

A high-performance fluorescent hybrid material for fluorometric detection and removal of toxic Pb (II) ion from aqueous media: performance and challenge

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Experimental section

Chemicals and apparatus

The NMR spectra (¹H and ¹³C) of the synthesized organic compounds were performed using a nuclear magnetic resonance spectrometer (Varian 400 MHz). The emission spectra and the linked spectroscopic measurements were performed by a Perkin Elmer LS 55 spectrofluorometer. The SEM images, FT-IR spectra and elemental analysis were performed with a HITACHI (SU5000), a Bruker Fourier Transform Infrared (ATR) and a Leco CHNS 932, respectively. The remaining lead ions in the suspension were determined by Analytic Jena, Contr AA 300 spectrophotometer using the atomic absorption values.

For the ordering of the used chemicals, various companies were preferred. Silica gel (70-230 mesh) used as both purification (column chromatography) and adsorbent materials was purchased from Fluka (Switzerland). Sodium azide, d-chloroform (CDCl₃), 3-aminopropyltrimethoxysilane (APTMS, 97%), propargylamine, triethylamine, 2,4-dimethyl-3-ethylpyrrole, borontrifluoride diethyl etherate, N,N-diisopropylethylamine (DIPEA), 4-(chloromethyl)benzyl chloride, sodium ascorbate, copper(II)sulphate were provided from Sigma-Aldrich. Solvents (dichloromethane, ethyl alcohol, toluene, petroleum ether (40-60%), N,N-

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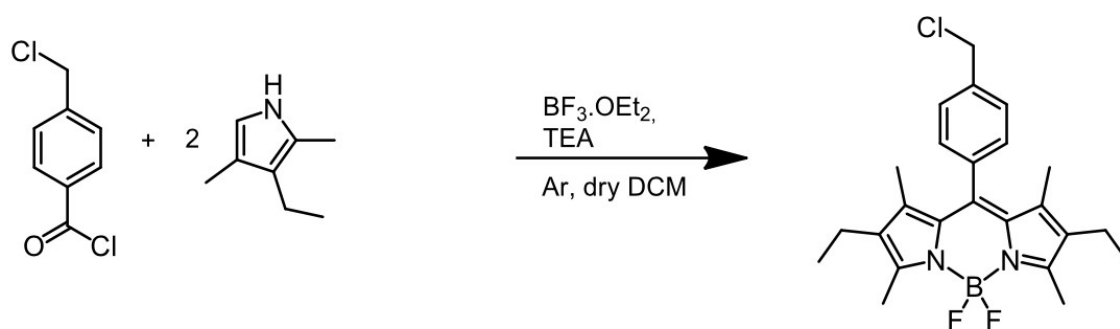
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dimethylformamide) and the metal nitrate salts were purchased from Merck Company (Germany, Darmstadt).

The synthesis of compounds

The compounds were prepared a known procedure [41].

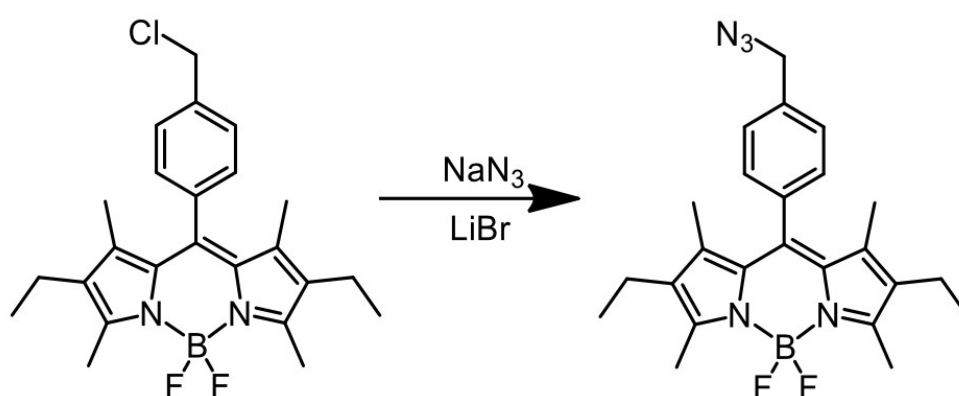
The synthesis of 8-{4-(chloromethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene



