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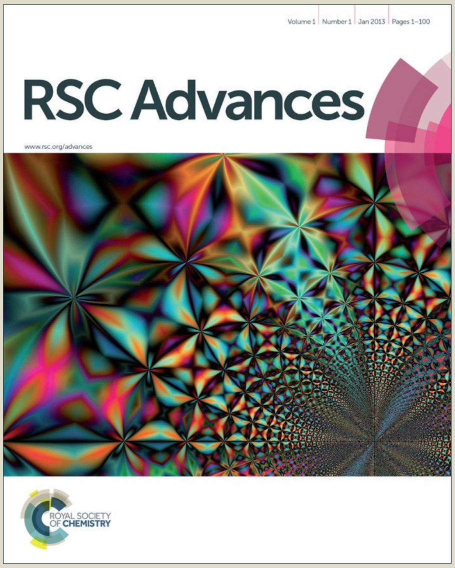

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A Stable 3D Porous Coordination Polymer as Multi-Chemosensor to Cr(IV) anion and Fe(III) cation and Its Selective Adsorption of Malachite Green Oxalate Dye †

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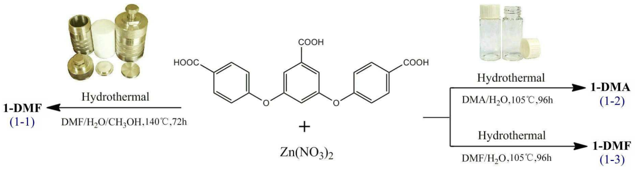
Based on $Zn(NO_3)_2{\cdot}6H_2O$ and 4,4'-((5-carboxy-1,3-phenylene)bis(oxy))dibenzoic acid (H_3cpbda), a 3D porous coordination polymer, $\{[Zn_{2.5}(cpbda)(OH)_2]{\cdot}solvent_2\}_n$ (Sovent= DMF and DMA (**1**), was synthesized by three solvent-thermal methods. The complex was characterized by single-crystal X-ray diffraction, IR spectroscopy, power X-ray diffraction, thermal-gravimetric analysis and fluorescence spectroscopy. Owing to its good thermal stability and fluorescence, the sensing experiments (eighteen kinds of cations and eleven kinds of anions) and the further titration processes show the complex can sensitively detect the Fe(III) metal cation and Cr(VI) anions ($Cr_2O_7^{2-}$ and CrO_4^{2-}) by the quenching responses. In addition, further adsorption research of seven dyes shows the complex **1** can selectively adsorb the Malachite Green Oxalate (MGO) dye.

Introduction

Luminescent coordination polymers (LCPs) have been proved to be excellent luminescent materials for their tunable structure, prominent optical properties, and relatively long emission wavelengths even in the visible region [1]. The porous coordination polymers (PCPs) are a new class of metal-organic materials with porous architectures, which have shown a variety of potential applications [2]. Particularly, numbers of luminescent PCPs have been synthesized, and widely investigated as sensing materials [3]. The chemosensors are of great importance for public health and environment protection due to their capabilities of detecting of heavy metal ions, toxic organic matters, etc [4].

As it is known, iron (Fe^{3+}) is an essential element in human body and plays an important role in the transport and storage of oxygen [5]. Besides, among the two common oxidation states of chromium, Cr(III) and Cr(VI), the Cr(VI) is highly toxic and can easily migrate in groundwater. Recently, it reported a metal-organic hybrid sorbent can reductive removal of Cr(VI) from aqueous solution [6]. The detection of such kind of metal ions and toxicants has been a hot topic for scientists. However the detection of Cr(III) and Cr(VI) in mixed solution is hard to accomplish because of their similarities. Especially the $Cr_2O_7^{2-}$ and CrO_4^{2-}, they both are Cr(VI) anions. Up to now, there is not an effective approach to detect Cr(III) cation and Cr(VI) anions respectively, using a coodination polymer sensor.

On the other hand, the separation and purification potentials of PCPs in the liquid phase are remarkable. The removal of organic dyes (such as Methylene Blue, Crystal Violet, Rhodamine B, Pyronin Y, Pyronin B, Thionine, Toluidine Blue O, Azure A, Brilliant Green and Methyl Yellow) from wastewater is vital for human life, which remains rarely explored to date [7]. Therefore, the guest-detection and dye-adsorption in liquid phase are becoming two significant applications for coordination polymers.



Scheme 1. The synthesis methods of complex **1**.

