Solvent and pH Dependent Fluorescent Properties of a Dimethylaminostyryl Borondipyrromethene Dye in Solution

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Steady-state and time-resolved fluorescence techniques have been used to study the photophysical properties of the fluorescent BODIPY-derived dye 3-{2-[4-(dimethylamino)phenyl]ethenyl}-1,3,5,7-trimethyl-3a,4a-diaza-4-bora-s-indacene. This compound has been synthesized via a microwave-assisted condensation of p,N,N-dimethylaminobenzaldehyde with the appropriate 1,3,5,7-tetramethyl substituted borondipyrromethene unit. The fluorescence properties of the dye are strongly solvent dependent: increasing the solvent polarity leads to lower fluorescence quantum yields and lifetimes, and the wavelength of maximum fluorescence emission shifts to the red. The Catalán solvent scales are found to be the most suitable for describing the solvatochromic shifts of the fluorescence emission. These are dominated by polarity/polarizability effects, as confirmed by quantum-chemical calculations performed in the dielectric continuum approximation. Fluorescence decay profiles of the dye can be described by a single-exponential fit in most solvents investigated, while two decay times are found in alcohols. The dye undergoes a reversible protonation—deprotonation reaction in the acidic pH range with a pKᵢ of 2.25 in acetonitrile solution. Fluorimetric titrations as a function of pH produce fluorescence emission enhancements at lower pH. The fluorescence excitation spectra show a hypsochromic shift from 600 nm for the neutral amine to 553 nm for the ammonium form, so that ratiometric measurements can be used to determine pKᵢ.

1. Introduction

The design and synthesis of novel, fluorescent chemosensors for the measurement of analytically important ions and molecules continues to be an exciting area of research.1,2 In recent years, much attention has been focused on the synthesis of 4,4-difluoro-8-(4-methoxy)phenyl)-1,3,5,7-tetramethyl-3a,4a-diaza-4-bora-s-indacene (BODIPY) based fluorescent probes and their application as selective and efficient chemosensors.3 The abundant applications of borondipyrromethene derivatives are facilitated by the well-known fluorophore characterized by valuable properties such as high (photo)chemical stability and relatively high fluorescence quantum yields (often approaching 1.0) and absorption coefficients.5,13–23 Moreover, borondipyrromethene dyes are excitable with visible light, have narrow emission bandwidths with high peak intensities, and are amenable to structural modification.

In this work, we synthesized1—via a microwave-assisted condensation reaction—a fluorescent pH sensor with 3a,4a-diaza-4-bora-s-indacene as fluorophore linked to a p,N,N-dimethylaminostyryl group at the 3-position. To investigate the photophysical properties of this new BODIPY dye (1), we recorded its steady-state absorption and fluorescence excitation and emission spectra and collected its time-resolved fluorescence profiles in several solvents. From these experiments, we determined the position of the spectral maxima (λabs, λem, and λcm), the full width at half-maximum of the absorption band (fwhmabs), the Stokes shifts (ΔS = λem – λabs), the fluorescence quantum yields (Φf) and lifetimes (τ), and the rate constants of radiative (ki) and nonradiative (knr) deactivation of this compound. We used the Lippert solvent parameter AΔf, the normalized Eν23(30) polarity scale, and the multiparameter Kamlet-Taft and Catalán solvent scales to describe the solvent effect on the fluorescence emission maxima and Stokes shift of 1. Semiempirical quantum-chemical calculations were performed to assess the amount of charge transfer in the excited state and explore the solvent dependent absorption and emission properties of the dye. Finally, fluorimetric titrations as a function of pH were used to determine the pKᵢ of the new dye in acetonitrile.

2. Results and Discussion

2.1. Synthesis. 4,4-Difluoro-8-(4-methoxyphenyl)-1,3,5,7-tetramethyl-3a,4a-diaza-4-bora-s-indacene (4) was synthesized from p-methoxybenzaldehyde (2) and 2,4-dimethylpyrrole (3) following a literature procedure.24 Compound 1 was synthesized in 26% yield by microwave-assisted condensation of compound 4 with p,N,N-dimethylaminobenzaldehyde (5) using acetic acid—piperidine as a catalyst (Scheme 1). The use of microwave irradiation drastically reduced the reaction time (from 26 h for conventional heating to 15 min for microwave heating) without affecting the chemical yield.
2.2. Spectroscopic Properties. The UV/vis absorption and fluorescence emission spectra of 1 dissolved in several solvents are depicted in Figure 1. The photophysical properties of 1 are compiled in Table 1. As is evident from this table, the main absorption band—attributed to the 0–0 vibrational band of a strong S°–S¹ transition—is centered between 593 and 610 nm in the pure solvents (1–18). In cyclohexane, methylcyclohexane, tetrahydrofuran (THF), toluene, diethyl ether, diisopropyl ether, and dibutyl ether, a shoulder at the short wavelength (high-energy) side can be observed—centered at approximately 565 nm—which is assigned to the 0–1 vibrational band of the same transition. In addition, weaker absorption bands are found at approximately 425 and 375 nm, the position of which is not appreciably affected by solvent polarity. These broader and weaker absorption bands are assigned to the S°–S² and S°–S³ transitions. The position of the S°–S¹ absorption band shows minor solvent-dependent shifts, indicating a weak charge-transfer character for the lowest electronic excitation in the ground-state geometry, vide infra. The typical, narrow BODIPY-like main absorption band⁵,¹³–²³ of 1 is, however, only seen in cyclohexane and methylcyclohexane. The full width at half-maximum (fwhm abs) increases from 938 cm⁻¹ in methylcyclohexane to 1902 cm⁻¹ in THF. The fluorescence excitation spectra match the absorption spectra.

Conversely, the fluorescence emission of 1 is strongly solvent dependent. The emission maximum steadily shifts to longer wavelengths in going from nonpolar to polar solvents (from 612 nm in cyclohexane and methylcyclohexane to 737 nm in DMSO), indicative of the charge transfer nature of the emitting state. This red shift is accompanied by a loss of fine structure and an increase of the bandwidth. Only the emission spectrum in cyclohexane and methylcyclohexane displays the typical BODIPY features,⁵,¹³–²³ i.e., a narrow, slightly Stokes-shifted band of mirror image shape.

