1,5-Prodan Emits from a Planar Intramolecular Charge-Transfer Excited State

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1,5-Prodan Emits from a Planar Intramolecular Charge-Transfer Excited State

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ABSTRACT: 1-Propionyl-5-dimethylaminonaphthalene (8, 1,5-Prodan) and two derivatives where the amino group is constrained in a seven-membered (9) and five-membered (10) ring are prepared. All three exhibit strong fluorescence and similar degrees of solvatochromism. Their fluorescence is strongly quenched in alcohol solvents. Because the amino group in 9 and especially 10 is forced to be coplanar with the naphthalene ring, the similar photophysical behavior of all three suggests that emission arises from a planar excited state (planar intramolecular charge transfer).

INTRODUCTION

Prodan (6-propionyl-2-dimethyaminonaphthalene), 1, is a highly fluorescent molecule whose Stokes shift varies strongly with solvent polarity.1 Its excited state has a dipole moment that is nearly double that of the ground state because of intramolecular charge transfer (ICT) from the amino group.2−4 The nature of the emissive excited state has been the subject of many studies. In nonpolar environments, fluorescence is thought to occur from a locally excited (LE) state whose structure is similar to that of the ground state. In fact, the LE state may be the second excited state (S2).6 In polar solvents, the excited state relaxes through ICT. Studies in micelles7 and related compound, dimethylaminobenzonitrile (Dmabn, 2), Figure 1, is known to emit from a twisted ICT (TICT) excited-state. The strongest evidence for this conclusion comes from the behavior of constrained Dmabn derivatives. Compound 3 locks the amino group in a small ring, and it shows only LE emission.7,8 Compound 4 locks the amino group in an orthogonal orientation, and it shows ICT emission.7,9

We have taken a similar approach to elucidating the structure of the emissive ICT state in Prodan. Derivatives (Figure 2) with a forced planar amino group (5)20 or propionyl group (6)21 show a fluorescence behavior that is similar to Prodan, while the twisted derivative 7 does not fluoresce.22 Thus, the behavior of the three model compounds suggests that Prodan emits from a PICT state and not from a TICT state.

Of the several regioisomers of Prodan, the 1,5-derivative (Figure 3) should be a strong fluorophore. While a derivative with an ethanoyl group was reported by Turro and Sames et al.,23 others bearing a cyclopenta[b]-ring fusion have been studied extensively by Brummond et al.24,25 The fused ring was not expected to significantly perturb the inherent photophysical behavior. The latter derivatives fluoresce nearly as strongly as 2,6-Prodan. Moreover, they absorb at shorter wavelengths, and they show large Stokes shifts. Unlike 2,6-Prodan, they are quenched in protic solvents. This research group has made a number of derivatives for bioconjugation studies.26

1,5-Prodan bears a striking similarity to the dansyl chromophore (Figure 3). Both have a dimethylamino electron-donating group in the 1-position and an electron-withdrawing group in the 5-position. The dansyl group is often used in the fluorescence tagging of proteins.27,28 The solvatochromism seen in these dansyl-tagged biomolecules has been interpreted assuming that the dansyl group emits from

Figure 1. Structures of Prodan (1), Dmabn (2), and two constrained derivatives 3 and 4.

Figure 2. Structures of constrained Prodan derivatives 5−7.

Figure 3.
We wondered if 1,5-Prodan might also emit from a TICT state. This paper reports the preparation of 1,5-Prodan (8) and two derivatives (9, 10) where the amino group is locked in a ring structure and compares their photophysical behavior.

**RESULTS AND DISCUSSION**

Compounds 8–10 were prepared using the routes in Scheme 1. The synthesis of the parent compound 8 follows the same route as our synthesis of Prodan.\(^{31}\) In the synthesis of 9, we were hoping that the carboxylic acid produced from the Michael addition of acrylic acid would cyclize adjacent to the amino group. Heating this acid in polyphosphoric acid at 120 °C did generate some of this isomer, but it mostly gave the methylamino precursor via a retro-Michael addition. The intramolecular Friedel–Crafts reaction of the carboxylic acid chloride is conducted at 40 °C, and cyclization occurs at the α-naphthalene position of the adjoining ring. The preparation of 10 makes use of an initial Bartoli indole synthesis.\(^{32,33}\)

