Supplementary Material

A conjugated BODIPY-triphenylamine multi-aldoxime: sonogashira coupling, ratiometric chemodosimeter and rapid detection of hypochlorite with two-photon excited fluorescence

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The synthesis of intermediates

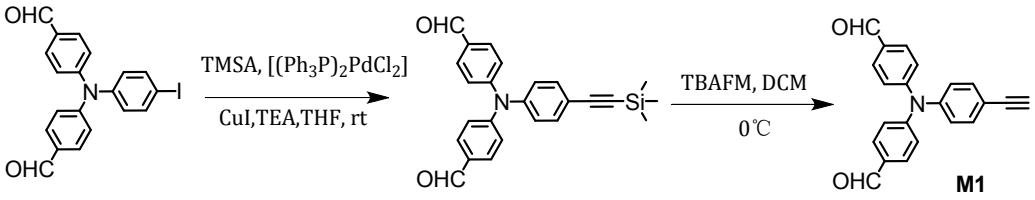


Fig S1. Synthese of alkynyl substitued triphenylamine M1.

Compound M1. Copper iodide (5.70 mg, 0.03 mmol)，N, N-di(4-formyl benzyl)-4-iodophenylamine (0.63 g, 1.47 mmol), Bis(triphenylphosphine) palladium dichloride (21.06 mg, 0.03mmol) and were placed in 10 mL of dry THF under N_2 for 30 min. Trimethylsilylacetylene (1.25 mL, 8.80 mmol) and triethylamine (10 mL) were added and stirred at ambient overnight under N_2. Then the crude product was purified by silica column chromatography to afford the product N, N-di (4-formylbenzyl)-4-trimethylsilylphenylamine as yellow solid (0.53 g), which (0.20 mg, 0.52 mmol) was placed in 45 mL CH_2Cl_2. Then, 0.62 mL 1 M tetrabutylammonium fluoride in THF was added at 0 °C and the mixture was stirred at 0 °C for 45 min. After removing the solvent, the crude product was purified by silica gel column chromatography to afford the product N, N-di (4-formylbenzyl)-4-acetenylphenylamine (M1) as a dark yellow solid. ^{1}H NMR (300 MHz, Chloroform-d) δ (ppm): 9.84 (s, 2H), 7.72 (d, 4H, J=9.01), 7.41(d, 2H, J=9.02), 7.12 (d, 4H, J=9.01), 7.03 (m, 2H, J=9.10), 3.06 (s, 1H). MS (m/z): calcd for $C_{12}H_{15}NO_2$: $[M+H]^+$ = 326.1136, found 326.1193.

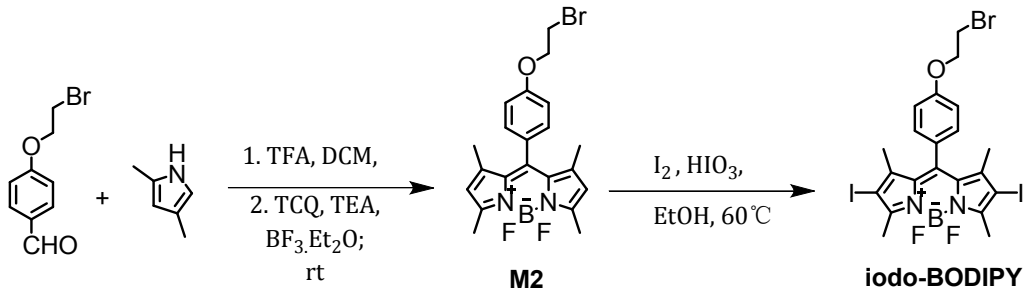


Fig S2. Synthesis of iodine substitued BODIPY dye iodo-BODIPY.

Compound iodo-BODIPY. 4-(2-bromoethoxy) benzaldehyde (1.1 g, 5.0 mmol) and 2, 4-dimethylpyrrole (1.0 g, 10.0 mmol) were dissolved in dry CH_2Cl_2 (150 mL). Ten drops of trifluoroacetic acid (TFA) were added, after TLC monitoring

showed complete disappearance of the aldehyde, a solution of tetra-chloro-benzo-quinone (TCQ) (2.5 g, 10.0 mmol) in anhydrous CH_2Cl_2 (50 mL) was added. This mixture was further stirred for 1h, then triethylamine (5.0 mL) and BF_3. OEt_2 (5.0 mL) were subsequently added. This mixture was stirred overnight. The mixture was washed with water and brine, dried over anhydrous Na_2SO_4, and evaporated under vacuum. The crude compound was purified by silica gel column chromatography to give a red powder as the pure BODIPY (50 %). M2 (447.0 mg, 1.0 mmol) and iodine (320.0 g, 2.5 mmol) in EtOH (40 mL). Iodic acid (352.0 mg, 2.0 mmol) was dissolved in 1 mL water and added dropwise over 20 min to the solution. This mixture was stirred at 60 °C for 30 min. After cooling, the mixture was evaporated under vacuum. The crude product was purified by silica gel column chromatography from ethyl acetate and n-hexane to afford a purple compound as pure iodo-BODIPY (86 %). ^{1}H NMR (500 MHz, Chloroform-d) δ (ppm): 7.17 (d, 2H, J = 10.11), 7.06 (d, 2H, J = 5.04), 4.37 (t, 2H, J = 6.20 Hz), 3.69 (t, 2H, J = 6.21 Hz), 2.64 (s, 6H), 1.44 (s, 6H). ^{13}C NMR (126 MHz, C Chloroform-d) δ (ppm): 159.15, 156.75, 145.31, 141.22, 131.70, 129.33, 127.58, 115.66, 85.61, 68.04, 28.70, 17.20, 16.02. MS (m/z): calcd for $C_{21}H_{20}BBrF_2I_2N_2O$：$[M+H]^+$= 696.8931, found: 696.8958.