8-{4-(chloromethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene was prepared following the synthesis procedure in our previous papers. p-(chloromethyl)benzoyl chloride (7.5 g, 0.04 mol) was added to a solution (in DCM, 200 mL) of Kryptopyrrole (10.8 mL, 0.08 mol) in Ar atmosphere at room temperature. Then, the stirring of the solution was allowed for 4 h. After cooling of the solution, 10 mL of triethylamine was added to the mixture, it was stirred at r. t. for half hour and boron trifluoride diethyl etherate (8 mL) was injected by syringe. The mixture was heated to 65 °C for 3 hours and the residue was purified by a solution of ethylacetate-cyclohexane in 1:8 ratio (3.47 g, Yield 40%). Mp: 189 °C. ¹H NMR [400 MHz, CDCl₃]: 7.42 (PhH, *J*=8.2 Hz, d, 2H), 7.20 (PhH, *J*=8.2 Hz, d, 2H), 4.65 (CH₂, s, 2H), 2.46 (CH₃, s, 6H) 2.23 (CH₂, *J*=7.5 Hz, q, 4H) 1.29 (CH₃, s, 6H) 0.91 (CH₃, *J*=7.5 Hz, t, 6H). ¹³C NMR [100

MHz, CDCl₃]: δ (ppm); 154.03, 139.49, 138.66, 135.88, 136.11, 133.02, 130.77, 128.99, 128.38, 45.66, 16.98, 14.66, 12.54, 11.66. Analytical Cal. for (%) C₂₄H₂₈N₂F₂ClB: H, 6.58; C, 67.22; N, 6.53; Found: H, 6.97; C, 66.98; N, 6.13. MS for C₂₄H₂₈N₂F₂ClB: 428 [M+H]⁺.

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



Compound **1** (0.44 mmol) and NaN₃ (0.344 g, 0.53 mol) were dissolved in N,N-dimethylformamide (20 mL) and mixed for 24 hours at room temperature. Under inert atmosphere. The residue was extracted with water/chloroform. The organic phases were collected, dried with Na₂SO₄. Following evaporation of chloroform, raw product was purified in column (only dichloromethane) (0.56 g, 96%). Caution: **3** must be handled with special care due to its explosive character, mp : 140 °C ¹H-NMR [400 MHz, CDCl₃]: 7.45 (PhH, *J*=8.0 Hz, d, 2H), 7.33 (PhH, *J*=8.1 Hz, d, 2H), 4.48 (CH₂, s, 2H), 2.57 (CH₃, s, 6H) 2.32 (CH₂, *J*=7.5 Hz, q, 4H), 1.28 (CH₃, s, 6H), 0.99 (CH₃, *J*=7.5 Hz, t, 6H). ¹³C NMR [100 MHz, CDCl₃]: δ (ppm); 154.04, 138.99, 138.03, 135.98, 135.62, 132.95, 130.81, 128.29, 129.03, 55.34, 17.44, 15.02, 12.32, 11.99. Analytical Cal. for (%) C₂₄H₂₈BF₂N₅: H, 6.48; C, 66.22; N, 16.09; Found: H, 6.67; C, 66.38; N, 16.15. MS for C₂₄H₂₈N₅F₂B: 435.3 [M+H]⁺.

