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Reactive fluorescent dye functionalized cotton fabric as a "Magic Cloth" for selective sensing and reversible separation of Cd^{2+} in water

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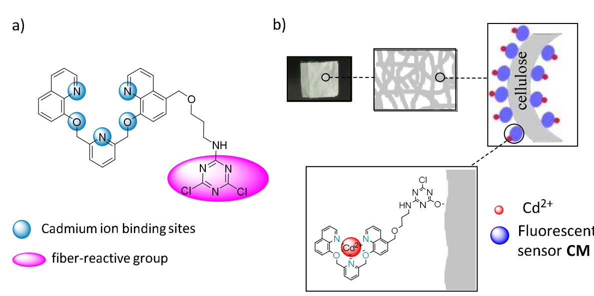
A reusable fluoresent material FCM, which was obtained through the dip-dyeing process of immobilizing the fluorescent sensor CM onto natural cotton fibers, exhibited high selectivity for detecting and separating Cd^{2+} in water.

Cadmium, an important heavy metal, is widely used in many fields such as metallurgy, military industry, agriculture, etc. As a highly toxic heavy metal, cadmium is listed by the U.S. Environmental Protection Agency (EPA) as one of 126 priority pollutants. Excessive exposure to Cd^{2+} sources can cause serious harm to the environment and human health due to its bioaccumulation through the food chain.[1] Cadmium poisoning leads to bone disease, heart disease, cancer and diabetes.[2,3] Thus, efficient methodologies for selective detection of Cd^{2+} are desperately needed. The traditional methods for cadmium analysis, e.g., inductively coupled plasma atomic emission spectroscopy, atomic absorption spectroscopy, anodic stripping voltammetric methods,[4-6] are time-consuming and costly. Fluorescence techniques, as powerful tools for onsite real-time detection, play significant roles in sensing heavy metal ions with high sensitivity and selectivity.[7-12] For years, some fluorescent sensor systems for the detection of Cd^{2+} have been reported, including organic dyes, gold nanoparticles, biomolecules, etc.[8] For example, our group has designed a Cd^{2+} sensor of BODIPY derivative based on the PET mechanism.[13] Yoon and co-workers have investigated a ratiometric fluorescent sensor for Cd^{2+} and Zn^{2+} detection, which can be distinguished by the naked eye.[14] Recently, our group also reported a quinoline-based "off-on" fluorescent sensor for Cd^{2+} with high selectivity and sensitivity.[15] However, most of them are only used in the homogeneous phase, thus unable to separate the target species. In recent years, the solid-substrate sensing materials for detecting and separating toxic metal ions, have been prepared as fluorescent polymers or fluorescent silica nanoparticles.[16-22] For example, our group has reported a fluorescent silica nanoparticles covalently grafted by the modified fluorescent small-molecule onto the surface, which was used to detect and absorb Hg^{2+} with high selectivity and sensitivity in serum and water samples.[20] Moreover, J. Jung and co-workers reported, Fe_3O_4@SiO_2 core/shell magnetic nanoparticles funtionalized by our aminonaphthalimide probe to separate and sense Hg^{2+} and CH_3Hg^{2+} efficiently [21] and this group also designed a BODIPY-functionalized magnetic silica nanoparticles which could remove Pb^{2+} from human blood.[22] We call such approach as "Selective Sensing and Separation Strategy" (3S strategy). However, such kinds of materials may suffer from the difficulty for manufacturing, scaling up, and using in real fields. Therefore, there is a great need for developing a novel material which can simultaneously detect and separate cadmium with high stability and reproducibility.

Cellulose, the most abundant natural material, is composed of long chains of repeated anhydroglucose units. The hydrogen bond network makes cellulose a stable polymer and insoluble in common solvents.[23] Owing to its hydrophilic nature and degradation, cellulose is an excellent candidate carrier.[24] Cotton fiber, as a natural cellulosic fiber, is widely used in textile industry. It has some important properties such as strong, durable, good permeability and easy to dye. Inspired by the dyeing process of cotton fabric, we



Scheme 1 (a) The structure of fluorescent sensor **CM**. (b) schematic illustration of fluorescent sensor **CM** modified cotton fiber (commercial cotton fabric) for detection of cadmium ions.

