxene-based scaffold, it is notable that the parent compound, 9, exhibits two reversible waves on oxidative scans but no observable peaks on reduction. These oxidative waves, which correspond to half-wave potentials of 0.86 and 1.45 V versus SCE, respectively (Table 1), are assigned to successive one-electron oxidation of the aminocarbazole units. The difference between the observed half-wave potentials is ascribed to electrostatic effects but the anticipated third oxidation step is not seen within the available anodic window. Appending a monostyryl BODIPY dye to the scaffold, thereby forming compounds TX or 7, lowers the half-wave potential for one-electron oxidation by approximately 200 mV owing to the increased conjugation provided by the styryl arm. Comparing this latter value with that derived for the analogous julolidinebased dye, 4, indicates that oxidation is more difficult for 7 by approximately 280 mV. It is also notable that, although the parent julolidine, 2, and triazatruxene, 9, compounds have the same half-wave potential when isolated, these units display quite disparate half-wave potentials when attached to the BODIPY unit. This is an important point that illustrates the differing degrees to which the principal donor couples to the extended BODIPY unit.

For JL, DFT calculations indicate that both HOMO and HOMO(-1) are spread over much of the molecule and include contributions from the BODIPY and julolidine residues (see the Supporting Information). As such, it is inaccurate to ascribe the first oxidation step as being localized on the julolidine unit. Identical calculations made with TX show that the HOMO is also spread over much of the molecule but incorporates only the amino group closest to the styryl arm. A similar distribution is observed for HOMO(-1) but the second amino group (this being separated from the styryl unit by 3 bonds compared with only 1 bond for the proximal amino group) makes an important contribution to HOMO(-2). The distal amino group (which is removed by 5 bonds from the styryl unit) is the major contributor to HOMO(-3) (see the Supporting Information). The energy-minimized structures indicate that the julolidine-based N atom present in JL is out of alignment with the styryl unit by only 2.5° but the proximal N atom on the triazatruxene unit present in TX is twisted out of alignment by approximately 10°. Such structural facets must contribute significantly towards the differing extents of electronic coupling found for these two electronic systems.

Further confirmation for the disparate electronic character of **JL** and **TX** comes from comparison of their absorption spectra recorded in 2-methyltetrahydrofuran (MTHF). Thus, the spectrum recorded for **TX** ($\lambda_{MAX} = 607$ nm, $\varepsilon_{MAX} =$ 103055 M⁻¹ cm⁻¹) resembles those reported for related styrylbased BODIPY dyes, although the half-width for the lowest-energy transition is somewhat elevated, and the total oscillator strength^[35] (*f*) is 0.86. This latter transition can be

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accounted for in terms of three vibrational modes of 1200 cm^{-1} , each with a half-width of 1135 cm^{-1} . For **JL** under the same conditions, the corresponding absorption transition ($\lambda_{\text{MAX}} = 631 \text{ nm}$, $\varepsilon_{\text{MAX}} = 89630 \text{ m}^{-1} \text{ cm}^{-1}$) is considerably broader, with f = 0.94, and redshifted. Spectral deconstruction into Gaussian-shaped bands requires three vibrational modes of 1200 cm^{-1} with half-widths of 1500 cm^{-1} .

One-electron reduction of the BODIPY core is easier by approximately 80 mV in both JL and 4 relative to the original dye, **1**. In fact, this observation is consistent with the optical properties of the monostyryl BODIPY dyes, as discussed later, and is a consequence of the extended π -delocalization pathway. In each case, the one-electron reduction step is quasireversible. Similar behavior is found for the triazatruxene-based dyes, **TX** and **7**, although the latter are somewhat easier to reduce (Table 1). This generic behavior follows from the situation outlined above for the corresponding oxidative processes. Quantum chemical

calculations performed at the DFT level (B3LYP 6-31G*) are suggestive of the LUMO being distributed over the styryl–BODIPY without significant penetration onto the amino-based donor (see the Supporting Information).

In the case of the prototypic push-pull dye, JLCV, reductive scans point to an irreversible wave attributable to one-electron reduction of the dicyanovinyl unit and a reversible wave due to reduction of the BODIPY core. Again, electrostatic repulsion perturbs the latter value. Similar properties are apparent for TXCV, although there are important disparities in the derived half-wave potentials for reduction of both units (Table 1), as might be anticipated in light of the above discussion comparing the electronic properties of the two sets of donors. It is interesting to note that this electronic effect carries over to reduction of the dicyanovinyl unit.



