

Supporting Information

Highly sensitive fluorescent sensor for Mg²⁺ and Ca²⁺ based on a multi-addressable diarylethene

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Contents

1. Experimental procedure details.
2. **Figure S1.** ¹H and ¹³C NMR spectra of compound **2** in CDCl₃.
3. **Figure S2.** ¹H and ¹³C NMR spectra of compound **4** in CDCl₃.
4. **Figure S3.** ¹H and ¹³C NMR spectra of compound **6** in CDCl₃.
5. **Figure S4.** ¹H and ¹³C NMR spectra of compound **7** in CDCl₃.
6. **Figure S5.** ¹H NMR spectra of **1o** in CDCl₃.
7. **Figure S6.** ¹³C NMR spectra of **1o** in CDCl₃.
8. **Figure S7.** IR spectra of **1o**.
9. **Figure S8.** Mass spectrum of **1o**, expected *m/z* for [M+ H]⁺ and [M+ Na]⁺, 637.1 and 659.1; found, 637.1 and 659.0, respectively.
10. **Figure S9.** Emission spectral changes of **1o** upon irradiation with UV/vis light (λ_{ex} = 400 nm).
11. **Figure S10.** Emission spectral and color changes of **1o** (a) and **1c** (b) induced by Ca²⁺/EDTA (λ_{ex} = 400 nm).
12. **Figure S11.** Emission spectral changes of **1o''** upon irradiation with UV/vis light (λ_{ex} = 400 nm).
13. **Figure S12.** Absorption spectral and color changes of **1o** (a) and **1c** (b) in acetonitrile (2.0 × 10⁻⁵ mol L⁻¹) induced by Ca²⁺/EDTA.
14. **Figure S13.** Absorption spectral and color changes of **1o''** upon irradiation with UV/vis light.

15. Figure S14. Job's plot showing the 1:1 complex of **1o**-Ca²⁺ in acetonitrile.

16. Figure S15. Mass spectra of [**1o**+MgOH]⁺ (a) and [**1o**+CaNO₃]⁺ (b).

17. Figure S16. Hildebrand-Benesi plot based on the 1:1 for **1o** with (a) $K_a(\text{Mg}^{2+}) = 6.4 \times 10^3 \text{ L mol}^{-1}$ and (b) $K_a(\text{Ca}^{2+}) = 1.7 \times 10^3 \text{ L mol}^{-1}$.

18. Figure S17. The normalized fluorescence intensity at 608 nm (a) and 599 nm (b) for **1o** ($2.0 \times 10^{-5} \text{ mol L}^{-1}$) in acetonitrile as a function of the concentration of Mg²⁺ ($\lambda_{\text{ex}} = 400 \text{ nm}$): LOD is $6.6 \times 10^{-10} \text{ mol L}^{-1}$ and Ca²⁺ ($\lambda_{\text{ex}} = 400 \text{ nm}$): LOD is $1.9 \times 10^{-9} \text{ mol L}^{-1}$, respectively.

1. Experimental procedure details

(1) Synthesis of compound **2**

Compound **2** was synthesized by reacting 3-bromo-2-methyl-5-thienylboronic acid (3.00 g; 13.57 mmol) with 5-bromo-2-methoxy benzaldehyde (2.92 g, 13.58 mmol) in the presence of Pd(PPh₃)₄ (250 mg) and Na₂CO₃ (6.36 g, 60 mmol) in tetrahydrofuran (THF) (80 mL containing 10% water) in a 250 ml three necked flask, for 15 h at 343 K. It was purified by column chromatography using petroleum ether/ethyl acetate (v/v 5:1) as the eluent to yield compound **2** as light yellow solid (3.92 g, 93%). ¹H NMR (CDCl₃, 400 MHz, TMS), δ (ppm): 2.35 (s, 3H), 3.90 (s, 3H), 6.95 (d, 1H, *J* = 8.0 Hz), 7.01 (s, 1H), 7.62 (d, 1H, *J* = 8.0 Hz), 7.89 (s, 1H), 10.41 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz, TMS), δ (ppm): 14.8, 55.9, 109.9, 112.3, 124.9, 125.1, 125.4, 126.6, 132.5, 133.5, 139.6, 161.3, 189.3.

(2) Synthesis of compound **3**

Compound **2** (3.53 g, 11.34 mmol), glycol (3.2 mL, 57.86 mmol), and p-toluenesulfonic acid (0.05 g, 0.26 mmol) were dissolved in toluene (160 mL). Under the Dean–Stark condition, the reaction mixture was refluxed overnight, and then washed sequentially three times with NaOH solution (2.0 mol L⁻¹) and water. The combined toluene layers were dried, and evaporated in vacuum to give compound **3** as yellow oil (3.35 g, 83%), which was used to the next reaction directly.

(3) Synthesis of compound **4**

To a stirred refined THF containing 4-bromo-1,5-dimethyl-1H-pyrrole-2-carbonitrile (4.0 g, 20.10 mmol) was added dropwise a 2.4 mol L⁻¹ n-BuLi solution (8.4 mL) at 195 K under argon atmosphere. After the mixture has been stirred for 1 h at 195 K, perfluorocyclopentene (C₅F₈) (2.7 mL, 20.10 mmol) was added. The reaction was further stirred at 195 K for 1 h, then the reaction was allowed to slowly warm to the room temperature and stirred for another 1 h. The reaction was quenched with distilled water. The product was extracted with ether, dried with MgSO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography using petroleum ether/ethyl acetate (v/v, 15:1) as the eluent to yield compound **4** as white solid (2.96 g, 47%). ¹H NMR (CDCl₃, 400 MHz, TMS), δ (ppm): 2.34 (s, 3H), 3.75 (s, 3H), 7.01 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz, TMS), δ (ppm): 11.4, 32.7, 104.5, 105.5, 112.1, 118.3, 136.3.

(4) Synthesis of compound **5**

To a stirred refined THF containing compound **3** (3.23 g, 9.10 mmol) was added dropwise a 2.4

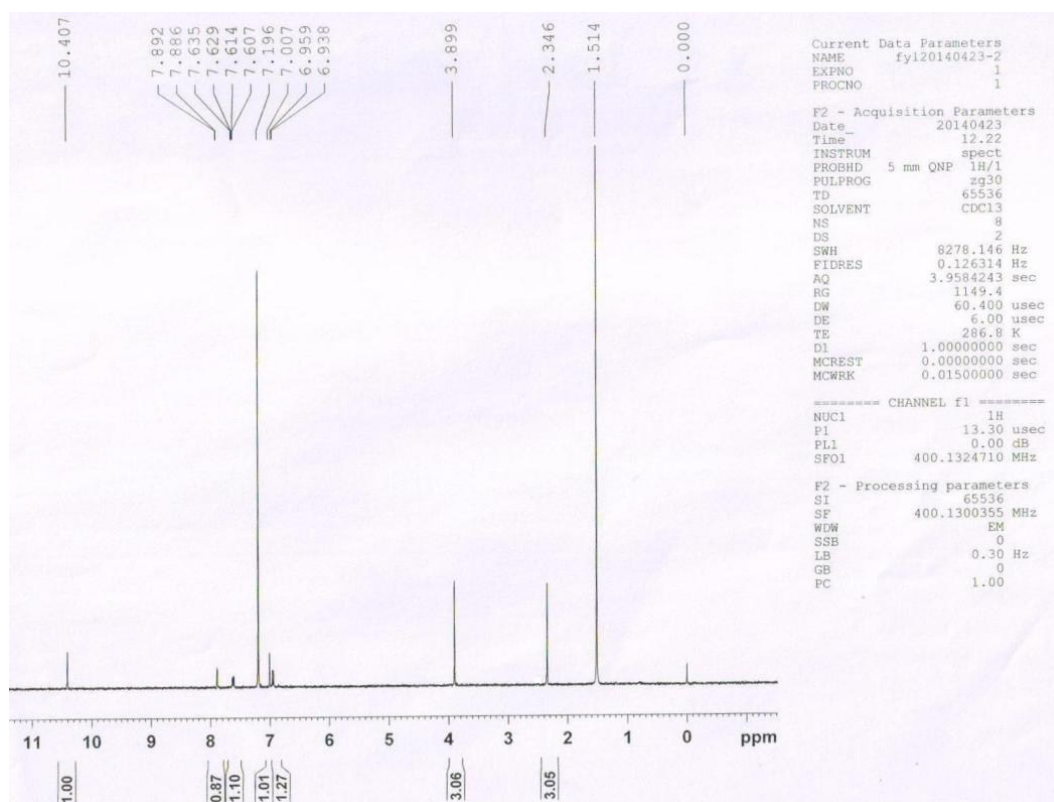
mol L⁻¹ n-BuLi solution (3.8 mL) at 195 K under argon atmosphere. After the mixture has been stirred for 1 h at 195 K, compound **4** (2.84 g, 9.10mmol, in 10 mL THF) was added slowly to the reaction mixture. The reaction was further stirred at 195 K for 1 h, and the reaction was slowly warmed up to the room temperature and stirred for 1 h. The reaction was quenched with distilled water. The product was extracted with ether, dried with MgSO₄, and concentrated under reduced pressure to give compound **5**, which was used to the next reaction directly.