^{1}H NMR, ^{13}C NMR and HRMS Spectra

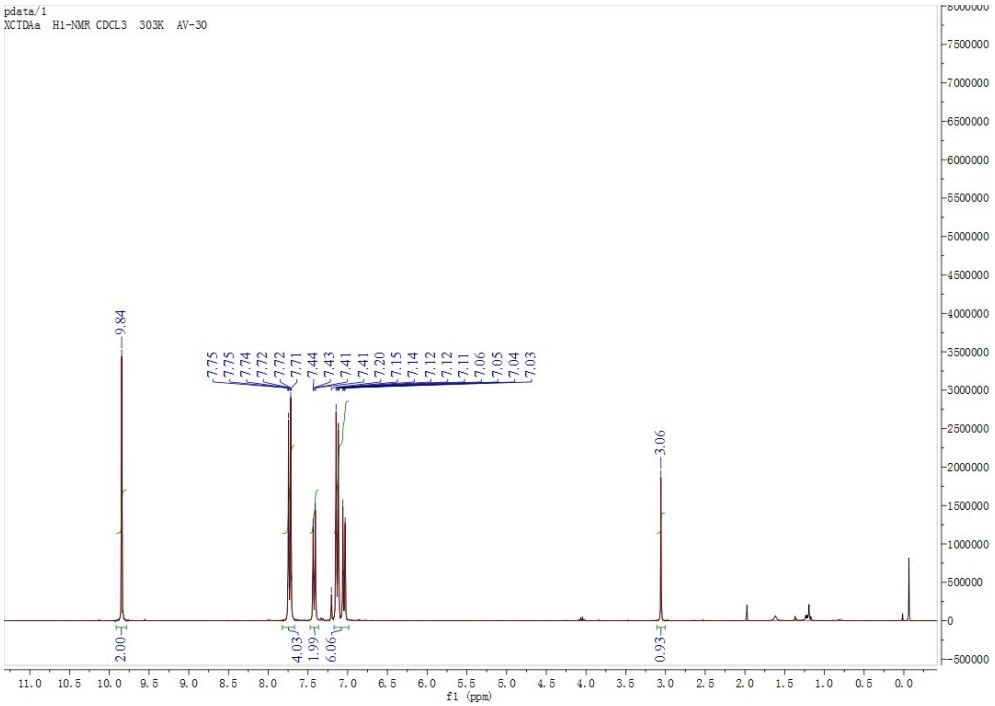


Fig S3. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of M1.

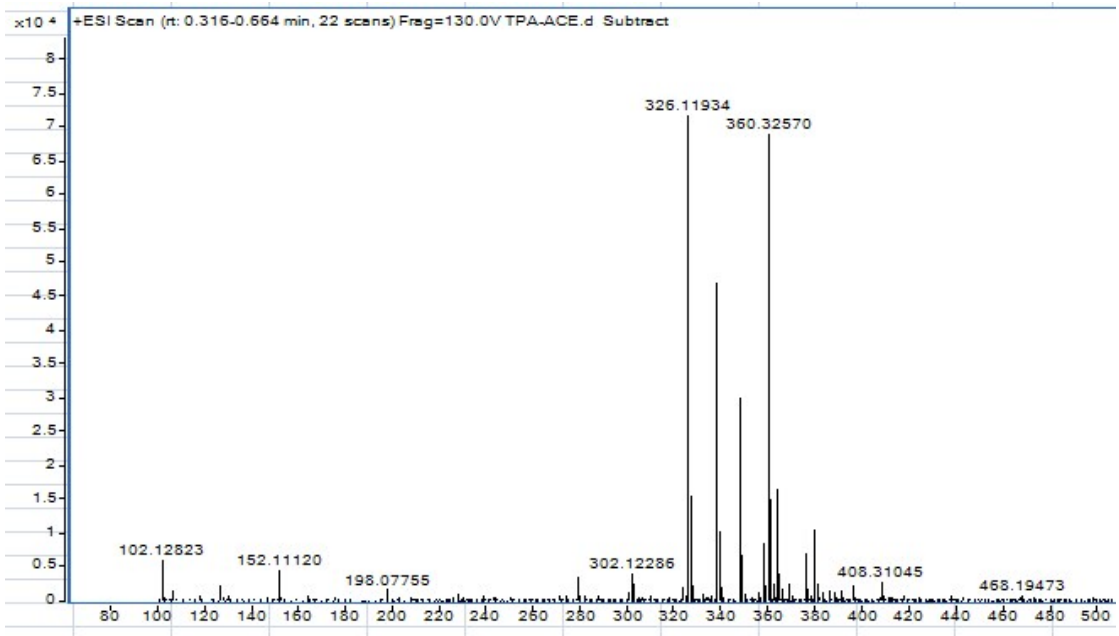


Fig S4. MS spectrum of M1.