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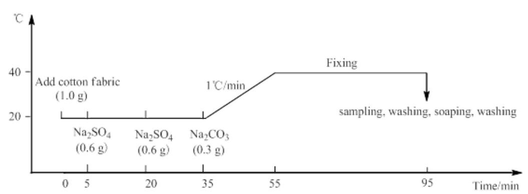
† Electronic Supplementary Information (ESI) available: Synthesis of FCM, FT-IR spectra, Fluorescence titration, Langmuir Isotherms, Reversibility experiments and Adsorption of Cd^{2+} included. See DOI: 10.1039/x0xx00000x

envision that, based on the industrial fiber and small molecular fluorescent probe, a novel kind of fluorescent sensor and material could be developed. Therefore, it's an ideal choice to apply cotton fabric as a carrier material to fabricate fluorescent sensors, which might provide a "Magic Cloth" to sense and separate toxic heavy metal cations. Reactive dyes are a class of organic substances commonly used in textiles, which form permanent covalent bonds with the cellulose fiber through chemical reactions. Cyanuric chloride, one type of reactive groups, is a trifunctional reagent which can react with the hydroxyl groups by temperature-modulated stepwise.[25] Employing the dip-dyeing process of reactive dyes, a cyanuric chloride modified fluorescent sensor is covalently grafted onto the surface of cotton fabric, which provides a new platform for sensor immobilization.

In this work, based on previous research,[15] a novel renewable fluorescent material (**FCM**) based on cotton fiber for simultaneous detection and separation of cadmium in aqueous solutions, was fabricated by immobilization of the cyanuric chloride modified Cd^{2+} sensor **CM** onto the surface of cotton fiber (e.g. commercial cotton fabric, Scheme 1). **CM** was used as a reactive dye, and its detailed synthesis procedures were shown in Scheme S1. **FCM** was prepared by the dip-dyeing process which included dye diffusion, adsorption and fixation stages as shown in Scheme 2.

To confirm whether the fluorescent sensor **CM** was successfully immobilized onto cotton fabric or not, Infrared spectroscopy of **FCM** was investigated. Fig. S1 exhibits the FT-IR spectra of pure cotton fabric (A), fluorescent material **FCM** (B) and fluorescent sensor **CM** (C), respectively. FT-IR spectrum of pure cotton fabric (A) was characterized by dominant O–H stretching vibration (3200 – 3500 cm^{-1}), C–H stretching vibration (2800 – 2900 cm^{-1}) and C–O stretching vibration (1010 cm^{-1}) as cellulose possesses plenty of hydroxyl groups. Fig. S1(C) showed the characteristic bands of fluorescent sensor **CM** at 1460 – 1700 cm^{-1} (C=N) which came from triazine and quinoline. Besides the existing groups in cellulose, the C=N bands also could be observed in the spectrum of the fluorescent material **FCM** (B). The present FT-IR data indicated that the fluorescent sensor **CM** has been successfully grafted onto cotton fabric.



Scheme 2 Preparation of fluorescent sensing material **FCM**

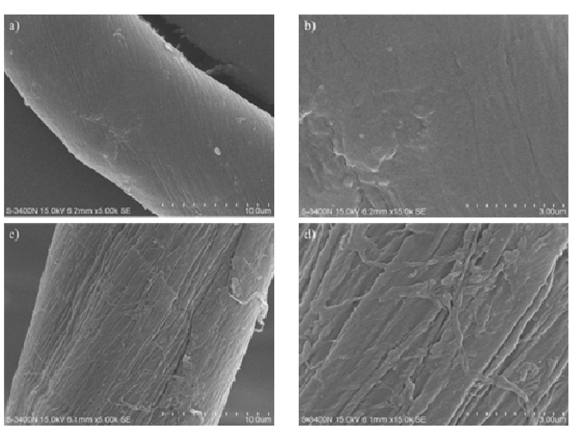


Fig. 1 TEM images of pure cotton fabric (a, b) and **FCM** (c, d)

A microscopic study was carried out using scanning electron microscopy (SEM) for better understanding of the surface properties of **FCM**. Fig. 1 showed the change in the morphology of the cotton fibers before (a, b) and after (c, d) modifications. The SEM images of pure cotton fibers (Fig. 1a and b) showed a relatively smooth and compact surface. In comparison, SEM photographs of **FCM** (Fig. 1c and d) illustrated notable changes in the structure. The surface of cotton fibers became rough and striated as the result of surface modification by the attachment of **CM** with the dip-dyeing method.