In this work, it reports a highly stable PCP, $\{[Zn_{2.5}(cpbda)(OH)_2]{\cdot}solvent_2\}_n$ (Sovent= DMF and DMA) (**1**). This crystal was first synthesized by Zheng's group, and its gas adsorptions and solvatochromic behaviors were investigated [8]. Furthermore, based on our previous research backgrounds on H_3cpbda ligands [9], it is considered that the PCPs constructed by H_3cpbda would be of great application potentials. Using $Zn(NO_3)_2{\cdot}6H_2O$ and H_3cpbda, the complex **1** was synthesized by three solvent-thermal methods (Scheme 1), which was further characterized by single-crystal X-ray diffraction, IR spectroscopy, power X-ray diffraction, thermal-gravimetric

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† Electronic Supplementary Information (ESI) available: Synthesis, crystallographic details, additional figures and tables. CCDC 888821 for **1** See http://dx.doi.org/10.1039/b000000x/

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analysis and fluorescence spectroscopy.

Owing to its good thermal stability and fluorescence, the sensing experiments of complex **1** on eighteen cations (Ni^{2+}, Pb^{2+}, Co^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Ag^{+}, Mn^{2+}, Cr^{3+}, Bi^{3+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}, Zr^{4+}, K^{+}, Na^{+}), eleven anions (Cl^{-}, Br^{-}, I^{-}, CO_3^{2-}, NO_3^{-}, SO_4^{2-}, ClO_3^{-} PO_4^{3-}, $Cr_2O_7^{2-}$, CrO_4^{2-}, SCN^{-}) and the further titration processes were investigated by the quenching responses. Moreover, the adsorptions of seven aqueous organic dye solutions, Methyl Green (MG), Xylenol Orange (XO), Malachite Green Oxalate (MGO), Congo Red (CR), Alizarin Red (AR), Methyl Orange (MO), Cresol Red (CR), have been investigated. Moreover, the maxsemum dye absorption capability and recycle absorption properties are also studied.

Experimental

Materials and Physical Measurements

The reagents were used directly as supplied commercially without further purification. Infrared spectra on KBr pellets were recorded on a Bruker Equinox-55 spectrometer in the range of 4000−400 cm^{-1}. Luminescence spectra for the solid samples were investigated with a Hitachi F-4500 fluorescence spectrophotometer. The X-ray powder diffraction pattern was examined with a Pigaku D/Max 3III diffractometer. Thermal analysis was determined with a Netzsch STA 449C microanalyzer under flowing N_2 atmosphere at a heating rate of 10 ºC /min.

Preparation of $\{[Zn_{2.5}(cpbda)(OH)_2]\cdot solvent_2\}_n$ (1).

1-1 (1-DMF). $Zn(NO_3)_2\cdot 6H_2O$ (0.125mmol/37.3mg), H_3cpbda (.05mmol/19.7mg), N,N-dimethylformamide (DMF, 3 mL), H_2O (3mL), methanol (CH_3OH, 3mL) and triethylamine (25%, 0.1mL) were mixed in a 25mL Teflon-lined stainless steel vessel. The mixture was sealed and heated at 140℃ for 72 h, and then cooled to room temperature at a rate of 5℃/h. Finally, colorless block-like crystals of **1-1** were obtained in 78% yield (based on H_3cpbda) and were isolated by washing with DMF/H_2O/CH_3OH, and dried in air. IR (KBr, cm^{-1}) (Figure S6): 3614s, 3437s, 3075s, 2923s, 1914w, 1663s, 1600vs, 1568vs, 1389vs, 1306m, 1234m, 1163m, 1111m, 1093m, 990m, 897w, 855w, 785s, 702m, 632w, 496w, 446w.

1-2 (1-DMA). $Zn(NO_3)_2\cdot 6H_2O$ (0.125mmol/37,3mg), H_3cpbda (0.05mmol/19.7mg), N,N-dimethylacetamide (DMA, 4 mL), H_2O (4mL) and NaOH (25%, 0.1mL) were mixed in a 10mL glass bottle. The mixture was heated at 105℃ for 72 h, and then colorless block-like crystals of **1-2** were obtained in 82% yield (based on H_3cpbda) and were isolated by washing with DMA/H_2O, and dried in air. IR (KBr, cm^{-1}) (Figure S7): 3734m, 3616m, 3438m, 3074m, 2923m, 1915w, 1662s, 1604s, 1563vs, 1501m, 1390vs, 1307m, 1231s, 1162m, 1114m, 1093m, 992m, 963w, 896m, 854m, 787m, 704m, 637m, 497w, 448w.

1-3 (1-DMF). The synthesis of **1-3** was similar to that described above, except that the solvent DMA was replaced by DMF. The yield was 84% (based on H_3cpbda).

