

Supporting Information

Light-driven Au(III)-promoted cleavage of triazole-bearing amine derivatives and its application in the detection of ionic gold

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Experimental Details

Materials and Measurements.

All commercially available reagents were reagent grade and used without further purification. Dichloromethane, n-hexane, and tetrahydrofuran (THF) were freshly distilled before each use. Following 23 kinds of metal salts were used for the metal ion selectivity test; 2: $\text{Fe}(\text{ClO}_4)_3$, 3: $\text{Fe}(\text{ClO}_4)_2$, 4: AuCl_3 , 5: $\text{Hg}(\text{OAc})_2$, 6: $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, 7: $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$, 8: $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 9: $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 10: $\text{MnSO}_4 \cdot x\text{H}_2\text{O}$, 11: $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 12: $\text{Cu}(\text{OAc})_2$, 13: $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 14: AlCl_3 , 15: $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, 16: AuCl , 17: $\text{AgClO}_4 \cdot x\text{H}_2\text{O}$, 18: NaClO_4 , 19: PtCl_2 , 20: PdCl_2 , 21: $\text{Rh}(\text{OAc})_2$, 21: $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 23: KClO_4 , 24: $\text{Ba}(\text{NO}_3)_2$. Electronic absorption spectra were recorded on a JASCO V-660 spectrometer. Fluorescence spectra were recorded on a JASCO FP-6300 spectrometer. All steady-state measurements were carried out by using a quartz cuvette with a pathlength of 1 cm at ambient temperatures. ^1H and ^{13}C NMR spectra were recorded on a Bruker Advance DPX 400 spectrometer at 25°C in CDCl_3 , CD_3CN , and $\text{DMSO}-d_6$. MALDI-TOF-MS was performed on Bruker Daltonics LRF20 with Dithranol (1,8,9-trihydroxyanthracene) as the matrix.

Synthesis

2: 4-nitrobenzaldehyde (300 mg, 1.985 mmol) and 2,4-dimethylpyrrole (420 μL , 4.079 mmol) were mixed in a 300 mL round bottomed flask. The flask was degassed three times under high vacuum and back-filled with N_2 . Dried MC (100 mL) and trifluoroacetic acid (several drops) were added and stirred for 12 h. Then, *p*-Chloranil (1 g, 4.067 mmol) was added and further stirred for 40 min at 25°C . Et_3N (2 mL) and BF_3OEt_2 (3.2 mL, 25.33 mmol) were added, and the reaction mixture was further stirred for 1 h at 25°C . The solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography (hexane/ethyl acetate, 8:1) to produce **2** as a reddish solid (91 mg, 14%). ^1H NMR (400 MHz, CDCl_3 , 25°C) δ = 8.40-8.38 (d, 2 H, J = 8.4 Hz), 7.55-7.53 (d, 2 H, J = 8.4 Hz), 6.02 (s, 2 H), 2.57 (s, 6 H), 1.36 ppm (s, 6 H); MALDI-TOF-MS: m/z : calcd. for $\text{C}_{19}\text{H}_{18}\text{BF}_2\text{N}_3\text{O}_2$: 369.17 $[\text{M}]^+$; found: 369.11.

3: 0.5 M HCl (4 mL) was added to a mixture solution of **2** (150 mg, 0.4063 mmol) and Fe (423.8 mg, 8.126 mmol) in THF (8.4 mL). The reaction mixture was refluxed for 7 h, and then

quenched with a saturated aqueous solution of Na_2CO_3 . The organic phase was extracted with CH_2Cl_2 , and then evaporated *in vacuo*. The residue was purified by column chromatography with CH_2Cl_2 as the eluent to give **3** as an orange solid (90 mg, 65%). ^1H NMR (400 MHz, CDCl_3 , 25 °C) δ = 7.00-6.98 (d, 8 H, J = 8.4 Hz), 6.77-6.75 (d, 2 H, J = 8.4 Hz), 5.97 (s, 2 H), 3.84 (s, 2 H), 2.54 (s, 6 H), 1.49 ppm (s, 6H); MALDI-TOF-MS: m/z : calcd. for $\text{C}_{19}\text{H}_{20}\text{BF}_2\text{N}_3$: 339.19 $[\text{M}]^+$; found: 339.37.

4: **3** (90 mg, 0.2653 mmol) and K_2CO_3 (366.7 mg, 2.653 mmol) were mixed in a 50 mL flask. Acetone (10 mL) and propargyl bromide (200 μL , 2.653 mmol) were added under nitrogen. The reaction mixture was refluxed for 12 h. After being cooled to room temperature, the solvent was removed. The residue was dissolved in CH_2Cl_2 (100 mL) and the solution was washed with water (100 mL). The organic layer was evaporated *in vacuo*, and purified by column chromatography with hexane/ CH_2Cl_2 (1:2) to produce **4** as a reddish solid (34 mg, 32%). ^1H NMR (400 MHz, CDCl_3 , 25 °C) δ = 7.16-7.14 (d, 2 H, J = 8.4 Hz), 7.04-7.02 (d, 2 H, J = 8.4 Hz), 5.97 (s, 2 H), 4.18 (s, 4 H), 2.55 (s, 6 H), 2.27 (s, 2 H), 1.45 ppm (s, 6H); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 155.30, 148.41, 143.45, 142.40, 132.15, 129.01, 125.88, 121.23, 116.01, 78.93, 73.09, 40.63, 14.81, 0.21 ppm; MALDI-TOF-MS: m/z : calcd. for $\text{C}_{25}\text{H}_{24}\text{BF}_2\text{N}_3$: 415.29 $[\text{M}]^+$; found: 414.83.

