

Supplementary Information

Reactive fluorescent dye functionalized cotton fabric as a “Magic Cloth” for selective sensing and reversible separation of Cd²⁺ in water

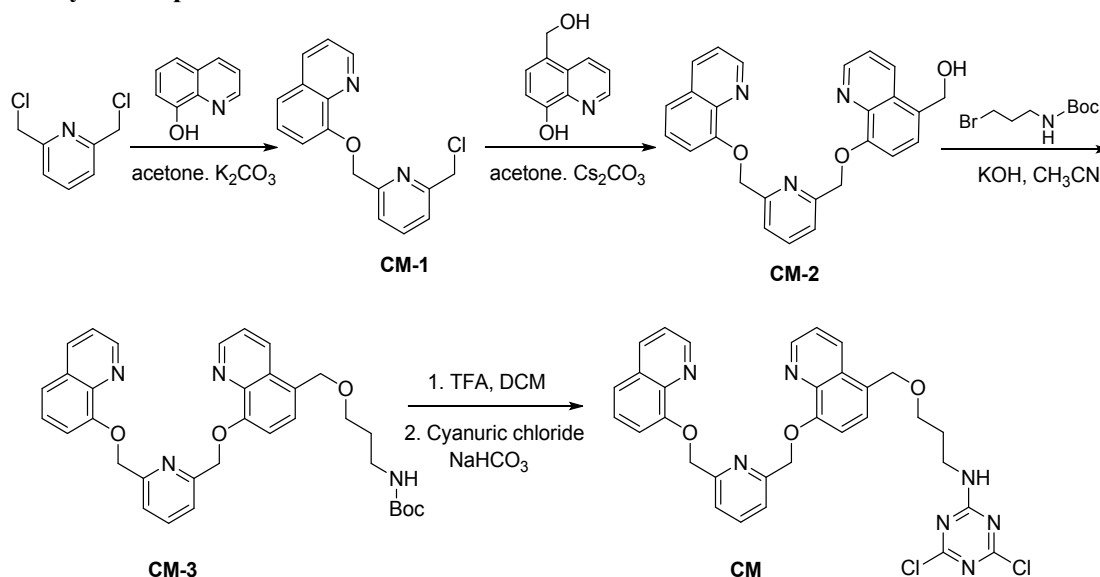
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1. Materials and apparatus

Unless otherwise noted, all the solvents used were of analytic grade and used without further purification. ¹H NMR and ¹³C NMR spectra were measured on a Bruker AM-400 spectrometer with chemical shifts reported in ppm (in CDCl₃, TMS as internal standard). Mass spectra were measured on a HP 5989A spectrometer. Fluorescence spectra were determined on a Varian Cary Eclipse Fluorescence Spectrometer. All absorption spectra and emission spectra were recorded at 24 ± 1 °C. The transmission electron microscopy (TEM) image was obtained by a JEM-2010HT transmission electron microscopy. Elemental analysis was performed by a Germany Elementar Vario EL III. Concentration of cadmium was analyzed by a Varian 710ES Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The solutions of metal ions were prepared from Hg(ClO₄)₂·3H₂O, Cd(ClO₄)₂·6H₂O, Pb(ClO₄)₂·3H₂O, AgClO₄·H₂O, Zn(ClO₄)₂·6H₂O, NaClO₄, FeSO₄·7H₂O, Mg(ClO₄)₂, KClO₄, Cr(ClO₄)₃·6H₂O, Co(ClO₄)₂·6H₂O, Cu(ClO₄)₂·6H₂O, Ni(ClO₄)₂·6H₂O, Ca(ClO₄)₂·4H₂O, BaCl₂, respectively, and were dissolved in deionized water.