The absorption and emission behavior of 8–10 are consistent with that of the reported cyclopentane-fused 1,5-Prodan derivative. Brummond et al. found that the latter has fluorescence quantum yields that are about 60% of those for 2,6-Prodan (1) across a range of aprotic solvents.\(^{24}\) The relative quantum yields for 8–10 were determined in toluene using anthracene (Φ = 0.30) as a reference. They are 0.42 ± 0.03, 0.40 ± 0.07, and 0.12 ± 0.01, respectively. The remaining reported yields in Table 1 are relative to these assignments. The absorption maxima of these compounds varies little with solvent: 332 ± 3 nm, 339 ± 3 nm, and 351 ± 3 nm for 8–10, respectively. Fluorescence spectra of 8–10 are shown in Figures S1–S3.

Relative to 8, constraining the amino group in a 7-membered ring (9) has little impact on the quantum yields and the absorption and emission positions. For the five-membered ring (10), however, both the absorption and emission maxima are significantly shifted to the red. One consequence of the emission red shift is that the fluorescence quantum yield is reduced because of the smaller energy gap between the excited state and the ground state. The origins of the red shifts in 10 are addressed in the computational modeling section (vide infra).

### Table 1. Fluorescence Quantum Yields (Φ\(_f\)) and Emission Maxima (λ\(_{em}\)) for 8–10 in Various Solvents\(^{4}\)

<table>
<thead>
<tr>
<th>solvent</th>
<th>8</th>
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<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tol</td>
<td>0.42</td>
<td>0.40</td>
<td>0.12</td>
</tr>
<tr>
<td>PhCl</td>
<td>0.44</td>
<td>0.43</td>
<td>0.12</td>
</tr>
<tr>
<td>CH(_2)Cl(_2)</td>
<td>0.33</td>
<td>0.43</td>
<td>0.12</td>
</tr>
<tr>
<td>EtOAc</td>
<td>0.35</td>
<td>0.37</td>
<td>0.06</td>
</tr>
<tr>
<td>Me(_2)CO</td>
<td>0.18</td>
<td>0.27</td>
<td>0.06</td>
</tr>
<tr>
<td>DMSO</td>
<td>0.12</td>
<td>0.26</td>
<td>0.06</td>
</tr>
<tr>
<td>iPrOH</td>
<td>0.021</td>
<td>0.046</td>
<td>0.026</td>
</tr>
<tr>
<td>MeOH</td>
<td>0.003</td>
<td>0.009</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

\(^{4}\)Solvents are listed in Figures S1–S3.
infra). All three compounds show strong fluorescence quenching in alcohols.

Despite the red-shifting in 10 relative to 8 and 9, all three show a similar ICT in the excited state. The displacement of electron density from the amino group to the carbonyl group gives rise to an increase in the molecular dipole moment. Higher polarity solvents are better able to stabilize the excited state, and, as a result, emission occurs at longer wavelengths. The degree of charge transfer is reflected in the magnitude of the solvatochromism. Figure 4 shows the solvatochromic behavior for 8–10. In these graphs, the emission maximum (wavenumbers) is plotted versus Reichardt’s $E_r(30)$ parameter. The latter is a composite scale used to characterize both the solvent polarity and the effect of solvent H-bonding. For Prodan and derivatives, multilinear regression analysis shows that their solvatochromism depends primarily on the polarity of the solvent but also slightly on the solvent acidity (H-bond donating ability). The three plots in Figure 4 are roughly linear for the aprotic solvents. The slopes of the best-fit lines are shown in Table 2. While the plots for 8 and 9 are linear

![Figure 4](image.png)

**Figure 4.** Plot of emission maximum ($E_r$, cm$^{-1}$) vs $E_r(30)$ for 8 (○, ---), 9 (□, −−−) and 10 (◊, --−). Solvents are toluene, chlorobenzene, ethyl ether, methylene chloride, ethyl acetate, acetone, dimethyl sulfoxide, acetonitrile, isopropanol, butanol, propanol, ethanol, and methanol.