5: Aniline (200 mg, 2.148 mmol) and K_2CO_3 (1.48 g, 10.74 mmol) were mixed in a 50 mL round bottomed flask. Acetone (20 mL) and propargyl bromide (805.6 μL , 10.74 mmol) were added under nitrogen. The reaction mixture was refluxed for 12 h. After being cooled to room temperature, the solvent was removed. The residue was dissolved in CH_2Cl_2 (100 mL) and the solution was washed with water (100 mL). The organic layer was evaporated *in vacuo*, and purified by column chromatography with hexane/ CH_2Cl_2 (6:4) to produce **5** as a white solid (381 mg, 75%). ^1H NMR (400 MHz, CDCl_3 , 25 °C) δ = 7.30-7.27 (t, 2 H, J = 7.0 Hz), 6.98-6.96 (d, 2 H, J = 8.8 Hz), 6.91-6.87 (t, 1 H, J = 7.4 Hz), 4.13 (s, 4 H), 2.25 (s, 2 H).

6: Ethylamine (1 g, 0.022 mol) and triethylamine (10 mL) were mixed in a 100 mL round bottomed flask at 0 °C. Propargyl bromide (2 mL, 0.047 mol) was added slowly and stirred at 0 °C. The residue was dissolved in CH_2Cl_2 (100 mL) and the solution was washed with a saturated aqueous solution of NaOH (100 mL). The organic layer was evaporated *in vacuo* to give a yellow liquid, which was dissolved in THF without further purification.

1_{Et}: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (560.8 mg, 2.246 mmol) and sodium ascorbate (445 mg, 2.25 mmol) were

added to a mixture of **6** (272 mg, 2.246 mmol) and methyl 4-(azidomethyl)benzoate (1.28 g, 6.738 mmol) in 10 mL THF/H₂O (1:1). The reaction mixture was stirred for 7 h at 50 °C, and then the organic layer was separated. After evaporation of the solvent under reduced pressure, the residue was purified using column chromatography with 50% CH₂Cl₂/ethyl acetate as the eluent to give **1_{Et}** as a white powder (678 mg, 60%). ¹H NMR (400 MHz, CDCl₃, 25 °C) δ = 8.04-8.02 (d, 4 H, J = 8.4 Hz), 7.55 (s, 2 H), 7.31-7.29 (d, 4 H, J = 8 Hz), 5.57 (s, 4 H), 3.92 (s, 6 H), 3.72 (s, 4 H), 2.54-2.52 (q, 4 H, J = 7.2 Hz), 1.14-1.11 ppm (t, 3 H, J = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 166.41, 144.99, 139.78, 130.39, 130.30, 127.72, 123.35, 53.54, 52.29, 47.49, 47.12, 12.39 ppm; MALDI-TOF-MS: m/z : calcd. for C₂₆H₂₉N₇O₄: 503.23 [M]⁺; found 501.72.

1_{Ph}: CuSO₄·5H₂O (560.8 mg, 2.246 mmol) and sodium ascorbate (445 mg, 2.246 mmol) were added to a mixture of **5** (380 mg, 2.246 mmol) and methyl 4-(azidomethyl)benzoate (1.28 g, 6.738 mmol) in 10 mL THF/H₂O (1:1). The reaction mixture was stirred for 7 h at 50 °C, and then the organic layer was separated. After evaporation of the solvent under reduced pressure, the residue was purified using column chromatography with 50% CH₂Cl₂/ethyl acetate as the eluent to give **1_{Ph}** as a white powder (1.05 g, 85%). ¹H NMR (400 MHz, DMSO-*d*₆, 25 °C) δ = 7.96 (s, 2 H), 7.88-7.86 (d, 4 H, J = 8.4 Hz), 7.29-7.27 (d, 4 H, J = 8.4 Hz), 7.11-7.07 (t, 2 H, J = 7.8 Hz), 6.82-6.80 (d, 2 H, J = 8 Hz), 6.62-6.59 (t, 1 H, J = 7.2 Hz), 5.58 (s, 4 H), 4.60 (s, 4 H), 3.81 (s, 6 H); ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 166.57, 147.94, 146.17, 139.72, 130.61, 130.48, 129.48, 127.77, 122.36, 118.16, 113.91, 53.73, 52.46, 47.04 ppm; MALDI-TOF-MS: m/z : calcd. for C₃₀H₂₉N₇O₄: 551.23 [M]⁺; found 552.46.