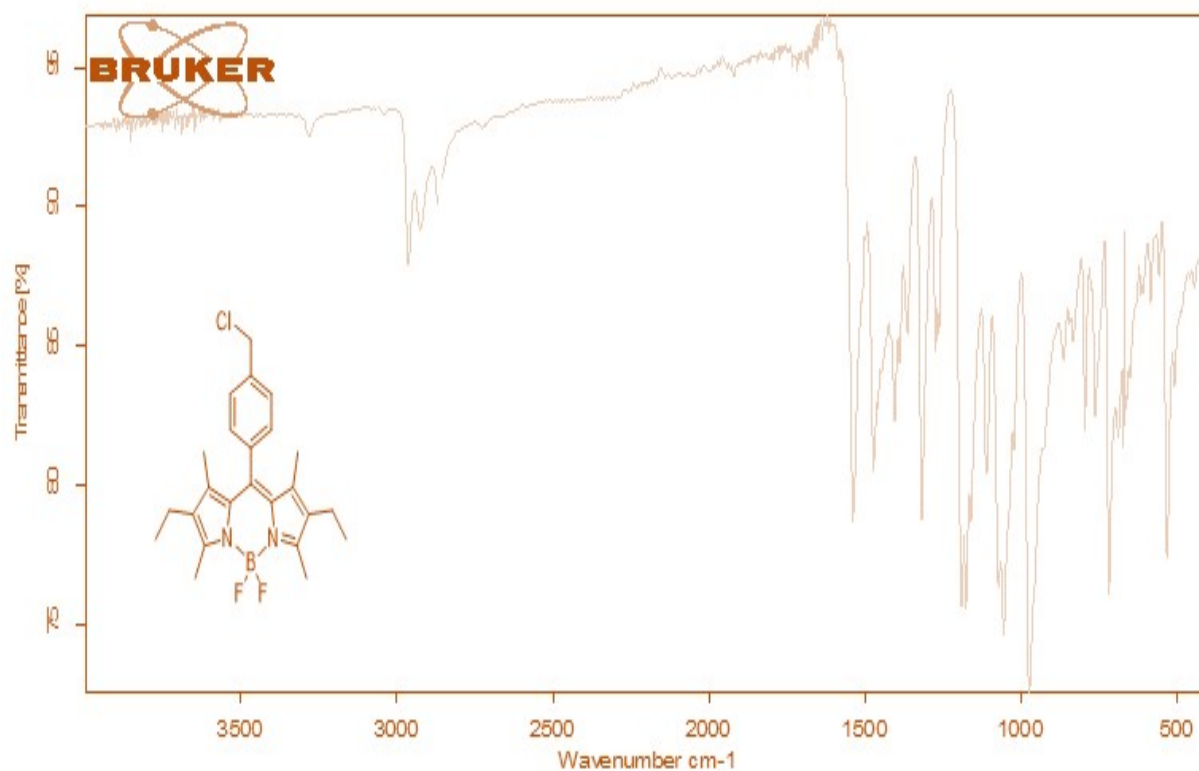


Fig.S1 FT-IR spectrum of 8-{4-(chloromethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene

