Naked-eye fluorescent sensor for copper (II) ion based on naphthalene conjugate BODIPY

dye

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Materials and Instruments

¹H and ¹³C-NMR spectra were obtained at room temperature on a Varian 400 MHz spectrometer in CDCl₃. Melting points were measured on a Gallenkamp apparatus. FTIR spectra were recorded on a Bruker Fourier Transform Infrared FTIR (ATR). UV-vis spectra were obtained with a Perkin Elmer Lambda 25 UV–vis spectrophotometer. The fluorescence spectra were recorded on a PerkinElmer LS 55 fluorescence spectrophotometer. All the measurements were carried out at 298 K. The emission slits were set as 5 nm in a fixed excitation. Elemental analyses were measured on a TruSpec elemental analyzer. Analytical TLC was used Merck plates (silicagel 60 F254 on aluminum). The synthesis of all compounds were performed under nitrogen atmosphere. The solutions of metal ions were prepared from their chloride salts. All chemicals were supplied from Fluka, Fisher Scientific (USA) and Acros Organics (USA), and Aldrich and used without further purification.

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2.2.1. The synthesis of 8-{4-(chloromethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7tetramethyl-4-bora-3a,4a-diaza-s-indacene (chloromethyl-Bodipy)

4-(chloromethyl)benzoyl chloride (3.750 g, 0.02 mol) was solved in dry dichloromethane (100 mL) and this solution was dropped to a dichloromethane solution of 2,4-dimethyl-3-ethylpyrrole (5.4 mL, 0.04 mol) at r. t. and under N₂. The mixture was stirred at 60 °C for 2 h. Then, the solution was get to room temperature and triethylamine (TEA) (5 equiv.) was injected with syringe. The mixture was stirred at r. t. for 30 min under N₂ and then boron trifluoride diethyl etherate (7 equiv.) was dropwise added [22]. After the refluxing of the solution for 2 h and evaporated to solvent and raw yield was purified by column chromatography (petroleum ether-EtOAc; in 8:1 ratio). A red solid (3.35 g, Yield 40 %). M.P.:188 °C. ¹H NMR [400 MHz, CDCl₃]: 7.40 (d, PhH, 2H), 7.19 (d PhH, 2H) 4.61 (s, -CH₂, 2H), 2.42 (s, -CH₃, 6H), 2.20 (q, -CH₂, 4H), 1.26 (s, -CH₃, 6H), 0.91 (t, -CH₃, 6H). ¹³C NMR [100 MHz, CDCl₃]: δ (ppm); 154.01, 138.99, 138.21, 135.93, 135.44, 133.01, 130.98, 128.81, 129.11, 45.77, 16.92, 14.51, 12.73, 11.88. Anal.Calc. for (%) C₂₄H₂₈N₂F₂ClB: C, 67.22; H, 6.57; N, 6.52; Found: C, 66.87; H, 6.55; N, 6.33. MS for C₂₄H₂₈N₂F₂ClB m/z: 428.1 [M+H]⁺.

2.2.2. The synthesis of 8-{4-(azidomethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7tetramethyl-4-bora-3a,4a-diaza-s-indacene (azidomethyl-Bodipy)

A mixture of chloromethyl-Bodipy (188 mg, 0.44 mmol), LiBr (174 mg, 0.44mmol) and NaN₃ (340 mg, 2.6 mmol) in DMF (10 mL) was mixture at r. t. for 24 h under N₂, then H₂O (45 mL) was added. The aqueous layer was extracted with ethylacetate and the organic phase was dried with MgSO₄, filtered, and concentrated. Column chromatography (SiO₂; CH₂Cl₂) gave 7

(278 mg, 97%) as a dark-red solid that was used as received. M.P.:140 °C. ¹H-NMR [400 MHz, CDCl₃]: ¹H NMR [400 MHz, CDCl₃]: 7.43 (d, PhH, 2H), 7.31 (d, PhH, 2H) 4.46 (s, -CH₂, 2H), 2.55 (s, -CH₃, 6H) 2.30 (q, -CH₂, 4H) 1.26 (s, -CH₃, 6H) 1.02 (t, -CH₃, 6H). ¹³C NMR [100 MHz, CDCl₃]: δ (ppm); 153.22, 139.33, 138.12, 136.17, 135.53, 132.81, 130.62, 128.32, 128.18, 55.19, 17.44, 15.14, 12.32, 11.99.