Crystallographic Data Collection and Refinement

Single-crystal X-ray diffraction analysis of the complex was carried out on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated Mo*K*α radiation (λ = 0.71073 Å) using ϕ/ω scan technique at room temperature. The structures were solved using direct methods and successive Fourier difference synthesis (SHELXS-97) [10], and refined using the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97) [11]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of organic ligands were placed in calculated positions and refined using a riding on attached atoms with isotropic thermal parameters 1.2 times those of their carrier atoms. Table S1 summarizes the crystal data for **1** and details of data refinements and collection. Table S2 gives the selected angles and bond lengths.

Results and Discussion

Description of the crystal structures

$[Zn_{2.5}(cpbda)(OH)_2]_n$ (1). Complex **1** crystallizes in the Triclinic $P\bar{1}$ space group, and the asymmetric unit consists of three Zn(II) atoms, one $cpbda^{3-}$ ligand and two deprotonated coordinated water molecules(Figure 1). The disordered solvent molecules in crystal lattice were omitted in the refining procedure. The Zn1 and Zn3 exhibit the distorted octahedral configurations, and the Zn2 shows four-coordinated tetrahedral configuration. The Zn-O bond distances range from 1.924(4) to 2.435(3) Å, and the bond angles around the Zn(II) atom are at the range of 78.40(12) and 180.00(19)°(Table S2).

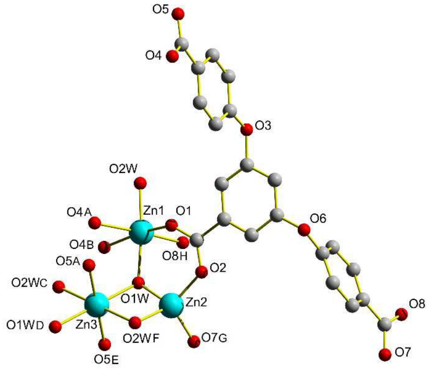

Fig. 1. The coordination environment of Zn(II) in **1**. Symmetry codes: A, –x + 2, –y + 1, –z + 1; B, x, y – 1, z; C, –x + 2, –y, –z + 1; D, –x + 3, – y, –z + 1; E, x + 1, y – 1, z ; F, x + 1, y, z; G, –x + 3, – y, –z; H, –x + 2, –y, –z .

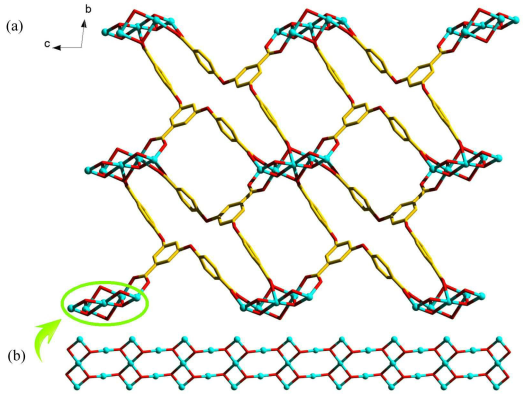

Fig. 2. The 3D structure of **1**. (a) The two 1D open channels in 3D framework, viewed along the *a* axis. (b) The double-strand 1D Zn-O-Zn chain in **1**, viewed along the *b* axis.

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The Zn(II) atoms are connected by coordinated water molecules, forming a novel double-strand 1D Zn-O-Zn chain (Figure 2b). The 1D chains bond to the T-shaped cpbda^{3-} ligands *via* the Zn-O bonds, showing a 3D structure (Figure S1-S2). It contains two different shapes of open channels with dimensions of approximately 8.8 × 7.4 and 15.7 × 3.4 Å^2 (excluding van der Walls radii of the atoms) along the [001] (Figure 2a). The removal of water and DMF molecules gives rise to the accessible void volume of 24.4%, as calculated by PLATON.

The topology of **1** viewed along the *a* axis is shown in Figure S3. The cpbda^{3-} bond with seven Zn(II) ions, can be simplified as a seven-connect node, while the two deprotonated water molecules (OH$^-$) act as the three-connect nodes. And the Zn1, Zn2 and Zn3 are 6-, 4- and 6- connect node respectively. The 3D structure of **1** can be described as a (5, 7, 8, 8)-network with the Point symbol of $(3^4 \cdot 4^4 \cdot 5^2)_2(3^4.4^5.5^6.6^6)_2(3^6.4^{11}.5^6.6^5)_2(3^8.4^8.5^8.6^4)$. The views of *b* and *c* axis are shown in Figure S4-S5.

PXRD and TGA results

The complexes exhibit highly synthesized yields. In order to confirm the phase purity of the bulk materials, PXRD analyses of **1-DMF** and **1-DMA** were carried out. The PXRD results with good agreements are listed in the supporting information (Figure S8).