Table 2. Slopes of the Solvatochromism Plots of $E$ vs $E_r(30)$ for 8–10

<table>
<thead>
<tr>
<th></th>
<th>8</th>
<th>9</th>
<th>$10^{-6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>slope</td>
<td>-169</td>
<td>-158</td>
<td>-156</td>
</tr>
<tr>
<td>std error</td>
<td>(5)</td>
<td>(7)</td>
<td>(14)</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.99</td>
<td>0.98</td>
<td>0.95</td>
</tr>
</tbody>
</table>

*Values in parentheses are from the regression analysis of the linear correlation. * Slope calculation excluding protic solvents.

with the protic solvents included, the plot for 10 is not. The deviations with the protic solvents are probably related to the extreme quenching in 10. One explanation for the deviation in the plot is that the H-bonding deactivation distorts the population of excited species, leaving only those of higher energy (more poorly H-bonded) to fluoresce. Alternatively, finding an emission maximum for a nearly completely quenched chromophore is problematic. While comparisons of 10 with 8 and 9 require some caution, there is no significant difference between the slopes for these compounds in aprotic solvents. Because the magnitude of the slopes is a reflection of the increase in the dipole moment of the excited state, all three must experience a similar degree of charge transfer in their excited states. Fluorophores 9 and 10 can only form a PICT excited state because the ring systems do not allow orthogonal twisting.

We have found that certain 2,6-Prodan derivatives are strongly quenched in alcohol solvents. In the excited state, the H-bonding interaction with the carbonyl becomes stronger as a result of the ICT. H-Bonding interactions with two solvent molecules have been implicated in the quenching mechanism, and the magnitude of quenching can be used as a sensor of solvent acidity. In Figure 5, the order of magnitude quenching is captured by taking the log$_{10}$ of the ratio of $I_{tol}/I_{sol}$ where $I$ refers to the fluorescence intensity maximum for a given solvent and $I_{tol}$ is the intensity in toluene. These values are plotted versus Catalán’s solvent acidity parameter, SA, a measure of the H-bond donating ability of the solvent. The intensity in toluene, where there is no H-bond induced quenching, is used as a reference. The plots are approximately linear over the range of alcohol solvents. The slopes are shown in Table 3 together with previous results with several 2,6-Prodan derivatives (Figures 2 and 6). The slopes for 8–10 are within the standard error of each other with an average of 2.3. The slopes for 1, 5–6 are also tightly clustered, but their average is much smaller (0.70). The slopes for 22–24 also fall close together, but their average (2.1) is much closer to that for 8–10. The clustering behavior for these three sets of compounds suggests that the H-bonding interactions are similar within each set and by extension that the charge densities of the carbonyl groups in the excited states are also similar. The stronger quenching for 22–24 relative to 1, 5–6 was ascribed to the carbonyl group being slightly twisted out of the plane of the naphthalene ring. In compounds 23–24, the tert-butyl group forces the nonplanarity, while in 22, it is the seven-membered ring. Evidently, these slight structural deviations turn on an efficient deactivation channel to the ground state with H-bonded complexes. With compounds 8–10, a similar deviation arises from the steric interaction with the

![Figure 5](image.png)

**Figure 5.** Plots of log ($I_{tol}/I_{sol}$) vs SA for 8 (○, ---), 9 (□, −−−) and 10 (◊, --−). Solvents (SA values) are 2-octanol (0.09), 2-butanol (0.22), cyclopentanol (0.26), 2-propanol (0.28), 1-pentanol (0.32), 1-butanol (0.34), 1-propanol (0.37), ethanol (0.40), and methanol (0.61).
The similarity in the behavior of all three compounds further supports the postulate of a PICT excited state.

The unusual behavior of 10 with respect to its absorption and emission positions is also captured by the computational results. The emission maximum for 10 is predicted to be shifted to the red by 900 cm\(^{-1}\) and its absorption by 850 cm\(^{-1}\). The other noticeable feature in the table is that the amino group in 10 is barely twisted in the ground state (about half as much) and essentially planar in the excited state (vs 20\(^\circ\)). The excited state dipole moment is slightly greater for 10. The enforced planarity of the amino group in 10 is likely responsible for its differing behavior relative to 8 and 9. The greater conjugation of the amino group leads to a slightly higher energy highest occupied molecular orbital and a lower energy lowest unoccupied molecular orbital (Figure S8).