1_{BODIPY}: CuSO₄·5H₂O (60 mg, 0.2402 mmol) and sodium ascorbate (48 mg, 0.2402 mmol) were added to a mixture of **4** (100 mg, 0.2402 mmol) and methyl 4-(azidomethyl)benzoate (200 mg, 0.9608 mmol) in 10 mL THF/H₂O (1:1). The reaction mixture was stirred for 7 h at 50 °C, and then the organic layer was separated. After evaporation of the solvent under reduced pressure, the residue was purified using column chromatography with 50% CH₂Cl₂/ethyl acetate as the eluent to give **1_{BODIPY}** as an orange powder (65.2 mg, 34%). ¹H NMR (400 MHz, CD₃CN, 25 °C) δ = 7.94-7.92 (d, 4 H, J = 8.4 Hz), 7.58 (s, 2 H), 7.27-7.25 (d, 4 H, J = 8.4 Hz), 7.04-7.02 (d, 2 H, J = 8.8 Hz), 6.99-6.96 (d, 2 H, J = 8.8 Hz), 6.02 (s, 2 H), 5.54 (s, 4 H), 4.71 (s, 4 H), 3.84 (s, 6 H), 2.46 (s, 6 H), 1.29 ppm (s, 6 H); ¹³C NMR (100 MHz, CD₃CN, 25 °C) δ = 167.56, 156.14, 149.85, 146.52, 144.86, 142.36, 133.18, 131.50,

131.16, 130.10, 129.99, 129.10, 124.45, 124.07, 122.31, 115.28, 54.24, 53.17, 47.64, 15.13 ppm; MALDI-TOF-MS: m/z : calcd. for $C_{43}H_{42}BF_2N_9O_4$: 797.66 $[M]^+$; found 798.79.

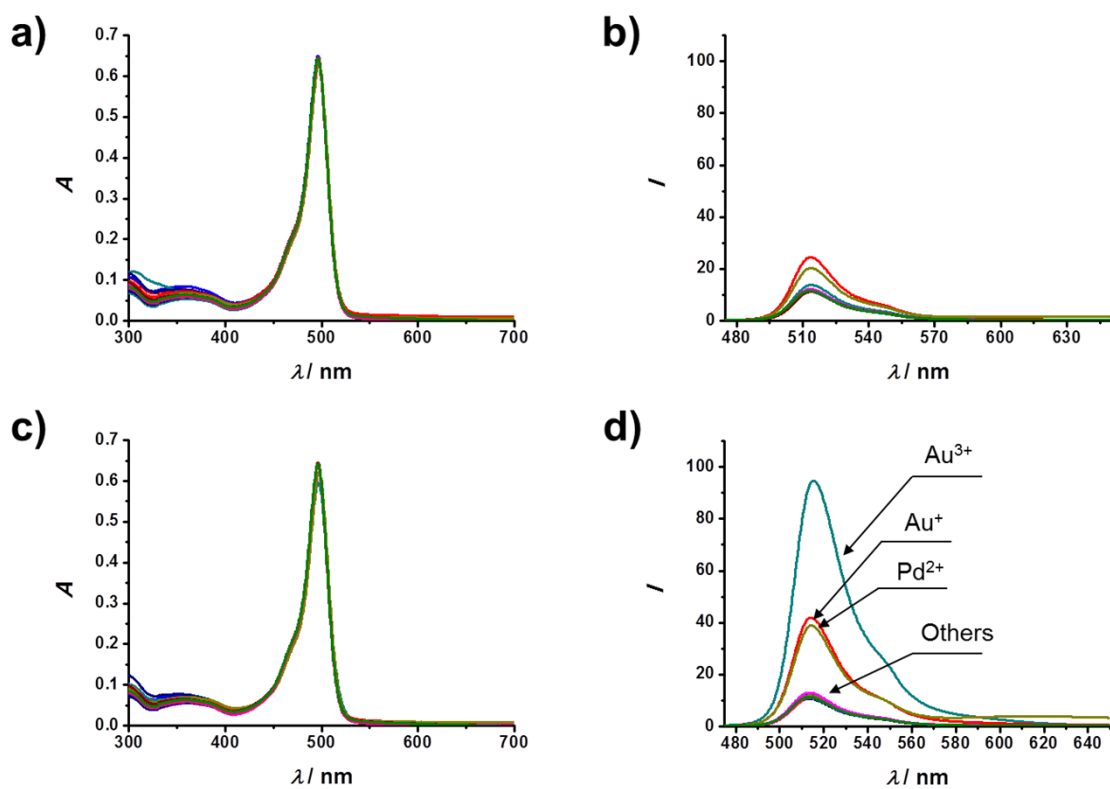


Figure S1. UV-Vis and Fluorescence response of **1**_{BODIPY} (10 μ M) to various metal cation (2 eq) additions in MeCN/H₂O (1:1 v/v); a), b) before light irradiation; c), d) after light irradiation (365 nm).