2. Synthetic procedures



Scheme S1 Synthetic route of fluorescent sensor CM

2.1 Synthesis of CM-2

Compound **CM-1** and 5-(hydroxymethyl)quinolin-8-ol were prepared according to the reported procedure (Scheme S1).^{1, 2} Compound **CM-2** was synthesized as follows: compound **CM-1** (0.20 g, 0.70 mmol), Cs₂CO₃ (0.45 g, 1.40 mmol) and 5-hydroxymethyl-quinolin-8-ol (0.12 g, 0.70 mmol) were dissolved in acetone (25 mL) under argon atmosphere. The solution was stirred for 4 h under reflux; then the mixture was filtered and the filtrate was removed by rotary evaporation. The residue was chromatographed on silica gel using CH₂Cl₂-CH₃OH (20:1, v/v) as an eluant to afford **CM-2** (0.19 g, 67%) as a white powder. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 8.90 (dd, *J*₁=2.0 Hz, *J*₂=4.0 Hz, 1H), 8.85 (dd, *J*₁ = 2.0 Hz, *J*₂ = 4.0 Hz, 1H), 8.41 (dd, *J*₁ = 1.6 Hz, *J*₂ = 8.8 Hz, 1H), 8.09 (dd, *J*₁ = 2.0 Hz, *J*₂ = 8.4 Hz, 1H), 7.48-7.60 (m, 3H), 7.38 (dd, *J*₁ = 4.0 Hz, *J*₂ = 8.4 Hz, 1H), 7.32-7.36 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.01-7.05 (m, 1H), 5.49 (s, 2H), 5.39 (s, 2H), 4.93 (s, 2H), 4.18 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 156.45, 156.41, 153.85, 153.58, 149.30, 148.96, 140.34, 140.13, 137.89, 136.07, 132.91, 129.50, 129.45, 127.77, 126.66, 126.13, 121.70, 121.57, 120.56, 120.54, 120.20, 109.81, 108.75, 77.44, 77.37, 77.33, 77.18, 77.13, 76.81, 71.17, 71.06, 62.49. MS (ESI) m/z 424[(M+H)⁺, 100%].

2.2 Synthesis of CM-3

Compound **CM-2** (0.04 g, 0.09 mmol), tert-butyl(3-bromopropyl)carbamate (0.03 g, 0.14 mmol) and potassium hydroxide (0.02 g, 0.35 mmol) were dissolved in acetonitrile (10 mL) under argon atmosphere. The solution was stirred for 16 h under reflux; then the mixture was filtered and the filtrate was removed by rotary evaporation. The residue was chromatographed on silica gel using CH₂Cl₂-CH₃OH (40:1, v/v) as an eluant to afford **CM-3** (40 mg, 73%) as a white powder. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 8.94 (dd, *J*₁ = 1.6 Hz, *J*₂ = 4.0 Hz, 1H), 8.91 (dd, *J*₁ = 1.6 Hz, *J*₂ = 4.4 Hz, 1H), 8.39 (dd, *J*₁ = 1.6 Hz, *J*₂ = 8.4 Hz, 1H), 8.06 (dd, *J*₁ = 1.6 Hz, *J*₂ = 8.4 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.42-7.51 (m, 3H), 7.37 (dd, *J*₁ = 4.0 Hz, *J*₂ = 8.0 Hz, 1H), 7.27-7.33 (m, 3H), 7.08 (dd, *J*₁ = 4.0 Hz, *J*₂ = 5.2 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 5.51 (s, 4H), 4.73 (s, 2H), 3.48 (t, *J* = 5.6 Hz, 2H), 3.10-3.15 (m, 2H), 1.67-1.73 (m, 2H), 1.34 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 156.56, 156.49, 155.94, 154.15, 153.91, 149.34, 149.17, 137.86, 135.94, 132.81, 129.46, 128.17, 127.49, 126.58, 126.19, 121.79, 121.67, 120.49, 120.46, 120.15, 109.78, 108.66, 78.91, 71.27, 71.24, 70.90, 68.26, 38.37, 29.83, 28.37. MS (ESI) m/z 581[(M+H)⁺, 100%].

2.3 Synthesis of CM

Compound **CM-3** (0.30 g, 0.52 mmol) was dissolved in dichloromethane (10 mL) and then added TFA (2 mL). The solution was stirred for 1 h at room temperature; then the solvent was removed by rotary evaporation. The mixture was dissolved in acetone (2 mL), then adjusted the