(5) Synthesis of compound **6**

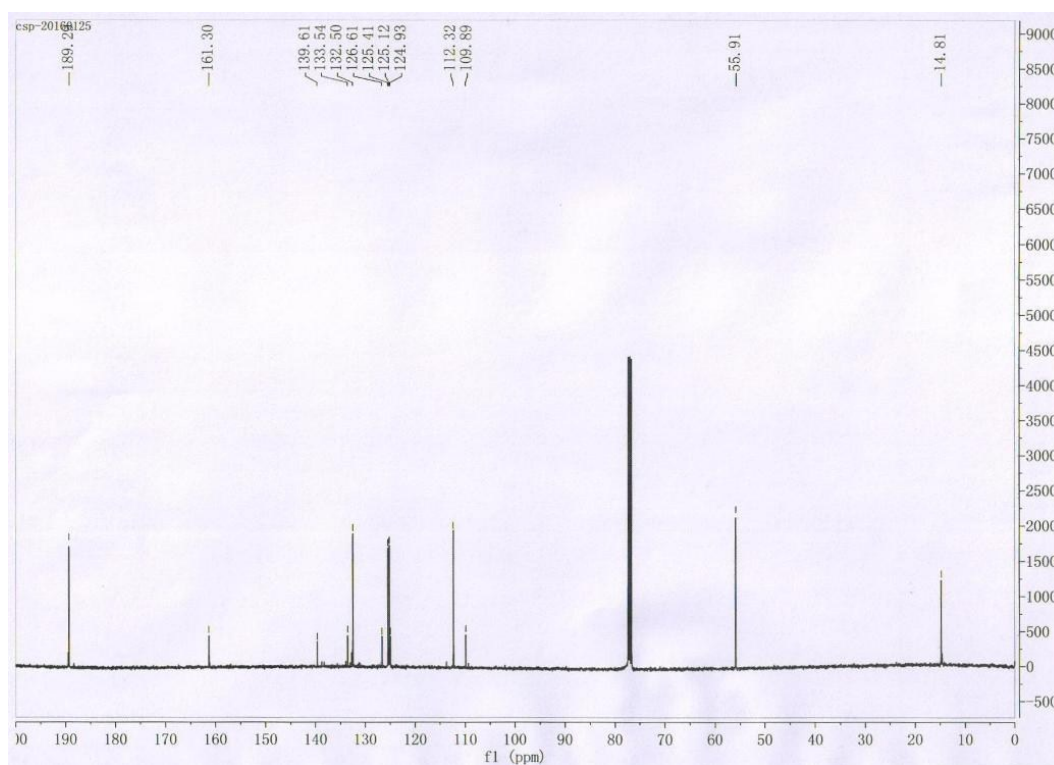
Compound **5** (2.70 g, 4.7 mmol), pyridine (0.4 ml, 4.7 mmol), and p-toluenesulfonic acid (0.81 g, 4.7 mmol) were dissolved in acetone/water (v/v, 4:1, 125 mL). The reaction mixture was refluxed for 5 h. After evaporated under vacuum, the mixture was extracted with diethyl ether, dried with MgSO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography using petroleum ether/ethyl acetate (v/v, 15:1) as the eluent to yield compound **6** as white solid (2.24 g, 91%). ¹H NMR (CDCl₃, 400 MHz, TMS), δ (ppm): 1.77 (s, 3H), 1.95 (s, 3H), 3.61 (s, 1H) 3.97 (s, 3H), 6.93 (s, 1H), 7.04 (d, 1H, *J* = 8.0 Hz), 7.19 (s, 1H), 7.71-7.74 (dd, 1H, *J*₁ = 2.4 Hz, *J*₂ = 8.0 Hz), 7.98 (d, 1H, *J* = 2.4 Hz), 10.49 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz, TMS), δ (ppm): 11.2, 14.0, 30.1, 55.7, 74.3, 111.4, 112.4, 118.1, 121.7, 122.6, 124.2, 124.7, 124.8, 125.3, 126.5, 132.8, 138.4, 140.6, 160.6, 190.0.

(6) Synthesis of compound **7**

Compound **6** (2.04 g, 3.9 mmol) was dissolved in refined CH₂Cl₂ (10 mL). After decreased the temperature to 195 K and permeated with argon atmosphere, a 1.0 mol L⁻¹ BBr₃ solution (3.9 mL, in CH₂Cl₂) was added dropwise. The reaction was further stirred at 195 K for 1 h, then it was slowly warmed up to the room temperature and stirred for another 24 h. The reaction was quenched with distilled water. The product was extracted with CH₂Cl₂, dried with MgSO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography using petroleum ether/ethyl acetate (v/v, 6:1) as the eluent to yield compound **7** as white solid (1.51 g, 76%). ¹H NMR (CDCl₃, 400 MHz, TMS), δ (ppm): 1.80 (s, 3H), 1.95 (s, 3H), 3.63 (s, 3H), 6.93 (s, 1H), 7.05 (d, 1H, *J* = 12.0 Hz), 7.19 (s, 1H), 7.72 (s, 2H), 9.97 (s, 1H), 11.06 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz, TMS), δ (ppm): 11.4, 14.5, 33.1, 105.6, 109.9, 112.8, 118.5, 118.8, 120.6, 122.3, 125.7, 126.1, 130.3, 134.2, 136.0, 140.2, 140.7, 161.3, 196.4.