Photophysics of the BODIPY-julolidine and BODIPY-triazatruxene dyes: The absorption spectral features of the two amino-substituted styryl-based BODIPY dyes were outlined

Figure 1. Absorption and fluorescence spectra recorded for compounds JL (black curves) and TX (grey curves) in MTHF at room temperature.

above and are reproduced in Figure 1. Fluorescence is readily apparent from both compounds in MTHF at room temperature and occurs in the far-red region (Figure 1). For **TX**, the emission spectrum is broad, but partially resolved, and has a maximum at 672 nm in MTHF. The entire spectral envelope can be deconstructed into Gaussian-shaped components with a common half-width of 1050 cm⁻¹. The accompanying vibronic modes coupled with nonradiative decay are estimated from spectral curve fitting to correspond to a mixture of torsional modes ($\nu = 750 \text{ cm}^{-1}$, S = 0.96, in which S refers to the Huang-Rhys factor) and skeletal bending modes ($\nu = 1400 \text{ cm}^{-1}$, S = 0.79).^[36] There is good agreement between the excitation and absorption spectra across the entire visible and near-UV regions. In MTHF, the fluorescence quantum yield is 0.56, and the excited-singlet-state lifetime, obtained from monoexponential decay curves, is 3.5 ns (Table 2). The spectrum has the appearance of a

Table 2. Summary of the photophysical properties recorded for the various aminosubstituted styryl-BODIPY compounds in MTHF at room temperature.

Property	JL	ТХ	JLCV	TXCV
$\lambda_{ABS} [nm]$	631	607	638	619
$\varepsilon_{MAX} \left[M^{-1} cm^{-1} \right]$	103 055	89630	88900	114720
f ^[a]	0.94	0.86	1.01	1.02
$d_{\rm GS} \left[{\rm D} \right]^{[b]}$	2.5	3.0	9.3	8.0
$\lambda_{\rm FLU}$ [nm]	720	672	725	685
S ^[c]	1.7:1.15	0.96:0.79	1.05:0.70	0.82:0.65
$\Phi_{ m F}$	0.30	0.56	0.0020	0.0023
$\tau_{\rm S}$ [ns]	2.8	3.5	0.13	0.26
$k_{\rm RAD} [10^7 {\rm s}^{-1}]$	10.7	15.6	1.5	0.9
$\lambda_{\rm CR} [{\rm eV}]^{[d]}$	0.10	0.06	0.075	0.068

[a] Oscillator strength calculated from the integrated absorption spectrum. [b] Computed dipole moment for the ground state. [c] Huang–Rhys factor calculated from the deconstructed emission spectrum, with the values referring to the medium- and lowfrequency modes, respectively. [d] Reorganisation energy accompanying charge-recombination emission extracted from spectral curve fitting.

single component. On cooling the solution, the emission maximum undergoes a substantive redshift until reaching 727 nm at 160 K from whence further lowering of the temperature causes the maximum to revert to higher energy. The emission intensity and lifetime decrease slightly during the redshift, in line with the Englman–Jortner energy-gap law,^[37] but recover during the subsequent blueshift (see the Supporting Information). These changes are modest but there is a larger effect as the solvent starts to freeze at around 140 K. Here, the emission maximum shifts rapidly with falling temperature until settling at 640 nm at approximately 115 K.

At <110 K, at which temperatures MTHF forms a glassy matrix,^[38] the emission profile resembles that expected for a monostyryl BODIPY dye lacking significant charge-transfer interactions (Figure 2).^[39] The emission peak lies at 640 nm (i.e., 15635 cm⁻¹) and the profile can be deconstructed into Gaussian-shaped bands with a common half-width of 680 cm⁻¹ and accompanying vibronic components of 1300 and 580 cm⁻¹. The Huang–Rhys factors (*S*), which are 0.96 (ν =750 cm⁻¹) and 0.79 (ν =1600 cm⁻¹) at room temperature,

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Figure 2. Effect of temperature on the fluorescence spectral profile recorded for **TX** in MTHF. The arrow indicates the effect of warming the solution from 80 to 290 K in equal increments.

have values of 0.30 ($\nu = 735 \text{ cm}^{-1}$) and 0.11 ($\nu = 1570 \text{ cm}^{-1}$) in the glassy matrix and are in better accord with those expected^[40] for a π - π * transition. The implication, therefore, is that the glassy matrix restricts internal charge transfer by virtue of its rigid nature; it might be noted that the polarity of glassy MTHF has been likened to that of N,N-dimethylformamide at room temperature.[41] In other solvents at room temperature, the fluorescence maximum recorded for TX shows a marked dependence on the static dielectric constant (ε_s) and undergoes a redshift as the polarity increases. Thus, the emission maximum transforms from 650 nm in dibutyl ether ($\varepsilon_s = 3.1$), to 668 nm in ethyl acetate ($\varepsilon_s = 6.02$), to 720 nm in dichloromethane ($\varepsilon_s = 8.93$), and to approximately 740 nm in acetonitrile ($\varepsilon_s = 37.5$). The quantum yield and lifetime fall steadily as the emission peak moves to lower energy and fluorescence is difficult to resolve in strongly polar solvents; for details see the Supporting Information.