pH of the solution to 6~7 by saturated aqueous solution of sodium bicarbonate. To the mixture, cyanuric chloride (0.12 g, 0.67 mmol) dissolved in ethyl acetate (20 mL) was added dropwise at 0 °C. After the completion of dropwise addition, the resulting solution was still stirred for 1 h, and then extracted with ethyl acetate three times. The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo to give a crude product, which was chromatographed on silica gel using EA-CH₃OH (10:1, v/v) as an eluant to afford **CM** (260 mg, 80%) as a white powder. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 9.02 (dd, *J*₁ = 1.6 Hz, *J*₂ = 4.0 Hz, 1H), 8.98 (dd, *J*₁ = 1.6 Hz, *J*₂ = 4.0 Hz, 1H), 8.44 (dd, *J*₁ = 1.6 Hz, *J*₂ = 8.4 Hz, 1H), 8.15 (dd, *J*₁ = 1.6 Hz, *J*₂ = 8.4 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.49-7.57 (m, 3H), 7.45 (dd, *J*₁ = 4.0 Hz, *J*₂ = 8.0 Hz, 1H), 7.32-7.41 (m, 3H), 7.08 (dd, *J*₁ = 2.8 Hz, *J*₂ = 6.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 5.59 (s, 2H), 5.58 (s, 2H), 4.83 (s, 2H), 3.57 (t, *J* = 5.6 Hz, 2H), 3.48-3.53 (m, 2H), 1.84-1.89 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 170.77, 169.65, 165.50, 156.66, 156.50, 154.43, 153.99, 149.43, 149.35, 140.72, 137.87, 135.98, 132.64, 129.52, 127.80, 126.62, 125.68, 121.94, 121.73, 120.51, 120.45, 120.19, 109.82, 108.67, 71.42, 71.16, 68.29, 40.16, 28.53. HRMS (ESI): [M+Na⁺] calcd for C₃₂H₂₇Cl₂N₇O₃, 650.1450; found, 650.1472 (100%).

3. Preparation of FCM

FCM was prepared by the dip-dyeing process (Scheme S2). Firstly, the cotton fabric samples (1.0 g) were introduced in dyeing bath containing 2% (o.w.f) compound **CM** at a liquor ratio of 1:20 (DMSO:H₂O, 1:1, V:V). Cotton fabrics were dipped in the bath involving sodium sulfate (60 g/L) at room temperature. After the exhaustion stage, 15 g/L sodium carbonate was added for fixation and the temperature was raised to 40 °C at 1 °C/min. Dyeing was continued at 40 °C for 40 min. The dyed fabrics that rinsed thoroughly in methanol-water were soaped in a aqueous solution of polyvinyl pyrrolidone (0.7 g/L) at 95 °C for 15 min, then washed with water again. After drying, the fluorescent material **FCM** was obtained.

4. The FT-IR spectra of pure cotton fabric, FCM and CM

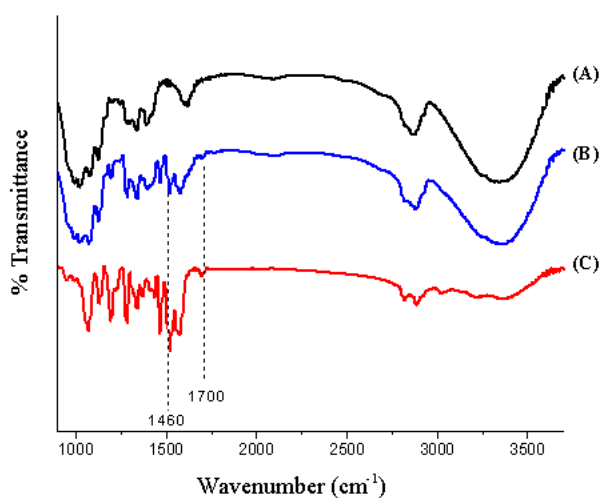


Fig. S1 The FT-IR spectra of pure cotton fabric (A), FCM (B) and CM (C)

5. Fluorescence titration

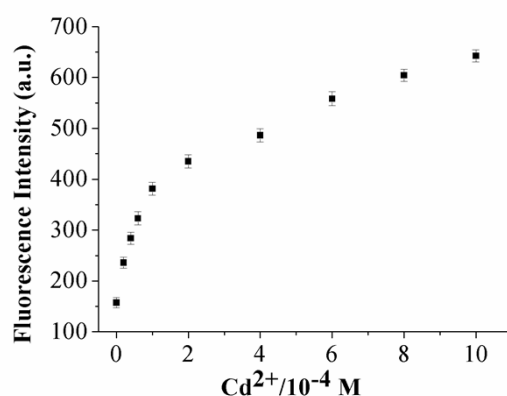


Fig. S2 Solid-state fluorescence spectra with error bars of FCM on exposure to various amount of Cd²⁺.