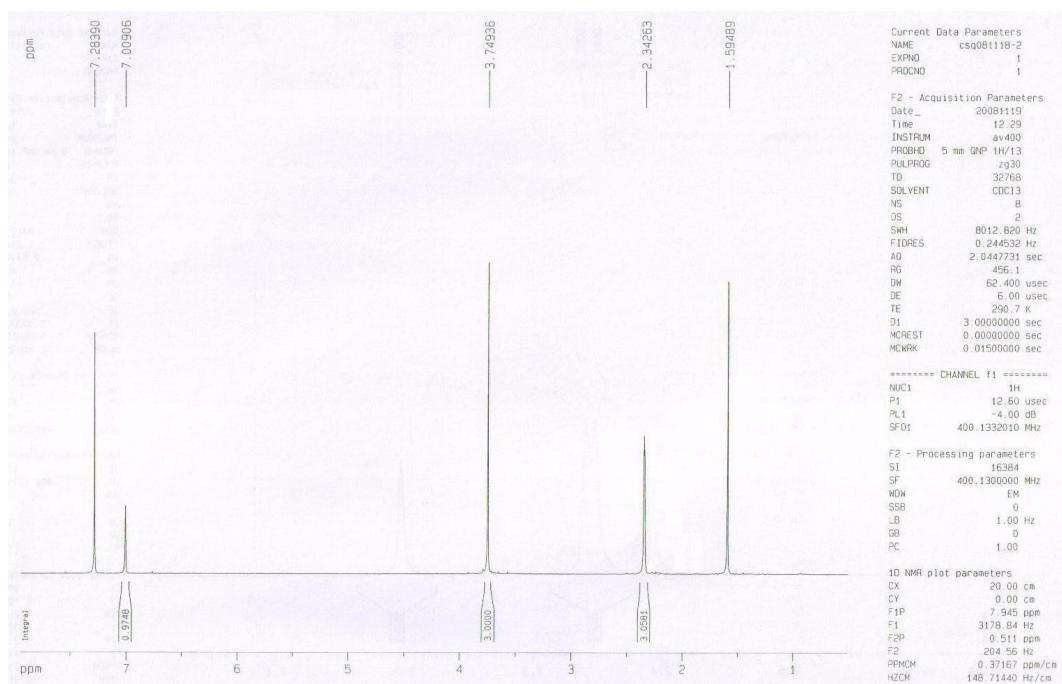


(a)

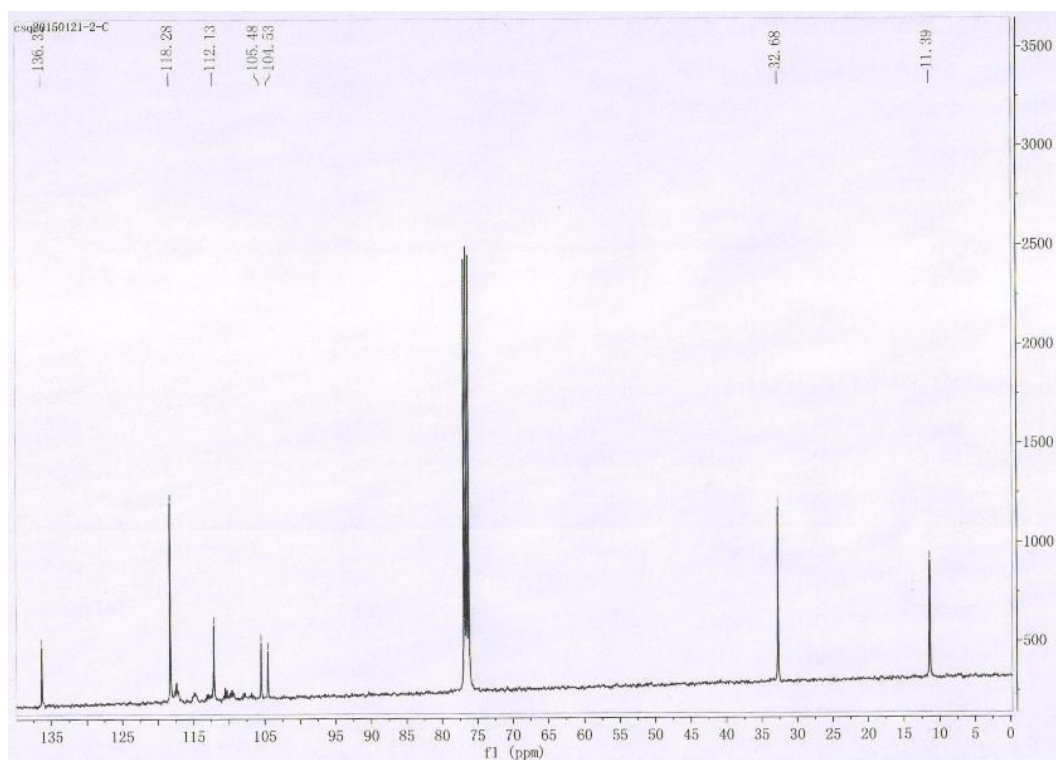


(b)

Figure S1. ^1H (a) and ^{13}C NMR (b) spectra of compound **2** in CDCl_3 .

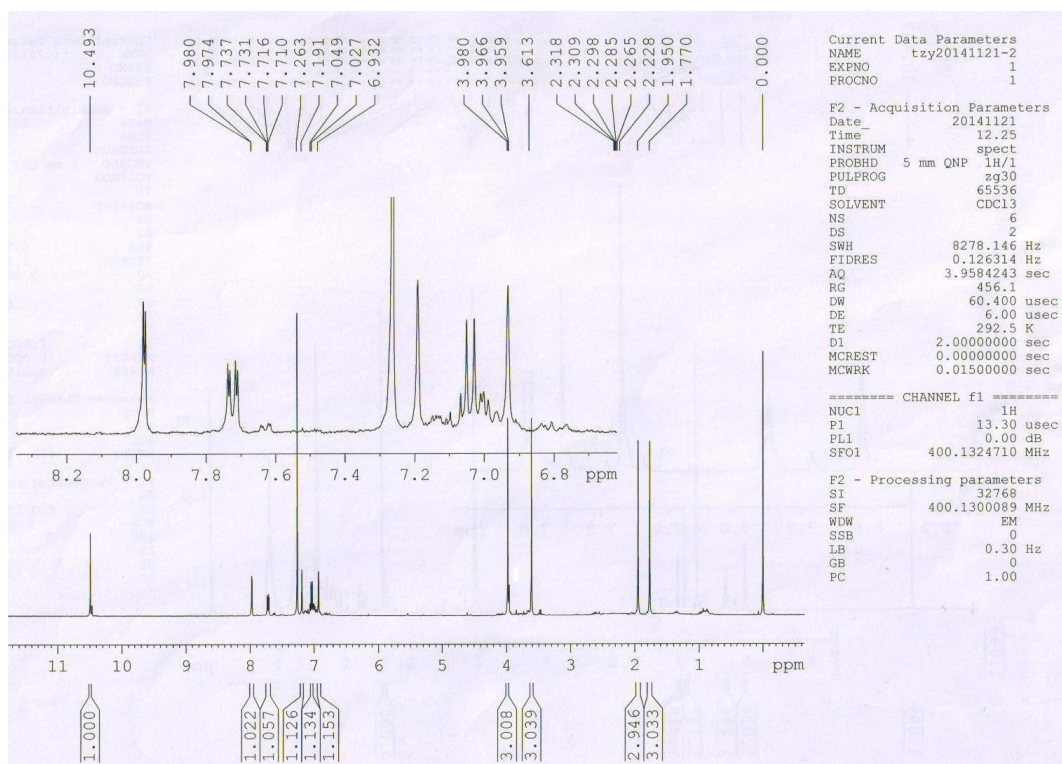


(a)