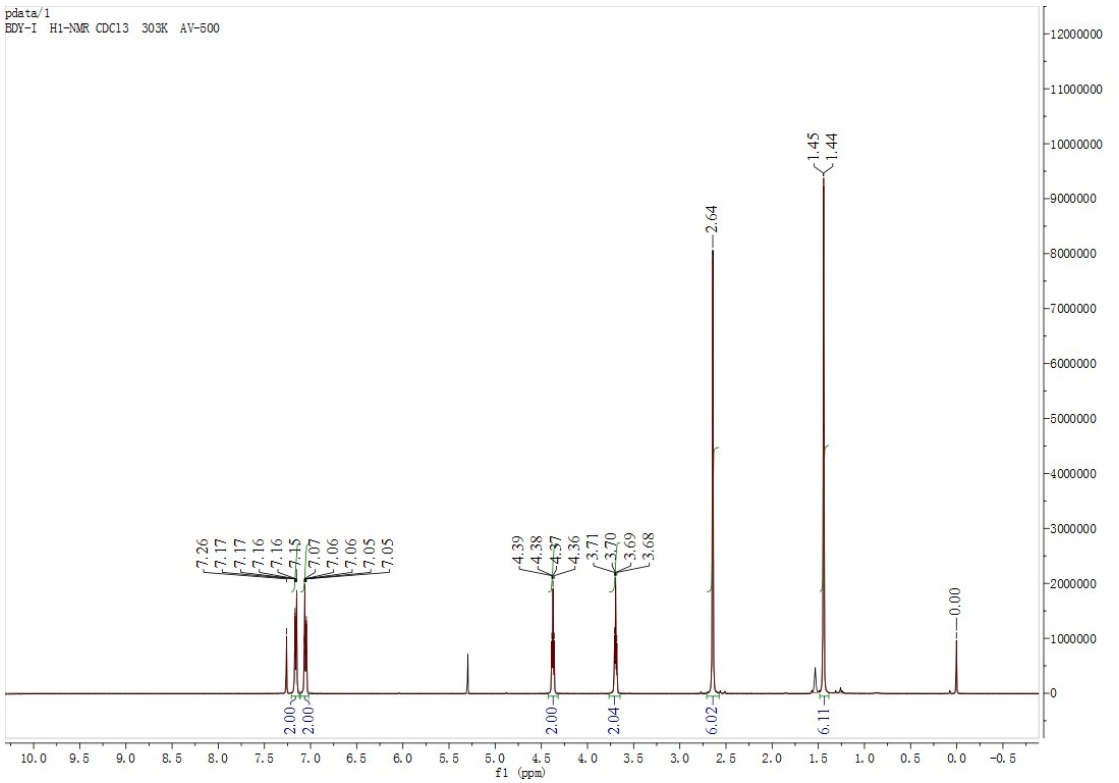


Fig S5. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of iodo-BODIPY.