Complex **1** is air-stable and can keep its crystalline integrity at ambient conditions. Thermogravimetric curves of **1-DMF** and **1-DMA** (Figure S9) show the great losses from 100°C to 280°C, corresponding to the release of guest molecules (**1-DMF**, calc. 19.9%, obser. 19.3%; **1-DMA**, calc. 22.8%, 22.6%). The structures of **1-DMF** and **1-DMA** are stable up to 450°C, and then quickly decompose.

Luminescence and sensing property

The solid-state luminescence of H_3cpbda and complex **1** were investigated at room temperature (Figure S10). Excitation wavelength of complex **1** is 310nm, resulting in a fluorescence emission peak at 343nm. The fluorescence of H_3L shows an emission peak at 366nm (Excitation 230nm). The blue shift of emission peak of **1** should be attributed to the $\pi \rightarrow \pi^*$ transitions or the ligand-to-metal charge transfer (LMCT), the incorporation of metal-ligand coordination interaction. After the ligands bond with metal ions, the increased rigidity of complex **1** enhances the intensity of emission peak.

To probe the sensing properties of complex **1** on metal cations and anions, 10mg of **1-DMF** and **1-DMA** were introduced into 5 mL of different $M(NO_3)_x$ (M = Ni^{2+}, Pb^{2+}, Co^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Ag^+, Mn^{2+}, Cr^{3+}, Bi^{3+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}, Zr^{4+}, K^+, Na^+) and $K_x(A)$ (A = Cl^-, Br^-, I^-, CO_3^{2-}, NO_3^-, SO_4^{2-}, ClO_3^- PO_4^{3-}, $Cr_2O_7^{2-}$, CrO_4^{2-}, SCN^-) solutions, and the emission data were recorded for luminescence studies. The studies of complex **1-DMF** (Figure 3 and Figure 4) showed that the Ag^+, Cr^{3+} and Fe^{3+} cations and the $Cr_2O_7^{2-}$, CrO_4^{2-} anions can distinctly induce the luminescence quenching. The similar sensing results of complex **1-DMA** were obtained, as listed in SI (Figure S11-S12).

In order to further detect the sensing sensitivities of complex **1**, the titration experiments were conducted. The **1-DMF** and **1-DMA** suspensions were prepared by dispersing 10 mg complexes into 3mL DMF/H_2O and DMA/H_2O (1:1). The concentrations of cations (Ag^+, Cr^{3+} and Fe^{3+}) and anions ($Cr_2O_7^{2-}$, CrO_4^{2-}) were increased from 0 to 2771 ppm to monitor the emission responses. The analysis results of **1-DMF** suspensions are shown in Figure 5-9. Along with the injections of Ag^+ and Cr^{3+} ions solutions, the luminescence slowly decrease. When the concentration of Ag^+ increases to 2308 ppm, the luminescence intensity decreases to 4% of the original one (Figure 5). It is worse for Cr^{3+}. The luminescence intensity is still 43.1% of the original one when the concentration increases to 2771 ppm (Figure 6). However, the injections of Fe^{3+}, $Cr_2O_7^{2-}$ and CrO_4^{2-} show such remarkable quenching effects that the ion concentration of merely 164 ppm can render the luminescence intensities decrease to 4.2%, 6.4% and 8.9% (Fe^{3+}, $Cr_2O_7^{2-}$ and CrO_4^{2-}) respectively (Figure 7-9). The titration results of **1-DMA** are listed in Figure S17-S18, and the quenching result is: $Fe^{3+} > Cr_2O_7^{2-} > CrO_4^{2-} >> Ag^+ > Cr^{3+}$. Obviously, complex **1** can sensitively detect the Fe(III) metal cation and Cr(VI) anions ($Cr_2O_7^{2-}$ and CrO_4^{2-}) by the quenching responses. Generally, there are two reasons for the sensing phenomena, photo induced electron transfer or resonance energy transfer or both[12]. Considering the dense 3D structure of the complex **1**, the changes of fluorescence intensity may not be attributed to the internal corporation, but the surface interactions and the photo-induced electron transfers between the excited frameworks and the guest molecules is more probable.

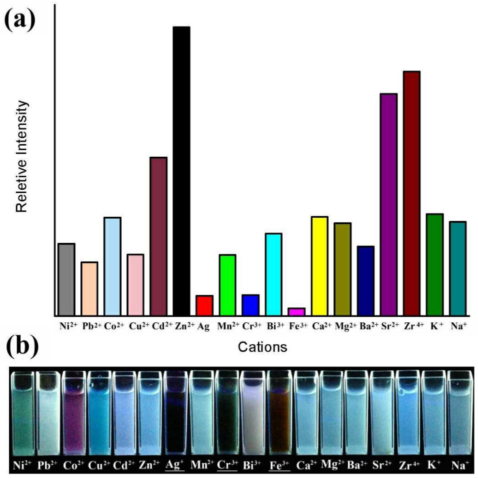

Fig. 3. The luminescence intensities of **1-DMF** suspensions with various metal cations.