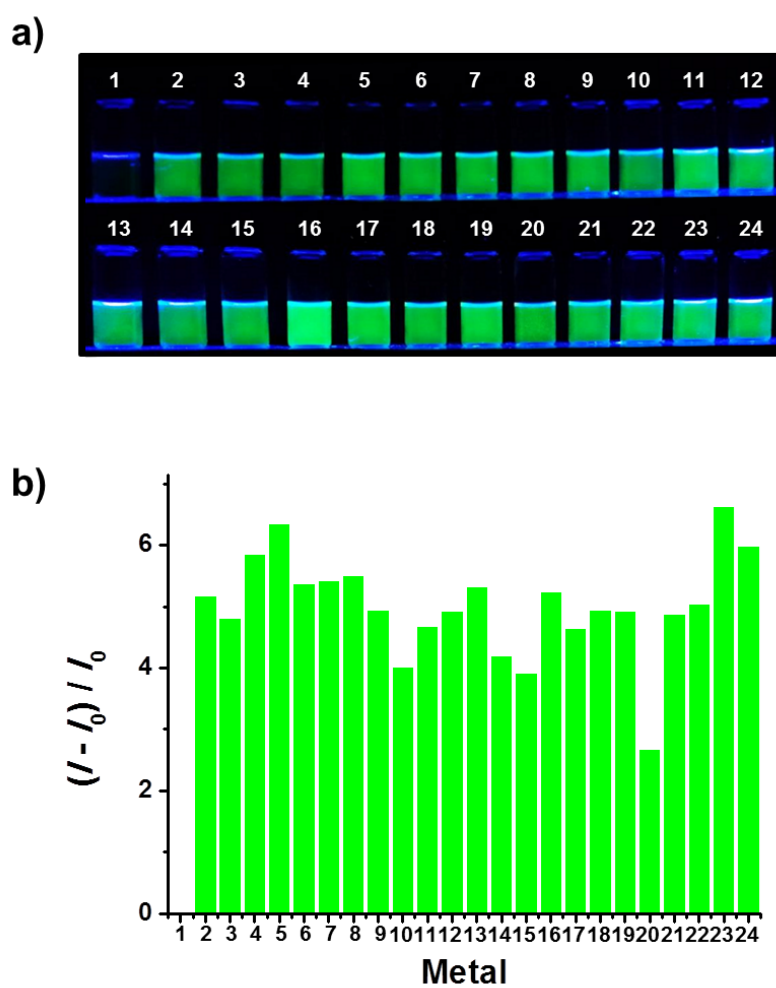


Figure S2. Fluorescence changes of **1**_{BODIPY} (10 μ M) by the addition of Au^{3+} ion (2 eq) with 2 min of UV irradiation (365 nm) in MeCN/ H_2O (1:1 v/v) containing various other metal ions (2 eq). a) fluorescence images, b) emission intensity changes at 515 nm upon excitation at 460 nm.