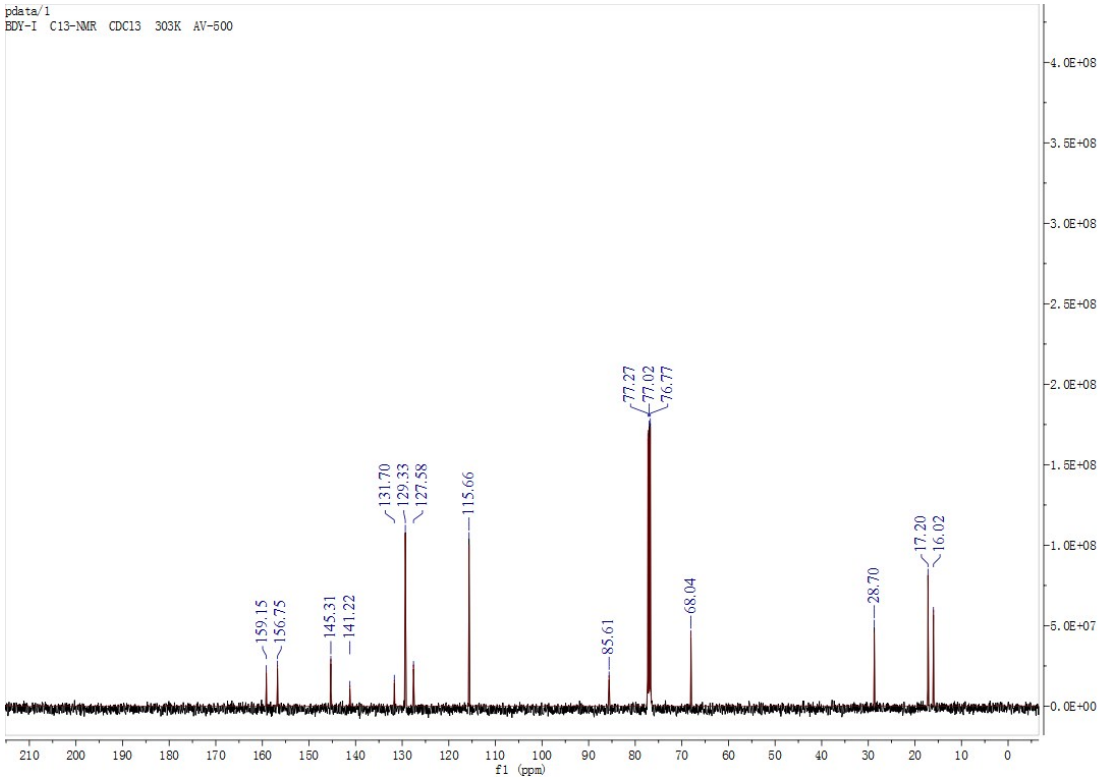


Fig S6. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of iodo-BODIPY.

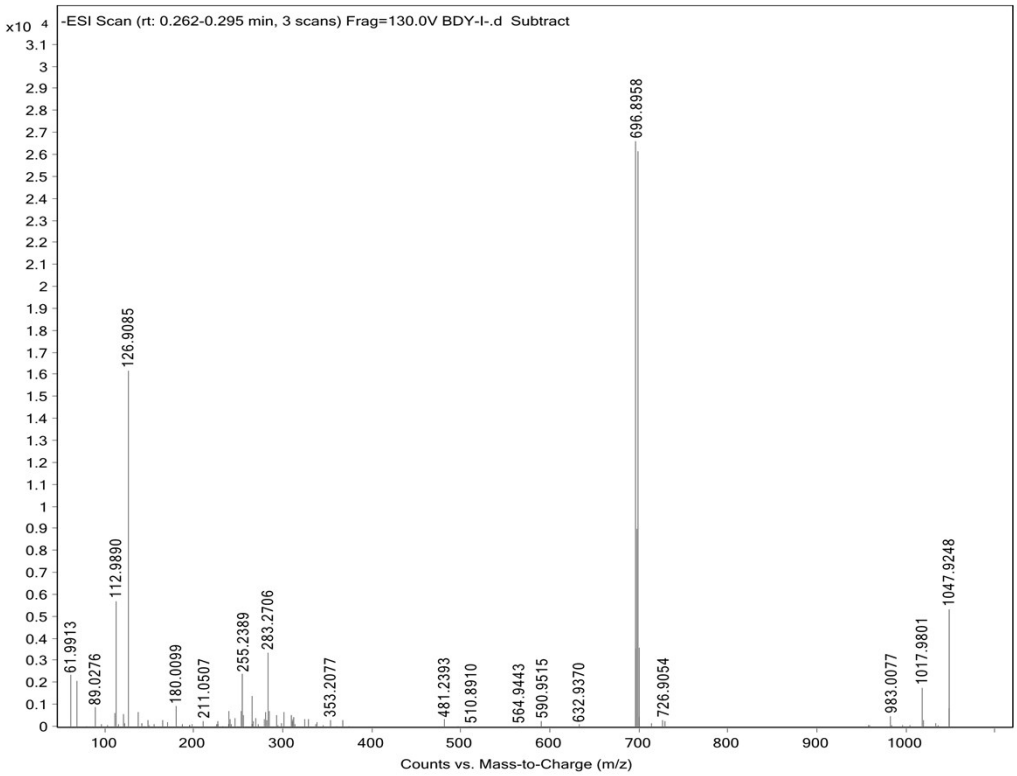


Fig S7. MS spectrum of iodo-BODIPY.