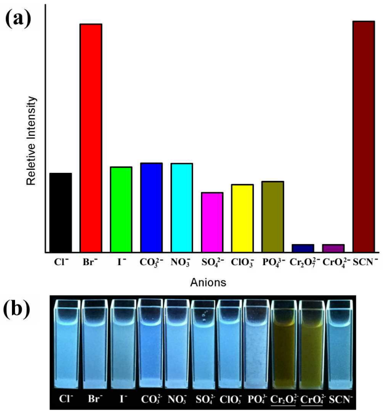

Fig. 4. The luminescence intensities of **1-DMF** suspensions with various anions.

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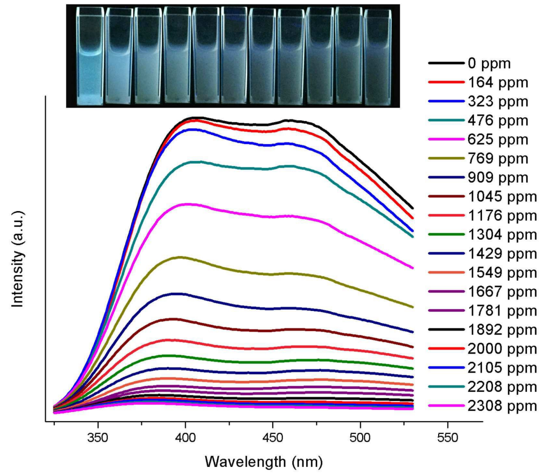

Fig. 5. The luminescence intensities of **1-DMF** suspensions with Ag(I) concentration varying from 0 to 2308 ppm.

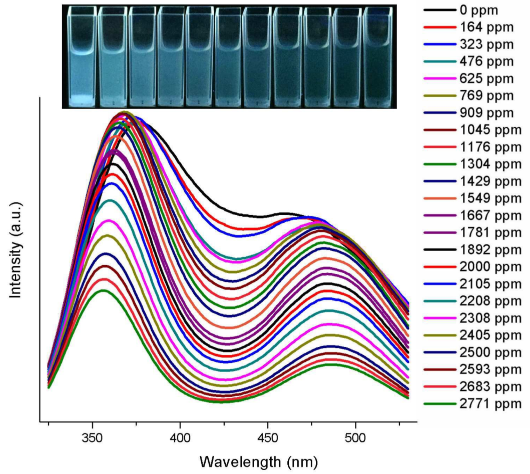

Fig. 6. The luminescence intensities of **1-DMF** suspensions with Cr(III) concentration varying from 0 to 2771 ppm.

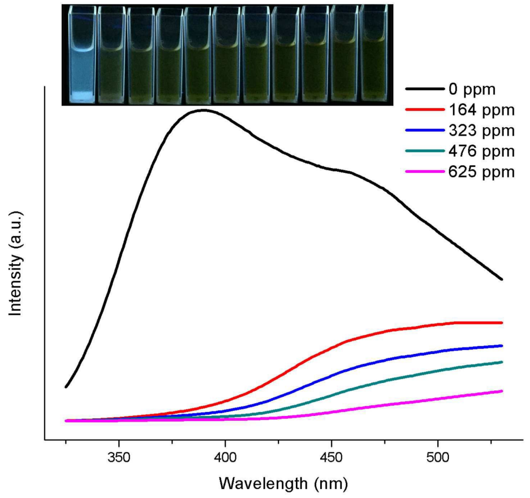

Fig. 7. The luminescence intensities of **1-DMF** suspensions with Fe(III) concentration varying from 0 to 1429 ppm.

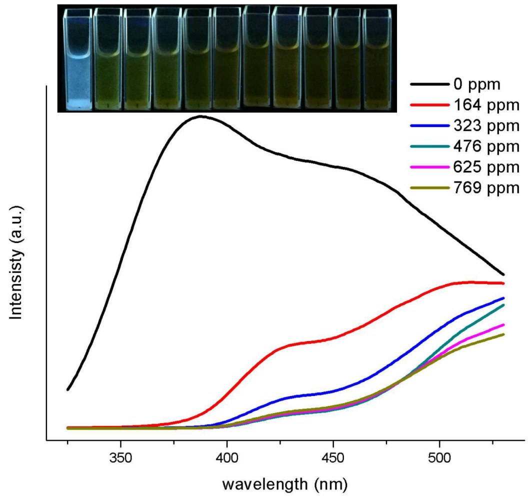

Fig. 8. The luminescence intensities of **1-DMF** suspensions with $Cr_2O_7^{2-}$ concentration varying from 0 to 1429