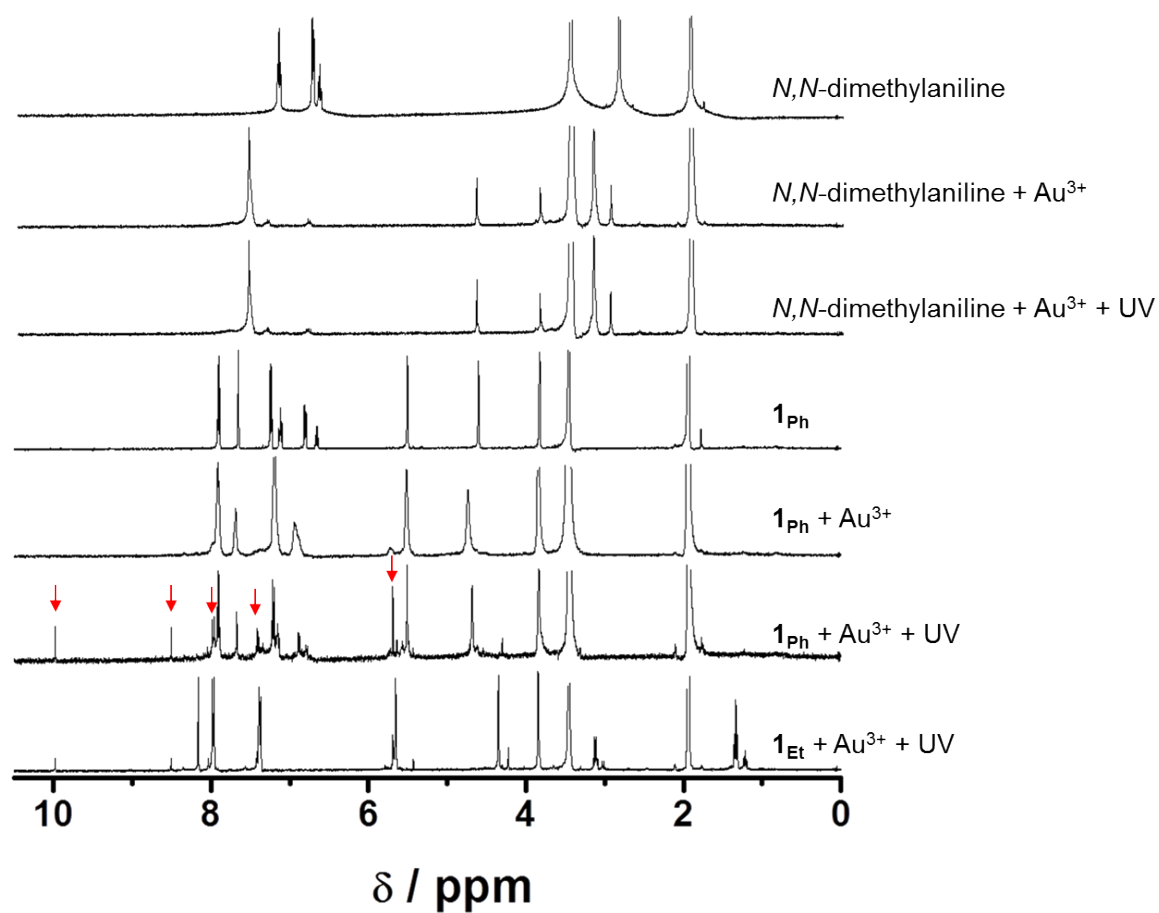


Figure S3. ^1H NMR spectral change of structural fragments of $\mathbf{1}_{\text{BODIPY}}$ by Au^{3+} addition and UV irradiation (365 nm). Red arrow indicates a new set of proton signals generated by UV irradiation.

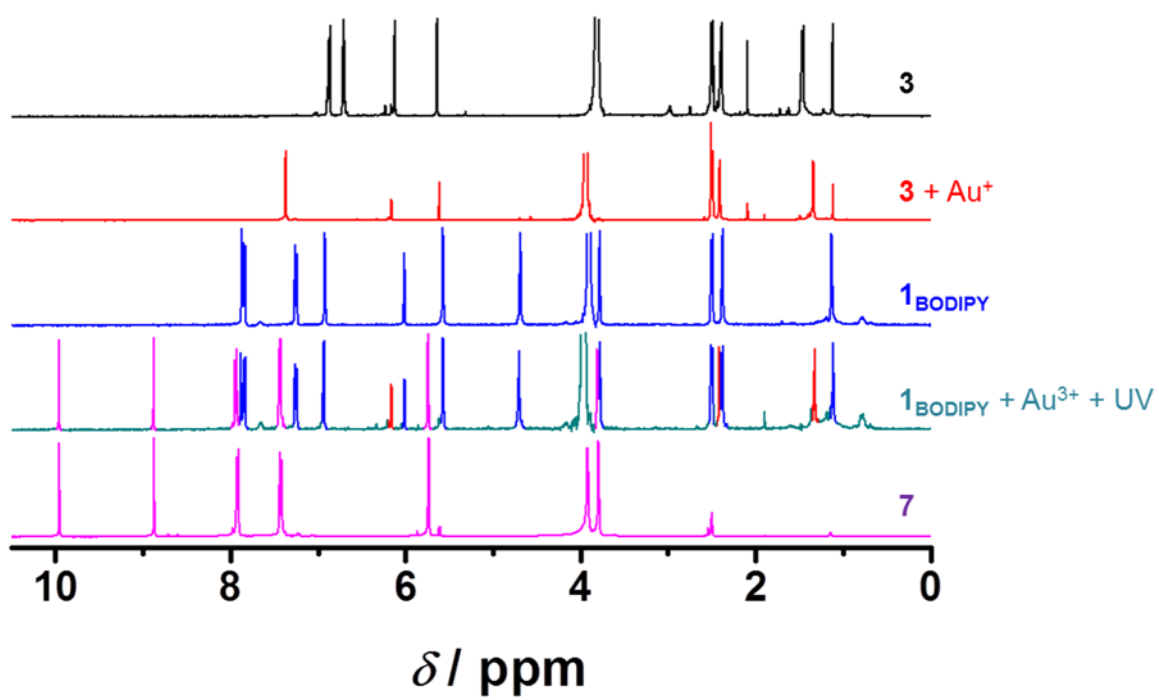


Figure S4. ^1H NMR spectra of **3**, **1_{BODIPY}**, and **7** in DMSO/D₂O (5:1 v/v) with different conditions.

$C_{12}H_{11}N_3O_3 = 245.0800$

[M+H⁺] 246.0873 [246.0860-246.0885]

1 #262 RT: 4.44 AV: 1 NL: 5.40E6
T: FTMS + p ESI Full ms [200.00-500.00]