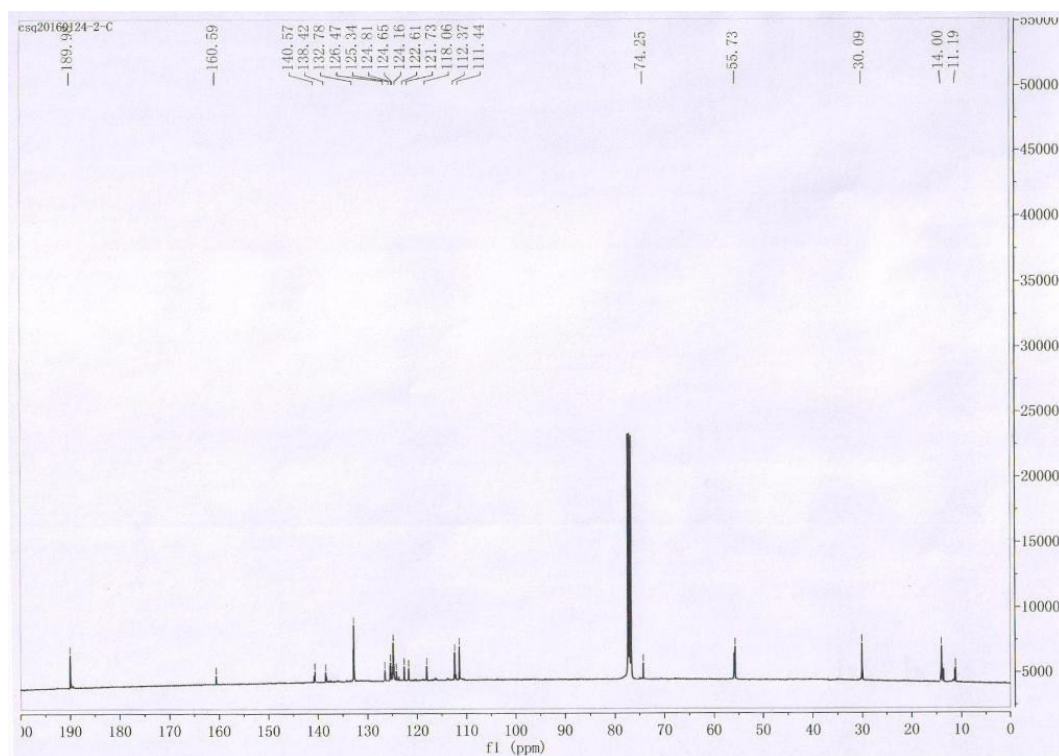


(b)

Figure S2. ^1H (a) and ^{13}C NMR (b) spectra of compound **4** in CDCl_3 .

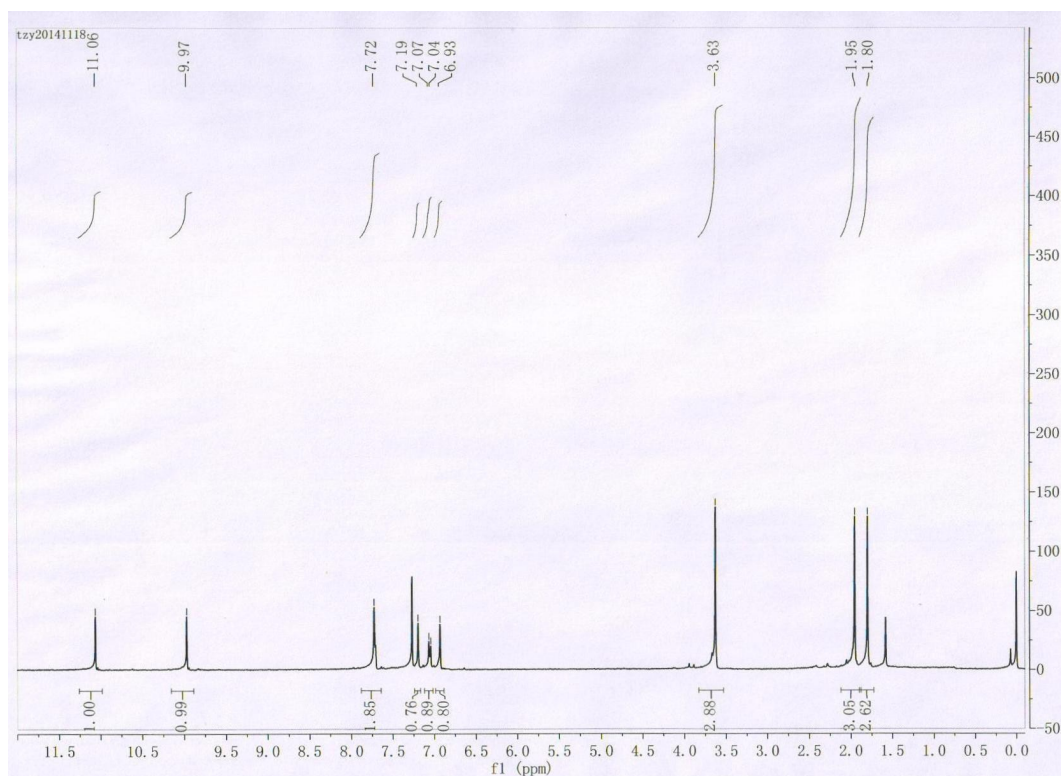


(a)

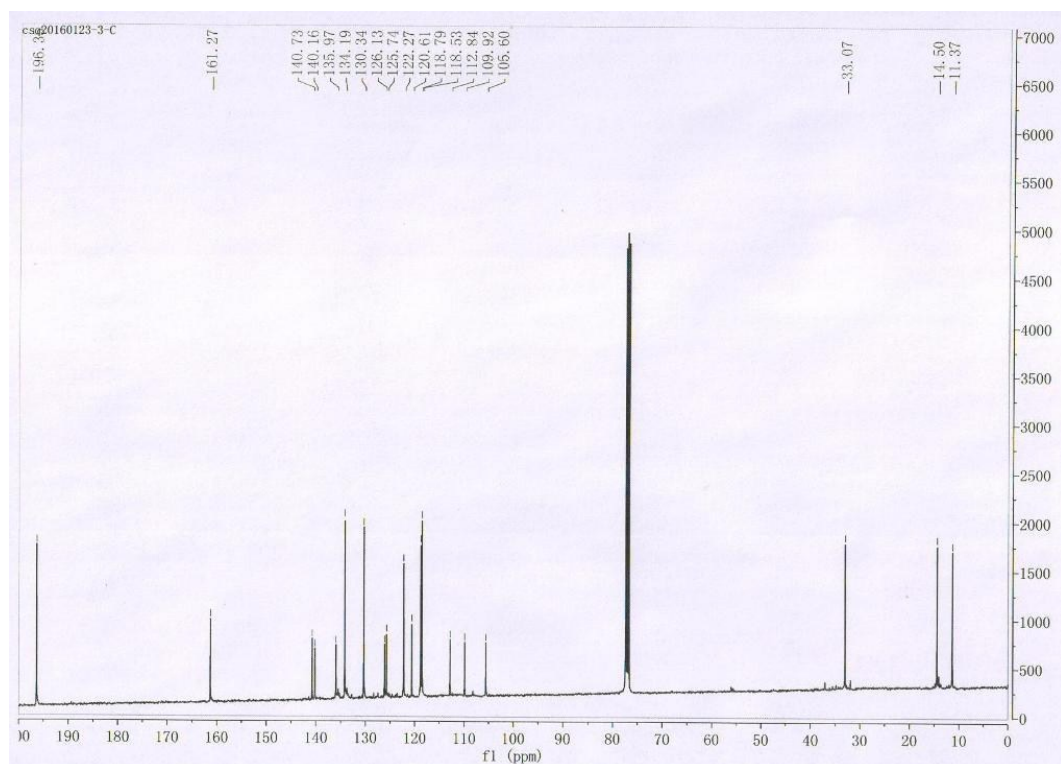


(b)

Figure S3. ^1H (a) and ^{13}C NMR (b) spectra of compound **6** in CDCl_3 .