Examination of the chemical structure of 1 suggests that the occurrence of an intramolecular charge transfer (ICT) process may be responsible for its high solvent sensitivity: the tertiary amino group is an electron donor and the boradiazaindacene moiety is electron-deficient, allowing for the occurrence of an excited state with some ICT character.

Figure 2 shows the delocalized forms that contribute to the real structure of 1 in a valence bond picture. Zwitterionic structures A and B²³ have dominant contributions to both the ground (S°) and the excited (S¹) state in the BODIPY chromophore. These structures will also be the main contributors to the ground state of 1, thereby rationalizing the slight sensitivity of the absorption peak with solvent polarity/polarizability. In the excited state, however, a larger weight is expected for the charge-separated structure C. This is confirmed by the quantum-chemical calculations (see below) and is enhanced by the geometric deformations in the relaxed excited state (which lead to an increased “quinoid” character of the styryl side chain, hence further favoring the charge-separated form C). As a result, a difference in dipole moment between the ground and excited states develops after geometric relaxation in the excited state, such that polar, nonprotic solvents stabilize the excited state and lead to a red-shifted emission. This also implies that, in the relaxed excited-state geometry (with a larger contribution of structure C), the nitrogen lone pair is less available for hydrogen bonding with a protic solvent. Hence, interaction between hydrogen donating solvents and the aniline nitrogen are expected to be weaker in the excited state than in the ground state, so that hydrogen bonding should
In addition, in the protic solvents (methanol and 1-butanol), a second, faster subnanosecond component was found. The time-resolved fluorescence measurements are also listed in Table 1. In all pure nonprotic solvents studied, a single decay component on the nanosecond time scale was found, ranging from 3.74 ns in diethyl ether to 1.20 ns in acetonitrile, with the emission to shorter wavelengths compared to a shift the emission to shorter wavelengths compared to aprotic solvents with the same dielectric constant. This should stabilize the ground state more than the excited state. This should stabilize the ground state more than the excited state.

The results of time-resolved fluorescence experiments are also listed in Table 1. In all pure nonprotic solvents studied, a single decay component on the nanosecond time scale was found, ranging from 3.74 ns in diethyl ether to 1.20 ns in acetonitrile, analogous to the borondipyrromethene derivative 3-rhodamine. The collected fluorescence decay surfaces were analyzed globally as biexponentials with linked decay times, analogous to the borondipyrromethene derivative 3-rhodamine. The collected fluorescence decay surfaces were analyzed globally as biexponentials with linked decay times, analogous to the borondipyrromethene derivative 3-rhodamine. The collected fluorescence decay surfaces were analyzed globally as biexponentials with linked decay times, analogous to the borondipyrromethene derivative 3-rhodamine. The collected fluorescence decay surfaces were analyzed globally as biexponentials with linked decay times, analogous to the borondipyrromethene derivative 3-rhodamine.

For the steady-state and time-resolved fluorescence measurements in solvent 19, HClO 4 was used as proton source. The results of time-resolved fluorescence measurements, the samples in solvents 2–4, 7–15, and 17 were excited at 580 nm whereas 530 nm excitation was used for solvent 19. For the steady-state and time-resolved fluorescence measurements in solvent 19, HClO 4 was used as proton source. The standard errors on τ1 are ±15 ps and ±3 ps on τ2. ϕ f values were determined by excitation at 560 nm (15 ps and 250 nm). 27 It is unlikely that the difference of τ2 between methanol and 1-butanol is related to a difference in solvent polarity. A lower-polarity solvent such as 1-butanol (dielectric constant ε = 17.1 compared to 32.6 for methanol) will lead to a less extensive bathochromic shift by dipolar interactions. This would slow the relaxation, and even longer relaxation times would be observed in solvents such as THF (ε = 7.4 and diethyl ether, ε = 4.3). This is, however, not the case. Conversely, a higher viscosity will slow the dipolar relaxation of the solvent by increased friction forces. Furthermore, the oxygen of 1-butanol competes more efficiently than the oxygen of methanol with the aniline nitrogen of BODIPY 1 for protons. Hence, one can also model a less important hydrogen bonding in 1-butanol leading again to a smaller red shift due to a rearrangement of the hydrogen bond after excitation. As the solvent relaxation involves a weakening of the hydrogen bond after excitation (see

### Table 1: Photophysical Properties of 1 in Several Solvents

<table>
<thead>
<tr>
<th>no.</th>
<th>solvent</th>
<th>λ_{abs} (max/nm)</th>
<th>λ_{em} (max/nm)</th>
<th>λ_{ex} (max/nm)</th>
<th>ΔD (cm⁻¹)</th>
<th>fwhm_{abs} (cm⁻¹)</th>
<th>ϕ_f (n.s.)</th>
<th>τ_1 (ps)</th>
<th>τ_2 (ps)</th>
<th>k_t (10^8 S⁻¹)</th>
<th>k_{la} (10^8 S⁻¹)</th>
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<td>methylcyclohexane</td>
<td>597</td>
<td>612</td>
<td>597</td>
<td>411</td>
<td>938</td>
<td>0.86 ± 0.02</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>2</td>
<td>cyclohexane</td>
<td>597</td>
<td>612</td>
<td>597</td>
<td>411</td>
<td>968</td>
<td>0.97 ± 0.03</td>
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<td>2.77</td>
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<td>620</td>
<td>602</td>
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<td>1370</td>
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<td>3.43</td>
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<td>640</td>
<td>607</td>
<td>850</td>
<td>1267</td>
<td>0.85 ± 0.02</td>
<td>3.25</td>
<td>2.62</td>
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<td>627</td>
<td>596</td>
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<td>1350</td>
<td>0.91 ± 0.02</td>
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<td>diisopropyl ether</td>
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<td>629</td>
<td>594</td>
<td>937</td>
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<td>0.87 ± 0.03</td>
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<tr>
<td>7</td>
<td>diethyl ether</td>
<td>593</td>
<td>641</td>
<td>593</td>
<td>1263</td>
<td>1444</td>
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<td>605</td>
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<td>665</td>
<td>596</td>
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<td>1513</td>
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<td>3.31</td>
<td>1.78</td>
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<td>600</td>
<td>664</td>
<td>600</td>
<td>1606</td>
<td>1902</td>
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<td>601</td>
<td>678</td>
<td>601</td>
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<td>597</td>
<td>695</td>
<td>597</td>
<td>2362</td>
<td>1648</td>
<td>0.27 ± 0.01</td>
<td>2.23</td>
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<td>butanenitrile</td>
<td>600</td>
<td>695</td>
<td>600</td>
<td>2278</td>
<td>1725</td>
<td>0.27 ± 0.02</td>
<td>2.26</td>
<td>1.19</td>
<td>3.23</td>
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<tr>
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<td>propanenitrile</td>
<td>598</td>
<td>710</td>
<td>598</td>
<td>2638</td>
<td>1762</td>
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<td>1.84</td>
<td>1.03</td>
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<tr>
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<td>696</td>
<td>598</td>
<td>2411</td>
<td>1838</td>
<td>0.16 ± 0.01</td>
<td>0.85</td>
<td>14</td>
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<tr>
<td>16</td>
<td>DMF</td>
<td>607</td>
<td>718</td>
<td>607</td>
<td>2547</td>
<td>1827</td>
<td>0.08 ± 0.01</td>
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<td>17</td>
<td>acetonitrile</td>
<td>597</td>
<td>717</td>
<td>597</td>
<td>2803</td>
<td>1762</td>
<td>0.090 ± 0.002</td>
<td>1.20</td>
<td>0.75</td>
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<tr>
<td>18</td>
<td>DMSO</td>
<td>610</td>
<td>737</td>
<td>609</td>
<td>2825</td>
<td>1876</td>
<td>0.056 ± 0.007</td>
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<tr>
<td>19</td>
<td>CHCN + H^+</td>
<td>553</td>
<td>561</td>
<td>553</td>
<td>258</td>
<td>725</td>
<td>1.00 ± 0.02</td>
<td>4.19</td>
<td>2.39</td>
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</table>