For the corresponding julolidine-based fluorophore, JL, fluorescence is redshifted relative to that of TX and has a maximum at 720 nm in MTHF at room temperature (Figure 1). Spectral curve fitting again requires the involvement of three Gaussian-shaped components with a common half-width of 950 cm⁻¹, and with underlying vibronic components of 755 and 1310 cm⁻¹. Excitation and absorption spectra are in accord across the relevant spectral window. At room temperature in MTHF solution, $\Phi_{\rm F}$ has a value of 0.30 and τ_s is 2.8 ns; again, decay curves are well explained in terms of monoexponential fits. Cooling the solution results in a redshift, the maximum reaching 755 nm at 160 K and with an accompanying decrease in emission yield, until approaching the freezing point of the solvent (see the Supporting Information). On lowering the temperature further, there is a substantial blueshift and a marked escalation in emission. At 80 K in glassy MTHF, $\Phi_{\rm F}$ reaches a limiting value of 0.58, and the emission maximum is found at 685 nm. The spectral profile remains fairly broad even in the glassy matrix but can be analyzed in terms of medium(i.e., $\nu = 1300 \text{ cm}^{-1}$, S = 0.21) and low-frequency (i.e., $\nu = 600 \text{ cm}^{-1}$, S = 0.53) vibronic peaks with a half-width of 815 cm⁻¹. The Huang–Rhys factors^[36] derived at 80 K, although much smaller than those found at room temperature, are still somewhat too high for a pure $\pi - \pi^*$ transition. These spectral shifts can be explained in terms of solvation of a polar species, taking into account that the dielectric constant of fluid MTHF increases with decreasing temperature.^[41] Again, it is proposed that freezing of the solvent hinders some important structural change that is essential for effective charge transfer along the molecular axis.

Aided by the quantum chemical studies outlined above, our understanding of the photophysical properties of TX can be summarized as follows (Table 2): Illumination creates an excited-singlet state possessing significant charge-transfer character, with the resultant transition dipole moment being spread over most of the molecule. The radiative rate constant (k_{RAD}) decreases with increasing polarity of the solvent, due to a corresponding change in geometry,^[42] while the competing nonradiative rate constant (k_{nr}) increases under the same conditions, due to the energy-gap law.[37] The net result is that fluorescence is reasonably pronounced in nonpolar media but is extinguished in strongly polar environments. It appears that formation of the excited state demands a change in geometry, as is evident by the unusually large Stokes' shift of 1550 cm⁻¹ in MTHF. This structural change, presumed to involve mutual alignment of the π cloud and the N lone pair, is restricted in rigid media in which the excited state more closely resembles a locally excited π - π * species. The ground state does not appear to be a polar species, in agreement with the DFT calculations $(\mu_{GS}=3.0 \text{ D})$, since the position of the absorption maximum varies with the polarizability (P_{ONS}) of the solvent^[43] but not with the dielectric constant. Indeed, there is a linear relationship between the wavenumber (v_{ABS}) at the maximum of the lowest-energy absorption transition and P_{ONS} (Figure 3), as has been reported for many classes of nonpolar chromophores,^[44] including BODIPY dyes.^[45] This linearity permits estimation of the radius of the solvent cavity housing the dye as being 4.3 Å and predicts the absorption maximum under vacuum to be at 560 nm, similar to that of the monostyryl dye lacking the amino group.^[39] Now the change in dipole moment accompanying excitation can be estimated from the Lippert-Mataga relationship^[46] as being 15.7 D for TX (Figure 2). Similar behavior is observed for JL (Table 2), where the change in dipole moment on excitation is calculated as approximately 17 D and the Stokes' shift in MTHF is 1960 cm^{-1} .

In glassy MTHF at 80 K, emission spectra recorded for the two compounds do not coincide and the julolidine-based system **JL** is subjected to a redshift of approximately 45 nm relative to **TX**. The same is true for excitation spectra. The parent monostyryl BODIPY dye^[39] that lacks charge-transfer interactions shows absorption and emission maxima at 573 and 583 nm, respectively, thereby giving a Stokes' shift of approximately 300 cm⁻¹. Extrapolation of the Lippert– Mataga plot recorded for **TX** also indicates that the Stokes'

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Figure 3. Effect of solvent on a) absorption and b) fluorescence spectral properties recorded for TX at room temperature: panel (a) represents the effect of solvent polarizability on the absorption maximum for the lowest-energy transition whereas panel (b) refers to a Lippert–Mataga plot for the Stokes' shift versus the solvent Pekkar function $(f(\varepsilon))$. The points are experimental values and the solid lines refer to fits to the corresponding theoretical model.

shift is 300 cm^{-1} under vacuum, where charge-transfer interactions are likely to be minimal. As such, the amino-substituted derivatives can be considered to possess increased conjugation lengths because of the N lone pair, which accounts for the redshifted absorption maximum, in addition to their inherent charge-transfer character. An important point to bear in mind is that this charge-transfer effect does not lead to light-induced charge separation.

