Supporting Information

Highly sensitive fluorescent sensor for Mg^{2+} and Ca^{2+} based on a multi-addressable diarylethene

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Contents

1. Experimental procedure details.

2. Figure S1. $^1$H and $^{13}$C NMR spectra of compound 2 in CDCl$_3$.

3. Figure S2. $^1$H and $^{13}$C NMR spectra of compound 4 in CDCl$_3$.

4. Figure S3. $^1$H and $^{13}$C NMR spectra of compound 6 in CDCl$_3$.

5. Figure S4. $^1$H and $^{13}$C NMR spectra of compound 7 in CDCl$_3$.

6. Figure S5. $^1$H NMR spectra of 1o in CDCl$_3$.

7. Figure S6. $^{13}$C NMR spectra of 1o in CDCl$_3$.

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 ($\lambda_{\text{ex}} = 400$ nm).

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

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

13. Figure S12. Absorption spectral and color changes of 1o (a) and 1c (b) in acetonitrile (2.0 $\times$ 10$^{-5}$ mol L$^{-1}$) induced by Ca$^{2+}$/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 $\text{Io-Ca}^{2+}$ in acetonitrile.

16. **Figure S15.** Mass spectra of $[\text{Io}+\text{MgOH}^+]$ (a) and $[\text{Io}+\text{CaNO}_3^+]$ (b).

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

18. **Figure S17.** The normalized fluorescence intensity at 608 nm (a) and 599 nm (b) for $\text{Io}$ ($2.0 \times 10^{-5}$ mol L$^{-1}$) in acetonitrile as a function of the concentration of Mg$^{2+}$ ($\lambda_{ex} = 400$ nm): LOD is $6.6 \times 10^{-10}$ mol L$^{-1}$ and Ca$^{2+}$ ($\lambda_{ex} = 400$ nm): LOD is $1.9 \times 10^{-9}$ 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, 9.10 mmol, 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 MgSO\(_4\), 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 MgSO\(_4\), 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%). \(^1\)H NMR (CDCl\(_3\), 400 MHz, TMS), \(\delta\) (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, \(J \approx 8.0\) Hz), 7.19 (s, 1H), 7.71-7.74 (dd, 1H, \(J_1 \approx 2.4\) Hz, \(J_2 \approx 8.0\) Hz), 7.98 (d, 1H, \(J \approx 2.4\) Hz), 10.49 (s, 1H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz, TMS), \(\delta\) (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 CH\(_2\)Cl\(_2\) (10 mL). After decreased the temperature to 195 K and permeated with argon atmosphere, a 1.0 mol L\(^{-1}\) BBr\(_3\) solution (3.9 mL, in CH\(_2\)Cl\(_2\)) 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 CH\(_2\)Cl\(_2\), dried with MgSO\(_4\), 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%). \(^1\)H NMR (CDCl\(_3\), 400 MHz, TMS), \(\delta\) (ppm): 1.80 (s, 3H), 1.95 (s, 3H), 3.63 (s, 3H), 6.93 (s, 1H), 7.05 (d, 1H, \(J \approx 12.0\) Hz), 7.19 (s, 1H), 7.72 (s, 2H), 9.97 (s, 1H), 11.06 (s, 1H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz, TMS), \(\delta\) (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.
Figure S1. $^1$H (a) and $^{13}$C NMR (b) spectra of compound 2 in CDCl$_3$. 
Figure S2. $^1$H (a) and $^{13}$C NMR (b) spectra of compound 4 in CDCl$_3$. 
**Figure S3.** $^1$H (a) and $^{13}$C NMR (b) spectra of compound 6 in CDCl$_3$. 
Figure S4. $^1$H (a) and $^{13}$C NMR (b) spectra of compound 7 in CDCl$_3$. 
Figure S5. $^1$H NMR spectra of 1o in CDCl$_3$. 

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Figure S13. Absorption spectral and color changes of 1o" upon irradiation with UV/vis light.
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$[\text{Mg}^{2+}]^{-1}(\text{mol}^{-1} \text{ L})$  

$Y = 2.82 \times 10^{-6} \times X + 0.018$  

$R = 0.998$  

$[\text{Ca}^{2+}]^{-1}(\text{mol}^{-1} \text{ L})$  

$Y = 7.56 \times 10^{-6} \times X + 0.013$  

$R = 0.998$
**Figure S17.** The normalized fluorescence intensity at 608 nm (a) and 599 nm (b) for 1o ($2.0 \times 10^{-5}$ mol L$^{-1}$) in acetonitrile as a function of the concentration of Mg$^{2+}$ ($\lambda_{\text{ex}} = 400$ nm): LOD is $6.6 \times 10^{-10}$ mol L$^{-1}$ and Ca$^{2+}$ ($\lambda_{\text{ex}} = 400$ nm): LOD is $1.9 \times 10^{-9}$ mol L$^{-1}$, respectively.