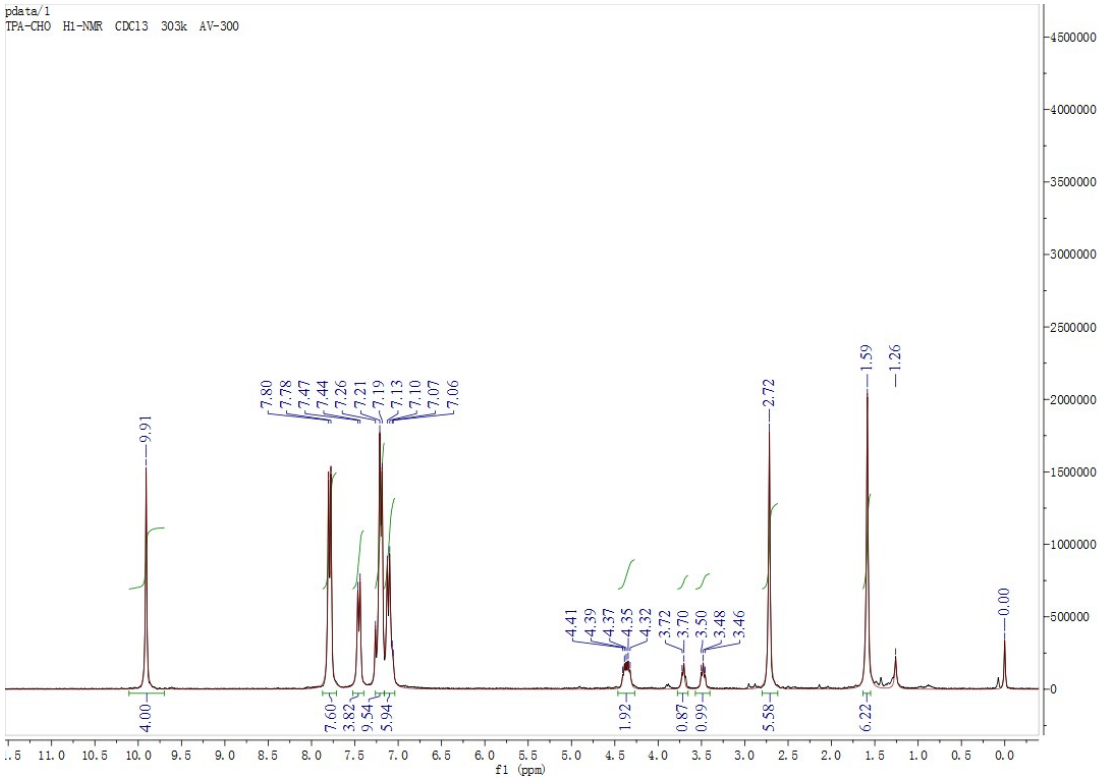


Fig S8. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of BTC.

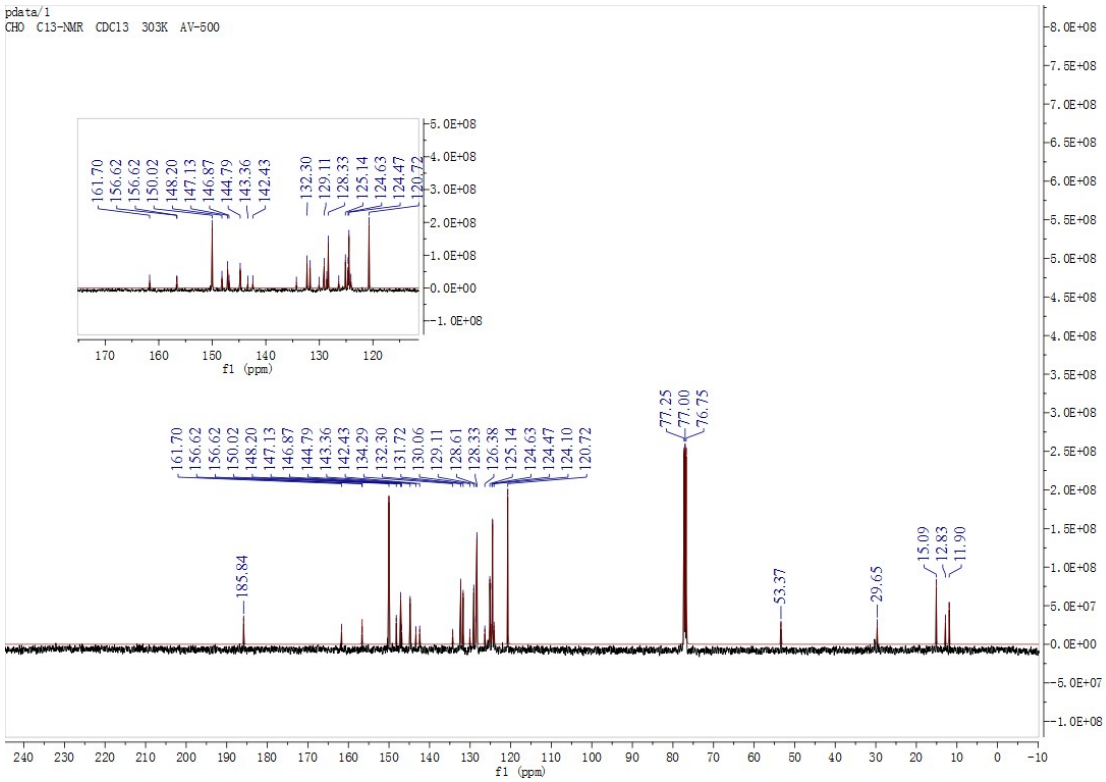


Fig S9. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of BTC.