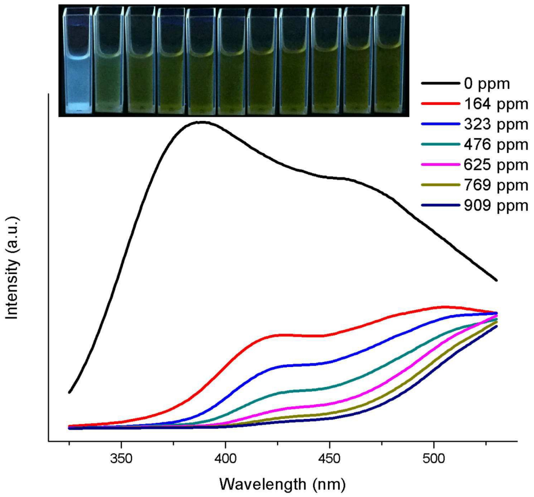

Fig. 9. The luminescence intensities of **1-DMF** suspensions with CrO_4^{2-} concentration varying from 0 to 1429 ppm.

Organic dyes adsorptions

The excellent sensing properties of polymers motivate the further investigation interests of the organic dyes adsorption. The 10 mg **1-DMF** and **1-DMA** complexes were put into seven kinds of aqueous organic dye solutions with concentration of 30 ppm, MG, XO, MGO, CR, AR, MO and CR (Figure S19). After two hours, the concentration of MGO decreased to 14.75 ppm. However, the others exhibited no obvious changes (MG is 29.22, XO is 28.16, CR is 29.27, AR is 28.53, MO is 29.00 and CR is 29.32), as shown in Figure 10. The complex **1** shows a great adsorption of MGO. There are some difficulties in the further demonstration that the complex could selective adsorb MGO dye in a mixed solution. As the Figure S22 and S23 shown, although the UV spectra of seven separate kinds of dye are different, the mixture of seven dyes (include MGO) and the mixture of six dye (exclude MGO) generate almost the same UV spectra. It is hard to measure and demonstrate whether the MGO dye is been selective absorbed in a mixture. The HPLC-MS was considered to separate the dyes in a mixed solution. However, the suitable

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mobile phase which can separate the similar seven dyes is difficult to seek. The further explorations on the ways to detect and separate the mixed dyes solutions are crucial.

After the soaking and washing by DMSO, the dyes can be released from the complex. The recycle adsorptions of MGO (30 ppm) are discussed, the complex reveals good stability and repeatability which can recycle absorb the MGO dye more than 13 times. The maximum adsorption capacity is 50.3 % (Figure 11). The detection of MGO concentration over time (Figure 12) shows that the adsorption process is very fast within 40 minutes. However, compared with the adsorption data of MO dye reported in the reference [13], the adsorption velocity and quantity of MGO in the present work are still unsatisfactory, which should be attributed to the lower porosity of complex **1**.

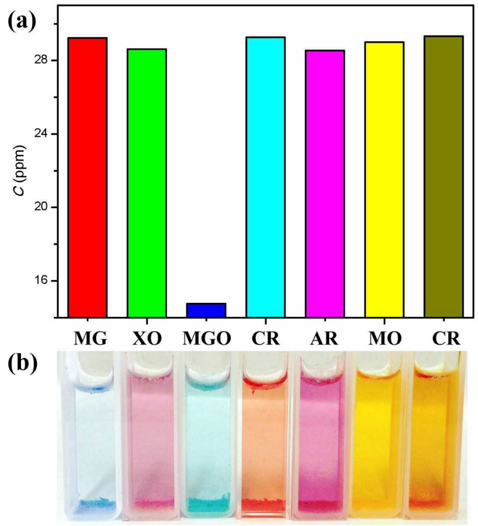

Fig. 10. The (a) concentrations and (b) naked-eye photos of different dyes in 2 hours after the additions of complexes **1-DMF.**

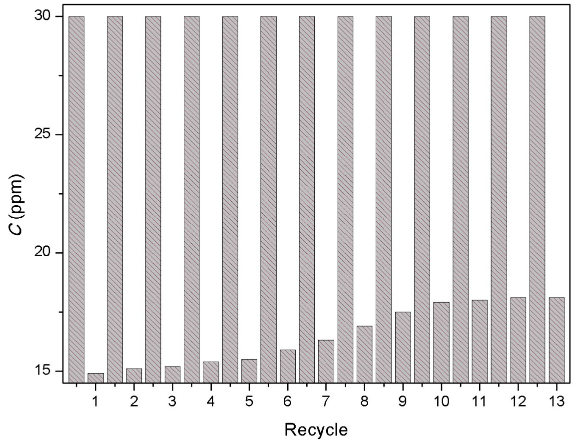

Fig. 11. The recycle adsorptions of Malachite Green Oxalate (MGO) by complex **1-DMF.**

