Electronic Supplementary Information

Synthesis

(E)-4,4-difluoro-5-(4-(dimethyl)amino)styryl)-1,3,7-trimethyl-8-phenyl-4-bora-3a,4a-diaza-s-indacene **B1**

4, 4-difluoro-1,3,5,7-tetramethyl-8-phenyl-4-bora-3a,4a-diaza-s-indacene (650 mg, 2 mmol) and 4-dimethylaminobenzaldehyde (350 mg, 2.3 mmol) were refluxed for 24 h in a mixture of toluene (50 mL), glacial acetic acid (1.5 mL) and piperidine (1.8 mL). Any water formed during the reaction was removed azeotropically by heating in a Dean-Stark apparatus. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure and then subjected to silica gel column chromatography with AcOEt/Hexane (2:1). The blue fraction was collected and recrystallized from $CHCl_3$/cyclohexane to give **B1** as deep blue needles (230 mg, 0.50 mmol, 25 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.36 (s, 3 H), 1.40 (s, 3 H), 2.45 (s, 3 H), 3.05 (s, 6 H), 5.99 (s, 1 H), 6.62 (s, 1 H), 6.71 (m, 2 H), 7.22 (d, 1 H, J=16.3 Hz), 7.30–7.34 (m, 2 H), 7.48–7.54 (m, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) 157.3, 151.1, 142.4, 138.8, 136.2, 135.7, 131.6, 129.4, 129.2, 129.1, 128.9, 128.2, 125.2, 121.2, 117.5, 116.9, 115.8, 112.6, 40.3, 14.7, 14.6, 14.3. HR-MS (EI, 70 eV): m/z found 456.2452, calcd for $[M+H]^+$ $C_{28}H_{28}N_3BF_2$ 456.2423. UV-Vis (CH_2Cl_2) λmax 598 nm.

(E)-4,4-difluoro-3,5-di-(4-(dimethyl)amino)styryl)-1,7-dimethyl-8-phenyl-4-bora-3a,4a-diaza-s-indacene **B2**

The same conditions were applied to 4, 4-difluoro-1,3,5,7-tetramethyl-8-phenyl-4-bora-3a, 4a-diaza-s-indacene (650 mg, 2 mmol) and 4-dimethylaminobenzaldehyde (760 mg, 5.0 mmol). After cooling to room temperature, the reaction mixture was concentrated under reduced pressure and then subjected to silica gel column chromatography with AcOEt/Hexane (2:1). The green fraction was collected and recrystallized from $CHCl_3$/cyclohexane to give **B2** as black needles (235 mg, 0.4 mmol, 20 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 6 H), 3.05 (s, 12 H), 6.62 (s, 2 H), 6.70 (m, 4 H), 7.21 (d, 2 H, J=16.3 Hz), 7.28–7.33 (m, 5 H), 7.45–7.55 (m, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.7, 150.8, 141.5, 136.8, 135.7, 135.6, 131.9, 129.2, 128.6, 128.4, 125.6, 125.2, 117.8, 115.1, 112.1, 40.3, 14.5. HR-MS (EI, 70 eV): m/z found 587.3152, calcd for $[M+H]^+$ $C_{37}H_{38}N_4BF_2$ 587.3158. UV-Vis ($CH2Cl_2$) λmax 692 nm.

Calculation of Fluorescence Quantum Yields

The fluorescence quantum yield (Φ) is the ratio of photons absorbed to photons emitted through fluorescence, *i.e.,* it gives the probability of the excited state being deactivated by fluorescence rather than by another, non-radiative mechanism. For the calculation of fluorescence quantum yields in B1 and B2 compounds dissolved in THF the comparative method of *Williams et al*. [1], which involves the use of standard fluorophore with known Φ value, was employed. In this method, it is assumed that solutions of studied and standard fluorophores with identical absorbance at the same excitation wavelength absorb the same number of photons. Therefore, the ratio of the integrated fluorescence intensities of two solutions at the same conditions will give the ratio of the quantum yields values, from which one is standard known. In order to obtain the trusted values of fluorescence quantum yield the measurements should be done at the same experimental conditions within a carefully chosen concentration range (normally, the absorbance in the 10 mm cuvette should not exceed 0.1 at the excitation wavelength) and the refractive

indexes of used solvents have to be taken into account. The standard fluorophore should be chosen to ensure that it absorb at the excitation wavelength and, if possible, emit in a similar region as studied sample. The measurements of the values of fluorescence quantum yield in B1 and B2 compounds have been performed in dilute solutions (1÷10 μM) using the excitation wavelength of 514 nm. As a standard fluorophore we used Rhodamine B dissolved in water (Φ_{RB}=0.31 at λ_{ex}=514 nm [2]).

In Fig.1-3 the absorption and emission spectra of B1, B2 and Rhodamine B obtained at different concentration are presented.

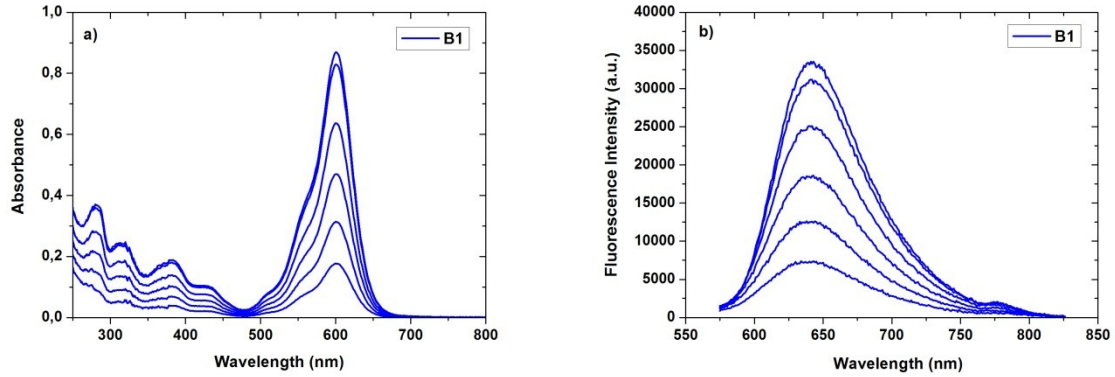

Fig.1. Absorption (a) and emission (b) spectra of B1 dissolved in THF obtained at different concentrations.