Overall, the photophysical properties recorded in fluid solution appear consistent with those reported by Rurack^[47] and Baruah^[48] and their co-workers for the corresponding monostyryl BODIPY dye bearing a terminal N,N-dimethylanilino unit. Here, the absorption spectrum is hardly affected by changes in solvent but the emission maximum moves to lower energy as the solvent polarity increases. A particular emphasis in the work outlined by Baruah et al.^[48] is placed on establishing the most appropriate descriptor for solvent polarity. We are less concerned with this point since our main interest lies with the push-pull dyes. Nonetheless, it is important to highlight the fact that k_{RAD} for the N,N-dimethylanilino-based dye^[47,48] is approximately $1.9 \times 10^8 \text{ s}^{-1}$, which is slightly higher than that found in this work, but consistent with the general observation that k_{RAD} decreases with increasing charge-transfer character. As reported by others for related compounds,^[47-49] the amino N atom is readily protonated in acidic solution and this causes a marked spectral shift for both absorption and emission maxima. In the case of JL, for example, protonation in MTHF shifts the absorption and fluorescence peaks to 575 and 585 nm, respectively, and $\Phi_{\rm F}$ increases to 0.95.

Photophysics of the push-pull compounds JLCV and TXCV: The push-pull compounds differ from the parent amino-substituted styryl-BODIPY dyes by virtue of having an electron-affinic dicyanovinyl unit appended through the *meso* position. It might be noted that this type of electron acceptor has a long history in the generic field of molecular photophysics.^[50] Absorption spectra recorded for these new push-pull molecules, **JLCV** and **TXCV**, in MTHF at room temperature are similar to those described for the corresponding BODIPY-amine compounds, **JL** and **TX**, but are redshifted by approximately 10 nm and slightly broadened (Figure 4). Oscillator strengths, which are 1.02 for both com-



Figure 4. a) Absorption and b) fluorescence spectra recorded for **JLCV** in MTHF at room temperature (see the Supporting Information for corresponding plots for **TXCV**). In part (a), the solid black curve is the experimental spectrum, the light grey curve is the deconstructed charge-transfer transition, and the dark grey curves are Gaussian components for the normal π - π * transition. In part (b), the solid black curve is the experimental spectrum, the light grey curve is the deconstructed spectrum for the emissive state and the dark grey curve is the proposed impurity.

pounds, are increased relative to the parent compounds and, most importantly, there are indications for the presence of a charge-transfer transition lying under the lowest-energy π - π * absorption band. The latter situation is most evident for **JLCV** but spectral curve fitting confirms the presence of a charge-transfer contribution to the total absorption spectral profile of **TXCV**. The maxima of these transitions are found at 660 and 724 nm for **TXCV** and **JLCV** in MTHF, respectively. The origin of both transitions is considered to involve charge transfer from the styryl-BODIPY to the dicyanovinyl unit since DFT calculations show the HOMO and LUMO(1) to be localized on the styryl-based BODIPY resi-

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due whereas the LUMO is centered on the dicyanovinyl appendage. Interestingly, the DFT calculations indicate substantially increased dipole moments for both push-pull compounds relative to the original amino derivative. Thus, the computed ground-state dipole moments are 9.3 and 8.0 D for **JLCV** and **TXCV**, respectively.

Fluorescence from the target push–pull systems is difficult to resolve in liquid MTHF and it is clear that the emission is extensively quenched relative to the analogues lacking the dicyanovinyl unit. For **TXCV**, fluorescence is decreased by a factor of approximately 300-fold relative to **TX** while the emission maximum is shifted to 695 nm (Table 2). In glassy MTHF at temperatures <115 K, the emission spectrum resembles that recorded for the control compound **TX**, and at 80 K Φ_F has a value of 0.32, which remains less than that measured for **TX** (Φ_F =0.85) under the same conditions (Figure 5). As the glass melts, there is a dramatic fall in Φ_F



Figure 5. Effect of temperature on the fluorescence spectral profile recorded for **TXCV** in MTHF. The arrow indicates the effect of warming the solution from 80 to 290 K in equal increments. The inset shows the effect of temperature on the relative emission quantum yield.

and a significant redshift, which reaches a maximum at 170 K where the fluorescence peak lies at 740 nm. Under critical examination of the emission spectral profiles it becomes clear that there are important differences between room-temperature spectra recorded for the push-pull system and the simpler amino derivative. Indeed, the total emission spectrum recorded for **TXCV** appears as a mixture of a fluorescence profile somewhat similar to that of **TX** and a new band lying at lower energy (Figure 5). This second component is broad and essentially featureless, with the maximum being strongly temperature dependent.