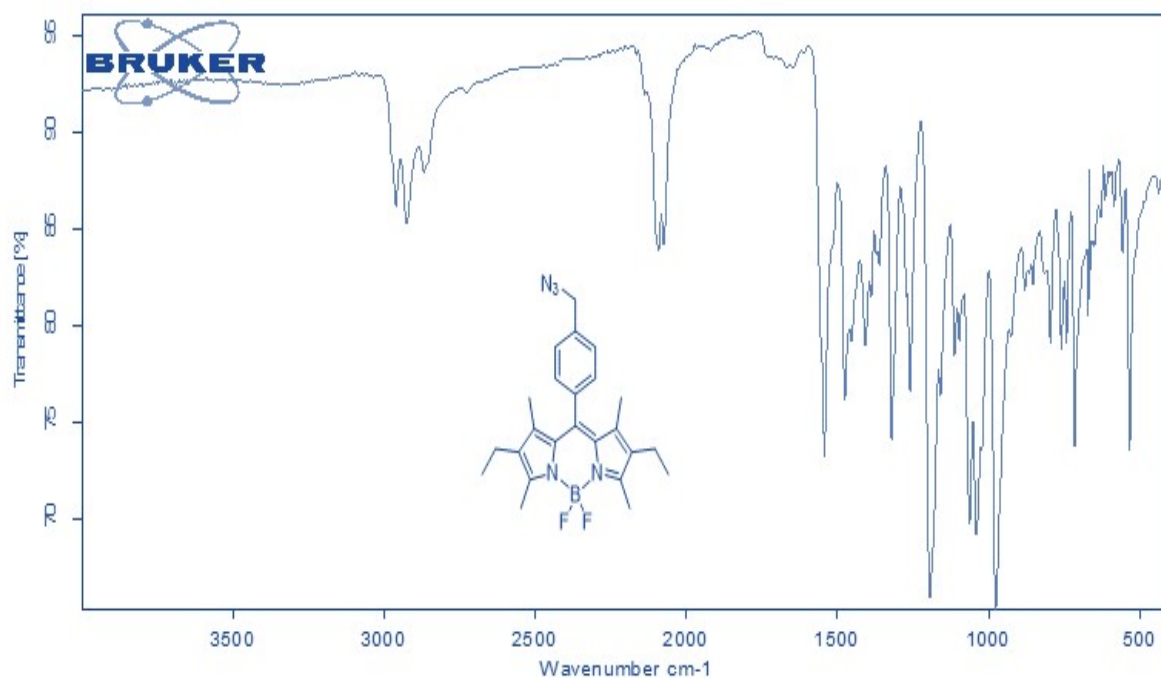


Fig. S2 FT-IR spectrum of Bodipy

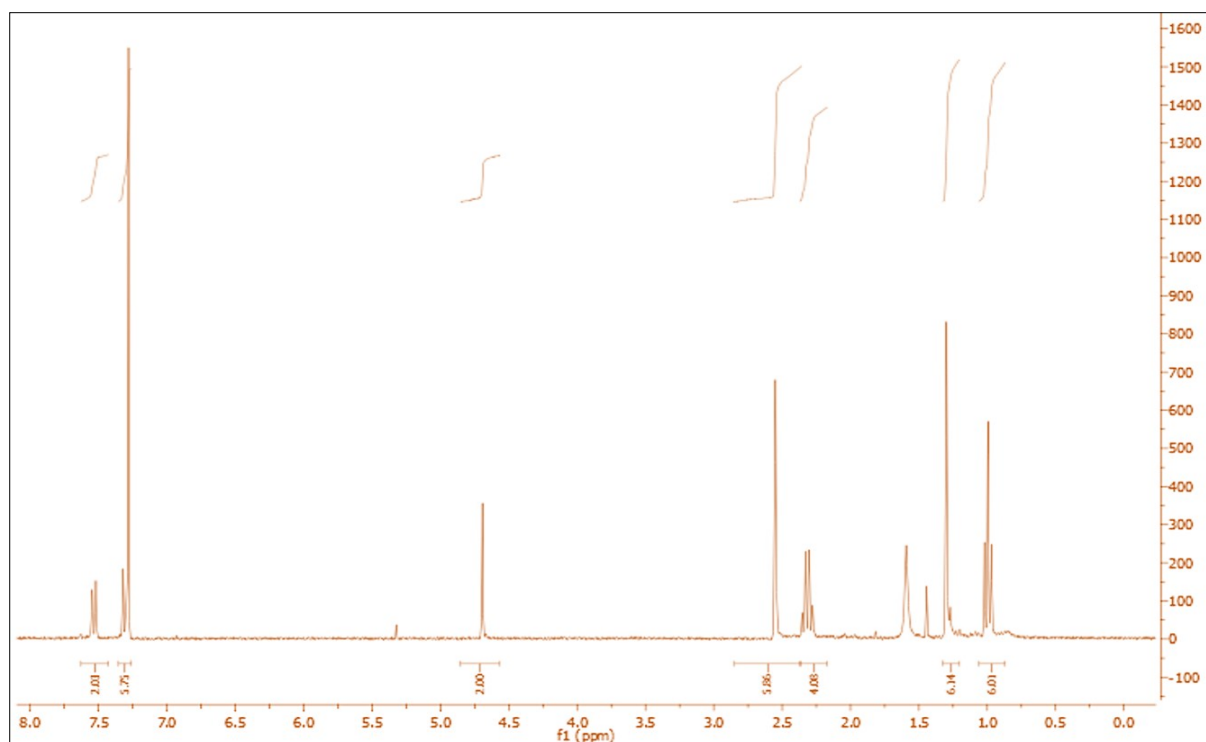


Fig.S3 ^1H -NMR spectrum of 8-{4-(chloromethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene