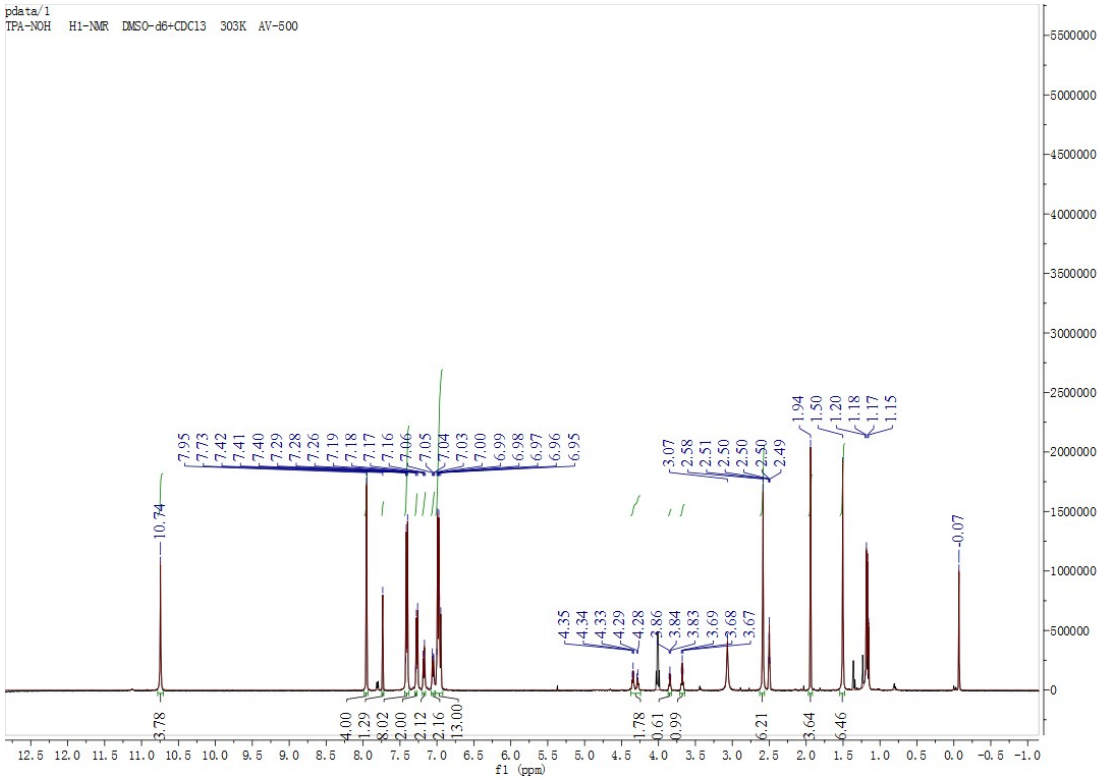


Fig S10. ^{1}H NMR spectrum ($CDCl_3$ + DMSO-d_6, 500 MHz) of BTN.

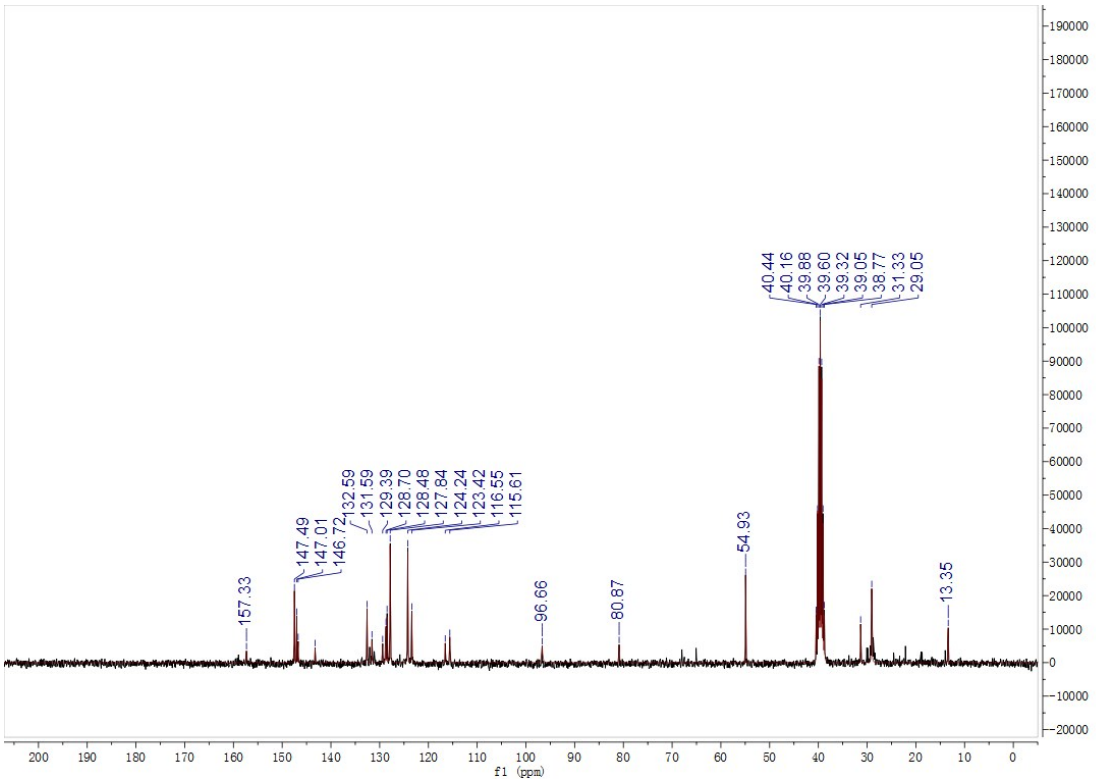


Fig S11. ^{13}C NMR spectrum (DMSO-d_6, 75 MHz) of BTN.