*For the time-resolved fluorescence measurements, the samples in solvents 2–4, 7–15, and 17 were excited at 580 nm whereas 530 nm excitation was used for solvent 19. For the steady-state and time-resolved fluorescence measurements in solvent 19, HClO 4 was used as proton source. The standard errors on τ1 are ±15 ps and ±3 ps on τ2. ϕ f values were determined by excitation at 560 nm (15 ps and 250 nm).*
above), it is difficult to understand why this should be slowed in the less polar 1-butanol where a less extensive rearrangement is necessary. However, the difference in viscosities (0.597 cP in methanol and 2.95 cP in 1-butanol) can explain why the rearrangement of this hydrogen bond after excitation is slower in 1-butanol.

2.3. Solvatochromic Effects. At the simplest level, solvent-dependent shifts of the fluorescence emission spectra are interpreted in terms of the Lippert–Mataga equation (eq 7, theoretical section), which describes the Stokes shift \( \Delta \lambda = \lambda_{\text{abs}} - \lambda_{\text{em}} \) as a function of the interaction between the change of the dipole moment of \( \mathbf{1} \) upon excitation, and the dipole in solvents with different dielectric constants (\( \epsilon \)) and refractive indices (\( n \)).

The use of eq 7 is limited to transitions where the excited-state reached after absorption is also the emissive state (hence for \( S_0 \rightarrow S_1 \) excitation and identical dipole moments for the Franck–Condon and relaxed excited states) and where the excited-state dipole moment is independent of solvent polarity. To go beyond the limitations imposed by the Lippert model, INDO/SCI calculations are presented here, in which self-consistent reaction field (SCRF) calculations are performed for pairs of states (ground state + excited state) considering full (i.e., electronic and inertial) relaxation in the initial state and only electronic relaxation in the final state (see Theoretical Section). The interaction between the final state and the mean reaction field created by the initial state leads to expressions similar to eqs 4 and 5 for a spherical cavity with radius \( a \) (but where the excitation energies and dipoles are obtained at the output of a SCRF process).

The INDO/SCI calculations indicate a significant increase in the vertical dipole moment difference \( \Delta \mu_{\text{ge}} \) when going from the (AM1/CAS-CI) ground-state equilibrium geometry (i.e., initial state for absorption) to the excited-state geometry (initial state for emission); in the gas phase, these values amount to \( \sim 2.6 \) and \( \sim 7.3 \) D, respectively. This is illustrated in Figure 3, displaying the changes in charge distribution between the ground and excited states, as obtained from a ZDO (zero differential overlap) analysis on both geometric structures. Although the excited-state wave function (the differential density between \( S_0 \) and \( S_1 \); see Figure 3) is still mostly confined on the BODIPY core, larger contributions on the \( p-N,N\text{-dimethylamino} \) side chain are computed in the excited-state configuration. These are consistent with increased charge-transfer contributions and, therefore, also a larger permanent dipole in the excited state.
As a consequence of the reshuffling in charge density upon electronic excitation, the ground-state vertical absorption is very slightly (blue) shifted with increasing solvent polarity (in the ground-state geometry, we have $\Delta \mu_{ge}(G) \approx \Delta \mu_{ge}(E)$ and the spectral shift mostly arises from solvent polarizability), while the excited-state vertical emission is strongly red-shifted (in the excited-state geometry, we have $\mu_{ge}(E) \gg \mu_{ge}(G)$), see Figure 4. The asymmetric evolution of the spectral shifts in absorption and emission predicted on the basis of the INDO/SCI results is fully supported by the experimental data (compare parts a and b of Figure 4).

Interestingly, both theory and experiment yield a poor linear relationship of the Stokes shift $\Delta \nu$ vs $\Delta f$ (Figure 5). This arises primarily from the nonlinear evolution of the Stokes shift in the more polar solvents, that is for $\Delta f \lesssim 0.2$.