### CONCLUSIONS

The photophysical behavior of two constrained derivatives (9 and 10) was compared with that of 1,5-Prodan (8). The former fluorophores can only emit from a PICT excited state because the amino group is locked in a seven- and five-membered ring, respectively. The change in the emission maxima in response to solvent polarity (solvatochromism) is a reflection of the excited-state dipole moment and hence the degree of ICT. Amino group twisting should result in a large ICT because of the resulting electronic decoupling with the aromatic system. However, all three show a similar level of solvatochromism in aprotic solvents. Further, ICT also results in increased H-bonding with the carbonyl oxygen in the excited state. With these three chromophores, H-bonding gives rise to efficient quenching. However, all three show similar sensitivity to H-bond-induced quenching. The planarity enforced by the five-membered ring in 10 gives rise to red-shifting of the absorption and emission maxima, resulting in a smaller quantum yield. Despite this difference in the behavior of 10, the solvatochromism and H-bond quenching results suggest a PICT excited-state structure for all three. By extension, these results cast suspicion on dansyl being a member of the class of TICT fluorophores.

### EXPERIMENTAL SECTION

**General Information.** NMR spectra were obtained with an Agilent DD2-400 or Varian Mercury VX-400 spectrometer. High-resolution ESI-MS were acquired with a Bruker Apex-Qe instrument. All solvents were of spectrophotometric grade. Reagents were obtained from Acros Organics or Sigma-Aldrich. Absorption and fluorescence data were collected using a fiber optic system with an Ocean Optics Maya CCD detector using a miniature deuterium/tungsten lamp and a 360 or 405 nm LED light source, respectively. Solution cells were thermostated at 23 \(^\circ\)C. Fluorescence spectra were reported after the following manipulations: (1) the electronic noise was subtracted from the

### Table 3. Slopes of the Quenching Plots in Figure 5 for 8–10 Compared with 2,6-Prodan (1) and Derivatives 5–6 (Figure 2) and 21–23 (Figure 6)

<table>
<thead>
<tr>
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<th>8</th>
<th>9</th>
<th>10</th>
<th>1</th>
<th>5</th>
<th>6</th>
<th>21</th>
<th>22</th>
<th>23</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope</td>
<td>2.48</td>
<td>2.13</td>
<td>2.32</td>
<td>0.74</td>
<td>0.74</td>
<td>0.60</td>
<td>1.96</td>
<td>2.20</td>
<td>2.02</td>
</tr>
<tr>
<td>std error</td>
<td>(0.15)</td>
<td>(0.17)</td>
<td>(0.29)</td>
<td>(0.08)</td>
<td>(0.05)</td>
<td>(0.08)</td>
<td>(0.07)</td>
<td>(0.13)</td>
<td>(0.19)</td>
</tr>
<tr>
<td>R(^2)</td>
<td>0.98</td>
<td>0.96</td>
<td>0.90</td>
<td>0.93</td>
<td>0.97</td>
<td>0.88</td>
<td>0.99</td>
<td>0.97</td>
<td>0.94</td>
</tr>
</tbody>
</table>
raw emission intensity and (2) the wavelength scale was converted to wavenumbers, and the net intensity was multiplied by $\lambda^2/\Delta\nu$ to account for the effect of the abscissa-scale conversion. The resulting intensity was divided by the spectral response of the Hamamatsu S10420 CCD. AM1/SM5C semiemirical calculations were conducted using AMPAC 9.1 from Semichem, Inc. Keywords employed were AM1, SDC.I = 53.64, 44.96, 41.66.

Syntheses (Scheme 1). Compounds 11–13 were prepared as described by Wang et al. Propionyl pyrrole was prepared previously. 3-((5-Bromonaphthalen-1-yl)(methyl)amino)propanoic acid, 4(1H)-one (8). A mixture of 5-bromo-1-dimethylaminonaphthalene, 13, (1.57 g, 6.28 mmol) in tetrahydrofuran (THF; 40 mL) was cooled to −78 °C under N₂. A solution of n-BuLi (4.5 mL, 1.6 M) in hexanes was added dropwise. The reaction was stirred for 15 min after the addition was complete. Propionyl pyrrole (920 mg, 7.48 mmol) was added slowly keeping the temperature below −60 °C. The cooling bath was removed, and the mixture was allowed to warm to −45 °C. Water (200 mL) was added, and the aqueous layer was extracted twice with CH₂Cl₂ (100 mL ea). The combined organic layers were dried over CaCl₂, and the solvent was evaporated in vacuo. The residue was purified by silica gel chromatography using a gradient elution with ethyl acetate in hexanes (0 → 10%). Fractions containing the compound were combined, concentrated, and distilled under high vacuum (0.2 Torr), giving compound 8 (860 mg, 60%) as a light brown oil. 1H NMR (400 MHz, CDCl₃): δ 7.91 (d, 3J = 8.3 Hz, 1H), 7.81 (d, 3J = 7.7 Hz, 1H), 7.50 (dd, 1J = 8.3, 7.8 Hz, 1H), 7.43 (d, 3J = 7.7 Hz, 1H), 7.06 (d, 3J = 7.8 Hz, 1H), 3.46 (t, 3J = 6.5 Hz, 2H), 3.10 (t, 3J = 6.6 Hz, 2H), 3.02 (s, 3H); 13C NMR (100 MHz, CDCl₃): δ 205.40, 150.27, 138.22, 133.10, 129.96, 127.95, 127.75, 127.20, 127.04, 112.74, 53.64, 44.96, 41.66. HRMS (ESI): [M + Na]⁺ calc for C₁₅H₁₅NONa⁺, 250.12024; found, 250.12012.