(a)



(b)

Figure S4. ¹H (a) and ¹³C NMR (b) spectra of compound 7 in CDCl₃.

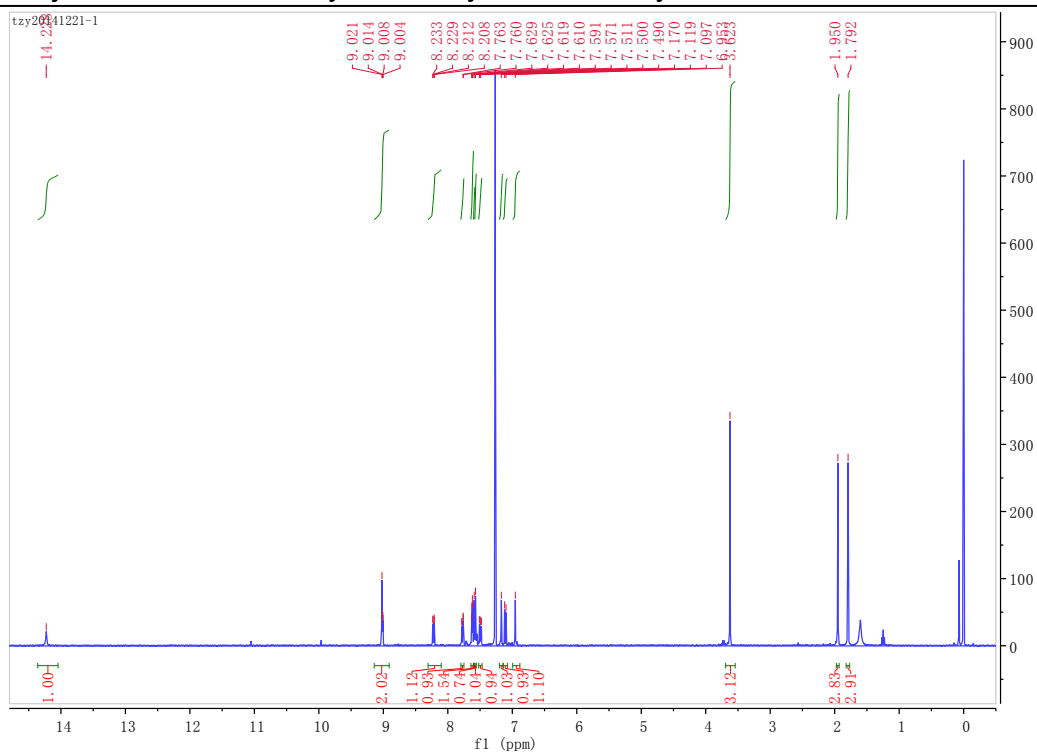


Figure S5. ^1H NMR spectra of **1o** in CDCl_3 .

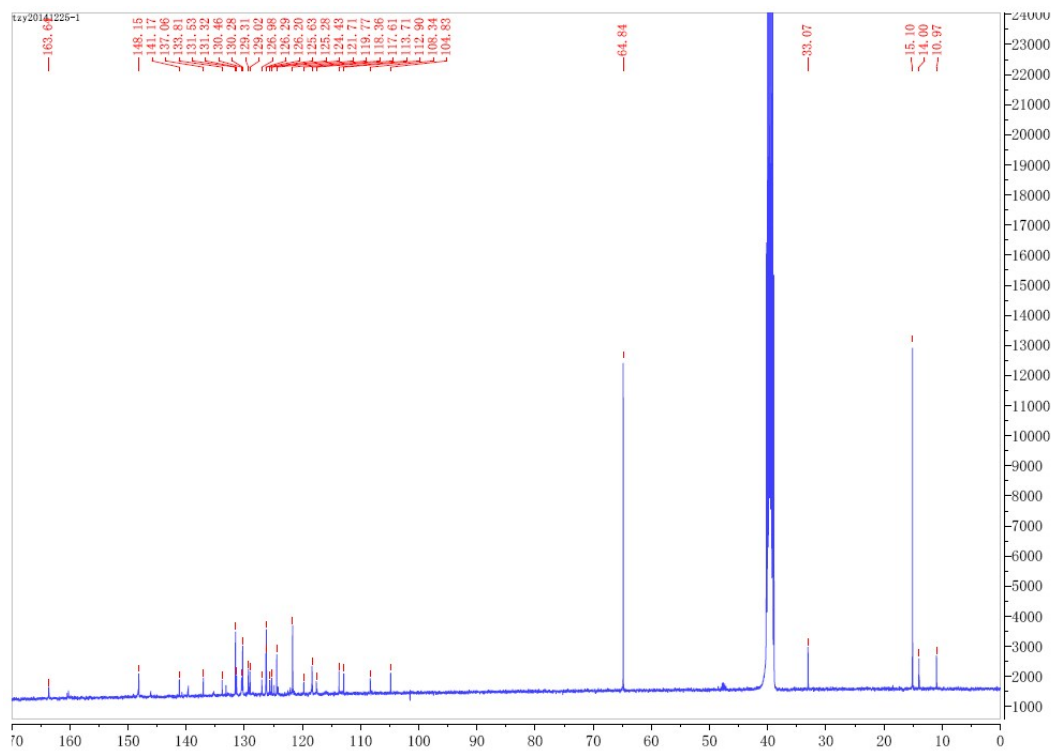


Figure S6. ^{13}C NMR spectra of **1o** in CDCl_3 .

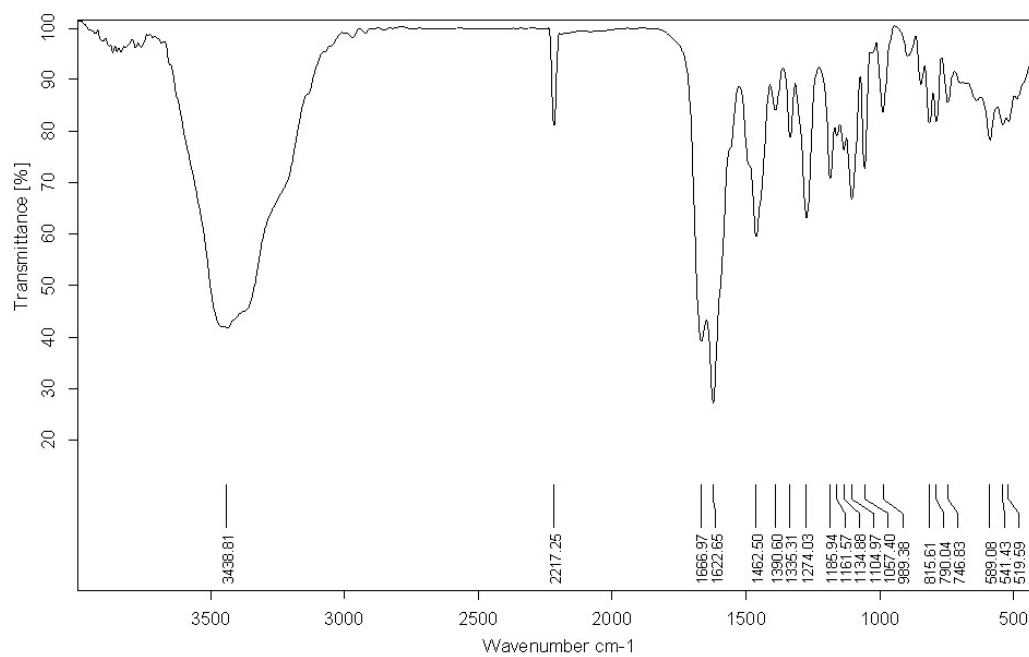


Figure S7. IR spectra of 1o.