Time-resolved emission studies carried out for **TXCV** in MTHF show that decay profiles require analysis in terms of dual-exponential kinetics (Figure 6). One component, with a lifetime of 2.4 ns, is a minor species and is tentatively assigned to a trace impurity on account of its spectral profile being similar to that of **TX**. The second component, which has a lifetime of 260 ps, is the dominant species and corresponds to the redshifted species (Figure 7). From the spectral curve fitting analysis, $\Phi_{\rm F}$ for this latter component is estimated to be approximately 0.002, hence $k_{\rm RAD}$ must be approximately 0.002.



Figure 6. Time-resolved fluorescence decay profile recorded for **TXCV** in MTHF following excitation at 635 nm and with detection at 710 nm. The instrument response function is shown as a black solid curve and the experimental data points appear as open circles. The analytical fit is shown as a red curve superimposed over the data points. For this analysis, $\chi^2 = 1.09$.



Figure 7. Decay-associated emission spectra derived from analysis of the time-resolved fluorescence spectra recorded for **TXCV** in MTHF following excitation at 590 nm. The grey curve corresponds to the longer-lived species and the black curve is for the shorter-lived component. See the Supporting Information for the analogous spectra derived for JLCV.

proximately 10⁷ s⁻¹ at room temperature. The same analysis can be made for JLCV, where the shorter lifetime is 130 ps and the residual impurity has a lifetime of 2.8 ns. In this case, the emission spectrum shows only a minor contribution from the "impurity" whilst the shorter-lived species has an emission maximum at 725 nm. The emission quantum yield for this latter species is very low in MTHF at room temperature, where k_{RAD} is estimated to be approximately $2 \times 10^7 \text{ s}^{-1}$. Temperature-dependent emission studies again show that the blueshifted emission characteristic of JL is apparent in the glassy matrix at < 110 K but disappears on melting. As for TXCV, the peak position for the redshifted species is strongly temperature dependent. On the basis that this emission arises from a charge-transfer state, the reorganization energy for charge recombination is approximately 0.1 eV (Table 2).

The photophysical properties of these push-pull dyes can be interpreted as follows: The lowest-lying singlet-excited state in both compounds is accessed through direct excitation into the charge-transfer transition identified on the red edge of the strong absorption band associated with the amino-substituted styryl-BODIPY dye. This state is weakly emissive. The excited-state lifetimes are fairly short, owing to the energy-gap law;^[37] the corresponding radiative rate constants are relatively small because of the low oscillator strengths for the charge-transfer absorption transition.^[42] Illumination into the BODIPY dye forms the corresponding localized state possessing considerable charge-transfer character but this species undergoes rapid internal conversion to populate the lower-energy state. The polar solvent stabilizes this latter state and thereby gives rise to the observed redshift as the temperature falls. In the glassy matrix, such stabilization is not possible,^[51] because the solvent cannot reorient around the emergent dipole, and the energy of the charge-transfer state increases dramatically. At <115 K, this state lies at higher energy than the singlet-excited state associated with the amino-substituted styryl-BODIPY dye. The net result is complete recovery of blueshifted fluorescence in the glass. In fact, the fluorescence properties (both integrated area and peak position) provide a convenient means by which to monitor global changes in the nature of the solvent as a function of temperature. Although other dyes have been used^[41,52] as optical probes for the temperatureinduced change in the dielectric constant of MTHF, these push-pull molecules are especially useful for following vitrification.

Conclusion

The two amino-substituted monostyryl BODIPY dyes undergo a significant increase in dipole moment on promotion to the first-allowed excited state. Both dyes are strongly fluorescent, without the anticipated quenching by the amino group, with the emission maximum depending on the local polarity. The relevant excited states, which possess strong charge-transfer character, are accessed by means of a key geometry change that is inhibited in a frozen glass at low temperature. Consequently, in the case of TX in MTHF, vitrification of the solvent is accompanied by a 90 nm blueshift, which occurs over a temperature range of approximately 30 K. These compounds are characterized by relatively high radiative rates and it is interesting to note how k_{RAD} depends on the strength of the donor. In fact, it can be argued that k_{RAD} provides an indirect measure of the internal charge-transfer characteristics for this class of styryl-BODIPY dyes. Data collected in different solvents for JL, **TX**, and the N,N-dimethylanilino^[47,48] derivative show reasonable linearity between k_{RAD} and the emission peak maximum, which suggests comparable coupling elements for all three dyes. In the same solvent, the measured Stokes' shifts are 1960, 1550, and 1420 cm⁻¹ for **JL**, **TX**, and the *N*,*N*-dimethylanilino compound, respectively, which could be taken as a relative measure of the donor ability.

