

Supporting Information

A Novel Triphenylamine-BODIPY Dendrons: Click Synthesis, Near-infrared Emission and Multi-channel Chemodosimeter for Hg²⁺ and Fe³⁺

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The synthesis of intermediates

Compound **pyrrole**: A mixture of diethyl 3,5-dimethyl-1H-pyrrole-2,4-dicarboxylate (30 g, 125 mmol) and potassium hydroxide (12 g, 214 mmol) in ethylene glycol (30 mL) was heated at 160°C for 5 h. After completion of the reaction, the solution was extracted with dichloromethane, dried with anhydrous sodium sulfate and then concentrated to give the crude product. The crude product was distilled in vacuum to give the pure product 3.5 g, yield: 29.5%.

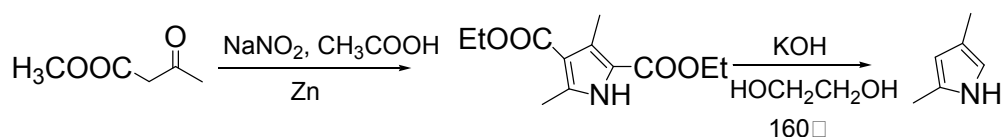


Fig. S1 Synthesis of 2, 4-dimethyl pyrrole

Compound **N₃-BODIPY**: 2, 4-dimethyl pyrrole (2.01 g, 21 mmol) and compound 4-(2-azidoethoxy) benzaldehyde (2.00 g, 10.47 mmol) were dissolved in dry dichloromethane (200 mL). Three drop of trifluoroacetic acid (TFA) was added to the solution. The reaction mixture was stirred at room temperature for 24 h. The reaction was monitored by TLC. After disappearance of the aldehyde, a solution of p-chloranil (2.57 g, 10.47 mmol) in dichloromethane was added. The reaction mixture was stirred at room temperature for 12 h. Absolute triethylamine (15 mL) was then added to the mixture. At last BF₃.OEt₂ (15 mL) was added dropwise at 0°C. The mixture was stirred 12 h again and then the reaction mixture was washed with water for three times (100 × 3 mL) and extracted with dichloromethane. The organic layer was dried over Na₂SO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography using dichloromethane as eluent to obtain a red solid 1.2 g, yield: 28 %. ¹H NMR (CDCl₃, ppm, 300 MHz) δ: 7.18 (d, *J*=8.34 Hz, 2H), 7.01 (d, *J*=8.37 Hz, 2H), 5.97 (s, 2H), 4.12 (t, *J*=5.85 Hz, 2H), 3.58 (t, *J*₁=6.51 Hz *J*₂=6.45 Hz, 2H), 2.55 (s, 6H), 1.43 (s, 6H).

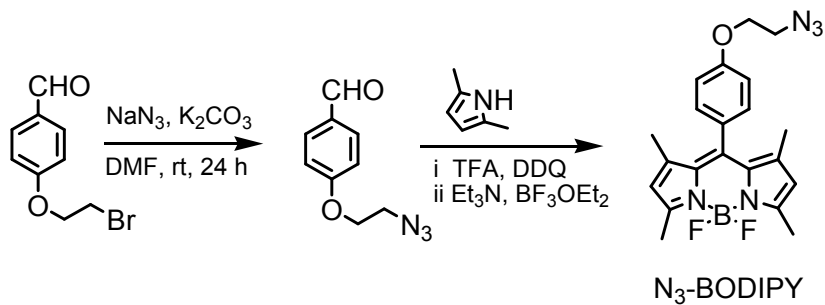


Fig. S2 Synthesis of compound **N₃-BODIPY**

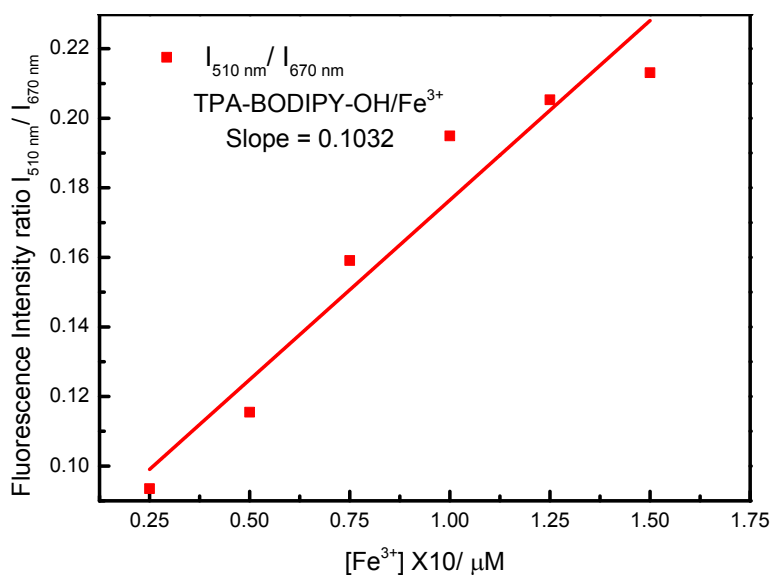


Fig. S3 Fluorescence Intensity ratio of 510 nm and 670 nm when TPA-BODIPY-OH on addition of Fe^{3+} (2.5-17.5 μM). ($C_{\text{TPA-BODIPY-OH}} = 10^{-5} \text{ M}$, in buffered with HEPES pH 7.4)