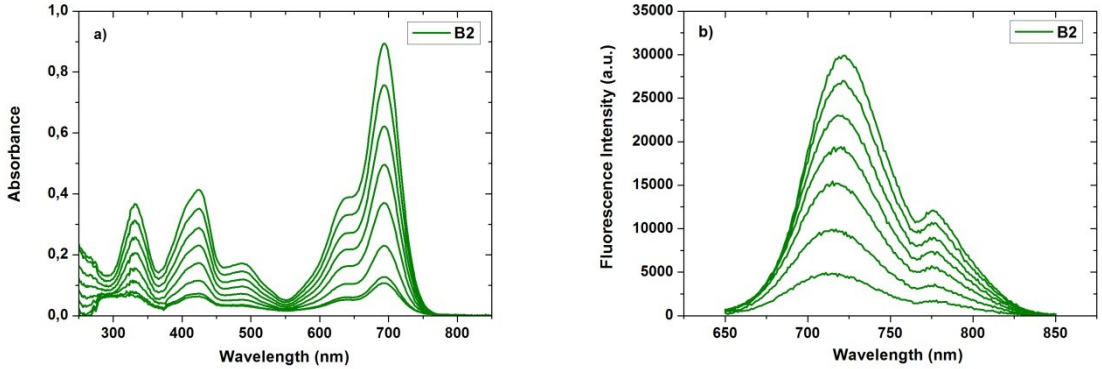

Fig.2. Absorption (a) and emission (b) spectra of B2 dissolved in THF obtained at different concentrations.

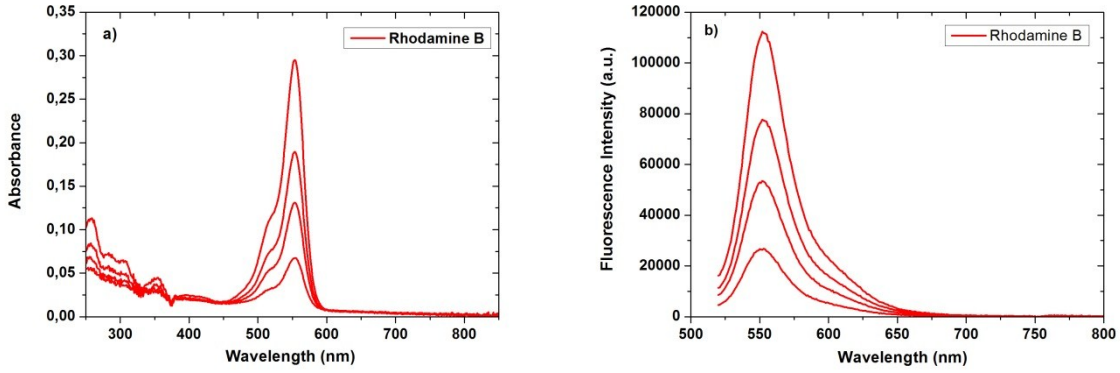

Fig.3. Absorption (a) and emission (b) spectra of Rhodamine B dissolved in water obtained at different concentrations.

The following equation has been used fir calculation of the values of fluorescence quantum yield:

$$\Phi_X = \Phi_{RB}\left(\frac{Grad_X}{Grad_{RB}}\right)\left(\frac{n_X^2}{n_{RB}^2}\right), \quad (1)$$

where Φ_{RB} is fluorescence quantum yield of rhodamine B, n_x, n_{RB} are the refractive indexes of used solvents (THF and water, respectively) and $Grad_X$ and $Grad_{RB}$ are the gradients from the plots of integrated fluorescence intensity versus absorbance (Fig.4).

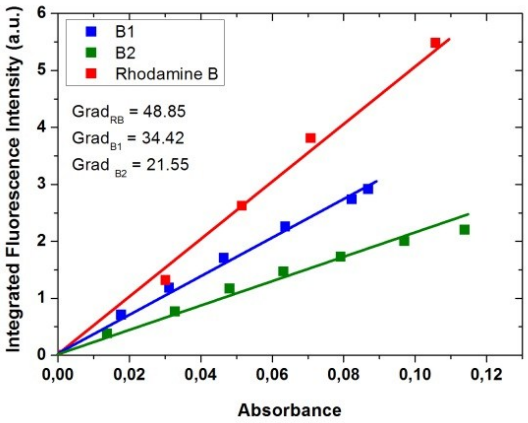

Fig.4. The dependences of integrated fluorescence intensity on absorbance values for B1, B2 and Rhodamine B with extracted values of gradients.

According to the Eq.1, the calculated values of fluorescence quantum yield at the excitation wavelength 514 nm were found to be Φ_{B1}=0.24 and Φ_{B2}=0.15.

References

1 A.T.R. Williams, S.A. Winfield and J. N. Miller, *Analyst*, 1983, **108**, 1067-1071.
2 D. Magde, G.E. Rojas and P. Seybold, *Photochem. Photobiol*., 1999, **70**, 737-744.