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Adding the dicyanovinyl acceptor, by means of an orthogonal phenylene ring, provides a route for increasing the molecular dipole moment and is accompanied by a large decrease in fluorescence. Electronic coupling is so strong, despite the bridge, that the absorption spectrum shows evidence of a low-lying charge-transfer state. On vitrification, the emission spectrum moves towards that of the amino-BODIPY derivative. This effect is explained in terms of the glass being unable to adequately solvate the charge-transfer state and preventing the essential geometry change. There is considerable interest in monitoring the properties of optical glasses formed by freezing an organic solvent, especially with regard to the local polarity.^[41] In this respect we note that compounds JLCV and TXCV function as exquisite mirrors for the vitrification of the solvent and clearly distinguish between a rigid glass and an amorphous glassy regime. These effects are due to changes in viscosity, rather than polarity, but could be adapted to develop improved optical sensors for glass transition temperatures.

Experimental Section

Synthesis and characterization

General procedure A: In a round-bottomed flask, piperidine and a crystal of p-toluenesulfonic acid (p-TsOH) were added to a solution of compound 1 (1 equiv) and 9-formyl-10-butoxy-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline (1.5 equiv) in toluene. The solution was heated at 140°C until it had evaporated to dryness. The colored solids were purified by silica gel chromatography before being recrystallized.

General procedure B: $[Pd(PPh_3)_2Cl_2]$ (10 mmol%) and sodium formate (1.2 equiv) were added to a solution of **3** (1 equiv) in anhydrous DMF (8 mL) in a two-necked flask equipped with a reflux condenser, a gas bubbler, and a magnetic stirring bar. The reaction mixture was degassed under a continuous flow of CO at atmospheric pressure and stirred at 90 °C for 3 h. After cooling to room temperature, the mixture was extracted with dichloromethane and washed several times with water. The organic phase was dried over hygroscopic cotton wool and evaporated. The crude residue was then purified by flash chromatography.

General procedure C: In a Schlenk tube equipped with a magnetic stirring bar, malonitrile (1.2 equiv) and several drops of piperidine/acetic acid were added to a suspension of the aldehyde precursor (1 equiv) in methanol (2.5 mL). The mixture was stirred at 85-95 °C for 1 h.

Details regarding the spectroscopic investigations are also provided in the Supporting Information.

Compound JL (3): Compound 3 was synthesized according to general procedure A, starting from 4,4-difluoro-8-(4-iodo)phenyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (BODIPY; 226 mg, 0.50 mmol). Column chromatography (silica gel, CH2Cl2/petroleum ether 4:6, v/v) and recrystallization from ethanol/CH2Cl2 gave 3 (220 mg, 58%) as a dark blue solid. $R_{\rm f} = 0.30$ (CH₂Cl₂/petroleum ether 4:6); ¹H NMR (CDCl₃, 300 MHz): $\delta = 0.99$ (t, ${}^{3}J = 7.3$ Hz, 3 H), 1.33 (s, 6 H), 1.41–1.42 (m, 9 H), 1.46 (s, 3H), 1.52-1.57 (m, 2H), 1.70-1.74 (m, 4H), 1.80-1.90 (m, 2H), 2.58 (s, 3H), 3.16 (t, ${}^{3}J=5.7$ Hz, 2H), 3.23 (t, ${}^{3}J=5.7$ Hz, 2H), 3.83 (t, ${}^{3}J = 6.6$ Hz, 2H), 5.95 (s, 1H), 6.58 (s, 1H), 7.08 (d, ${}^{3}J = 8.2$ Hz, 2H), 7.32 (d, ${}^{3}J=16.2$ Hz, 1 H), 7.37 (s, 1 H), 7.42 (d, ${}^{3}J=16.2$ Hz, 1 H), 7.83 ppm (d, ${}^{3}J$ = 8.2 Hz, 2 H); ${}^{13}C$ NMR (CDCl₃, 50 MHz): δ = 14.3, 14.1, 14.7, 14.7, 15.2, 19.6, 30.2, 31.0, 32.4, 32.4, 32.8, 36.6, 40.1, 47.0, 47.6, 94.6, 113.2, 113.3, 113.3, 113.3, 117.4, 118.3, 120.3, 120.3, 122.0, 123.6, 126.9, 130.7, 135.3, 136.4, 138.3, 139.5, 142.7, 144.7, 152.2, 156.6, 157.6 ppm; ¹¹B NMR (CDCl₃, 128 MHz): $\delta = 1.07$ ppm (t, J(B,F) = 32.6 Hz); EIMS (neat matter): m/z calcd for C₄₀H₄₇BF₂IN₃O: 761.2; found: 761.1 (100) [M^+],