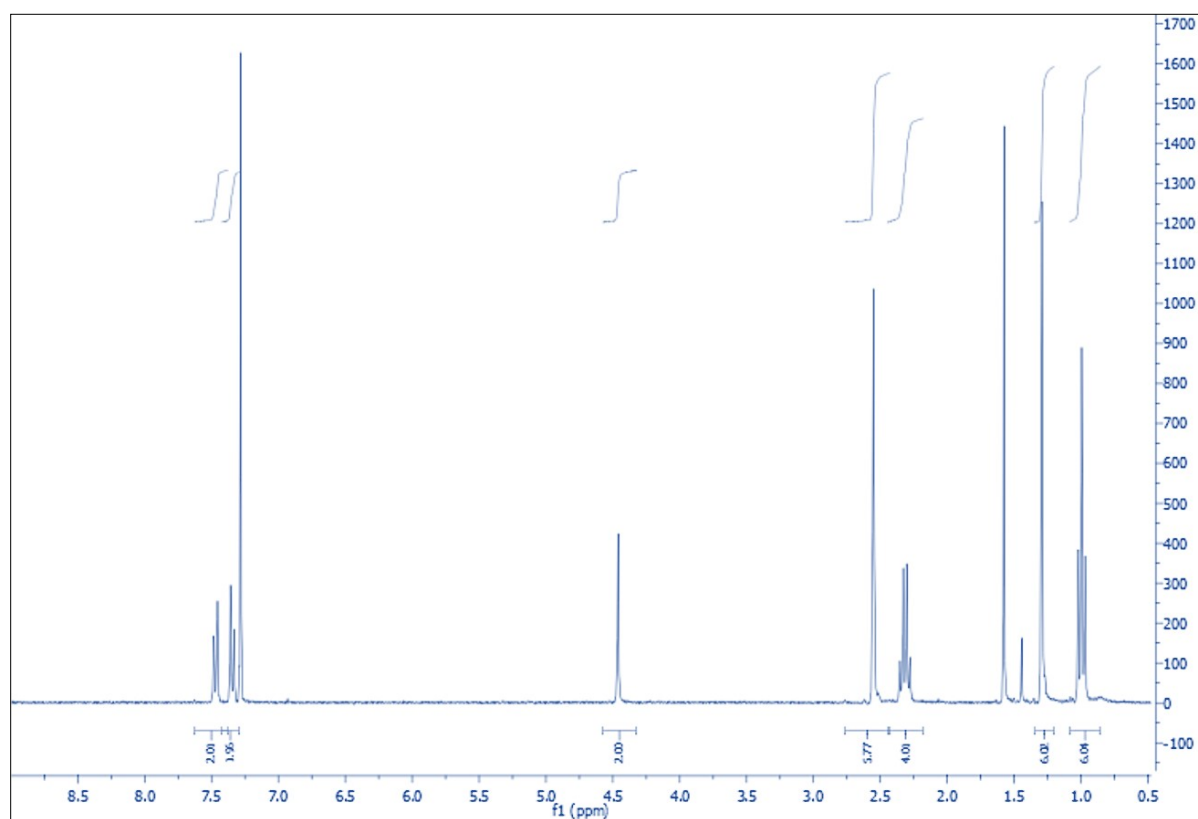


Fig.S4 ^1H -NMR spectrum of Bodipy (25 °C)

