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.** Syntheses of alkynyl substituted 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, 0.03 mmol) and were placed in 10 mL of dry THF under N₂ for 30 min. Trimethylsilylacetylene (1.25 mL, 8.80 mmol) and triethylamine (10 mL) were added and stirred at ambient overnight under N₂. 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 CH₂Cl₂. 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) $\delta$ (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 substituted 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 CH₂Cl₂ (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 CH₂Cl₂ (50 mL) was added. This mixture was further stirred for 1 h, then triethylamine (5.0 mL) and BF₃·OEt₂ (5.0 mL) were subsequently added. This mixture was stirred overnight. The mixture was washed with water and brine, dried over anhydrous Na₂SO₄, 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 %). ¹H 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). ¹³C 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 C₂₁H₂₀BBrF₂I₂N₂O: [M+H]⁺ = 696.8931, found: 696.8958.

¹H NMR, ¹³C NMR and HRMS Spectra

Fig S3. ¹H NMR spectrum (CDCl₃, 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.

DFT calculations of BTN before reacting with OCl⁻
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 (50-100 μM). Condition: [BTN] = 10 μM, PBS (10 mM, pH = 7.4): THF (1/1, v/v), $\lambda_{ex}$ = 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. $\lambda_{ex}$ = 380 nm.
<table>
<thead>
<tr>
<th>Compounds</th>
<th>References</th>
<th>Recognition sites</th>
<th>(\lambda_{\text{max-em}})</th>
<th>LOD</th>
<th>Signal representation</th>
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<td><img src="image" alt="Compound 1" /></td>
<td>Dyes and Pigments, 2017, 136, 852-858.</td>
<td>2</td>
<td>589 nm</td>
<td>0.85 (\mu)M</td>
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<td><img src="image" alt="Compound 2" /></td>
<td>Sensors and Actuators B: Chemical, 2017, 244, 307-313.</td>
<td>2</td>
<td>519 nm</td>
<td>0.039 (\mu)M</td>
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<td><img src="image" alt="Compound 3" /></td>
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<td>3.3 (\mu)M</td>
<td>Single fluorescence intensity</td>
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<td><img src="image" alt="Compound 4" /></td>
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<td>524 nm</td>
<td>5.0 (\mu)M</td>
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<td>BTN</td>
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<td>4</td>
<td>670 nm</td>
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Fig S16. The fluorescent probes reported for multi-sites toward hypochlorite