7-Bromo-1-methyl-1,2,3,4-tetrahydronaphtho[1,8-bc]-azepine (17). 7-Bromo-1-methyl-2,3-dihydronaphtho[1,8-bc]-azepin-4(1H)-one, 16, (1.3 g, 25%) was used without further purification. 1H NMR (400 MHz, CDCl₃): δ 7.91 (d, 3J = 8.6 Hz, 1H), 7.81 (d, 3J = 7.8 Hz, 1H), 7.50 (t, 3J = 8.0 Hz, 1H), 7.44 (d, 3J = 7.5 Hz 1H), 7.06 (d, 3J = 7.8 Hz, 1H), 3.46 (t, 3J = 6.7 Hz, 2H), 3.10 (t, 3J = 6.5 Hz, 2H), 2.17 (s, 3H).

7-Bromo-1-methyl-1,2,3,4-tetrahydronaphtho[1,8-bc]-azepin-4(1H)-one (9). 7-Bromo-1-methyl-2,3,4-tetrahydronaphtho[1,8-bc]-azepine, 17, (730 mg, 2.64 mmol) was dissolved in dry THF (15 mL), and the mixture was cooled to −78 °C under N₂. A solution of n-BuLi in hexanes (2.2 mL, 1.6 M, 3.5 mmol) was added dropwise with stirring. The mixture was allowed to stir for 20 min after the addition. Propionyl pyrrole (350 mg, 2.84 mmol) was added in one portion. The reaction was allowed to warm slowly to −25 °C, whereupon water was added (3 mL) with stirring. When the mixture reached 0 °C, it was diluted with Et₂O (200 mL), and the organic phase was washed twice with 5% aq NH₄Cl (100 mL ea), dried over Na₂SO₄ and concentrated in vacuo. The residue was purified using column chromatography (SiO₂, 0–10% EtOAc/hexanes). The yellow fluorescent band was added followed by the dropwise addition of oxalyl chloride (6.64 g, 52.7 mmol). The reaction was stirred at 0 °C under CaCl₂ drying for 1.5 h. The solvent was removed in vacuo, and the remaining oxalyl chloride was removed under high vacuum. The residue was dissolved in CH₂Cl₂ (75 mL), and aluminum chloride (6.7 g, 19.9 mmol) was added. The mixture was heated to reflux for 3 h. The reaction was allowed to cool and then it was quenched with aq NaHCO₃ (12.5 g/300 mL) with stirring. The aq phase was extracted with 10% CH₂Cl₂/hexanes (2 × 75 mL ea) and once with 20% CH₂Cl₂/hexanes (75 mL). The combined organic layers were washed with ice-cold water (100 mL), dried over Na₂SO₄ and concentrated in vacuo. The fraction boiling between 160 and 210 °C at 0.2 Torr gave crude 7-bromo-1-methyl-2,3-dihydronaphtho[1,8-bc]azepin-4(1H)-one, 16, (13.3 g, 25%) which was used without further purification. 1H NMR (400 MHz, CDCl₃): δ 7.91 (d, 3J = 8.6 Hz, 1H), 7.80 (d, 3J = 8.6 Hz, 1H), 7.50 (t, 3J = 8.0 Hz, 1H), 7.44 (d, 3J = 7.5 Hz 1H), 7.06 (d, 3J = 7.8 Hz, 1H), 3.46 (t, 3J = 6.7 Hz, 2H), 3.10 (t, 3J = 6.5 Hz, 2H), 2.17 (s, 3H).
collected and concentrated. The residue was distilled bulb-to-bulb under vacuum giving 1-(1-methyl-1,2,3,4-tetraydroanaphtho[1,8-bc]azepin-7-yl)-propan-1-one, 9, as a yellow oil (240 mg, 36%).