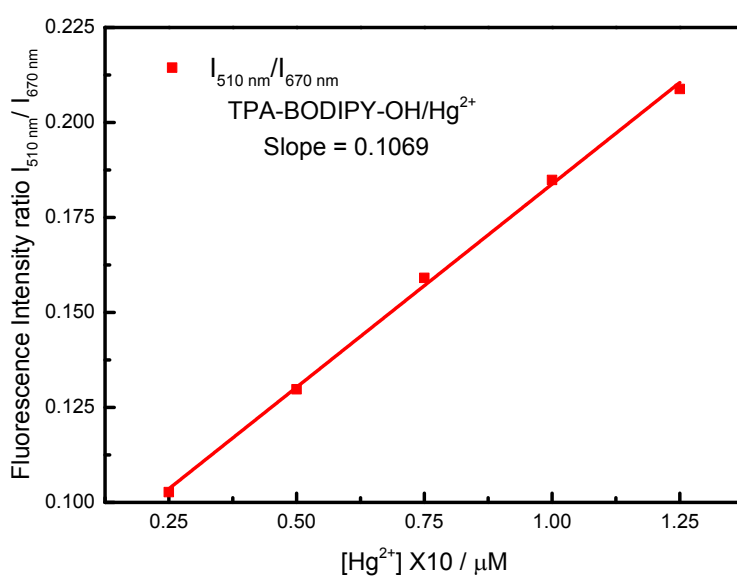


Fig. S4 Fluorescence Intensity ratio of 510 nm and 670 nm when TPA-BODIPY-OH on addition of Hg^{2+} (2.5-12.5 μM). ($C_{\text{TPA-BODIPY-OH}} = 10^{-5} \text{ M}$, in buffered with HEPES pH 7.4)

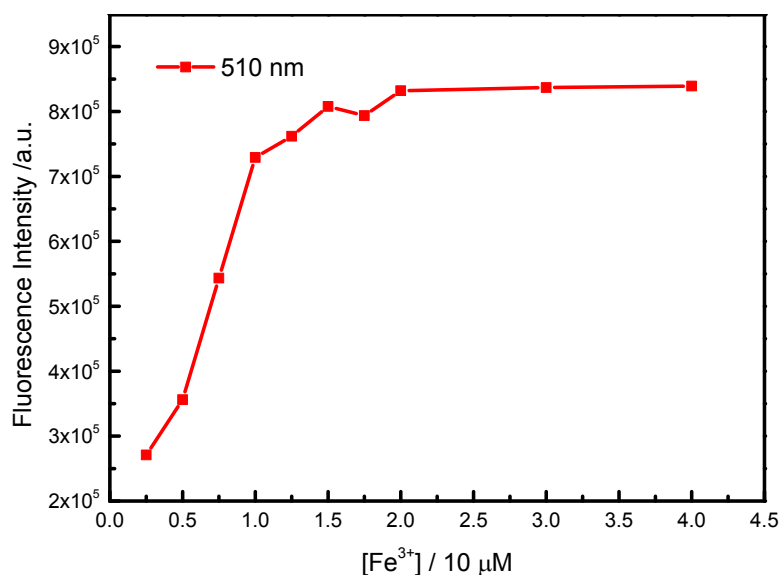


Fig. S5 Fluorescence changes of TPA-BODIPY-OH (10^{-5} M) in buffered with HEPES (pH 7.4) upon addition of Fe³⁺ (0 - 40 μM).