The performance tests were carried out by exposing **FCM** to aqueous solutions of Cd^{2+}. Changes in the solid-state fluorescence spectra of **FCM** with Cd^{2+} are shown in Fig.2 (a) and Fig. S2. **FCM** displayed a weak solid-state fluorescence before coordination with Cd^{2+}, which could be ascribed to the photo-induced electron transfer (PET) process from the N atom in pyridine moiety to the 8-hydroxyquinoline fluorophores, which quenched the fluorescence. However, with the increase of the concentration of Cd^{2+}, the solid-state fluorescence intensity of **FCM** at 415 nm was gradually enhanced at 415 nm was gradually enhanced owing to the blocking of the PET pathway. Based on the fluorescence titration, we couled calculate the detection limit of **FCM**. From 2 × 10^{-5} M to 1 × 10^{-4} M Cd^{2+}, there was a good correlation coefficient (R^2 = 0.9782, Fig. 2b). Then based on the definition by IUPAC, the detection limit was 2.6 × 10^{-6} M. [26]As can be seen from Fig.2 (c), after being dipped into Cd^{2+} solution, the fluorescent colour of **FCM** turned strong blue. The result indicated that the fluorescent sensor **CM**, which was loaded on the surface of cotton fabric, interacted with cadmium ions.

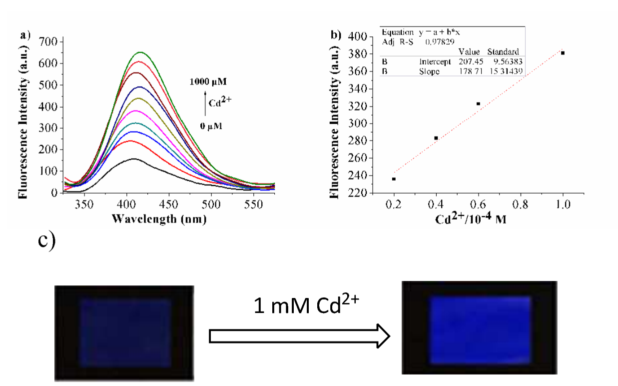


Fig. 2 (a) Solid-state fluorescence spectra of **FCM** on exposure to various amount of Cd^{2+}. (b) Solid-state fluorescence intensity change as a function of Cd^{2+} concentration (2 × 10^{-5} M to 1 × 10^{-4} M). (c) Visual fluorescence change for **FCM** exposed to Cd^{2+} (1 mM) at 365 nm UV lamp light. Condition: [**FCM**] = 5 mg mL^{-1}, [Cd^{2+}] = 0 – 1.0 × 10^{-3} M, λ_{ex} = 302 nm.

The high selectivity of **FCM** to Cd^{2+} is further conducted. The experiments were carried out to investigate the effect of different metal ions by fixing the ion concentration at 1 mM. As shown in Fig. 3, except for Cd^{2+}, nearly no change in solid - state fluorescence intensity was observed while exposing **FCM** to other metal ions such as Hg^{2+}, Pb^{2+}, Ag^{+}, Zn^{2+}, Na^{+}, Mg^{2+}, K^{+}, Cr^{3+}, Co^{2+}, Cu^{2+}. Furthermore, in order to survey the interference of other common metal ions, the competition experiments were done, which showed that in the presence of Cd^{2+}, the solid-state fluorescence was not seriously affected by other metal ions besides Cu^{2+}. All results indicated that **FCM** was a highly selective fluorescent sensor for the detection of Cd^{2+}.

The adsorption ability of **FCM** with Cd^{2+} was next investigated. **FCM** (150 mg, 35 mm × 45 mm) was added to water solution (25 mL) containing Cd^{2+} (4.5×10^{-5} M) in a breaker. After stirring and shocking, the fluorescent material **FCM** was taken out and the concentration of cadmium ions in the solutions were analysed by ICP-AES. As seen from Fig. 4, **FCM** showed good adsorption capability towards Cd^{2+} in water. After adsorption, the residual concentration of cadmium ions in water was only 0.6 ppm (ca. 5.3×10^{-6} M). The result indicated that **FCM** is an effective adsorbent for Cd^{2+}.