1H NMR (400 MHz, CDCl3): δ 7.17 (d, J = 8.2 Hz, 1H), 7.07 (d, J = 7.2 Hz, 1H), 3.18 (m, 4H), 3.02 (s, 3H), 1.39 (q, J = 7.3 Hz, 2H), 2.14 (quin, J = 6.7 Hz, 2H), 1.25 (t, J = 7.3 Hz, 3H).

13C NMR (100 MHz, CDCl3): δ 205.89, 152.86, 144.10, 134.90, 132.63, 128.19, 127.14, 126.66, 123.40, 116.53, 108.67, 56.34, 41.02, 35.55, 34.52, 29.50, 8.84.


6-Bromo-1H-benzog[gl]indole (18). 5-Bromo-1-nitronaphthalene, 11, (4.00 g, 15.9 mmol) was added all at once with stirring to a solution of vinyl magnesium bromide in THF (100 mL, 0.7 M, 70 mmol) that had been cooled to 10 °C in an ice-water bath under N2. The reaction immediately warmed to 40 °C. When the mixture cooled to 20 °C, the ice bath was removed and stirring was continued for 1 h. The reaction was cooled in an ice-water bath while a sat. aq solution of NH4Cl (5 mL) was added. The solvent was removed in vacuo, leaving crude 6-bromo-1-methyl-1H-benzog[gl]indole, 11, (2.01 g, 8.17 mmol) which was used without further purification.

1H NMR (400 MHz, CDCl3): δ 8.91 (br s, NH), 7.94 (d, J = 8.8 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.8 Hz, 1H), 7.72 (dd, J = 7.6, 0.7 Hz, 1H), 7.33 (dd, J = 8.0, 7.6 Hz, 1H), 7.29 (d, J = 2.9 Hz, 1H), 6.71 (dd, J = 2.9, 0.7 Hz, 1H), 13C NMR (100 MHz, CDCl3): δ 130.50, 128.95, 128.24, 125.89, 124.66, 124.31, 123.43, 123.09, 122.45, 119.85, 119.29, 104.60.

6-Bromo-1H-benzog[gl]indole (19). 6-Bromo-1H-benzog[gl]indole, 18, (2.01 g, 8.17 mmol) was dissolved in dry DMF (10 mL). The solution was cooled in an ice-water bath, and NaH (0.90 g, 60% in oil, 22.5 mmol) was added in several portions. The reaction was stirred for 30 min before adding CH3I (2.26 g, 9.55 mmol). Stirring was continued overnight. The reaction mixture was added dropwise to a rapidly stirred solution of NaCl (60 g) and NH4Cl in water (800 mL). Next, NaCl (130 g) was added, and the aqueous mixture was extracted twice with CH2Cl2. The combined organic layers were dried over CaCl2 and concentrated in vacuo. The residue was filtered with 250 mL of 15% ethyl acetate/hexanes through a silica gel column (~10 cm). The filtrate was concentrated in vacuo, giving crude 6-bromo-1-methyl-2,3-dihydro-1H-benzog[gl]indole, 20, (1.22 g, 61%). This material was dried on a vacuum pump before the next step.

1H NMR (400 MHz, CDCl3): δ 8.05 (d, J = 8.6 Hz, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.64 (d, J = 7.3 Hz, 1H), 7.34 (d, J = 8.4 Hz, 1H), 7.14 (dd, J = 8.0, 7.9 Hz, 1H), 3.53 (t, J = 8.7 Hz, 2H), 3.12 (s, 3H), 3.10 (t, J = 8.7 Hz, 2H).

13C NMR (100 MHz, CDCl3): δ 149.76, 132.93, 129.15, 126.73, 124.48, 124.32, 123.89, 123.55, 122.76, 119.47, 58.34, 42.97, 29.33.

Emission spectra of 8−10 in various solvents; plots of computed emission maxima vs experimental values; and optimized structures for the ground and first excited states of 8−10 (PDF)

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Author Contributions
The manuscript was written through contributions of all authors.

Notes
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