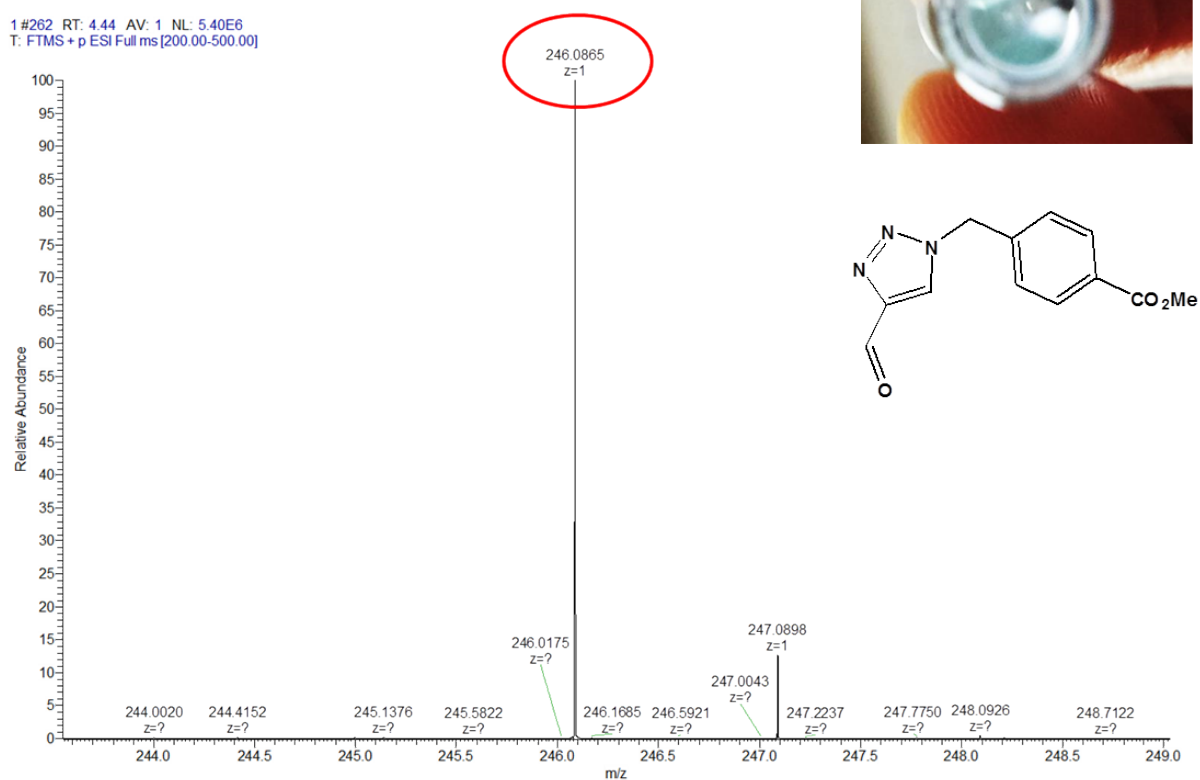


Figure S5. High resolution mass spectrum of **7** and an image of Tollen's test for aldehyde.

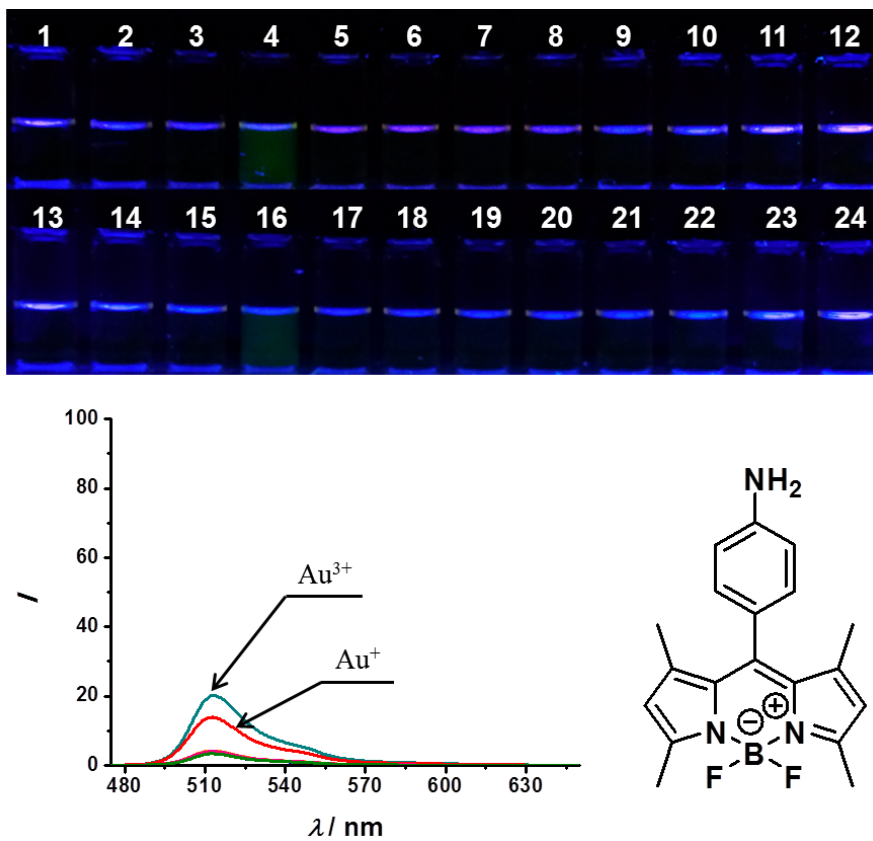


Figure S6. Fluorescence response of **3** (10 μM) to various metal ions (2 eq) in MeCN/H₂O (1:1 v/v).