To rationalize this evolution, it is useful to look at the relevant state dipole moment differences, namely $|\Delta \mu_{ge}(G)|$, $|\Delta \mu_{ge}(E)|$, and $|\Delta \mu_{ge(ad)}|$ (the difference between the dipoles in the relaxed ground and excited states, i.e., the “adiabatic” dipole moment difference) (see Figure 6). The vertical dipole differences $|\Delta \mu_{ge}(G)|$ and $|\Delta \mu_{ge}(E)|$ show hardly any dependence on solvent polarity, while the adiabatic quantity $|\Delta \mu_{ge(ad)}|$ increases significantly in more polar solvents (for $\Delta f$ values larger than $\sim 0.15$). For compound 1, it turns out that: $|\Delta \mu_{ge}(E)| \gg |\Delta \mu_{ge}(G)|$. In addition, $\mu_{ge}(E) \approx |\Delta \mu_{ge}(E)|$ for small $\Delta f$ values ($<0.15$). (In more polar solvents the ground-state dipole becomes significant.) When only the (dominant) contribution from emission to the Stokes shift is retained, eqs 4 and 5 can then be combined into the Lippert–Mataga expression (eq 7), but where $\Delta \mu_{ge}$ is the dipole difference computed in the excited-state equilibrium geometry. The best linear fit of the measured Stokes shift $\Delta \nu$ in the solvent polarity range ($0 < \Delta f < 0.15$) (Figure 5) yields $\Delta \mu_{ge}(E) \approx 7.4$ D for $a = 5.25$ Å, in excellent agreement with the calculated value (Figure 6). For more polar solvents, $\mu_{ge}(E)$ and $\Delta \mu_{ge(ad)}$ increase substantially, the dependence of the Stokes shift $\Delta \nu$ on $\Delta f$ is nonlinear and eq 7 fails to reproduce the experimental data. The more pronounced evolution of $\mu_{ge}(E)$ with $\Delta f$ (as compared to $\mu_{ge}(G)$) and the resulting increase in $\Delta \mu_{ge(ad)}$ [and to a lesser extent $\Delta \mu_{ge}(E)$] likely arise from the larger polarizability of 1 in its excited state. In the SCRF procedure applied here, the total dipole of the solute molecule in a given excited state is the sum of the source (initial) dipole and an induced contribution associated with the solvent reaction field. As the latter contribution is proportional to the polarizability ($\alpha$) of the solute in that state, a larger induced dipole in the excited state follows from $\alpha_e > \alpha_g$. Although we did not pursue this further, we note that expressions for the
spectral shifts accounting for such changes in polarizability between ground and excited state have been derived.32,33

While the Lippert solvent parameter $\Delta \nu$ only considers the permanent dipole moment and to some extent the polarizability of the solvent, other solvent polarity scales—e.g., the normalized $E_{T}^{N}(30)$ scale34—used to describe the solvatochromic shifts observed in the absorption and fluorescence spectra also take into account the hydrogen bond donating and accepting character of the solvent. Figure 7 shows the Stokes shift $\Delta \nu$ of I as a function of the $E_{T}^{N}(30)$ solvent parameter. From this figure, two different groups of solvents can be distinguished: nonprotic and protic (methanol and 1-butanol) solvents. There is an adequate linear relationship ($r = 0.982$) between the Stokes shift and the $E_{T}^{N}(30)$ polarity scale for the nonprotic solvents (i.e., excluding methanol and 1-butanol). A similar linear relationship ($r = 0.984$) was found between the fluorescence emission maximum $\bar{v}_{em}$ and $E_{T}^{N}(30)$ for the nonprotic solvents. For the protic solvents methanol and 1-butanol, the Stokes shift is much smaller than expected based on the $E_{T}^{N}(30)$ scale. For I, an increase of the permanent dipole moment of the solvent leads to a large red shift of the emission while increasing the hydrogen donating character of the solvent leads to a negligible red shift or perhaps even a blue shift of the emission from the relaxed excited state. This corresponds to our earlier discussion on the delocalized structures shown in Figure 2.

The solvent effect on $\bar{v}_{abs}$, $\bar{v}_{em}$, and the Stokes shift $\Delta \nu$ can also be described on the basis of a multilinear expression (eq 1a):

$$y = y_0 + aA + bB + cC$$

in which $y_0$ stands for the physicochemical property of interest in the absence of solvent (i.e., in the gas phase); $a$, $b$, and $c$ are adjustable coefficients that reflect the dependency of the physicochemical property ($y$) in a given solvent on the various (A, B, C) solvent parameters. At least two different sets of solvent scales can be found in the literature to characterize these solvent properties. In the present analysis, the polarity/polarizability, the acidity, and the basicity of the solvent are taken into account. Kamlet and Taft35 put forward the $\pi^*$, $\alpha$, and $\beta$ parameters to characterize, respectively, the polarity/polarizability, the acidity, and the basicity of a solvent (eq 1b). Conversely, Catalán et al. proposed empirical solvent scales for polarity/polarizability (SPP36,37), for acidity (SA37), and for basicity (SB37,38) to describe the respective properties of a given solvent (eq 1c). The essential difference between the two sets of scales lies in the fact that the Catalán scales have been constructed with data obtained from the same laboratory, by using always the adequate probe/homomorph pair, and therefore, these scales represent the corresponding pure effects. The data values from the scales by Kamlet and Taft, however, have in many cases been obtained from an average of about 40 probes, measured by different authors from several laboratories.

$$y = y_0 + a_{SA} + b_{SB} + c_{SPP}$$

(Kamlet–Taft) (1b)

$$y = y_0 + a_{SA} + b_{SB} + c_{SPP}$$

(Catalán) (1c)

Table 2 lists the estimated coefficients $y_0$, $a$, $b$, $c$ (see eq 1) and correlation coefficients ($r$) for the multiple linear regression analysis of the absorption ($\bar{v}_{abs}$) and fluorescence emission maxima ($\bar{v}_{em}$), and the Stokes shift $\Delta \nu$ of I as a function of the Kamlet–Taft (eq 1b) and Catalán (eq 1c) solvent scales for the pure solvents (1–18 of Table 1). The Kamlet–Taft solvatochromic parameters $\alpha$, $\beta$, and $\pi^*$ parameters are taken from ref 39, while the Catalán solvent parameters SA, SB, and SPP are from refs. 36–38. Both sets of solvent scales produce similar qualitative results, although the Catalán scales yields somewhat better fits for $\bar{v}_{em}$ and $\Delta \nu$ (as judged by the correlation coefficient $r$ as goodness-of-fit criterion).

