Electronic Supplementary Information for


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S1
General.

$^1$H and $^{13}$C NMR spectra were recorded on a Varian Gemini 200 (200 MHz) spectrometer in deuteriochloroform (CDCl$_3$) with either tetramethylsilane (TMS) (0.00 ppm $^1$H, 0.00 ppm $^{13}$C) or chloroform (7.26 ppm $^1$H, 77.00 ppm $^{13}$C) or as internal reference, unless otherwise stated. Data are reported in the following order: chemical shift in ppm, multiplicities (br (broadened), s (singlet), d (doublet), t (triplet), q (quartet), sex (sextet), hex (hextet), m (multiplet), exch (exchangeable), app (apparent)), coupling constants, $J$ (Hz), and integration. Infrared spectra were recorded on a Perkin-Elmer FTIR 1600 series spectrophotometer. Peaks are reported (cm$^{-1}$) with the following relative intensities: s (strong, 67-100%), m (medium 40-67%), and w (weak 20-40%). Melting points were determined on a Stanford Research Systems EZ-Melt apparatus and are not corrected.

Materials. Solvents for laser and photophysical studies were of spectroscopic grade (Merck, Aldrich or Sigma) and were used without purification. Those used in synthetic work were purified by standard methods. Other reagents were from commercial sources, and used as received. The commercial laser dye Coumarin 480, also called Coumarin 102 (laser grade, Exciton) was used as received with a purity >99% (checked by spectroscopic and chromatographic methods). ThiomethylBODIPY 1 is commercially available; alternatively, it can be prepared according to the literature starting from thiophosgene.$^{[1]}$ Propargylamine is commercially available and was used as received.
**Synthesis of 8-PAB.** A 20 mL scintillation vial was charged with thiomethylBODIPY 1 (100 mg, 0.42 mmol, 1 equiv.), a stir-bar, and dichloromethane (2 mL), then propargylamine (35 mg, 0.63 mmol, 1.5 equiv.) was added via syringe. The vial was capped and after 60 min, 1 was consumed. The solvent was removed under vacuum, and the product was purified by crystallization (CH$_2$Cl$_2$/petroleum ether) to give a yellow crystalline powder (97 mg, 94 % yield). TLC (30% EtOAc/hexanes, $R_f$ = 0.17); mp 176-178 °C (dec); IR (KBr, cm$^{-1}$): 3379 (m), 3363 (m), 3282 (m), 1592 (s), 1554 (s), 1402 (s); $^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 7.67 (br s, 2H), 7.13 (br s, 2H), 6.70 (br s, 1H), 6.51 (br s, 2H), 4.52 (m, 2H), 2.56 (t, $J = 2.6$ Hz, 1H; $^{13}$C (50 MHz, Acetone-$d_6$) $\delta$: 149.5, 136.3, 133.0, 126.2, 125.7, 122.9, 117.5, 115.7, 114.4, 78.0, 75.8, 36.8. Anal. Calcd for C$_{12}$H$_{10}$BF$_2$N$_3$: C, 58.82; H, 4.11; N, 17.15. Found: C, 58.66; H, 4.05; N, 17.25.

**Sample preparation.** The intrinsic photophysical properties of 8-PAB in solution were registered in diluted solutions (2×10$^{-6}$ M) using a 1 cm optical pathway quartz cuvettes. The samples were prepared by adding the corresponding solvent to an adequate amount of a concentrated stock solution (ca. 10$^{-3}$ M) of the dye in acetone, after vacuum evaporation of the solvent.

**Spectroscopic techniques.** UV-Vis absorption and fluorescence spectra were recorded on a Varian model CARY 4E spectrophotometer and a SPEX Fluorolog 3-22 spectrofluorimeter, respectively. Fluorescence quantum yield ($\phi$) was obtained using an ethanolic solution of Coumarin 1 as reference ($\phi_r =$0.75). Radiative decay curves were registered with the time correlated single-photon counting technique (Edinburgh
Instruments, model FL920, with picosecond time-resolution). Emission was monitored at the maximum emission wavelength after excitation at 370 nm by means of a diode laser (PicoQuant, model LDH370). The recorded fluorescence decay curves were deconvoluted from the pulse signal by means of an iterative software supplied with the instrument.

**Computational details.** All the quantum mechanical calculations were performed by means of the Gaussian 03 package. Ground and excited state geometries were optimised at the Density Functional Theory (DFT) method (using the B3LYP) and the Configuration Interaction Singles (CIS) *ab initio* method, respectively. In both cases the 6-31G* basis set was used.

**Laser experiments.** Liquid solutions of dyes were contained in 1 cm optical-path quartz cells that were carefully sealed to avoid solvent evaporation during experiments. The liquid cells of the blue-edge dyes were transversely pumped at 355 nm with 5.5 mJ, 12 ns FWHM pulses from the third-harmonic of Q-switched Nd:YAG laser (Spectron SL282G) at a repetition rate of up to 10 Hz. The exciting pulses were line-focused onto the cell, providing pump fluences on the active medium of 180 mJ/cm². The oscillation cavity (2 cm length) consisted of a 90% reflectivity aluminum mirror, with the end face of the sample as output coupler.