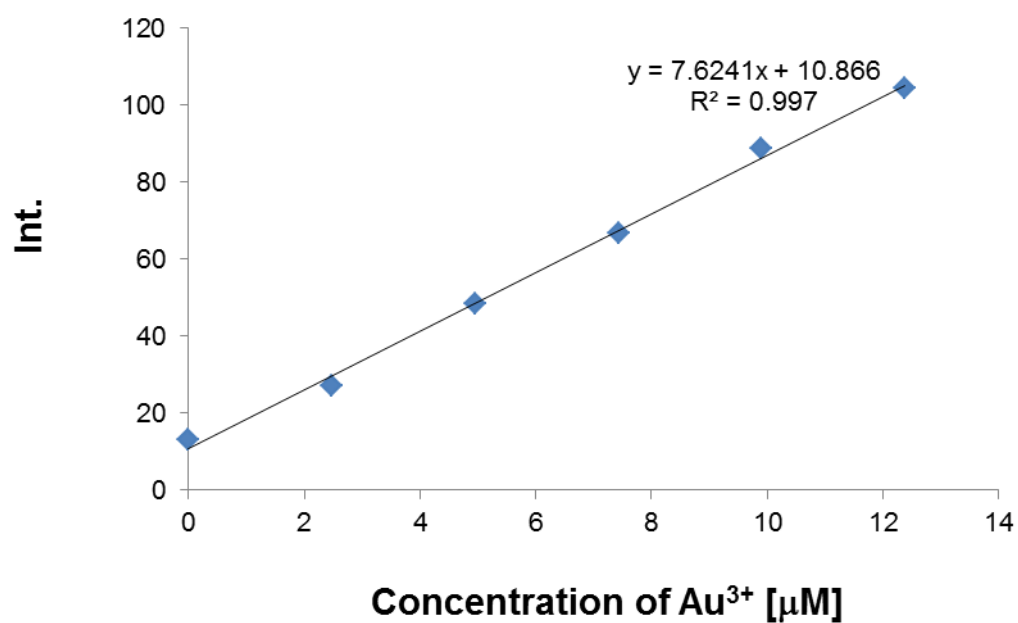


Figure S7. Linear correlation between fluorescence intensity of **1_{BODIPY}** and Au³⁺ concentration. The fluorescence emission intensity was measure after 2 min of UV irradiation.

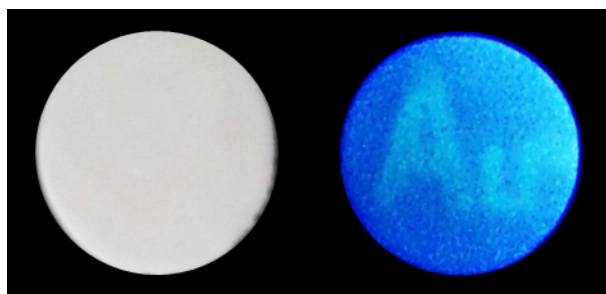


Figure S8. Fluorescence pattern obtained by **1_{BODIPY}** and AuCl₃ solution. To get the fluorescence pattern a filter paper was dipped into the solution of **1_{BODIPY}** and then AuCl₃ solution was thinly coated onto the surface of filter paper. Finally, the paper was covered with photomask and exposure to UV-handy lamp (365 nm) for 1 min.

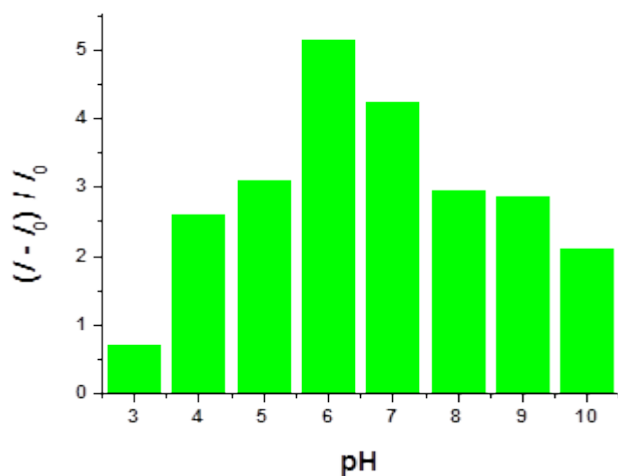


Figure S9. pH dependent fluorescence changes of **1**_{BODIPY} (10 μ M) to Au^{3+} ion (2 eq) in MeCN/0.01 M PBS buffer (1:1 v/v, pH 3-10), $\lambda_{\text{ex}} = 460$ nm, $\lambda_{\text{em}} = 515$ nm.