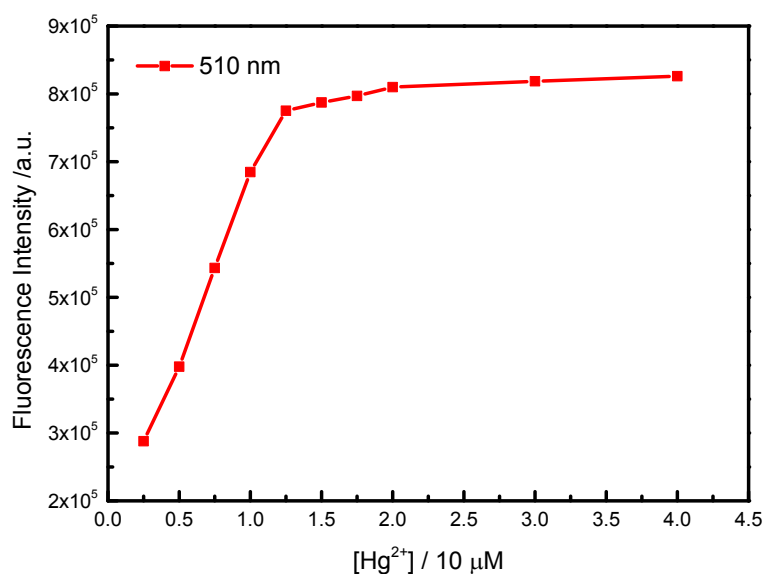


Fig. S6 Fluorescence changes of TPA-BODIPY-OH (10^{-5} M) in buffered with HEPES (pH 7.4) upon addition of Hg²⁺ (0 - 40 μM).

pH dependence of TPA-BODIPY-OH

The effects of pH on the fluorescence response of TPA-BODIPY-OH were studied. As shown in Fig. S7, with the pH decreased from 12.76 to 1.09, the emission band centered at 510 nm increased gradually and a distinct emission enhancement was observed with the change of fluorescence intensity increased 1.3-fold. If compared with the emission band at 510 nm, the fluorescence intensity at band 598 nm and

670 nm almost keeps unchanged because only -C=N group can reaction with H proton. The reason why fluorescence intensity at 510 nm increased is that the broken of C=N group. The band at 510 nm was the typical emission band of BODIPY dyes and in TPA-BODIPY-OH dendrons it can be attributed to the Schiff base BODIPY unit. With the increase of acid, the H proton reaction with the C=N group and generate aldehyde group (actually it was formyl group). So the -C=N isomerization and rotation was diminished and thus enhances the fluorescence intensity.

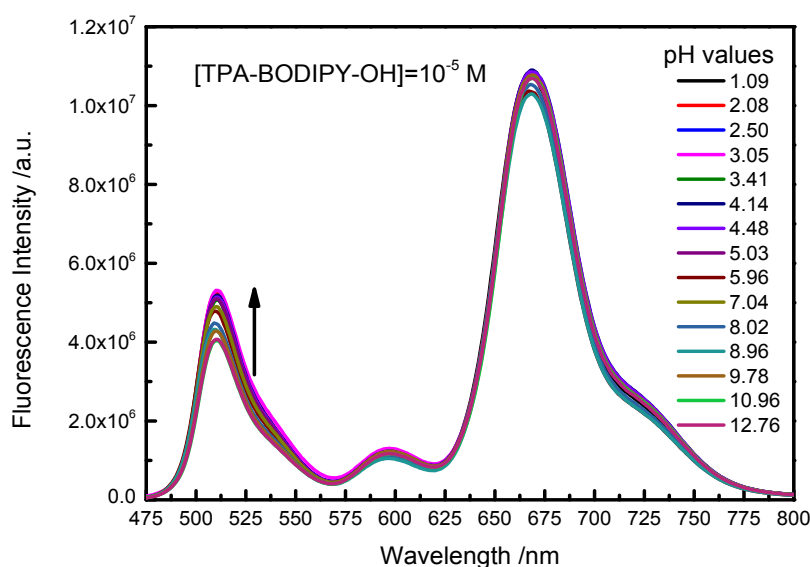


Fig. S7. The fluorescence spectrums of TPA-BODIPY-OH at various pH values. Conditions: $C_{\text{TPA-BODIPY-OH}} = 10^{-5} \text{ M}$; $V_{\text{THF}}:V_{\text{H}_2\text{O}}=1:1$.

The fluorescence intensity ratio of band 510 nm and band 670 nm was shown in Fig. S8. Notably, the fluorescence intensity ratio showed a steady increase until a plateau was reached (pH < 5) with a 1.3-fold increase at the plateau of the fluorescence intensity ratio of band 510 nm and band 670 nm. The results showed that the probe TPA-BODIPY-OH was steadily in strong basic medium and the emission band keeps unchanged when pH > 11. The titration curve of pH values reveals that emission band intensity changes linearly with the decrease of pH values in the range of 5-11. That means the TPA-BODIPY-OH can be served as the probe to protons.