The correlation coefficients ($r$) for the multilinear fits of the absorption maxima of I vs solvent polarity/polarizability, acidity, and basicity are far from 1.0. However, there is a linear relationship between $\bar{v}_{abs}$ and the Catalán solvent polarizability parameter SP (see below). Conversely, much better $r$ values

![Figure 7. Stokes shift ($\Delta \nu$) (in cm$^{-1}$) of I as a function of the solvent polarity parameter $E_{T}^{N}(30)$. The numbers refer to the same solvents as in Figure 1 and Table 1. The straight line is the best linear fit ($r = 0.982$) for the nonprotic solvents (i.e., excluding methanol and 1-butanol).](image-url)
are found for the multilinear fitting of the fluorescence emission maxima \( \bar{v}_{em} \). For both sets of solvent scales, the estimated coefficients describing the solvent polarity/polarizability (large and negative \( c_{SPP} \) and \( c_{c}^* \) values) indicate that the solvent polarity/polarizability is the main parameter responsible for the shift of the fluorescence emission band (\( \bar{v}_{em} \)) to lower energies, corroborating the observed bathochromic shifts of the emission maximum \( \bar{v}_{em} \) with higher \([f(\epsilon) - \frac{1}{2}f(n^2)]\) (see Figure 4). The (absolute) values of the coefficients \( a_{SB} \) and \( b_{SB} \) are indeed much smaller than \( c_{SPP} \). The same is true for \( a_{a} \) and \( b_{j} \) compared to \( c_{c}^* \). Furthermore, for the fits of \( \bar{v}_{em} \), the standard errors on the parameters \( a_{SA} \) and \( b_{SB} \) (and \( a_{a} \) and \( b_{j} \)) are of comparable magnitude as the parameters themselves. The errors on \( y_{obs}, c_{SPP} \), and \( c_{c}^* \), however, are much smaller. Fitting a linear equation with the solvent scale SPP as the only independent variable to \( \bar{v}_{em} \) (eq 1b with \( a_{SA} = 0 \) and \( b_{SB} = 0 \)) confirms that the polarity/polarizability of the solvent is the most important factor determining the fluorescence emission maximum. Indeed, this linear fit (Catalán, Table 2) has a similar r value (0.973) as the multilinear fit (\( r = 0.978 \)). An analogous result is obtained for the Kamlet–Taft scale: if the solvent parameter \( \pi^* \) is used as the only independent variable in the linear equation to fit \( \bar{v}_{em} \) (eq 1c with \( a_{a} = 0 \) and \( b_{j} = 0 \)), the obtained correlation coefficient \( r = 0.929 \) is somewhat smaller than for the multilinear fit (\( r = 0.947 \)).

Figure 8 shows the relationship between the fluorescence maxima \( \bar{v}_{em} \) predicted by the multicomponent linear regression using the estimated \( a_{SA}, b_{SB}, \) and \( c_{SPP} \) coefficients (Catalán scale, eq 1c) vs the respective experimental values. There is a linear relationship encompassing all solvents (1–18), corroborating the high correlation coefficient found for the multilinear Catalán fit. An analogous curve of \( \bar{v}_{em} \) for the Kamlet–Taft solvent scales (figure not shown) indicates that the Kamlet–Taft scales is slightly less appropriate than the Catalán scales for describing the solvent dependent fluorescence emission shifts of \( \mathbf{1} \).

The small solvatochromism of \( \mathbf{1} \) for absorption is noteworthy. Indeed, the data of Table 2 indicate that \( \bar{v}_{abs} \) does not depend on solvent polarity/polarizability, acidity, or basicity. However, this small change may reflect just a slight change in polarizability on the environment of the chromophore. Indeed, when one plots \( \bar{v}_{abs} \) as a function of the Catalán solvent polarizability parameter SP (SP40 scale) for 16 solvents of Table 1 [the SP values for dibutyl ether (solvent 5) and diisopropyl ether (solvent 6) are not available right now], an excellent linear relationship (eq 2, \( r = -0.948 \)) is found between \( \bar{v}_{abs} \) and SP (Figure 9),

\[
\bar{v}_{abs} = \bar{v}_{abs}^0 + a_{SP} \text{SP}
\]

with \( \bar{v}_{abs}^0 = (18.1 \pm 0.1) \times 10^3 \text{ cm}^{-1} \) and \( a_{SP} = (20 \pm 2) \times 10^2 \). This clearly indicates that the absorption spectra depend only on the change of polarizability of the environment of the chromophore.

Using the fluorescence decay time \( \tau \) and the fluorescence quantum yield \( \phi_f \), the rate constants for fluorescence \( k_f \) and nonradiative decay \( k_n \) can be calculated according to eq 9 (see Experimental Section). The data in Table 1 show that \( k_f \) decreases with increasing solvent polarity. Since \( k_f \) is proportional to the product of the squared transition dipole moment \( \langle \psi_c^* \mid \mu \mid \psi_f \rangle^2 \), \( n^3 \), and \( \bar{v}_{em}^{-3} \) (eq 3),

\[
k_f = \frac{64\pi^4}{3h^3} \bar{v}_{em}^{-3} \langle \psi_c^* \mid \mu \mid \psi_f \rangle^2
\]

we plotted \( k_f(n^3\bar{v}_{em}^{-3}) \) of \( \mathbf{1} \) vs \( \Delta f \) in Figure 10. In eq 3, \( \mu \) stands for the dipole moment operator. This ratio remains practically constant up to \( \Delta f \approx 0.20 \) and then decreases with increasing \( \Delta f \) to reach about half its value in acetonitrile compared to the apolar solvents. This means that the transition dipole moment...
(ψ/C|H|ψ/E) has decreased by 30%. This corresponds to the increase of the excited-state dipole moment in more polar solvents as suggested by the nonlinear Lippert–Mataga plot (Figure 5) and theoretical calculations.42

The strong increase of $k_{nr}$ upon increasing solvent polarity (Figure 11) can be rationalized if $k_{nr}$ can be attributed mainly to internal conversion. This nonradiative transition is accompanied by a large change in dipole moment. Although there is no full electron transfer as in exciplexes,43 the nonradiative processes can be considered to be due to some extent to a partial charge transfer between the strongly coupled BODIPY and aniline moieties. The free energy dependence of the rate of charge transfer is currently described in Marcus’ theory.44 In the framework of this theory, the solvation will act as accepting modes for this internal conversion process.45 The energy gap between the singlet excited state and the ground state is, in all solvents, close to or above 2 eV; thus, it always exceeds the reorganization energy, and the nonradiative process proceeds in the “inverted” region.46 Increasing the solvent polarity decreases the energy gap and simultaneously increases the reorganization energy. In the “inverted” region, both factors will increase the rate of the nonradiative process. As the increased value of $k_{nr}$ can be rationalized in the framework of Marcus’ theory, the effect of the changing electronic structure in more polar solvents is apparently less relevant than for $k_{f}$.  