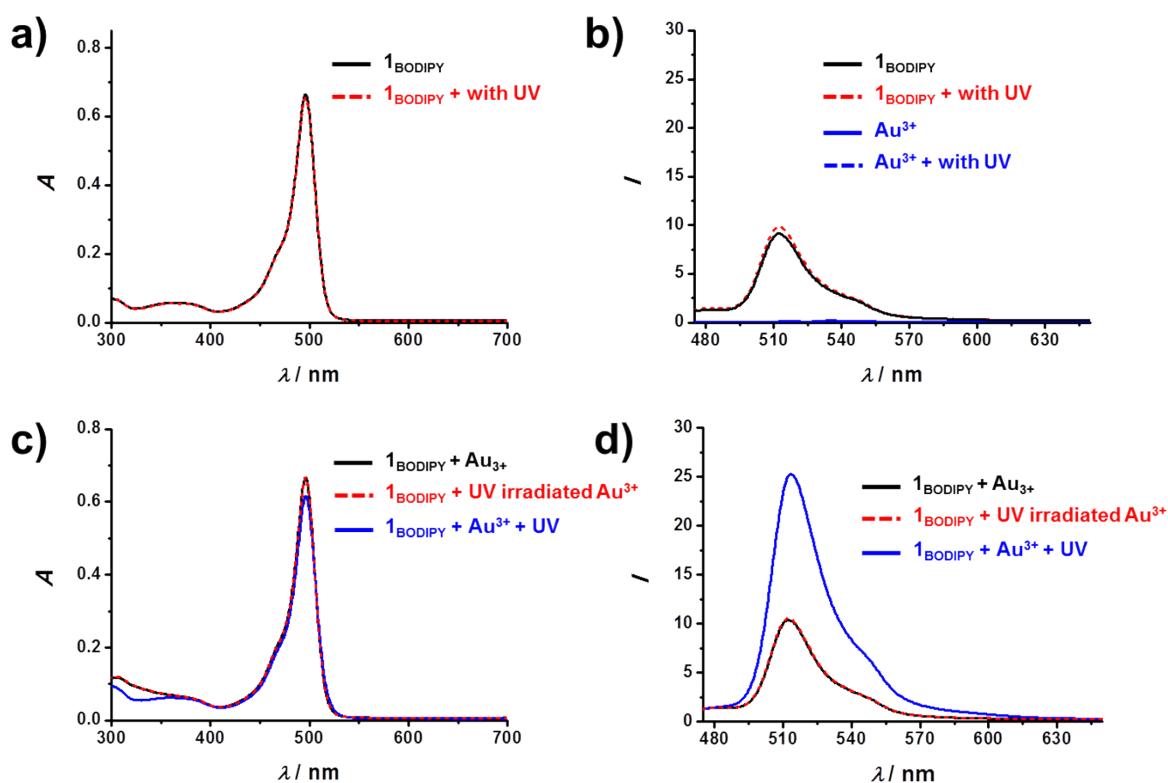


Figure S10. The influence of UV irradiation on **1**_{BODIPY} (10 μ M) and Au^{3+} (20 μ M) in MeCN/ H_2O (1:1 v/v). a) Absorption and b) emission spectra of **1**_{BODIPY} without addition of Au^{3+} , c) absorption and d) emission spectra of **1**_{BODIPY} with Au^{3+} , where red dashed line is the result of mixing **1**_{BODIPY} with UV-irradiated Au^{3+} . UV-irradiation was carried out using UV-handly lamp (365 nm) for 2 min.

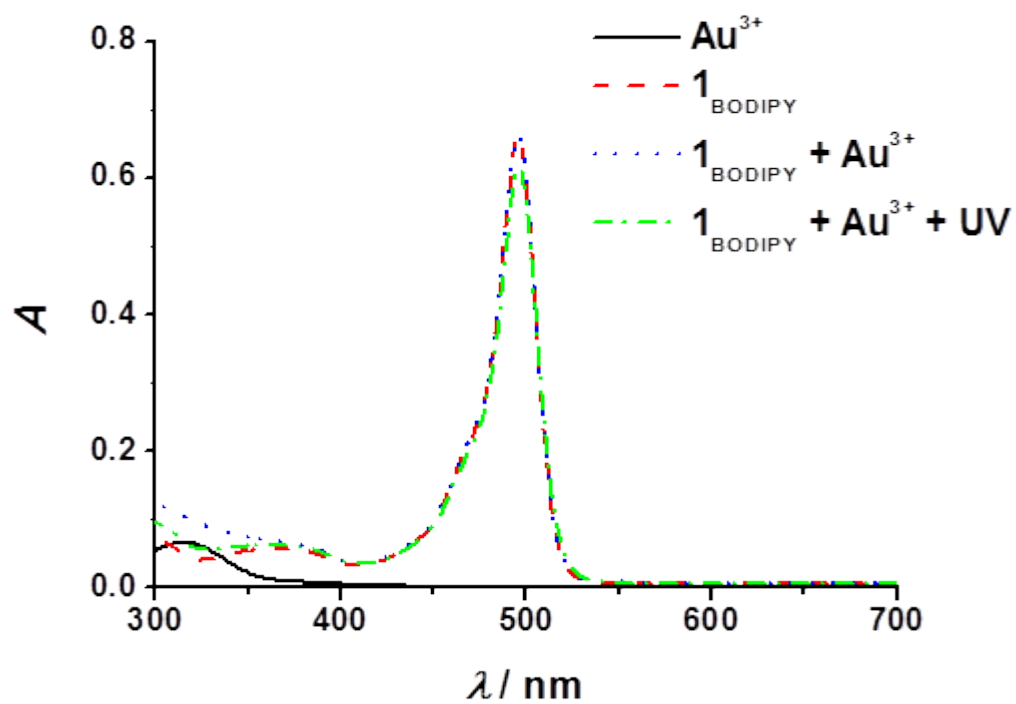


Figure S11. UV-Vis absorption spectra of Au^{3+} (20 μM), 1_{BODIPY} (10 μM), and Au^{3+} containing 1_{BODIPY} (10 μM) in MeCN/ H_2O (1:1 v/v).