2.2.3. The synthesis of 8-{4-(aminomethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7tetramethyl-4-bora-3a,4a-diaza-s-indacene (aminomethyl-Bodipy)

A mixture of azidomethyl-Bodipy (435 mg, 1 mmol,) and PPh₃ (1 mmol, 262 mg) in dry THF (20 mL) was stirred for 5 h at room temperature under Ar, then H₂O (2 drops) was added. This mixture was stirred for overnight and evaporated to solvent. Column chromatography (SiO₂; DCM/MeOH: 10/1) gave aminomethyl-Bodipy (298 mg, 73%) as a red solid. M.P. \approx 170 °C

¹H–NMR [400 MHz, CDCl₃]: ¹H NMR [400 MHz, CDCl₃]: 7.43 (d, PhH, 2H), 7.25 (d, PhH, 2H), 4.02 (s, -CH₂, 2H), 2.55 (s, -CH₃, 6H) 2.35 (q, -CH₂, 4H) 1.22 (s, -CH₃, 6H) 1.0 (t, -CH₃, 6H). ¹³C NMR [100 MHz, CDCl₃]: δ (ppm); 154.22, 142.33, 139.82, 137.17, 134.83, 132.99, 130.76, 128.32, 128.00, 46.22, 17.34, 14.84, 12.42, 12.02.

2.2.4. The synthesis of 8-{4-((E)-1-((methylimino)methyl)naphthalen-2-ol)phenyl}-2,6diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (N-Bodipy)

Aminomethyl-Bodipy (0.409 g, 1 mmol) was dissolved in methanol (10 mL) and added dropwise a solution of 2-hydroxy-1-naphthaldehyde (0.122 g, 1 mmol) in methanol (10 mL). The mixture was stirred at r. t. for overnight. After the evaporation of solvent, raw product

was purified on column. An orange-red solid. (516 mg, Yield 92%). M.P.: 295 °C. ¹H-NMR [400 MHz, CDCl₃]: 11.55 (bs, -OH, 1H), 8.75 (s, N=CH, 1H), 7.45 (m, PhH, 4H), 7.28 (m, PhH, 4H) 7.18 (d, PhH, 2H), 4.70 (s, -CH₂, 2H), 2.55 (s, -CH₃, 6H), 2.35 (q, -CH₂, 4H) 1.22 (s, -CH₃, 6H) 1.0 (t, -CH₃, 6H). ¹³C NMR [100 MHz, CDCl₃]: δ (ppm); 165.21, 155.32, 141.98, 138.85, 137.61, 136.32, 136.19, 134.42, 132.96, 132.81, 131.55, 130.61, 128.02, 127.21, 125.11, 124.53, 62.22, 17.49, 14.77, 12.22, 11.99. Anal.Calc. for (%) C₃₅H₃₆BF₂N₃O: C, 74.60; H, 6.44; N, 7.46; Found: C, 74.97; H, 6.88; N, 7.32. MS for C₃₅H₃₆BF₂N₃O m/z: 564.1 [M+H]⁺.



Scheme 1 The synthesis procedure of N-Bodipy



FT-IR spectrum of Chloro-methyl Bodipy



FT-IR spectrum of Azido-methyl Bodipy



FT-IR spectrum of Amino-methyl Bodipy



FT-IR spectrum of N-Bodipy



FT-IR spectrum of N-Bodipy/Cu(II) complex



¹H-NMR spectrum of Chloro-methyl Bodipy



¹H-NMR spectrum of Azido-methyl Bodipy



¹H-NMR spectrum of Amino-methyl Bodipy















¹³C-NMR spectrum of Amino-methyl Bodipy



¹H-NMR spectrum of N-Bodipy



¹³C-NMR spectrum of N-Bodipy