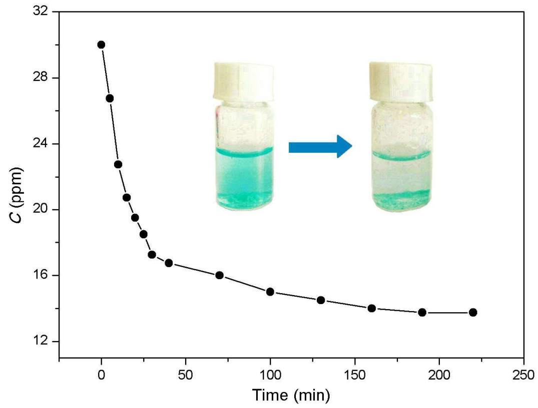

Fig. 12. The MGO concentration changing over time, after the addition of **1-DMF.**

Conclusion

In summary, the 3D porous coordination polymer **1-DMF** (or **1-DMA**) based on H_3cpbda ligand was synthesized by multiple methods and exhibited good thermal stability. According to its fluorescence property, complex **1** showed the sensitive detections of Fe(III) metal cation and Cr(VI) anions ($Cr_2O_7^{2-}$ and CrO_4^{2-}) by the quenching responses. In addition, further research revealed the complex **1** demonstrated high selective and recycled adsorption of the Malachite Green Oxalate (MGO) dye. The results indicated that the polymer **1** could be employed as a stable multi-functional material acting as good luminescent sensor and dye absorber.

Acknowledgements

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Notes and references

1 (a) K. Chen, Q. H. Shu, and M. Schmittel, Chem. Soc. Rev., 2015, 44, 136; (b) P. C. A. Swamy, S. Mukherjee, and P. Thilagar, Anal. Chem., 2014, 86, 3616; (c) S. Heng, A. M. Mak, D. Stubing, et al, Anal. Chem., 2014, 86, 3268.

2 (a) R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R. V. Belosludov, T. C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe, Y. Mita, Nature., 2005, 436, 238; (b) S. Ma, D. Sun, J. M. Simmons, C. D. Collier, D. Yuan, H. C. Zhou, J. Am. Chem. Soc., 2008, 130, 1012; (c) S. Horike, M. Dinca, K. Tamaki, J. R. Long, J. Am. Chem. Soc., 2008, 130, 5854; (d) S. Yang, X. Lin, A. J. Blake, G. Walker, P. Hubberstey, N. R. Champness, M. Schröder, Nat. Chem., 2009, 1, 487; (e) Z. Z. Lu, R. Zhang, Y. Z. Li, Z. J. Guo, H. G. Zheng, J. Am. Chem. Soc., 2011, 133, 4172.

3 (a) L. Liu, J. H. Hao, C. Hao, et al, RSC Adv., 2015, 5, 3045; (b) J. W. Ye, L. M. Zhao, G. L. Ning, et al, Chem. Eur. J., 2015, 21, 2029; (c) M. Carboni, Z. Lin, W. B. Lin, et al, Chem. Eur. J., 2014, 20, 14965; (d) J. S. Qin, S. R. Zhang, Z. M. Su, et al, Chem. Eur. J., 2014, 20,

RSC Advances Accepted Manuscript

5625; (e) Y. Yu, X. M. Zhang, Y. B. Dong, et al, Chem. Comm., 2014, 50, 1444.

4 (a) C. Bazzicalupi, C. Caltagirone, N. Zaccheroni, et al, Chem. Eur. J., 2013, 19,14639; (b) Y. P. Zhu, T. Y. Ma, Z. Y. Yuan, et al, ACS Appl. Mater. Interfaces, 2014, 6, 16344; (c) S. Bhattacharyya, A. Chakraborty, T. K. Maji, et al, Chem Comm, 2014, 50, 13567.

5 (a) Z. H. Xiang, C. Q. Fang, S. H. Leng and D. P. Cao, J. Mater. Chem A, 2014, 2, 7662; (b) Y. Lu, B. Yan, J. L. Liu, Chem Comm, 2014, 50, 9969; (c) H. B. Xu, S. H. Zhou, Q. H. Yuan, et al, J. Mater. Chem. C, 2015, 3, 291.

