AZADIPYRROMETHENE DYE WITH A FULLY CHELATED BORON ATOM

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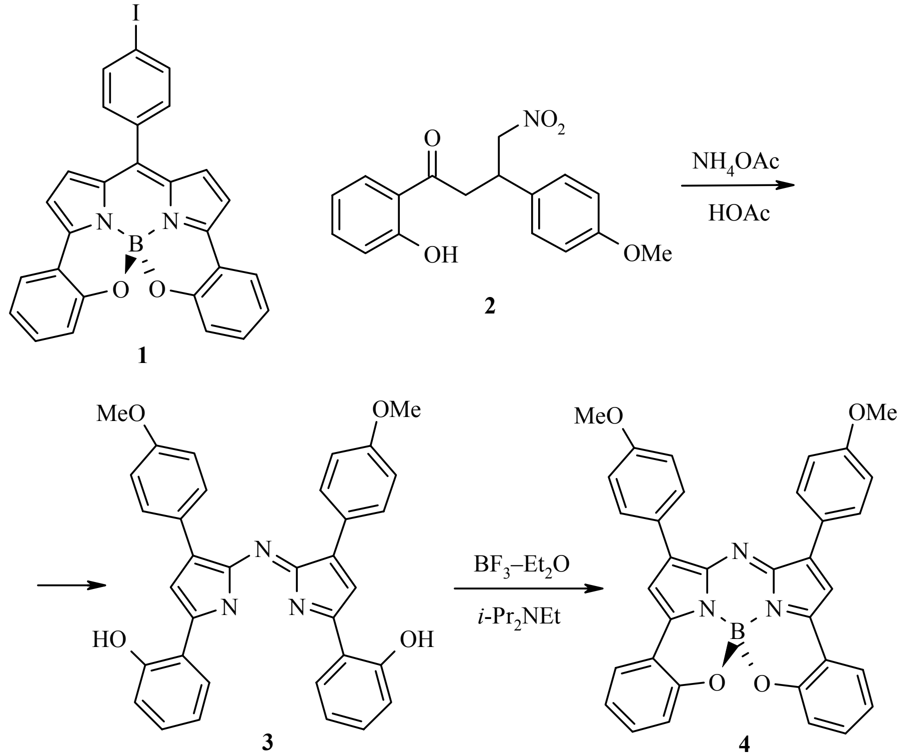
Among the variety of approaches to the modification of the basic structure of boron complexes of dipyrromethene dyes, also known as 4-bora-3a,4a-diaza-s-indacenes or BODIPY (BDP), the method proposed by Kim et al. [1] stands out for its originality. Structure **2** described by Kim [1] is a dipyrromethene with a fully chelated boron atom.



1 **2** **3** **4**

1 – λ_{max} 630 nm (ε 46 000), λ_{em} 654 nm, φ 0.41; **3** – λ_{max} 623 nm (ε 54 000);
4 – λ_{max} 726 nm (ε 70 000), λ_{em} = 741 nm, φ 0.38

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This dye is much more intense in its color than starting difluoroboryl derivative and its fluorescence properties also are significantly altered (here and subsequently, the spectral properties are given for chloroform solutions). However, the most interesting feature for dye **1** is its spiral chirality, the first example for this type of compound.

Azapyrromethenes are preparatively more available because their synthesis needs no correspondingly substituted pyrroles. Out of the known Scheme (for example, [2]) we obtained the azaanalogue of dye **1**.

As expected, dye **4** has a more intense color than its analog **1**, while its quantum yield at 38% for the near IR region is very high, which makes preparatively-available azadipyrromethene **4** among the most efficient long-wavelength luminophores.

The ^{1}H NMR spectra were taken on a Varian VXR-300 spectrometer at 300 MHz with TMS as the internal standard. The electronic absorption spectra were taken on a Shimadzu UV-3100 spectrophotometer. The fluorescence spectra were taken on a Varian Cary Eclipse spectrometer.

[5-(2-Hydroxyphenyl)-3-(4-methoxyphenyl)-1H-pyrrol-2-yl][5-(2-hydroxyphenyl)-3-(4-methoxyphenyl)pyrrol-2-ylidene]amine (3). A mixture of nitro ketone **2** (1.5 g, 5 mmol), ammonium acetate (7.7 g, 100 mmol), and acetic acid (18 ml) was heated at 100°C for 4 h. After cooling, the precipitate was filtered off and washed with acetic acid to give 0.41 g (38%) compound **3**, mp >250°C. ^{1}H NMR spectrum (DMSO), δ, ppm (*J*, Hz): 3.85 (6H, s, 2OCH$_3$); 7.03 (6H, m, H arom); 7.13 (2H, d, *J* = 8.1, H arom); 7.37 (2H, t, *J* = 7.8, H arom); 7.65 (2H, s, H-4); 8.05 (6H, m, H arom); 11.7 (2H, br. s, OH). Found, %: C 75.32; H 4.94; N 7.81. $C_{34}H_{27}N_3O_4$. Calculated, %: C 75.40; H 5.02; N 7.76.

Boron Chelate of [5-(2-Hydroxyphenyl)-3-(4-methoxyphenyl)-1H-pyyrol-2-yl][5-(2-hydroxyphenyl)-3-(4-methoxyphenyl)pyrrol-2-ylidene]amine (4). A mixture of dipyrromethene **3** (0.27 g, 0.5 mmol), diisopropylethylamine (0.64 g, 5 mmol), and boron trifluoride etherate (1.06 g, 7.5 mmol) in anhydrous toluene (40 ml) was heated at reflux for 1 h. Then, the solution was washed with water, dried over sodium sulfate, evaporated, and subjected to chromatography on an alumina column using carbon tetrachloride–ethyl acetate as the eluent to give 0.14 g (50%) compound **4** mp >250°C. ^{1}H NMR spectrum (CDCl$_3$), δ, ppm (*J*, Hz): 3.91 (6H, s, 2OCH$_3$); 7.01 (6H, m, H arom); 7.09 (2H, d, *J* = 7.5, H arom); 7.13 (2H, s, H-4); 7.40 (2H, t, *J* = 8.4, H arom); 7.85 (2H, d, *J* = 7.8, H arom); 8.13 (2H, d, *J* = 9.0, H arom). Mass spectrum, *m/z* (I_{rel}, %): 549 $[M]^+$ (100). Found, %: C 74.82; H 4.51; N 7.81. $C_{34}H_{24}BN_3O_4$. Calculated, %: C 74.33; H 4.40; N 7.65.

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