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T: ITMS + c ESI Full ms [50.00-2000.00]

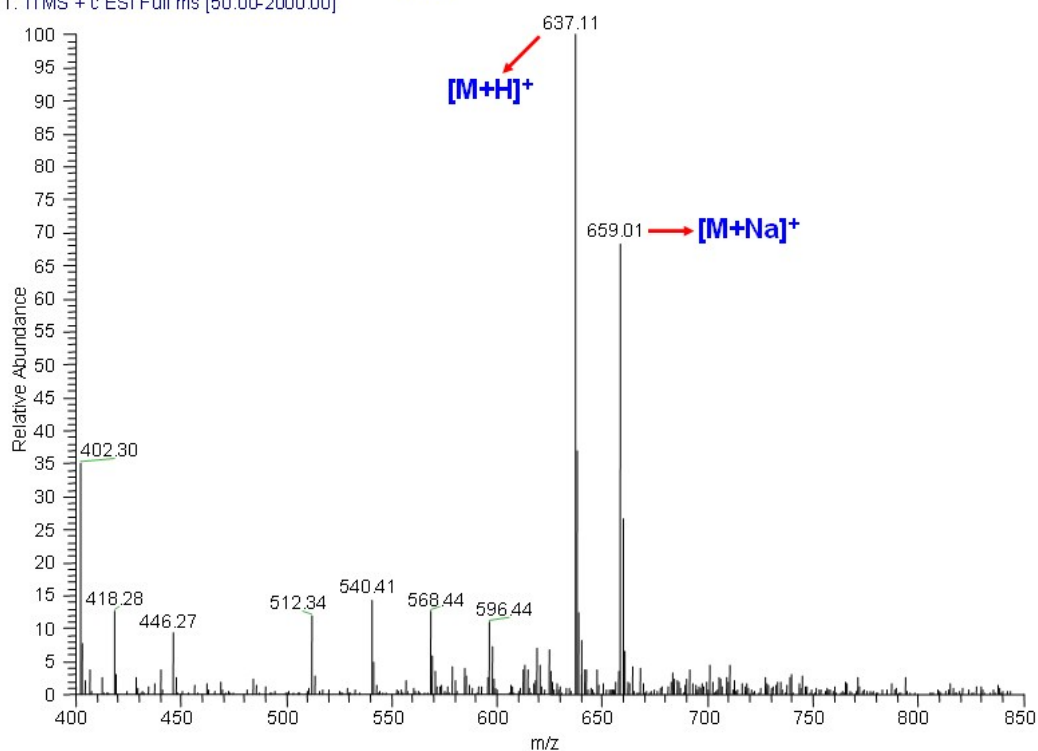


Figure S8. Mass spectrum of **1o**, expected m/z for $[M+H]^+$ and $[M+Na]^+$, 637.1 and 659.1; found, 637.1 and 659.0, respectively.

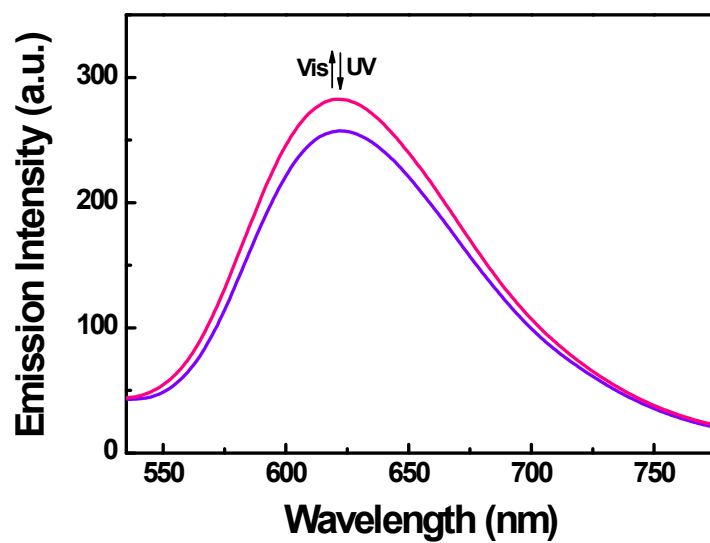
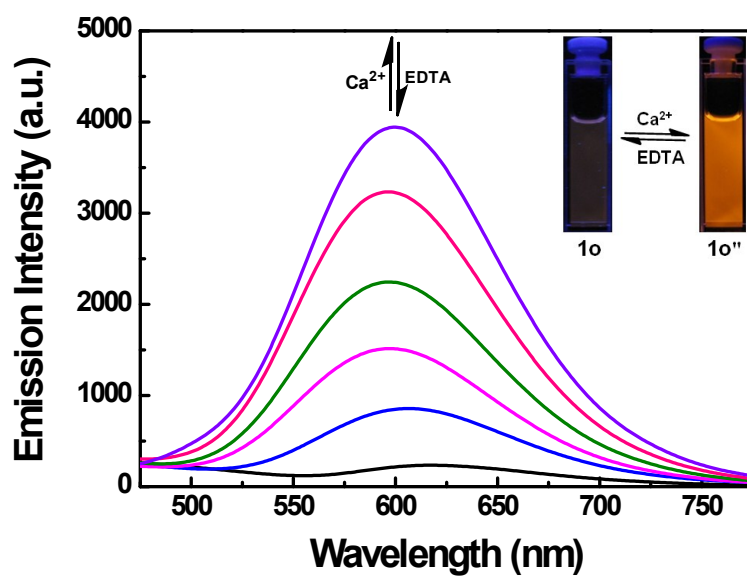
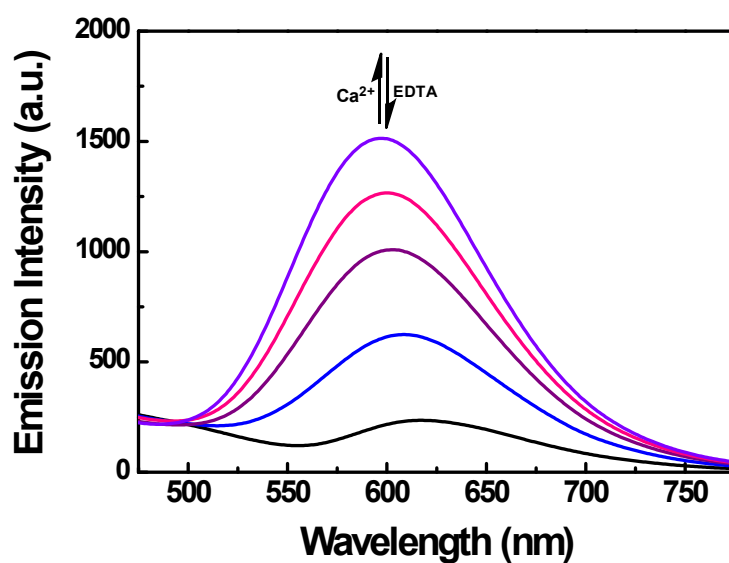


Figure S9. Emission spectral changes of **1o** upon irradiation with UV/vis light ($\lambda_{\text{ex}} = 400$ nm).



(a)



(b)

Figure S10. Emission spectral and color changes of **1o** (a) and **1c** (b) induced by Ca^{2+} /EDTA (λ_{ex} = 400 nm).