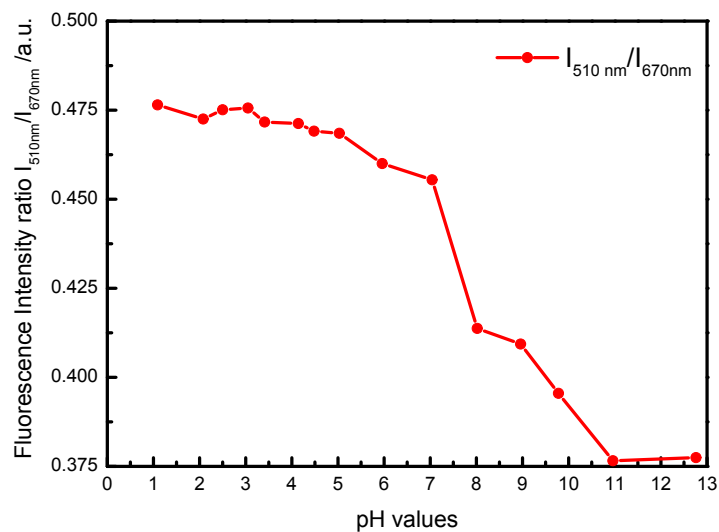


Fig. S8. Fluorescence Intensity ratio ($I_{510\text{nm}} / I_{670\text{nm}}$) of probe TPA-BODIPY-OH at different pH values. Conditions: $C_{\text{TPA-BODIPY-OH}}=10^{-5}$ M; $V_{\text{THF}} : V_{\text{H}_2\text{O}} = 1:1$.