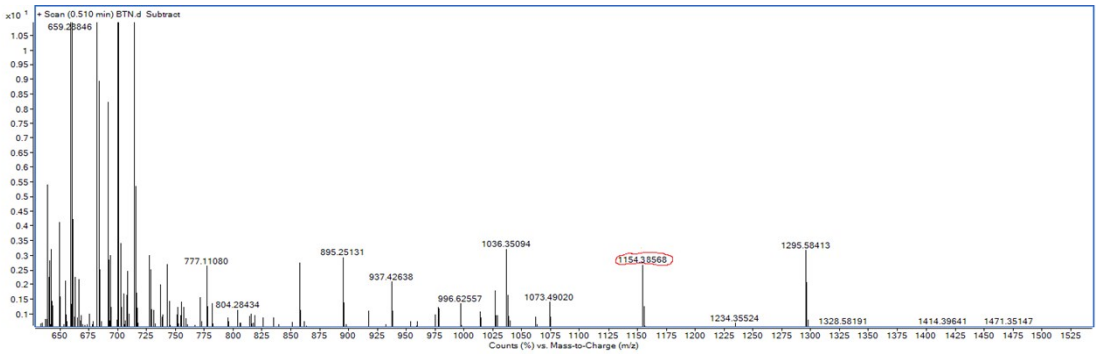
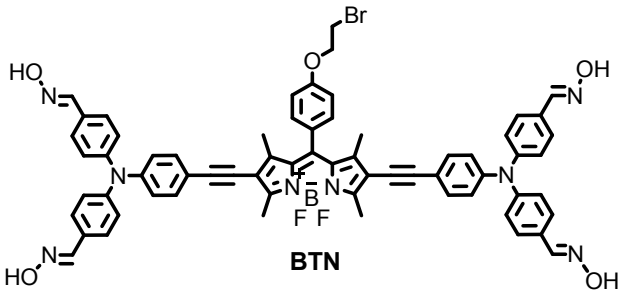
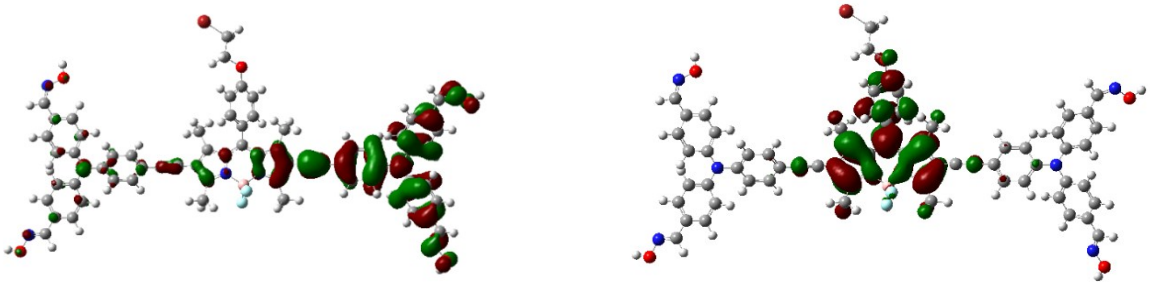


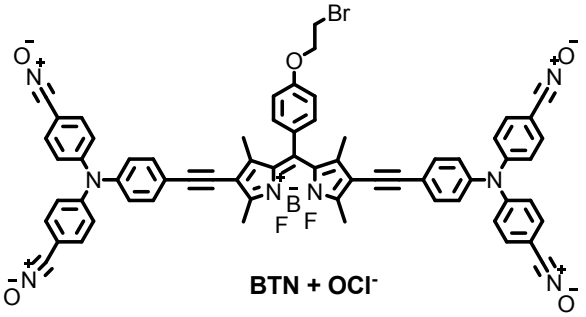
Fig S12. MS spectrum of BTN.