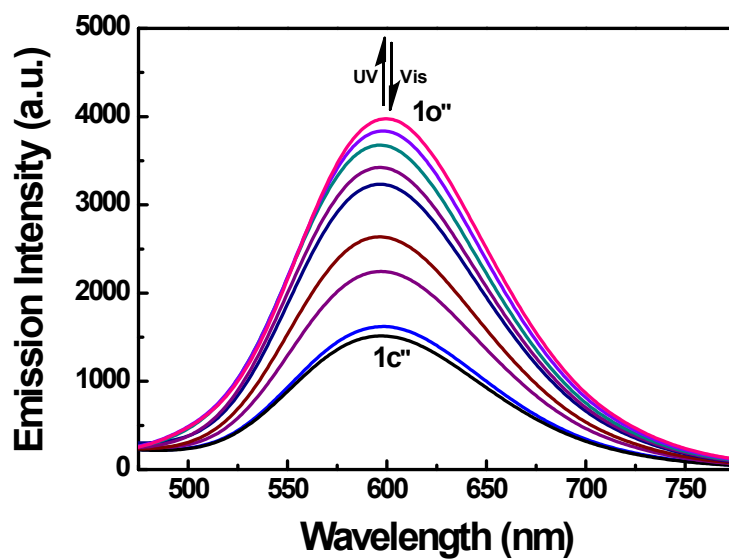
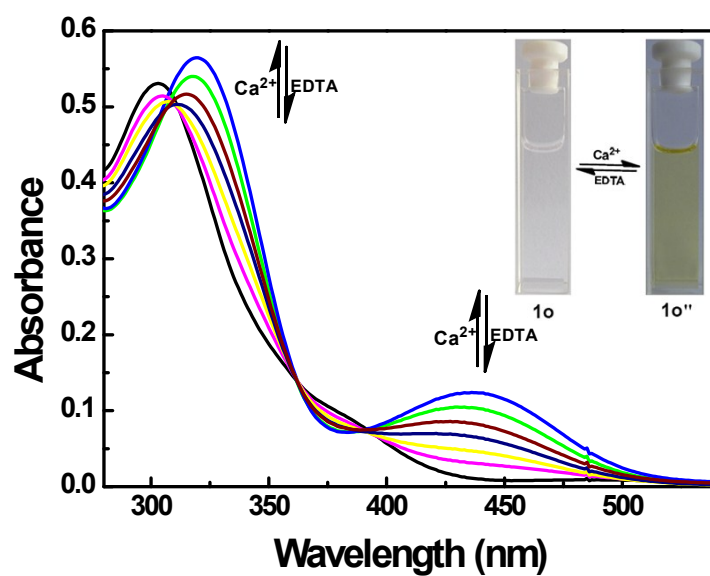
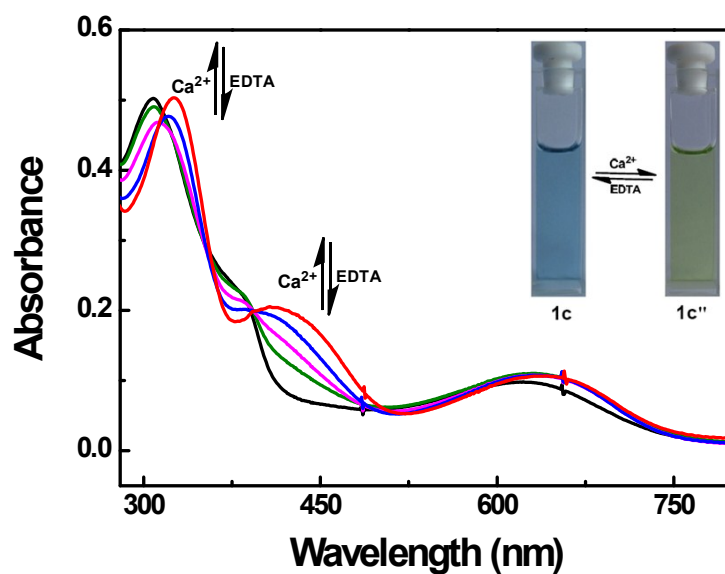


Figure S11. Emission spectral changes of **1o''** upon irradiation with UV/vis light ($\lambda_{\text{ex}} = 400$ nm).



(a)



(b)

Figure S12. Absorption spectral and color changes of **1o** (a) and **1c** (b) in acetonitrile (2.0×10^{-5} mol L^{-1}) induced by Ca^{2+} /EDTA.

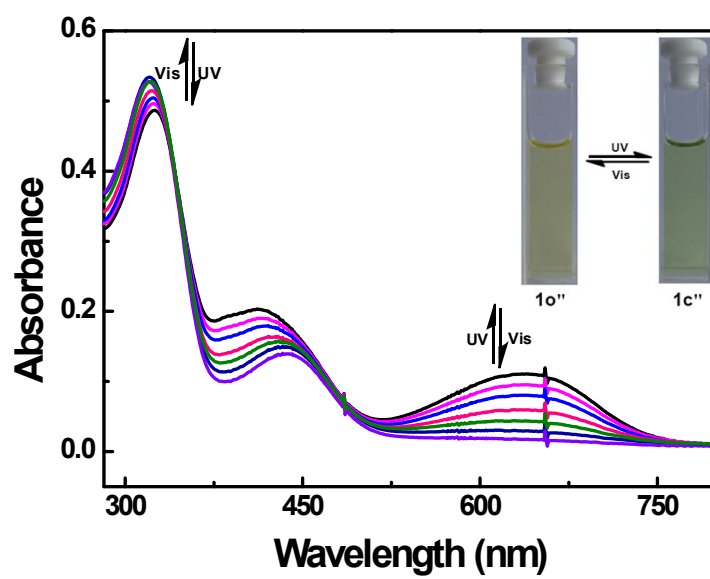


Figure S13. Absorption spectral and color changes of **1o''** upon irradiation with UV/vis light.

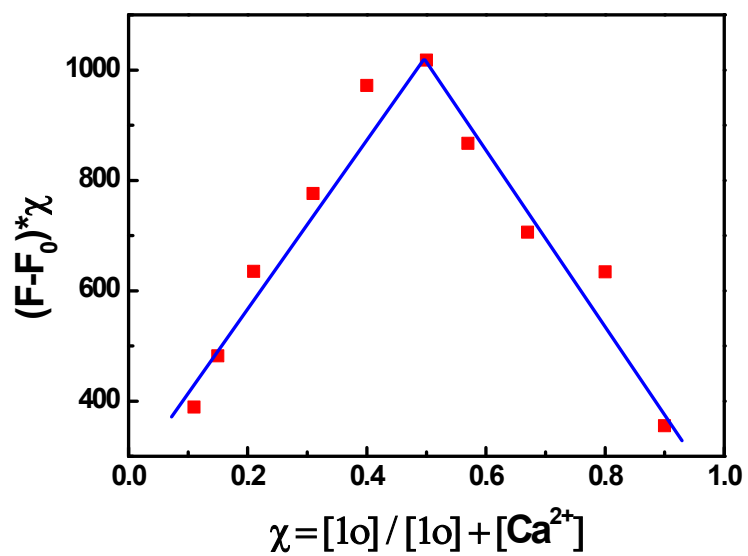


Figure S14. Job's plot showing the 1:1 complex of **1o**-Ca²⁺ in acetonitrile.