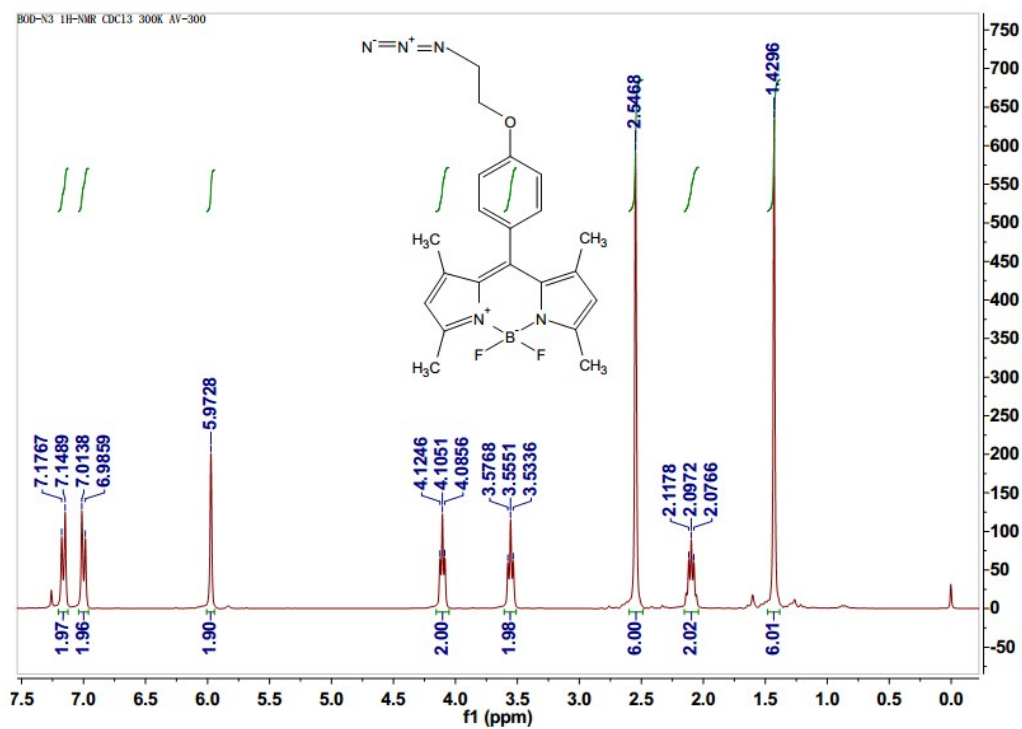


Fig. S9 ^1H NMR spectra of compound $\text{N}_3\text{-BODIPY}$

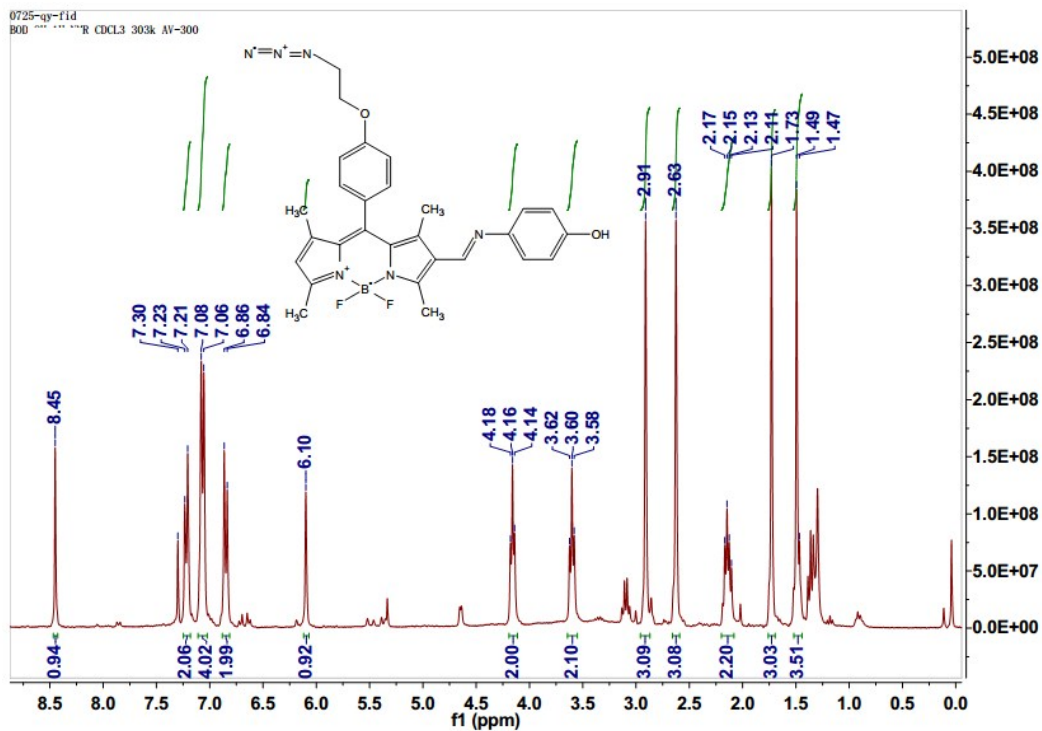


Fig. S10 ^1H NMR spectra of compound **BODIPY-OH**