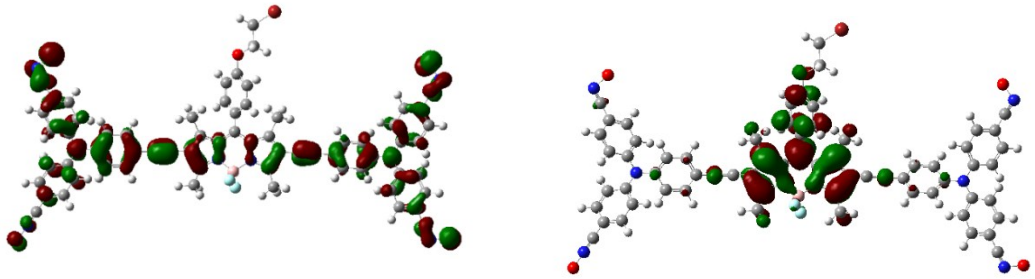




HOMO (-4.77ev) LUMO (-2.77ev)

DFT calculations of BTN before reacting with OCl^-





HOMO (-5.33ev) LUMO (-3.20ev)

DFT calculations of BTN after reacting with OCl^-

Figure S13 The DFT calculations of BTN based on B3LYP/6-31G(d) basis set before and after reacting with OCl^-.

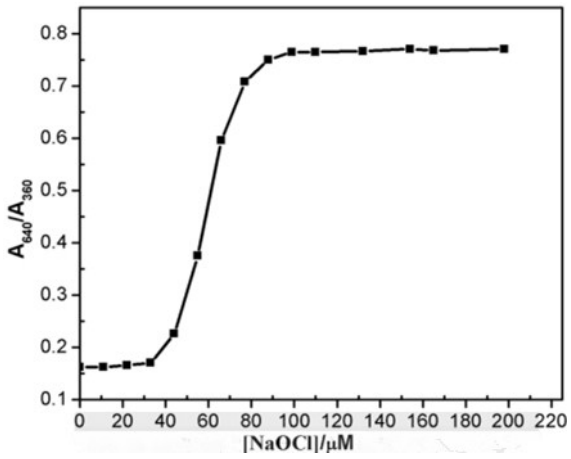


Fig S14. The UV-Vis absorption ratio (A_{640} /A_{360}) changes with the addition of NaOCl (50-100μM). Condition: [BTN] =10 μM, PBS (10 m M, pH = 7.4): THF (1/1 , v/v), λ_{ex}=380 nm (slit: 5 nm).

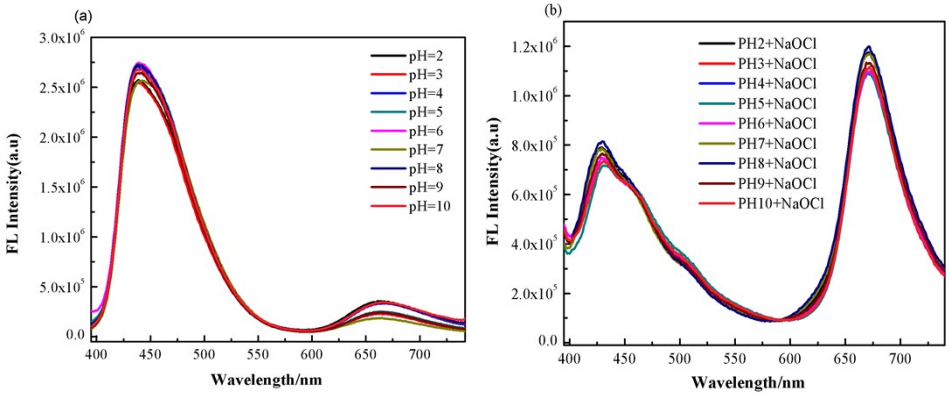


Fig S15. Effect of pH on the fluorescence intensity of probe (10 μM) in buffered/THF (1/1, v/v, pH= 2.0~10.0, 10 mM). Fluorescence responses are shown before (a) and after (b) addition of NaOCl (50 μM) at 440 nm and 660 nm, respectively, after incubation of NaOCl for 30 min. λ_{ex} = 380 nm.

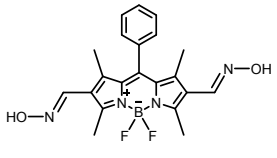
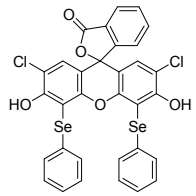
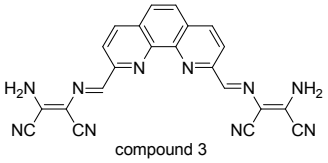
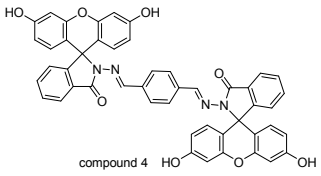
Compounds	References	Recognition sites	$\lambda_{max\text{-}em}$	LOD	Signal representation
 compound 1	Dyes and Pigments, 2017 , 136, 852-858.	2	589 nm	0. 85 μM	ratiometric
 compound 2	Sensors and Actuators B: Chemical, 2017, 244, 307-313.	2	519 nm	0.039 μM	Single fluorescence intensity
 compound 3	Sensors and Actuators B: Chemical 2014, 204, 741-745.	2	447 nm	3.3 μM	Single fluorescence intensity
 compound 4	Sensors and Actuators B: Chemical 2014, 202, 656-662.	2	524 nm	5.0 μM	Single fluorescence intensity
BTN	this work	4	670 nm	4.9 μM	ratiometric

Fig S16. The fluorescent probes reported for multi-sites toward hypochlorite