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688.2 (30) $[M-(OC_4H_9)]^+$; elemental analysis calcd (%) for $C_{40}H_{47}BF_2IN_3O$: C 63.09, H 6.22, N 5.52; found: C 62.76, H 6.04, N 5.38. **Compound 4**: Compound **4** was synthesized according to general proce-

dure B, starting from compound 3 (155 mg, 0.203 mmol). The crude residue so obtained was purified by column chromatography (silica gel), eluting with toluene/CH2Cl2 (8:2, v/v) to give the desired compound as a dark blue solid (95 mg, 71%). $R_f = 0.46$ (toluene/CH₂Cl₂ 8:2); ¹H NMR (CDCl₃, 300 MHz): $\delta = 0.98$ (t, ${}^{3}J = 7.2$ Hz, 3 H), 1.33–1.42 (m, 18 H), 1.51–1.57 (m, 2H), 1.73 (t, ${}^{3}J=6.0$ Hz, 4H), 1.81–1.88 (m, 2H), 2.59 (s, 3H), 3.16–3.24 (m, 4H), 3.83 (t, ${}^{3}J=6.7$ Hz, 2H), 5.96 (s, 1H), 6.59 (s, 1H), 7.46–7.48 (m, 3H), 7.54 (d, ${}^{3}J=8.1$ Hz, 2H), 8.02 (d, ${}^{3}J=8.1$ Hz, 2H), 10.12 ppm (s, 1H); ¹³C NMR (CDCl₃, 50 MHz): $\delta = 14.2$, 14.4, 14.6, 15.0, 19.5, 29.74, 30.1, 30.8, 30.9, 32.3, 32.7, 36.4, 40.0, 46.9, 47.5, 113.1, 117.3, 118.4, 120.3, 121.9, 123.5, 125.3, 126.9, 128.3, 129.1, 129.8, 130.2, 132.8, 135.6, 135.8, 136.5, 137.9, 139.1, 142.2, 142.3, 142.4, 144.7, 152.3, 156.8, 157.6, 191.7 ppm; ¹¹B NMR (CDCl₃, 128 MHz): $\delta = 1.07$ ppm (t, J(B,F) = 33.2 Hz; IR: $\tilde{\nu} = 701$, 763, 976, 1061, 1116, 1156, 1194, 1254, 1290, 1317, 1464, 1497, 1532, 1581, 1702 (CHO), 2869, 2927, 2957 cm⁻¹; EIMS (neat matter): m/z calcd for $C_{41}H_{48}BF_2N_3O_2$: 663.3; found: 663.2 (100) $[M]^+$, 590.2 (35) $[M-(OC_4H_9)]^+$; elemental analysis calcd (%) for C41H48BF2N3O2: C 74.20, H 7.29, N 6.33; found: C 73.92, H 6.98, N 6.12.

Compound JLCV (5): Compound 5 was synthesized according to general procedure C, starting from compound 4 (39 mg, 0.056 mmol). After cooling the reaction to room temperature, the precipitate formed was isolated by centrifugation and washed several times with methanol, giving the product as a dark blue powder (20 mg, 50%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 0.98$ (t, ${}^{3}J = 7.3$ Hz, 3 H), 1.33–1.42 (s, 18 H), 1.50–1.55 (m, 2H), 1.71–1.75 (m, 4H), 1.80–1.90 (m, 2H), 2.59 (s, 3H), 3.17 (t, ${}^{3}J=$ 5.8 Hz, 2H), 3.25 (t, ${}^{3}J=5.8$ Hz, 2H), 3.82 (t, ${}^{3}J=6.7$ Hz, 2H), 5.96 (s, 1 H), 6.60 (s, 1 H), 7.73–7.48 (m, 3 H), 7.55 (d, ${}^{3}J=8.2$ Hz, 2 H), 7.84 (s, 1H), 8.05 ppm (d, ${}^{3}J=8.3$ Hz, 2H); ${}^{13}C$ NMR (CDCl₃, 100 MHz): $\delta =$ 14.3, 14.5, 14.6, 15.1, 19.5, 29.4, 29.7, 30.0, 30.8, 32.3, 32.3, 32.7, 36.4, 39.9, 46.9, 47.5, 75.9, 83.9, 112.5, 112.9, 113.5, 117.2, 118.7, 120.4, 121.9, 123.5, 126.9, 129.8, 130.0, 130.5, 131.1, 131.2, 132.7, 134.7, 135.9, 138.7, 142.2, 142.6, 144.8, 152.3, 157.1, 157.7, 158.9, 165.5 ppm; $^{11}\mathrm{B}\ \mathrm{NMR}\ (\mathrm{CDCl}_3,$ 128 MHz): $\delta = 1.04$ (t, J(B,F) = 32.9 Hz); IR: $\tilde{\nu} = 702$, 795, 854, 984, 1014, 1156, 1196, 1257, 1294, 1320, 1465, 1496, 1533, 1583, 2228 (-CN), 2963, 2961, 2926 cm⁻¹; EIMS (neat matter): m/z calcd for $C_{44}H_{48}BF_2N_5O$: 711.4; found: 711.2 (100) $[M]^+$, 692.2 (30) $[M-F]^+$; elemental analysis calcd (%) for C44H48BF2N5O: C 74.26, H 6.80, N 9.84; found: C 73.94, H 6.62, N 9.62.