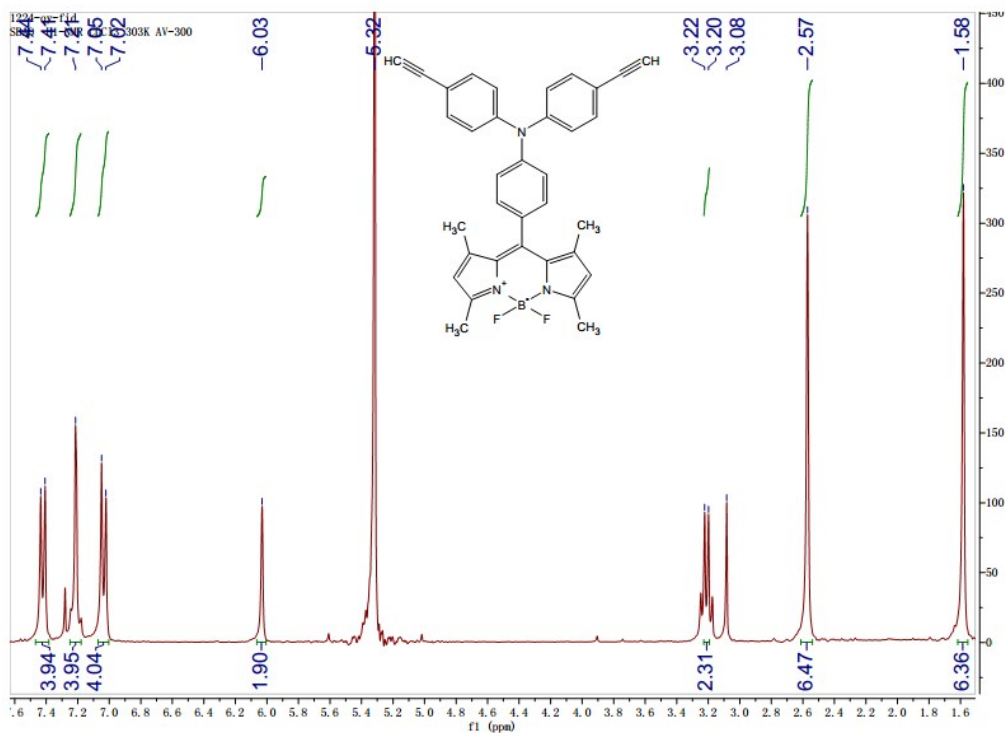


Fig. S11 ^1H NMR spectra of compound **Ey-BODIPY**

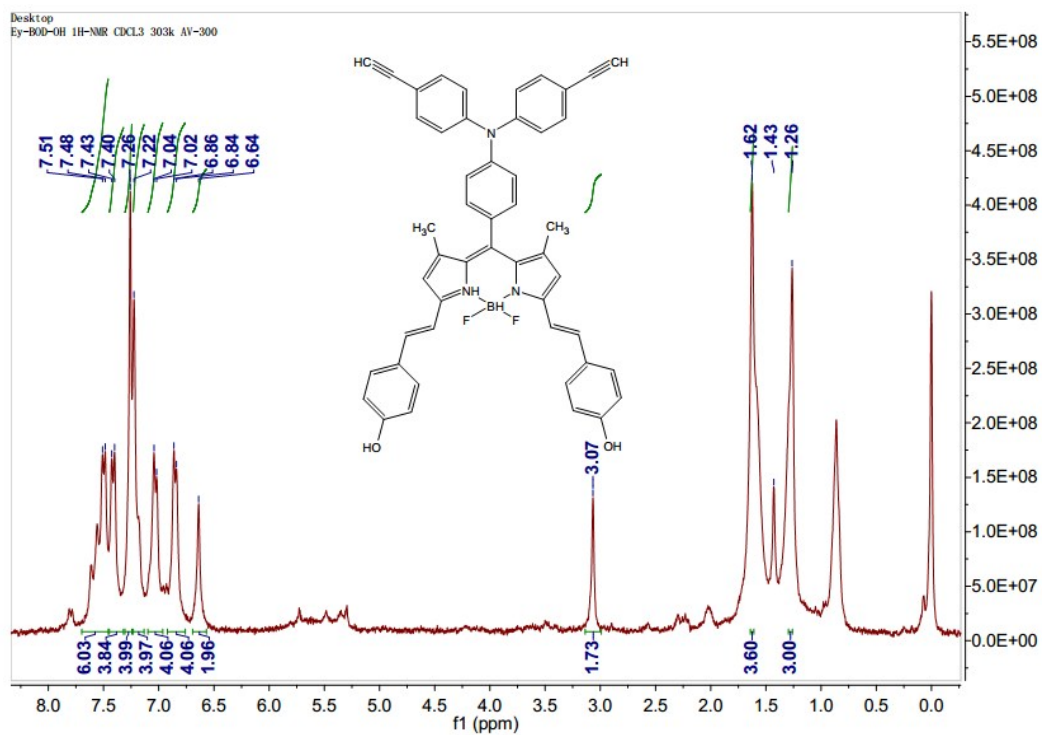


Fig. S12 ^1H NMR spectra of compound **Ey-BODIPY-OH**

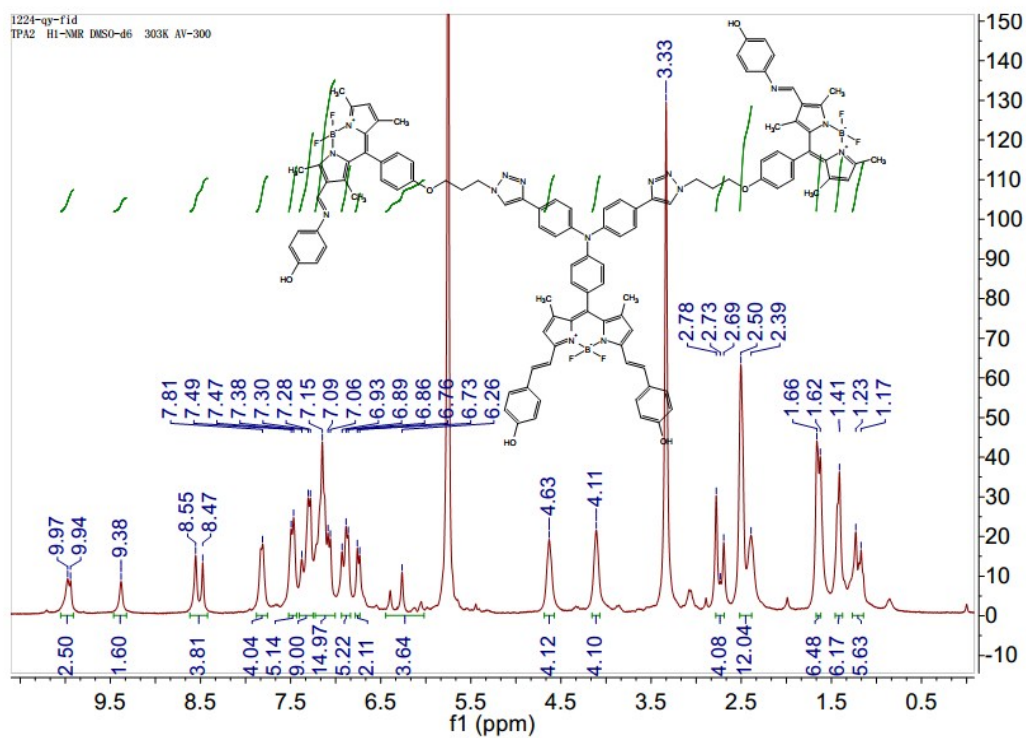