2.4. pH Dependence of the Absorption and Fluorescence Spectra in Acetonitrile Solution. Protonation of the tertiary amine function drastically alters the electron-donating properties of the tertiary amine group and consequently is expected to switch off the ICT to the borondipyrromethene moiety. In acidified acetonitrile, this produces the typical BODIPY-like narrow absorption and emission bands with a very high fluorescence yield.5,13–23 The absorption spectra of 1 in acetonitrile are shown as a function of pH in Figure 12a. The absorption spectra of 1 show a decrease of the absorbance band with a maximum at 597 nm with increasing HCl concentration (i.e., lower pH) and a simultaneous increase of the absorption at 553 nm. Varying the pH also gives rise to several isosbestic points (at 566, 465, 336, and 280 nm). The lowest-energy absorption band of the ammonium form of the dye is blue-shifted by about 40 nm in comparison to that of the neutral amine form. The width of the absorption band of the neutral amine (fwhm$_{abs}$ = 1794 cm$^{-1}$) is ~50% smaller in the ammonium form (fwhm$_{abs}$ = 791 cm$^{-1}$).

The fluorescence excitation ($\lambda_{em}$ = 660 nm) and emission spectra ($\lambda_{em}$ = 530 nm) of 1 in acetonitrile are shown as a function of pH in Figure 12, parts b and c, respectively. The fluorescence signals increase significantly with increasing HCl concentration. In the same way as the absorption spectra, the fluorescence excitation maximum at 597 nm (neutral amine form) moves to 552 nm (positively charged ammonium form) at lower pH. The highest $f$ value (0.91, determined by excitation at 530 nm) is found for the ammonium form (at the lowest pH, namely 0.38). The width of the fluorescence excitation band is also reduced in going from the amine (fwhm = 1908 cm$^{-1}$) to the ammonium form (fwhm = 825 cm$^{-1}$ in acidified acetonitrile), stressing the influence of the conjugated (unprotonated)
the spectra of Figure 12b (direct titration of the amine group on the spectroscopic properties of I). The solid line represents the best fit of eq 10 with the data of Figure 13. (a) Best fit of eq 10 with the emission spectra of Figure 12b (λem = 660 nm, λex = 553 nm). (b) Best fit of eq 11 with the emission spectra of Figure 12c (λem = 660 nm, λex = 553 nm).

Figure 13. (a) The solid line represents the best fit of eq 10 with n = 1 to the direct excitation fluorimetric titration data of I obtained from the spectra of Figure 12b (λem = 660 nm, λex = 553 nm). (b) Best fit of eq 11 with n = 1 to the ratiometric excitation fluorimetric titration data of I obtained from the spectra of Figure 12b (λem = 660 nm, λex = λex = 660/553 nm).

The acidity constant \( K_a \) and the stoichiometry (n) of the binding of H\(^+\) by the tertiary amine group of compound I were determined by fitting eq 10 or eq 11 (see Experimental Section) to the fluorescence excitation or emission spectral data.

The first method for estimating \( K_a \) and the stoichiometry (n) is the direct fluorimetric titration (eq 10, see Experimental Section). The results of the direct fluorimetric titration using the excitation data of Figure 12b (λem = 660 nm, λex = 553 nm) are displayed in Figure 13a and yield a pK\(_a\) value of 2.27 ± 0.05 and a well-defined 1:1 stoichiometry between I and H\(^+\), indicative of ammonium ion formation. A similar titration using the excitation spectra of Figure 12b (λem = 660 nm) at an excitation wavelength where the intensity decreases with lower pH (λex = 600 nm) yields the same pK\(_a\) value (2.28 ± 0.05). These results are in perfect agreement with the curve-fittings using the absorption spectra of Figure 12a (at 552 nm: pK\(_a\) = 2.21 ± 0.05, at 595 nm: pK\(_a\) = 2.28 ± 0.05) and the emission spectra of Figure 12c (λem = 562 nm: pK\(_a\) = 2.25 ± 0.04, at λem = 605 nm: pK\(_a\) = 2.17 ± 0.03). These results show that the obtained pK\(_a\) values are independent of which spectral data are used and of the selected wavelengths. All estimated n values are indicative of a 1 to 1 binding between dye I and H\(^+\). Since large spectral shifts are observed in the fluorescence excitation spectra, the ratiometric method (eq 11, see Experimental Section) can be used to estimate values of \( K_a \). The ratio \( R = \frac{F(\lambda_{em}, \lambda_{ex})}{F(\lambda_{em}, \lambda_{ex}^2)} \) of two fluorescence excitation intensities (at λex\(_1\) = 600 nm and λex\(_2\) = 553 nm) with observation at λem = 660 nm as a function of pH was used to estimate \( K_a \) and n. Figure 13b shows the best fit of eq 11 to the above-defined ratiometric fluorescence excitation data, from which values of \( K_a \) and n are obtained. The pK\(_a\) value from ratiometric excitation data estimated on the basis of eq 11 is 2.3 ± 0.1, in good agreement with that obtained by the direct titration method. The estimated n value indicates that I binds one proton.

3. Experimental and Theoretical Sections

3.1. Materials. All solvents for the spectroscopic measurements were of spectroscopic grade and were used without further purification. The chemicals for the synthesis were of reagent grade quality, procured from commercial sources and used as received. Boron trifluoride etherate was ca. 48% BF\(_3\). 3.2. NMR and Mass Spectra. 1H and 13C NMR spectra were recorded on a Bruker Avance 300 instrument operating at a frequency of 300 MHz for 1H and 75 MHz for 13C. 1H NMR spectra were referenced to tetramethylsilane (0.00 ppm) as an internal standard and chemical shift multiplicities are reported as s = singlet, d = doublet, and m = multiplet. 13C spectra were referenced to the residual CDCl\(_3\) signal (77.67). Low-resolution mass spectra were recorded on a Hewlett-Packard 5989A mass spectrometer in electron impact (EI) mode. High-resolution EI mass spectra were recorded on a Kratos MS50TC system coupled to a Mach 3 processing unit with a resolution of 10000.