Compound 7: Compound **7** was synthesized according to general procedure B, starting from compound **6a** (101 mg, 0.077 mmol). Flash chromatography from silica gel (toluene/petroleum ether 7:3, v/v) gave the product as a dark blue solid (78%, 73 mg). $R_{\rm f}$ =0.48 (toluene/petroleum ether 7:3); ¹H NMR (CDCl₃, 300 MHz): δ =0.78–0.85 (m, 9H), 1.19–1.43 (m, 25H), 1.93–2.04 (m, 6H), 2.66 (s, 3H), 4.88–4.96 (m, 6H), 6.04 (s, 1H), 6.73 (s, 1H), 7.35 (t, ³*J*=7.4 Hz, 2H), 7.43–7.50 (m, 3H), 6.04 (s, 1H), 8.04 (d, ³*J*=8.0 Hz, 2H), 7.62–7.70 (m, 3H), 7.71 (s, 1H), 7.85 (d, ³*J*=16.0 Hz, 1H), 8.04 (d, ³*J*=8.0 Hz, 2H), 8.22–8.29 (m, 3H), 10.12 ppm (s, 1H); ¹¹B NMR (CDCl₃, 128 MHz): δ =1.10 ppm (t, *J*(B,F)=32.6 Hz); IR: \hat{v} =706, 727, 794, 984, 1015, 1075, 1157, 1193, 1260, 1298, 1372, 1464, 1499, 1538, 1705 (-CHO), 2852, 2923, 2958 cm⁻¹; EIMS (neat matter): *m*/*z* calcd for C₆₃H₆₈B_{F2}N₅O: C 78.82, H 7.14, N 7.29; found: C 78.54, H 6.72, N 6.82.

Compound TXCV (8): Malonitrile (7 mg, 0.112 mmol) and several drops of piperidine/acetic acid were added to a Schlenk tube equipped with a stirrer bar and containing a solution of aldehyde precursor **7** (68 mg, 0.056 mmol) in THF (3 mL). The mixture was stirred at 95 °C for 20–30 min. After purification by column chromatography (silica gel, toluene/CH₂Cl₂ 8:2, v/v), the product was obtained as a dark blue solid (22 mg, 50%). $R_{\rm f}$ =0.64 (toluene/CH₂Cl₂ 8:2); ¹H NMR (CDCl₃, 400 MHz): δ = 0.78–0.85 (m, 9H), 1.21–1.33 (m, 18H), 1.41 (s, 3H), 1.47 (s, 3H), 1.94–2.03 (m, 6H), 2.65 (s, 3H), 4.91–4.98 (m, 6H), 6.05 (s, 1H), 6.76 (s, 1H), 7.36 (t, ³J=7.4 Hz, 2H), 7.46 (t, ³J=8.1 Hz, 2H), 7.54 (d, ³J=7.6 Hz, 1H), 7.58 (d, ³J=8.3 Hz, 2H), 7.36–7.66 (m, 2H), 7.69 (d, ³J=8.5 Hz, 1H), 7.75 (s, 1H), 7.85 (d, ³J=16.2 Hz, 1H), 7.86 (s, 1H), 8.08 (d, ³J=

8.3 Hz, 2H), 8.26 (d, ${}^{3}J=8.5$, 1H), 8.29 ppm (d, ${}^{3}J=7.9$ Hz, 2H); ${}^{13}C$ NMR (CDCl₃, 50 MHz): δ =13.9, 13.9, 14.1, 14.6, 14.9, 22.4, 22.5, 22.7, 26.3, 26.4, 29.3, 29.7, 31.4, 31.4, 31.4, 31.9, 47.1, 84.2, 110.3, 110.6, 119.3, 119.8, 119.8, 119.8, 121.4, 121.5, 121.6, 122.7, 123.3, 123.4, 124.6, 129.7, 130.2, 130.9, 131.3, 138.5, 138.8, 139.4, 140.9, 141.0, 141.2, 142.0, 154.5, 155.1, 158.7 ppm; ${}^{11}B$ NMR (CDCl₃, 128 MHz): δ =1.07 ppm (t, J(B,F)=32.0 Hz); IR: $\bar{\nu}=710$, 727, 800, 984, 1018, 1039, 1077, 1158, 1194, 1299, 1373, 1409, 1463, 1500, 1540, 1589, 2229 (-CN), 2853, 2923, 2954 cm⁻¹; EIMS (neat matter): m/z calcd for C₆₆H₆₈BF₂N₇: 1007.5; found: 1007.3 (100) $[M]^+$, 988.3 (20) $[M-F]^+$; elemental analysis calcd (%) for C₆₆H₆₈BF₂N₇: C 78.63, H 6.80, N 9.73; found: C 78.42, H 6.62, N 9.42.

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