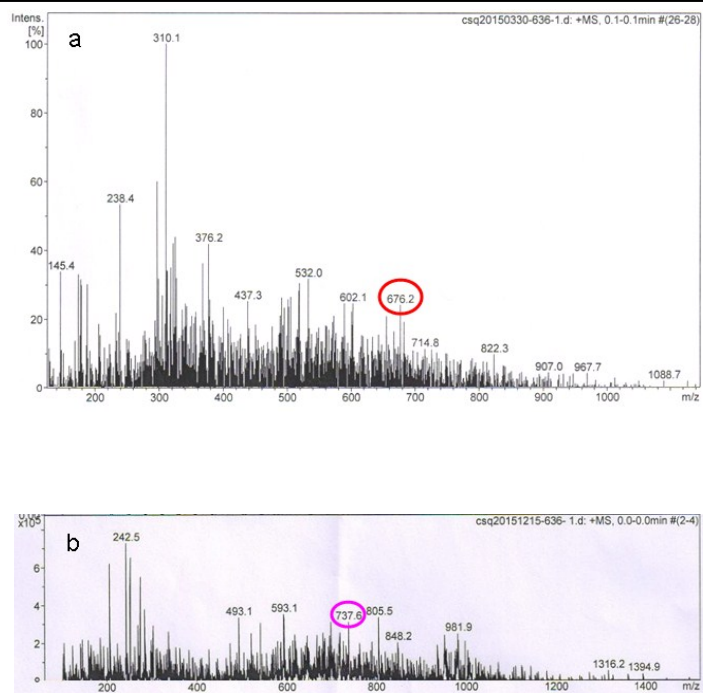
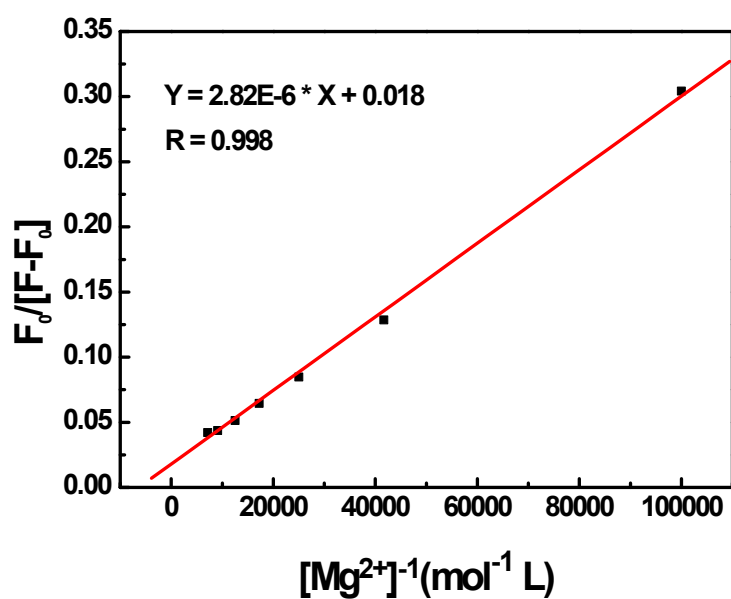
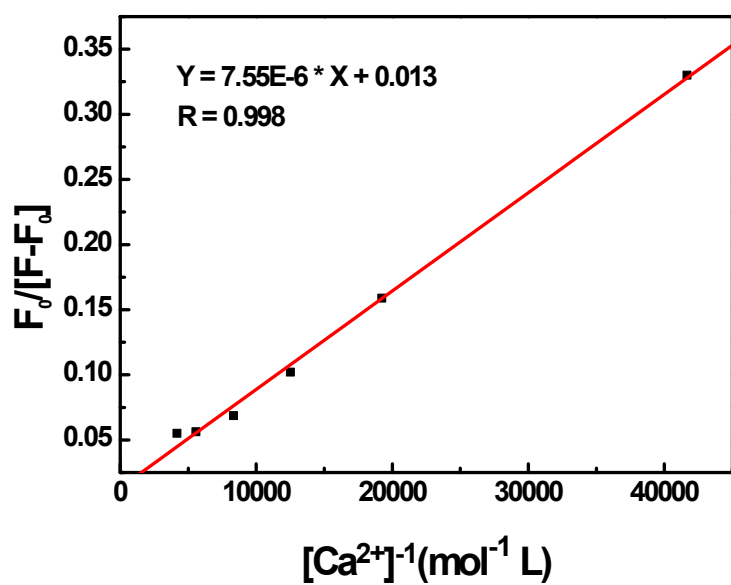


Figure S15. Mass spectra of $[10+MgOH]^+$ (a) and $[10+CaNO_3]^+$ (b).

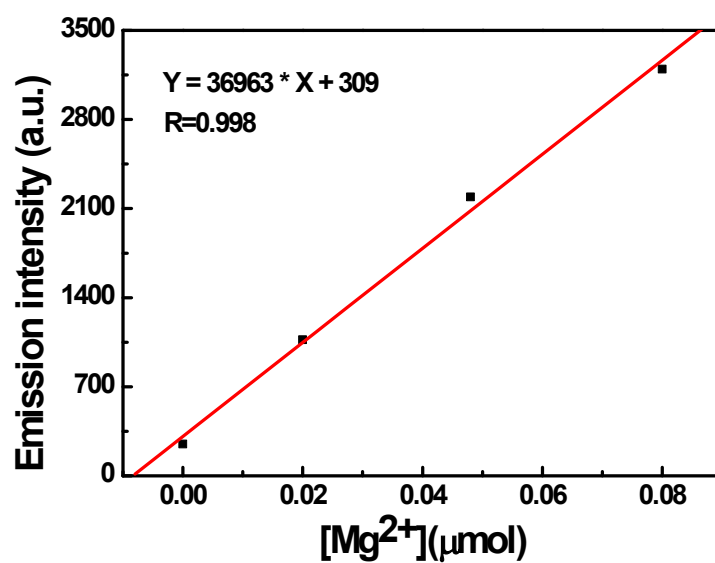


(a)

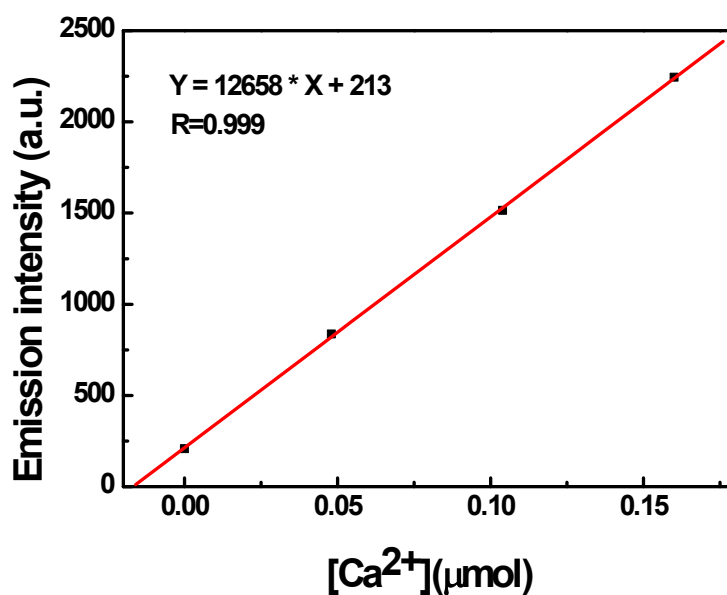


(b)

Figure S16. Hildebrand-Benesi plot based on the 1:1 for **1o** with (a) $K_a(Mg^{2+}) = 6.4 \times 10^3 \text{ L mol}^{-1}$ and (b) $K_a(Ca^{2+}) = 1.7 \times 10^3 \text{ L mol}^{-1}$.



(a)



(b)

Figure S17. The normalized fluorescence intensity at 608 nm (a) and 599 nm (b) for **1o** (2.0×10^{-5} mol L⁻¹) in acetonitrile as a function of the concentration of Mg^{2+} ($\lambda_{ex} = 400$ nm): LOD is 6.6×10^{-10} mol L⁻¹ and Ca^{2+} ($\lambda_{ex} = 400$ nm): LOD is 1.9×10^{-9} mol L⁻¹, respectively.