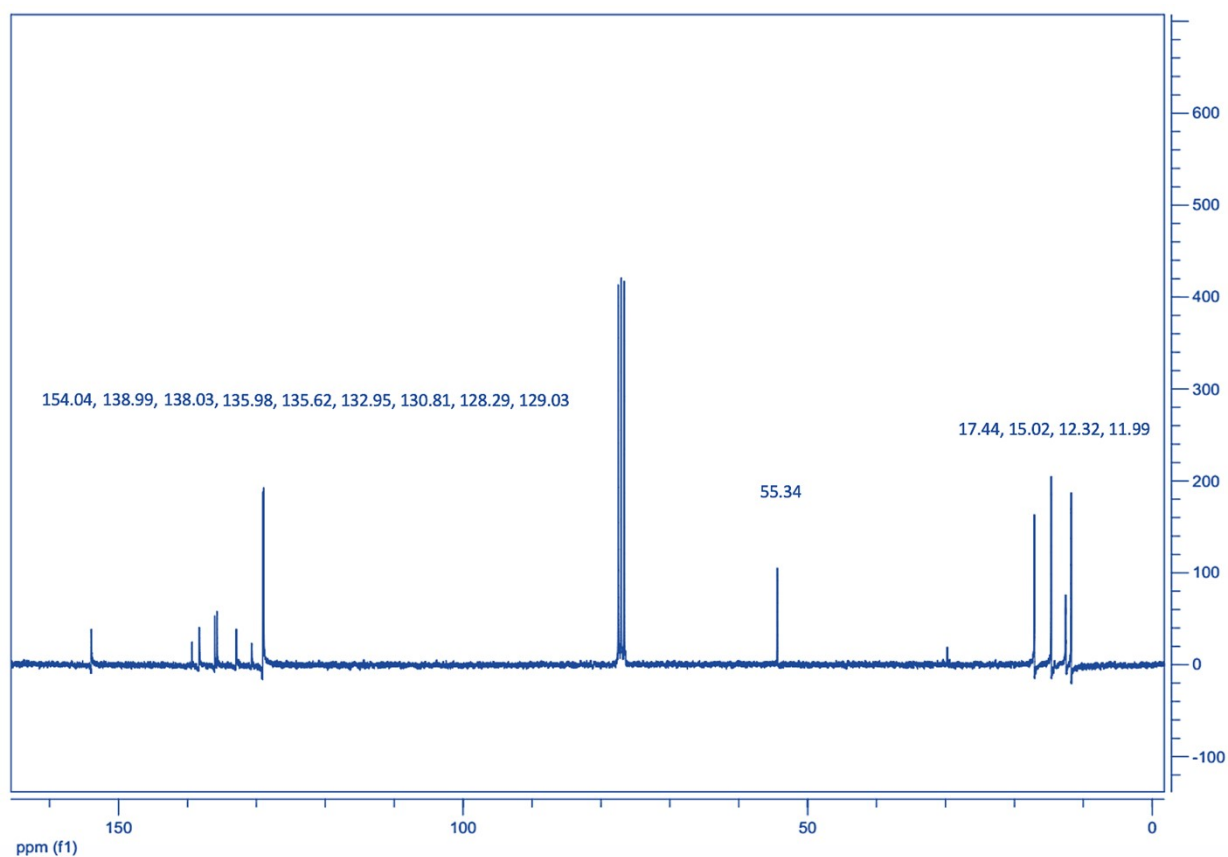
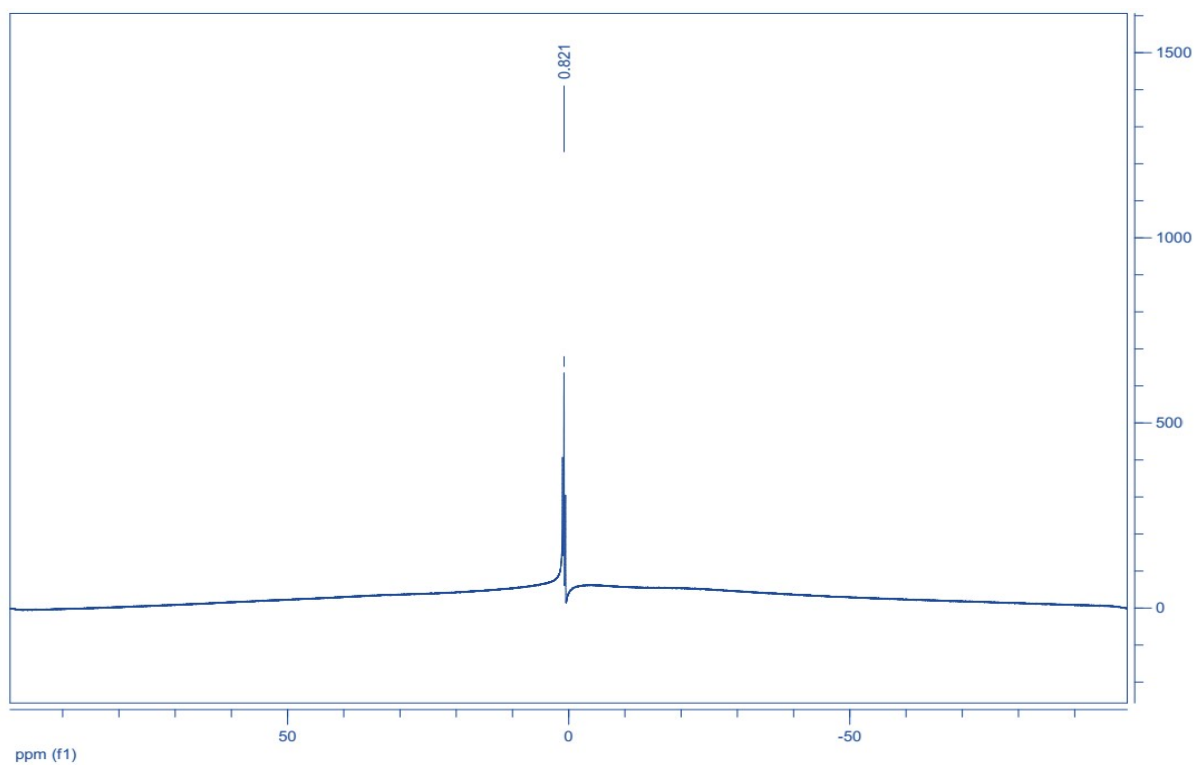