6 S. Sarkar, S. Dutta, P. Bairi, and T. Pal, *Langmuir*. 2014, 30, 7833.

7 (b) S. Han, Y. Wei, C. Valente, I. Lagzi,J. J. Gassensmith, A. Coskun, J. F. Stoddart and B. A. Grzybowski,J. Am. Chem. Soc., 2010,132, 16358; (e) C. Zou, Z. Zhang, X. Xu, Q. Gong, J. Li and C. D. Wu,J. Am. Chem. Soc., 2012,134,87; (f) R. A. Smaldone,R. S. Forgan, H. Furukawa, J. J. Gassensmith, A. M. Z. Slawin,O. M. Yaghi and J. F. Stoddart, Angew. Chem., Int. Ed., 2010, 49, 8630; (g) L. Li, F. Sun, J. Jia, T. Borjigin and G. Zhu, CrystEngComm, 2013, 15, 4094.

8 J. H. Cui, Y. Z. Li, Z. J. Guo and H.-G. Zheng, Chem. Comm., 2013, 49, 555.

9 (a) W. H. Huang, G. P. Yang, Y. Y. Wang, et al, Cryst. Growth Des., 2013, 13, 66; (b) W. H. Huang, X. J. Luan, Y. Y. Wang, et al, CrystEngComm., 2013, 15, 10389; (c) W. H. Huang, Y. Y. Wang, Y. N. Zhang, et al, Inorg. Chim. Acta, 2015, 433, 52.

10 Sheldrick G M. *SHELXL-97*, *Program for Crystal Structure Determination*, University of Göttingen, Germany, 1997.

11 Sheldrick G M. *SHELXL-97*, P*rogram for Crystal Structure Refinement*, University of Göttingen, Germany, 1997.

12 (a) A. J. Lan, K. H. Li, H. H. Wu, et al, *Angew. Chem. Int. Ed.* **2009**, *48*, 2334; (b) S. Pramanik, C. Zheng, X. Zhang, et al, *J. Am. Chem. Soc.* **2011**, *133*, 4153; (c) S. S. Nagarkar, B. Joarder, A. K. Chaudhari, et al, *Angew. Chem. Int. Ed.* **2013**, *52*, 2881; (d) S. J. Toal, W. C. Trogler, *J. Mater. Chem.*, **2006**, *16*, 2871; (e) J. C. Sanchez, A. G. DiPasquale, A. L. Rheingold, W. C. Trogler, *Chem. Mater.*, **2007**, *19*, 6459.

13 Y. X. Tan, Y. P. He, M. Wang, J. Zhang, RSC Adv., 2014, 4, 1480.

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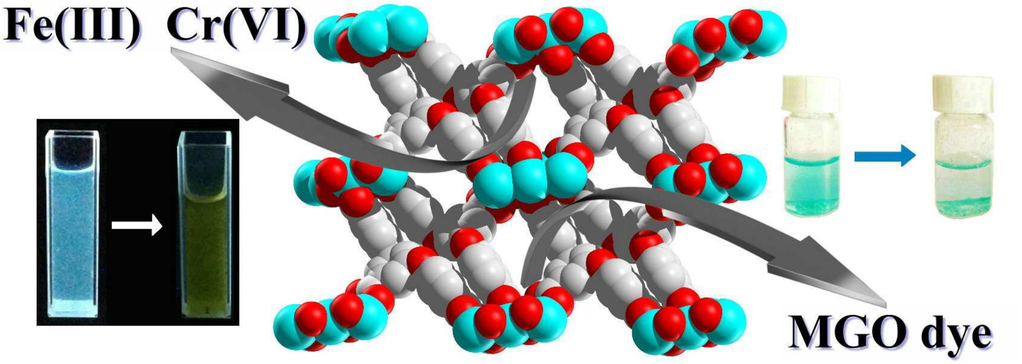
A Stable 3D Porous Coordination Polymer as Multi-Chemosensor to Cr(IV) anion and Fe(III) cation and Its Selective Adsorption of Malachite Green Oxalate Dye

Based on $Zn(NO_3)_2·6H_2O$ and 4,4'-((5-carboxy-1,3-phenylene)bis(oxy))dibenzoic acid (H_3cpbda), a 3D porous coordination polymer, $\{[Zn_{2.5}(cpbda)(OH)_2]·solvent_2\}_n$ (Sovent= DMF and DMA (**1**), was synthesized by three solvent-thermal methods. The complex was characterized by single-crystal X-ray diffraction, IR spectroscopy, power X-ray diffraction, thermal-gravimetric analysis and fluorescence spectroscopy. Owing to its good thermal stability and fluorescence, the sensing experiments (eighteen kinds of cations and eleven kinds of anions) and the further titration processes show the complex can sensitively detect the Fe(III) metal cation and Cr(VI) anions ($Cr_2O_7^{2-}$ and CrO_4^{2-}) by the quenching responses. In addition, further adsorption research of seven dyes shows the complex **1** can selectively adsorb the Malachite Green Oxalate (MGO) dye.



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