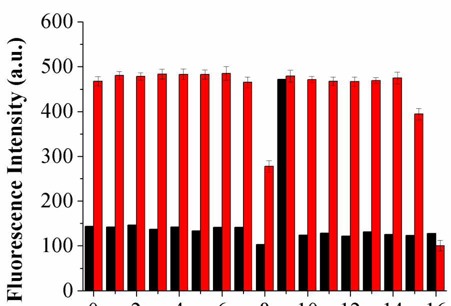


Fig. 3 Solid-state fluorescence response of **FCM** with various metal ions. Black bars represent the response of **FCM** in the presence of the appropriate metal ion of interest (2×10^{-3} M). Red bars represent the solid-state fluorescence response of **FCM** upon addition of Cd^{2+} (1×10^{-3} M) to a solution of the appropriate metal ion of interest. 0, none; 1, Ni^{2+}; 2, Mn^{2+}; 3, Li^{+}; 4, Na^{+}; 5, K^{+}; 6, Cr^{3+}; 7, Fe^{2+}; 8, Hg^{2+}; 9, Cd^{2+}; 10, Mg^{2+}; 11, Ba^{2+}; 12, Zn^{2+}; 13, Ca^{2+}; 14, Co^{2+}; 15, Ag^{+}; 16, Cu^{2+}. [**FCM**] = 5 mg mL^{-1}, λ_{ex} = 302 nm.

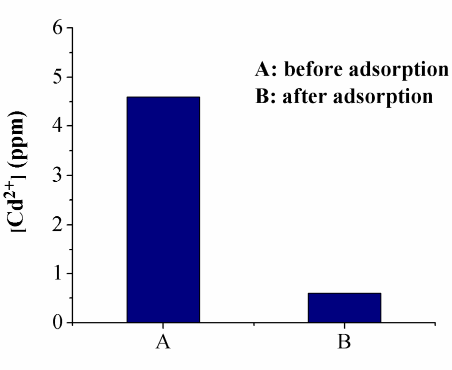


Fig. 4 The concentration of Cd^{2+} in aqueous solutions before and after adsorption by **FCM**. Condition: [**FCM**] = 5 mg mL^{-1}, $[Cd^{2+}] = 4 \times 10^{-5}$ M, at room temperature.

Then we carefully studied the adsorption capacity of **FCM**. Fig. 5 showed the adsorption isotherm of Cd^{2+} on **FCM**. In the isotherm measurements, the Cd^{2+} concentration was from 2×10^{-5} M to 1×10^{-3} M, and the **FCM** concentration was 5 mg mL^{-1}. The Cd^{2+} removal by **FCM** has been already normalized by the non-immobilized fiber. According to the adsorption isotherm, we also found the Q_{max} of **FCM** was 3.4 mg g^{-1} (30 μmol g^{-1}). As shown in Fig. S3, there was a good agreement (R^2 = 0.9960) between the experimental adsorption data and the Langmuir adsorption model. According to the Langmuir curves, K_L was 0.025 L mg^{-1} (eqs 1 and 2 from SI). We also studied the effect of [**FCM**] on adsorption of Cd^{2+}. As shown in Fig. 6, the adsorption of Cd^{2+} improved significantly while increasing the concentration of **FCM** from 0.5 – 2 mg mL^{-1}. However, while increasing the concentration of **FCM** from 2 – 6 mg mL^{-1}, the improvement in adsorption of Cd^{2+} was not significant.

As seen in the dual functionality of **FCM** (Fig. 7), after the interaction of **FCM** and Cd^{2+}, the removal of Cd^{2+} and solid-state fluorescence of **FCM** showed a similar tendency. The adsorption capacity and solid-state fluorescence of **FCM** were both enhanced with increasing the concentration of Cd^{2+}. The results implied the extraction capacity of **FCM** was depended on the amount of fluorescent sensor **CM** grafted onto surface of cotton fabric. As the Job's plot of **CM** with Cd^{2+} was 1:1 [15] and the Q_{max} of **FCM** was 3.4 mg g^{-1} (30 μmol g^{-1}), then we calculated the amount of immobilized **CM** on cotton fabric was 19 mg g^{-1} (30 μmol g^{-1}).

The fluorescent material **FCM** possesses excellent detection and separation reversibility of Cd^{2+}. By treated with HCl aqueous solution (0.1 mM), the bound cadmium ions can be dissociated from the fluorescent sensor **CM**. As displayed by the solid-state fluorescence spectra (Fig. S4a), the solid-state fluorescence intensity at 415 nm of **FCM** was increased while exposed to the aqueous solution of Cd^{2+}. After the treatment with HCl aqueous solution, the solid-state fluorescence intensity at 415 nm decreased. The fluorescent colour of **FCM** coordinated cadmium ions returned to the initial weak blue while dipped in HCl solution and washed with aqueous solution, then again turned to strong blue by exposing to Cd^{2+} (Fig. S4b). As shown in Fig. 8, **FCM** was found to be