Fig.S5 ^{13}C -NMR spectrum of Bodipy (25 °C)



.S6 ^{11}B -NMR spectrum of Bodipy (25 °C)

Fig

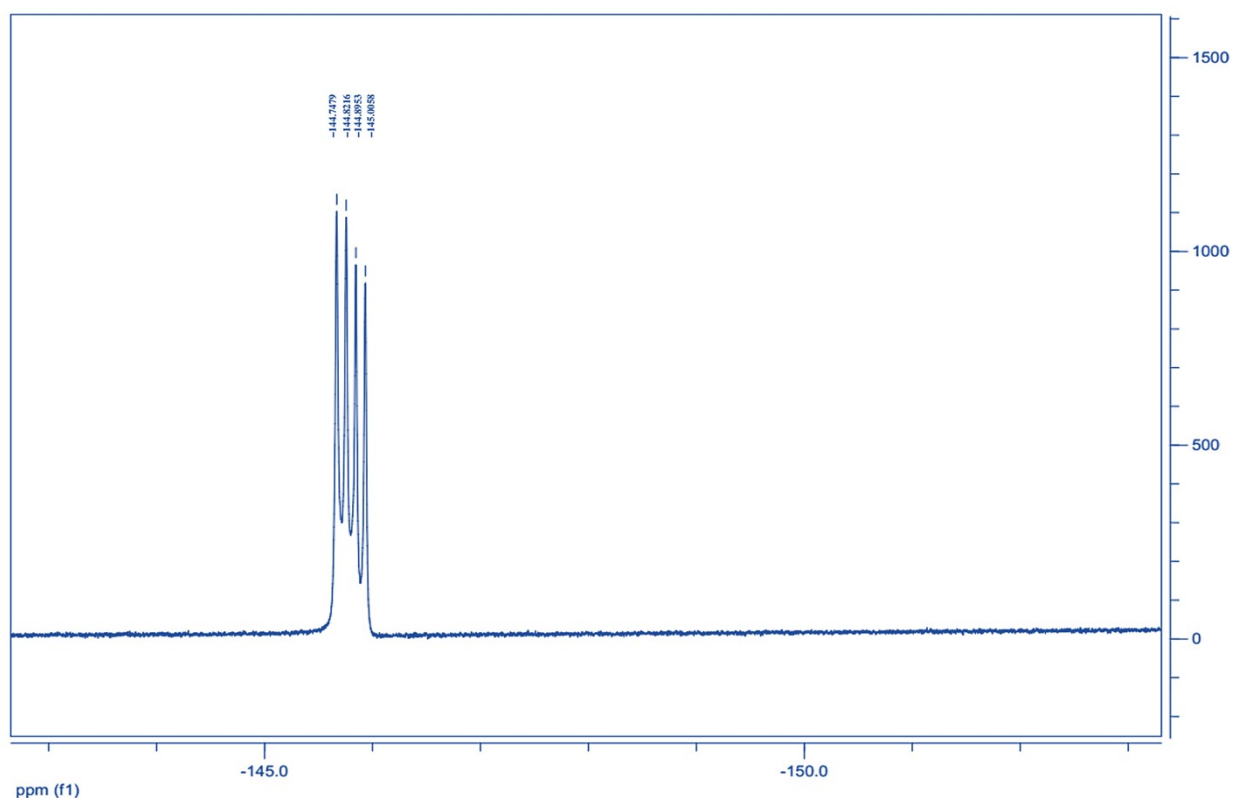


Fig.S7 ^{19}F -NMR spectrum of Bodipy (25 °C)