Fig. S13 ^1H NMR spectra of compound **TPA-BODIPY-OH**

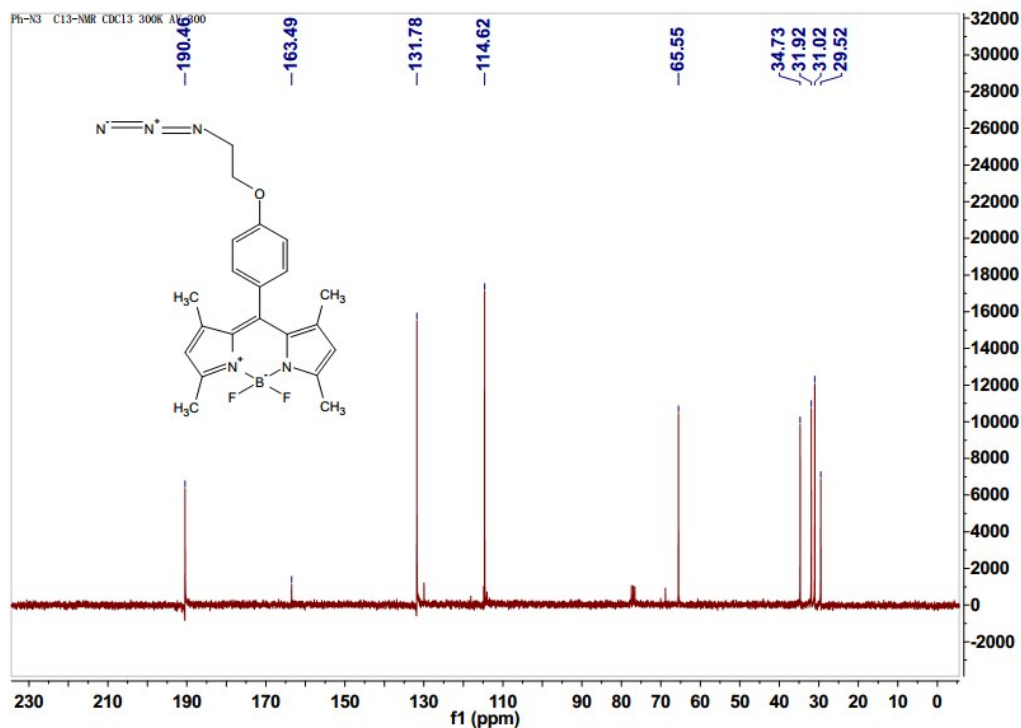


Fig. S14 ^{13}C NMR spectra of compound **N₃-BODIPY**

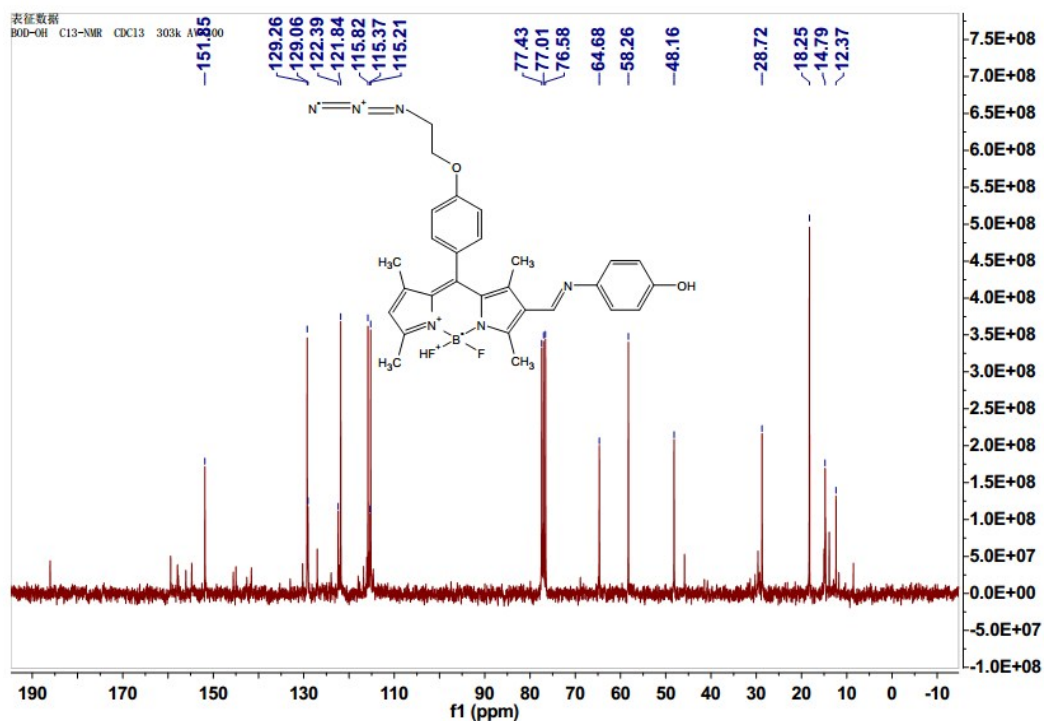