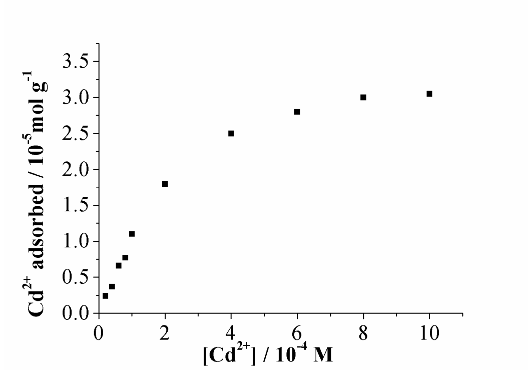


Fig. 5 Adsorption isotherm of Cd^{2+} on **FCM**. Condition: [**FCM**] = 5 mg mL^{-1}, [Cd^{2+}] = 2 × 10^{-5} M – 1.0 × 10^{-3} M, at room temperature.

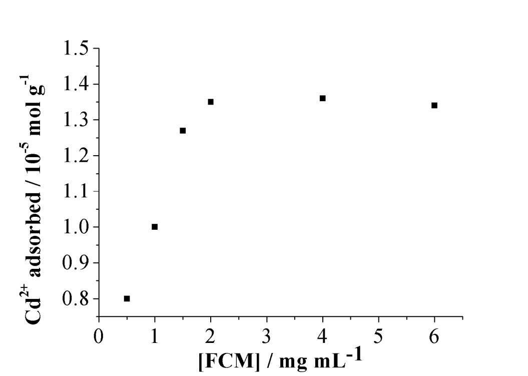


Fig. 6 Effect of **FCM** concentration on adsorption of Cd^{2+}. Condition: [Cd^{2+}] = 2 × 10^{-5} M, [**FCM**] = 0.5 – 6 mg mL^{-1}, at room temperature.

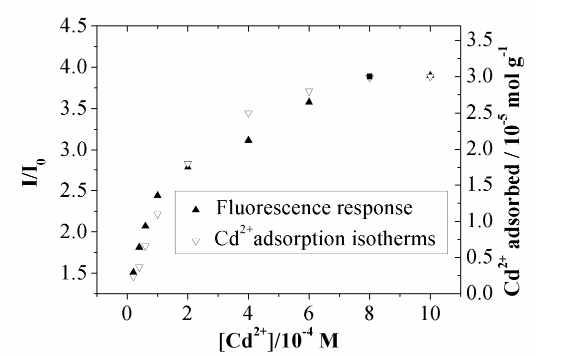


Fig. 7 Cd^{2+} adsorption isotherms and fluorescence response.▽ : the amount of Cd^{2+} adsorbed by **FCM** (5 mg mL^{-1}) for different concentrations of Cd^{2+} at room temperature;▲:Solid-state fluorescence intensity of **FCM** (5 mg mL^{-1}) for different concentrations of Cd^{2+} at room temperature.

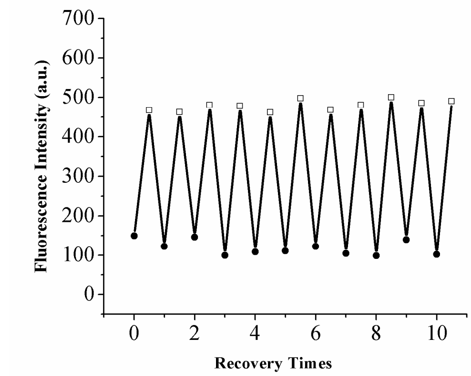


Fig. 8 Solid-state fluorescence spectra of **FCM** in the 1 × 10^{-3} M of Cd^{2+} over ten complex/stripping cycles, λ_{ex} = 302 nm.

●: represents the emission intensity of **FCM** without Cd^{2+};

□: represents the emission intensity of **FCM** with free Cd^{2+}.

able to recombine with Cd^{2+} for more than ten times without significant performance loss, which demonstrated the regenerability of the **CM** modified cotton fabric for Cd^{2+} detection and separation.

In conclusion, we have carried out "Selective Sensing and Separation Strategy" (3S strategy), successfully designed and prepared an inexpensive material by covalently grafting ligand-based fluorescent sensors **CM** onto cotton fibers based on the dip-dyeing process to provide a "Magic Cloth" for detecting and separating of cadmium ions. The prepared material **FCM** displayed high selective fluorescent responses to Cd^{2+} in aqueous solution based on coordinated complexation. The modified material **FCM** used as a reusable adsorbent with high stability to extract cadmium ions was also achieved. We believe that this methodology would provide a very promising alternative for developing high performance materials for the detection and separation of heavy metal ions in aqueous media for practical applications.

Acknowledgements

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