The photostability of the dyes was evaluated by irradiating under lasing conditions 10 μL of a solution in ethanol. The solutions were contained in a cylindrical Pyrex tube (1 cm height, 1 mm internal diameter) carefully sealed to avoid solvent evaporation during the experiments. Monitoring of sample photolysis was carried out by recording the laser-induced fluorescence emission, excited transversally to the capillary with the same pump
pulses from the Nd:YAG laser used for producing dye laser emission, as a function of the pump pulses at 1 Hz repetition rate. The fluorescence emission was monitored perpendicular to the exciting beam, collected by an optical fiber, and imaged onto the input slit of a monochromator (Acton Research corporation) and detected with a charge-coupled device (CCD) (SpectruMM:GS128B). The fluorescence emission was recorded by feeding the signal to the boxcar (Stanford Research, model 250) to be integrated before being digitized and processed by a computer. Each experience was repeated at least three times. The estimated error of the energy measurements was 10% and the experimental error in the photostability measurements was estimated to be on the order of 7%. Details of the experimental setup can be found elsewhere.[3,4]

Narrow-line-width laser emission and tuning ranges of dye solutions were obtained by placing the samples in a home-made Shoshan-type oscillator[5] consisting of full-reflecting aluminum back and tuning mirrors, and a 2400 lines·mm⁻¹ holographic grating in grazing incidence, with outcoupling via the grating zero order. Wavelength tuning was accomplished by rotation of the tuning mirror. Tuning mirror and grating (both from Optometrics) were 5 cm wide and the angle of incidence on the grating was 88.5°. Laser line width was measured with a Fabry-Perot etalon (IC Optical Systems) with a free spectral range of 15.9 GHz.
### Table S1. Photophysical\(^a\) properties of 8-PAB in different solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(\lambda_{ab})</th>
<th>(\varepsilon_{\text{max}})</th>
<th>(\lambda_{fl})</th>
<th>(\Delta\nu_{St})</th>
<th>(\phi^{b})</th>
<th>(\tau)</th>
<th>(k_{fl})</th>
<th>(k_{nr})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td>398.0</td>
<td>2.6</td>
<td>481.5</td>
<td>4360</td>
<td>0.32</td>
<td>2.04</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CF(_3)CH(_2)OH</td>
<td>404.0</td>
<td>2.9</td>
<td>480.5</td>
<td>3940</td>
<td>0.88</td>
<td>6.33</td>
<td>1.4</td>
<td>0.2</td>
</tr>
<tr>
<td>MeOH</td>
<td>405.0</td>
<td>3.3</td>
<td>464.5</td>
<td>3160</td>
<td>0.52</td>
<td>3.22</td>
<td>1.6</td>
<td>1.5</td>
</tr>
<tr>
<td>EtOH</td>
<td>406.5</td>
<td>3.2</td>
<td>463.0</td>
<td>3010</td>
<td>0.66</td>
<td>3.81</td>
<td>1.7</td>
<td>0.9</td>
</tr>
<tr>
<td>Me(_2)CO</td>
<td>406.0</td>
<td>3.1</td>
<td>466.5</td>
<td>3190</td>
<td>0.86</td>
<td>4.92</td>
<td>1.7</td>
<td>0.4</td>
</tr>
<tr>
<td>EtOAc</td>
<td>408.5</td>
<td>3.3</td>
<td>469.5</td>
<td>3180</td>
<td>0.94</td>
<td>5.13</td>
<td>1.8</td>
<td>0.2</td>
</tr>
<tr>
<td>c-hexane</td>
<td>422.5</td>
<td>3.5</td>
<td>482.0</td>
<td>2920</td>
<td>0.93</td>
<td>5.35</td>
<td>1.7</td>
<td>0.1</td>
</tr>
</tbody>
</table>

\(^a\) Absorption (\(\lambda_{ab}\)) and fluorescence (\(\lambda_{fl}\)) wavelengths (±0.5 nm), molar absorption coefficient at maximal absorption (\(\varepsilon_{\text{max}}\) in 10\(^4\) M\(^{-1}\) cm\(^{-1}\)), fluorescence quantum yield (\(\phi\), ±0.05 ), lifetime (\(\tau\), ±0.05 ns), Stokes shift (\(\Delta\nu_{St}\), in cm\(^{-1}\)) and rate constant of radiative and non-radiative deactivation (\(k_{fl}\) and \(k_{nr}\), in 10\(^8\) s\(^{-1}\))

\(^b\) using coumarin 1 in ethanol (\(\phi=0.75^{[6]}\)) as reference.

\(^c\) Decay curve analyzed as a two-exponential decay: \(\tau_2=4.96\) ns with a minor contribution (\(A_2 < 4\%\)).
Figure S1. Lasing efficiency of 8-PAB as a function of the dye concentration in ethyl acetate registered in the non-tunable-plane cavity. As it was expected, the lasing efficiency of the dye increased rapidly with the dye concentration until a maximum value for a solution with an optical density of ca. 18. From this point on, further increases in the dye concentration result in a slight decrease of the lasing efficiency which is related to the effect of reabsorption/reemission phenomena on the emission intensity, because the possibility of exciting molecules by absorption of a photon previously emitted by another molecule in the medium depends on the overlapping between absorption and fluorescence spectra, which is affected by the dye concentration.\[7\]

Figure S2. Efficiency and spectra of the laser emission of the dye 8-PAB (7×10^{-4} M) in different solvents: EtOAc (ethyl acetate, dashed line); acetone (dark grey line); EtOH (ethanol, light grey line) and F₃-EtOH (2,2,2-trifluoroethanol, black line).
References