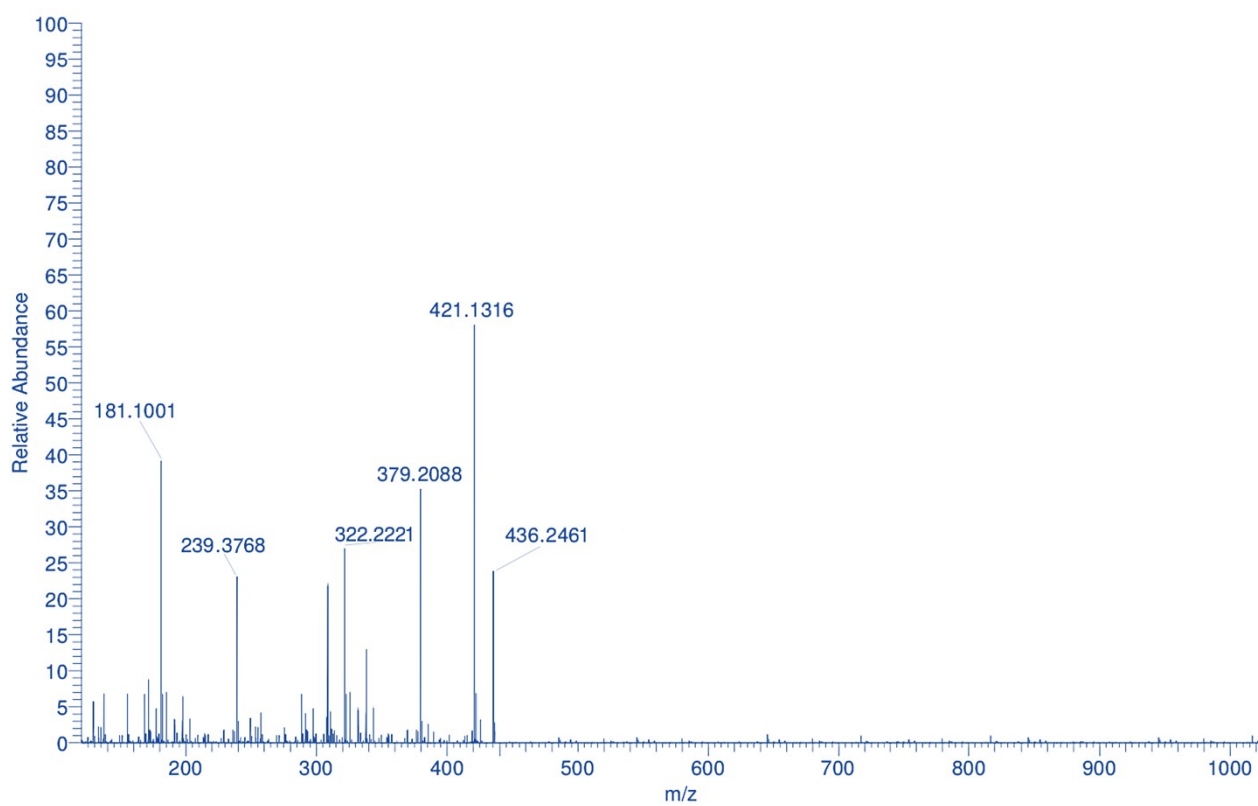


Fig.S8 Mass spectrum of Bodipy

[41] Bilgic A., Cimen A., Kursunlu A.N., 2021. Fluorescent and Easy-Make Hybrid Sensor Based-on Silica Gel & BODIPY for the Detection of Cu (II) in Aqueous Medium: Fully Characterized, Effective and Visual Data, IEEE Sensors J., 22 (3), 1882-1889.