3.3. Synthesis of 4. First, 408 mg (3 mmol) of p-methoxybenzaldehyde and 570 mg (6 mmol) of 2,4-dimethylpyrrole were dissolved in 50 mL of dry dichloromethane. One drop of trifluoroacetic acid (TFA) was added to the solution and the reaction mixture was stirred for 16 h at room temperature under argon. After disappearance of the aldehyde (monitored via thin-layer chromatography), a solution of 500 mg of p-chloranil in dichloromethane (30 mL) was added to the solution and stirring was continued for another 0.5 h. 3 mL of absolute triethylamine was then added to the mixture and after stirring for 15 min, 3 mL of BF\(_3\)-OEt\(_2\) was added dropwise. The stirring was continued for the next 2 h and then the mixture was washed with water. The separated organic phase was washed over MgSO\(_4\), evaporated, and purified through a silica column (eluent: hexane/ethyl acetate 7/3 v/v) to obtain 402 mg (38%) of shiny red crystals of compound 4, mp 214–216 °C.

1H NMR (300 MHz, in CDCl\(_3\)): 7.20 (d, 2H, J = 8.2 Hz, ArH); 7.03 (d, 2H, J = 9.1 Hz, ArH); 5.9 (s, 2H, H2 and H6); 3.8 (s, 3H, OCH\(_3\)); 2.5 (s, 6H, 2 × CH\(_3\)); 1.4 (s, 6H, 2 × CH\(_3\)). LRMS: (EI, 70 eV) 354 (M+ 100), 339 (20), 335 (11), 334 (41). HRMS (EI): calculated for C\(_{20}\)H\(_{21}\)BF\(_2\)N\(_2\)O, 354.1715; found, 354.1715.
3.4. Synthesis of 1. Compound 4 (70 mg, 0.2 mmol), p-N,N-dimethylanilino-phenylborane (40 mg, 0.28 mmol), piperidine (0.1 mL), acetic acid (0.1 mL), and a small amount of molecular sieves were suspended in 2 mL of toluene in a 10 mL glass tube sealed with a Teflon cap. The sample was irradiated at 200 W and 190 °C for 20 min in a CEM-Discover monomode microwave apparatus. After completion of the reaction, the cold mixture was directly poured into a silica gel column and eluted with a 1/1 (v/v) dichloromethane/hexane mixture. The collected blue fraction was subsequently recrystallized from chloroform/hexane to yield 25 mg (26%) of deep blue crystals of Dimethylaminostyryl Borondipyrromethene Dye.

INDO/S 49 /SCI (single configuration interaction) calculations of the ground-state geometry (capital "G"); similarly, \( \bar{\mu}_g(G) \) is the excited-state dipole in the excited-state geometry; \( \bar{\Delta}_{ge}(G) = \bar{\mu}_g(G) - \bar{\mu}_g(G) \) corresponds to the dipole moment difference between the ground state and the excited state in the geometry of the ground state [respectively, excited state]. The bar on top of \( \mu \) indicates the vector nature of the dipole moment. \( \epsilon \), \( n \), and \( a \) stand for the solvent dielectric constant, the solvent refractive index, and the radius of the spherical cavity in which the fluorophore is contained, respectively. If the same excited state is involved in absorption and emission, i.e., neglecting the influence of geometric relaxation in the excited state: \( \bar{\mu}_g(G) = \bar{\mu}_g(E) = \bar{\mu}_g, \bar{\Delta}_{ge}(G) = \Delta_{ge}(E) = \Delta_{ge} \). Subtracting eq 4 from eq 5 yields the well-known Lippert–Mataga expression for the Stokes shift:29

\[
\Delta \nu = \frac{2\Delta f}{4\epsilon_0 \hbar c a} (\bar{\mu}_e - \bar{\mu}_e) \left( \frac{\epsilon}{\epsilon_a} + \frac{\epsilon_a}{\epsilon} \right) + \text{constant} \quad (7)
\]

3.5. Quantum-Chemical Calculations. Ground-state and excited-state geometry optimizations of the isolated molecule in the gas phase have been performed at the AM1/CAS-CI level.47,48 These geometries have been subsequently used as input for INDO/S/SCI (single configuration interaction) calculations of the vertical electronic excitations.50

The solvent effects have been modeled within a self-consistent reaction field (SCRF) model in the presence of a dielectric medium.51 The solvent effects have been modeled within a self-consistent reaction field (SCRF) model in the presence of a dielectric medium.51 The solvent effects have been modeled within a self-consistent reaction field (SCRF) model in the presence of a dielectric medium.51 The solvent effects have been modeled within a self-consistent reaction field (SCRF) model in the presence of a dielectric medium.51 The solvent effects have been modeled within a self-consistent reaction field (SCRF) model in the presence of a dielectric medium.51 The solvent effects have been modeled within a self-consistent reaction field (SCRF) model in the presence of a dielectric medium.51 The solvent effects have been modeled within a self-consistent reaction field (SCRF) model in the presence of a dielectric medium.51 The solvent effects have been modeled within a self-consistent reaction field (SCRF) model in the presence of a dielectric medium.51 The solvent effects have been modeled within a self-consistent reaction field (SCRF) model in the presence of a dielectric medium.51 The solvent effects have been modeled within a self-consistent reaction field (SCRF) model in the presence of a dielectric medium.51 The solvent effects have been modeled within a self-consistent reaction field (SCRF) model in the presence of a dielectric medium.51 The solvent effects have been modeled within a self-consistent reaction field (SCRF) model in the presence of a dielectric medium.51 The solvent effects have been modeled within a self-consistent reaction field (SCRF) model in the presence of a dielectric medium.51

3.6. Steady-State Spectroscopy. The absorption measurements were done on a Perkin-Elmer Lambda 40 UV/vis spectrophotometer. Corrected steady-state excitation and emission spectra were recorded on a SPEX Fluorolog. For the determination of the fluorescence quantum yields (\( \phi_f \)) in solvents 1–18, dilute solutions with an absorbance below 0.1 at \( \lambda_{ex} = 560 \text{ nm} \) were used. Cresylviolet in methanol (\( \phi_f = 0.55 \)) was used as fluorescence standard.51 For solvent 19, \( \phi_f \) was determined by excitation at 530 nm. The \( \phi_f \) values reported in Table 1 are the averages of multiple (generally 4), fully independent measurements. The \( \phi_f \) values as a function of pH were measured by excitation at 530 nm. In all cases, correction for the refractive index was applied. All spectra were recorded at room temperature on nondegassed samples.