Fig. S15 ^{13}C NMR spectra of compound **BODIPY-OH**

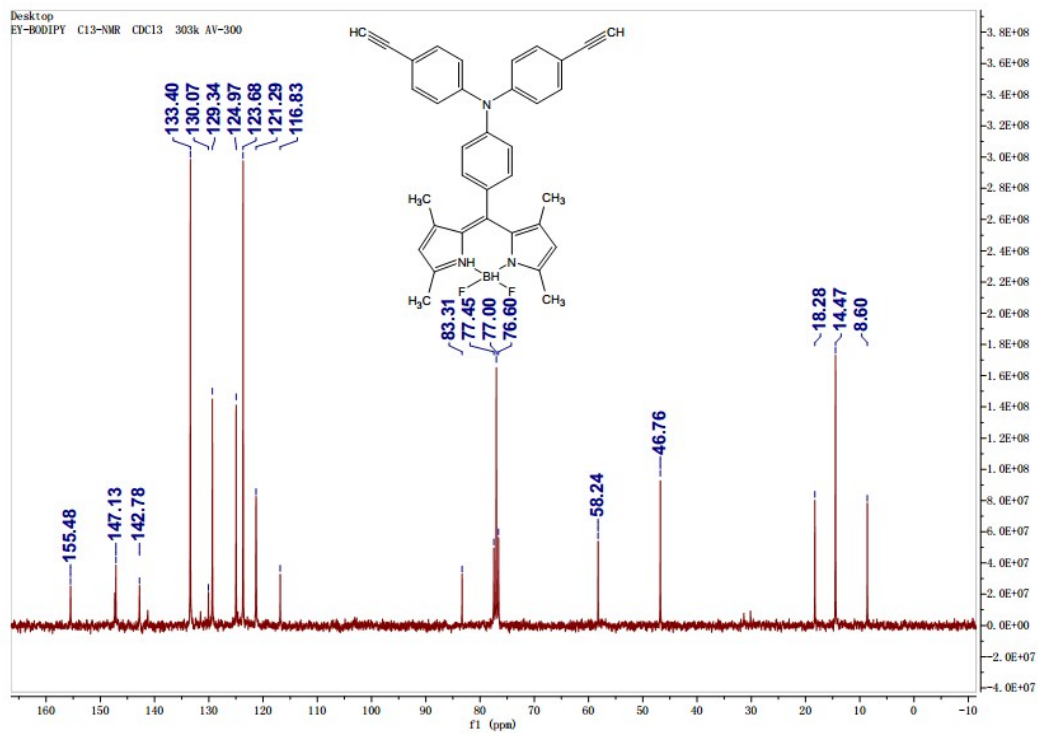


Fig. S16 ^{13}C NMR spectra of compound Ey-BODIPY

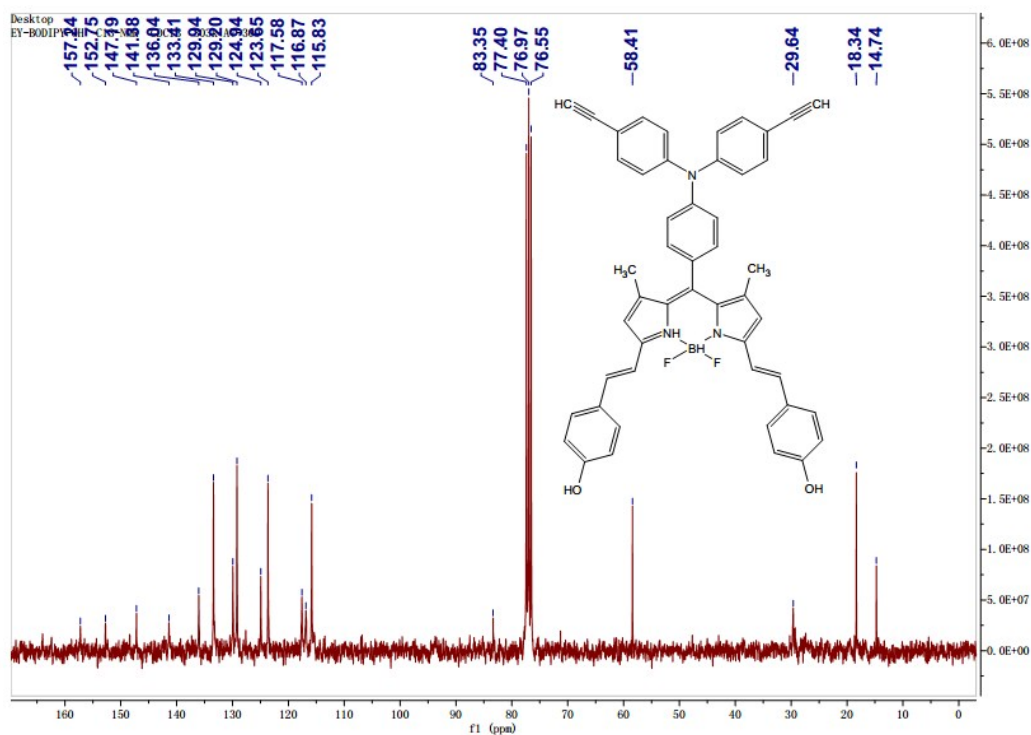


Fig. S17 ^{13}C NMR spectra of compound Ey-BODIPY-OH