6. Langmuir Isotherms

The equilibrium data were also represented by the Langmuir adsorption model, which is given by

$$Q_e = \frac{Q_{\max} K_L C_e}{1 + K_L C_e} \quad (\text{eq.1})$$

where Q_{\max} is the adsorption capacity (mg of metal ion/g of sorbent) when all adsorption sites are occupied, C_e is the equilibrium concentration of the metal ion, and the Langmuir constant K_L (L of solution/mg of metal ion) represents the ratio of the adsorption rate constant to the

desorption rate constant. Linearization of the Langmuir equation yields:

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_{\max}} + \frac{1}{Q_{\max}} C_e \quad (\text{eq.2})$$

Fig. S3 shows the Langmuir parameters derived from the linear regression of the Cd^{2+} adsorption isotherm data on **FCM**.

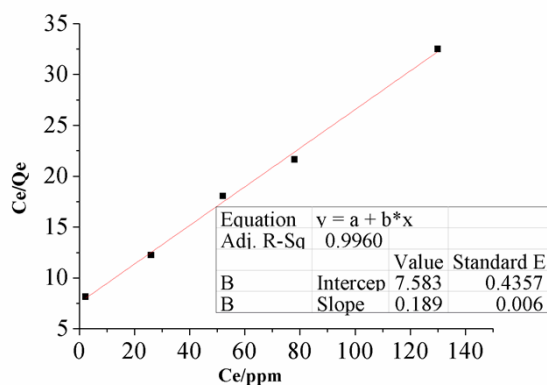


Fig. S3 Langmuir modeling of the adsorption isotherm of Cd^{2+} on **FCM**

7. Reversibility experiments

The fluorescent sensors **CM** modified cotton fabric **FCM** (50 mg, 25 mm × 21 mm) was firstly exposed to the aqueous solution (10 mL) of Cd^{2+} (1 mM). After taking out and drying, the solid-state fluorescence intensity at 415 nm was measured. Secondly, it was treated with HCl aqueous solution (0.1 mM), then washed with aqueous solution and dried. The solid-state fluorescence intensity at 415 nm decreased to the original condition. **FCM** was found to be able to recombine with Cd^{2+} for more than ten times.

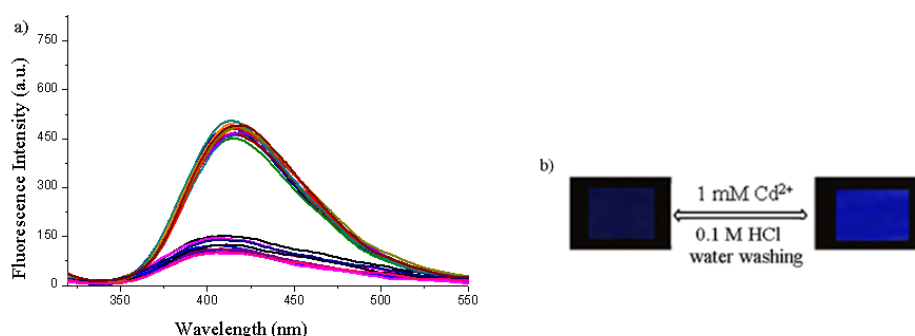


Fig. S4 (a) Solid-state fluorescence spectra of **FCM** in the 1×10^{-3} M of Cd^{2+} over ten complex/stripping cycles, $\lambda_{\text{ex}} = 302$ nm. (b) Fluorescent color change of **FCM** before and after combined with Cd^{2+} under 365 nm UV lamp illumination.

8. Adsorption of Cd^{2+} from water by **FCM**

FCM (150 mg, 35 mm × 45 mm) was added to water solution (25 mL) containing Cd^{2+} ($4.5 \times$

10^{-5} M) in a breaker. After stirring and shocking for 10 min, the fluorescent material **FCM** was taken out and the concentration of cadmium ions in the solutions were analyzed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The adsorption capacity per gram **FCM** (Q , mg/g) was calculated from the equation: $Q = [(C_0 - C) \times V] m^{-1}$, where C_0 and C were the initial and final concentrations of metal ion in solution (mg L^{-1}), V is the sample volume (L), m is the weight of **FCM** (g).

9. References

1. L. Xu, M.-L. He, H.-B. Yang and X. Qian, *Dalton Trans.*, 2013, **42**, 8218-8222.
2. J. Burckhalter and R. I. Leib, *J. Org. Chem.*, 1961, **26**, 4078-4083.