3.7. Time-Resolved Spectroscopy. Fluorescence decay traces of 1 were recorded at several emission wavelengths by the single-photon timing method.52 Details of the instrumentation used53 and experimental procedures54 have been described elsewhere. The samples were excited at 530 or 580 nm with a repetition rate of 8.18 MHz. Fluorescence decay histograms were collected in 4096 channels using 10 × 10 mm cuvettes. The absorbance at the excitation wavelength was always below 0.1. All lifetime measurements were performed on nondegassed samples at 20 °C. Histograms of the instrument response functions (using a LUDOX scatterer) and sample decays were recorded until they typically reached 10^4 counts in the peak channel. The total width at half-maximum of the instrument response function was ~30 ps.

The fitting parameters were determined by nonlinear least-squares estimation by minimizing the global reduced chi-square

\[
\chi^2 = \sum_i \sum_j w_{ij}(g_{ij}^0 - g_{ij}^f)^2/n
\]

where the index \( i \) sums over \( q \) experiments, and the index \( j \) sums over the appropriate channel limits for each individual experiment. \( g_{ij}^0 \) and \( g_{ij}^f \) denote respectively the observed and calculated (fitted) values corresponding to the \( i+j \)th channel of the \( i+j \)h experiment, and \( w_{ij} \) is the corresponding statistical weight. \( v \) represents the number of degrees of freedom for the entire multidimensional fluorescence decay surface.

The statistical criteria to judge the quality of the fit included both graphical and numerical tests and have been described previously.55 The decays were analyzed first individually by a (multi) exponential decay law in terms of decay times \( \tau_i \) and their associated preexponential factors \( a_i \). A minimum of three
different observation wavelengths \( \lambda_{em} \) covering the emission spectrum were selected for the construction of the fluorescence decay surface. The final curve-fitting was done by global (or simultaneous) analysis in which decay traces recorded at several \( \lambda_{em} \) were described by a (multi) exponential decay function with linked (global) decay times \( \tau \) and local preexponentials \( \alpha \). The goodness-of-fit was judged for each fluorescence decay trace separately as well as for the global fluorescence decay surface. All reported curve fittings had \( \chi^2 \) values below 1.1.

When the fluorescence decays were monoeponential, the rate constants of radiative (\( k_i \)) and nonradiative (\( k_{nr} \)) deactivation were calculated from the measured fluorescence quantum yield \( \phi_i \) and lifetime \( \tau \) according to eq 9:

\[
\begin{align*}
  k_i &= \frac{\phi_i}{\tau} \\
  k_{nr} &= \left(1 - \frac{\phi_i}{\tau}\right)
\end{align*}
\] (9a) (9b)

3.8. Fluorimetric Titrations. The ground-state acidity constant \( K_a \) of the ammonium salt of 1 was determined in acetonitrile solution at 20 °C by direct fluorimetric titration as a function of pH using the fluorescence excitation or emission spectra. To adjust the pH of the acetonitrile solutions, 0.1 and 0.01 M solutions of HCl and NaOH in acetonitrile were used. Fitting nonlinear eq 10 (see ref 56 for more information,) to the steady-state fluorescence data \( F \) recorded as a function of pH yields values of \( K_a \), the fluorescence signals \( F_{\text{min}} \) and \( F_{\text{max}} \) at minimal and maximal [H’], respectively (corresponding to the amine and ammonium forms of the dye, respectively), and \( n \) (the number of protons bound per amine molecule).

\[
F = \frac{F_{\text{max}} [H^+]^n + F_{\text{min}} K_a}{K_a + [H^+]^n}
\] (10)

Fitting eq 10 to the steady-state fluorescence data \( F \) with \( n, K_a, F_{\text{min}}, \) and \( F_{\text{max}} \) as freely adjustable parameters always gave values of \( n \) close to 1, indicating that one proton is bound per tertiary amine molecule. Therefore, \( n \) was kept fixed at 1 in the final curve fittings, from which the estimated values of \( K_a \) are reported here.

Since large spectral shifts are observed in the fluorescence excitation spectra, the ratiometric method (eq 11; see ref 56) can be used to calculate values of \( K_a \). In the excitation ratiometric method, one measures \( R = F(\lambda_{em}, \lambda_{ex})/F(\lambda_{em}, \lambda_{ex}^2) \) at a common emission wavelength, \( \lambda_{em} \), and two different excitation wavelengths, \( \lambda_{ex} \) and \( \lambda_{ex}^2 \). \( R_{\text{min}} \) and \( R_{\text{max}} \) correspond to the ratios at minimal and maximal [H’], respectively, and \( \xi = F_{\text{min}} (\lambda_{em}, \lambda_{ex}^2) / F_{\text{max}} (\lambda_{em}, \lambda_{ex}^2) \). Next, we evaluate \( R \) according to eq 11:

\[
R = \frac{R_{\text{max}} [H^+]^n + R_{\text{min}} K_a \xi}{K_a \xi + [H^+]^n}
\] (11)

Fitting nonlinear eq 11 to the excitation ratiometric fluorescence data \( R \) as a function of [H’] yields values for \( K_a \xi, n, R_{\text{min}}, \) and \( R_{\text{max}} \). Since \( \xi (\lambda_{em}, \lambda_{ex}^2) = \) the ratio of the fluorescence signal of the amine form of I over that of the ammonium form at the indicated excitation and emission wavelengths—\( \xi \) is experimentally accessible, a value for \( K_a \) can be recovered from ratiometric excitation fluorescence data.

4. Conclusions

We have used a microwave-assisted condensation reaction to synthesize the visible light excitable, fluorescent BODIPY-based dye 3-[2-[4-(dimethylamino)phenyl]ethenyl]-4,4-difluoro-8-(4-methoxyphenyl)-1,5,7-trimethyl-3a,4a-diaza-4-bora-s-indacene, which shows strongly soluble dependent fluorescence emission properties. The fluorescence quantum yield and the lifetime decrease in polar solvents in conjunction with large bathochromic shifts. In acetonitrile solution, large spectral shifts are observed in the fluorescence excitation and absorption spectra upon protonation of the tertiary amine function. The value of the acidity constant \( K_a \) (pK\(_a\) = 2.25) of the ammonium form—determined via both direct and ratiometric fluorimetric titrations—indicates that the dye can be used as a pH indicator in the acidic pH range.

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References and Notes

Dimethylaminostyryl Borondipyrromethene Dye


(44) This is the “gap law”.
(46) The active space comprises the eight most frontier molecular orbitals.
(48) The active space includes the 60 highest occupied molecular orbitals (MOs) and 60 lowest unoccupied MOs.