CHEMISTRY
A European Journal

A Journal of
ChemPubSoc Europe

Accepted Article

Title: A Water-Stable Luminescent Zn(II) Metal-Organic Framework as Chemosensor for High-Efficiency Detection of CrVI-Anions (Cr2O72- and CrO42-) in Aqueous Solution

Authors: Tong-Liang Hu, Zhao-Quan Yao, Guang-Yu Li, Jian Xu, and Xian-He Bu

To be cited as: *Chem. Eur. J.* 10.1002/chem.201705328

Link to VoR: http://dx.doi.org/10.1002/chem.201705328

Supported by ACES

WILEY-VCH

A Water-Stable Luminescent Zn(II) Metal-Organic Framework as Chemosensor for High-Efficiency Detection of Cr^{VI}-Anions ($Cr_2O_7^{2-}$ and CrO_4^{2-}) in Aqueous Solution

Zhao-Quan Yao,†[a] Guang-Yu Li,†[a] Jian Xu,[a] Tong-Liang Hu,*[a,b] and Xian-He Bu*[a,b,c]

Abstract: A new luminescent Zn(II)-MOF with 1D triangular channels along the *b* axis, namely **NUM-5**, has been successfully assembled and well characterized, which features good stability, especially in aqueous solution. Interestingly, this compound exhibits a fast, sensitive and selective luminescence quenching response towards Cr^{VI} ($Cr_2O_7^{2-}$/CrO_4^{2-}) in aqueous solution. The detection limits towards $Cr_2O_7^{2-}$ and CrO_4^{2-} ions are estimated to be 0.7 and 0.3 ppm, respectively, which are among the lowest detection limits reported for the MOF-based fluorescent probes that can simultaneously detect $Cr_2O_7^{2-}$ and CrO_4^{2-} in aqueous environment. The possible detection mechanism has been discussed in detail. Moreover, it can be easily regenerated after detection experiments, indicative of excellent recyclability. All these results suggest **NUM-5** to be a highly selective and recyclable luminescent sensing material for the quantitative detection of Cr^{VI}-anions in aqueous solution.

Introduction

Chromium, especially hexavalent chromium, is one of most common toxic heavy metal pollutants present in water. Very dangerously, it causes permanent damage to human health and living environment, even at a low concentration.[1-4] Thus, World Health Organization (WHO) guidelines limit Cr^{VI} ($Cr_2O_7^{2-}$/CrO_4^{2-}) to 50 µg L^{-1} in groundwater.[5] Up to now, the prevailing detection of Cr^{VI} ($Cr_2O_7^{2-}$/CrO_4^{2-}) is mainly based on instrumental methods, including atomic absorption spectroscopy, ICP-MS and electrochemical analysis.[6-8] However, these methods are often time-consuming, high cost, hardly portable and require trained personnel. Therefore, developing a new convenient, reliable and inexpensive method for the detection of Cr^{VI} contaminants is urgently needed.

It is well established that optical sensing is a simple, real-time and cost-effective detection method,[9-14] thereby promising for the detection of Cr^{VI}. As a new class of optical materials, luminescent metal-organic frameworks (LMOFs) have recently attracted immense interests because of their specific photophysical properties, easily tailorable structures and permanent porosity.[15-23] All these fascinating properties endow them with potential applications in chemosensors,[24-28] photonic devices,[29-33] and optoelectronic technologies.[34-36] Importantly, the reported LMOF-based sensors display advantages in quick response time,[37] excellent sensitivity and selectivity,[38] etc. Therefore, they are a good candidate for detecting Cr^{VI} ($Cr_2O_7^{2-}$/CrO_4^{2-}) in aqueous solution.[39,40] In this regard, some LMOF probes for Cr^{VI} ($Cr_2O_7^{2-}$/CrO_4^{2-}) have been reported recently; however, the lack of water stability and recyclability impedes their applications in practice.[41] Thus, the development of a new LMOF for sensing Cr^{VI} ($Cr_2O_7^{2-}$/CrO_4^{2-}) in aqueous solution with high sensitivity, selectivity and excellent recyclability is extremely beneficial.

On the basis of above discussions, we herein employ luminescent 9,10-bis(4-pyridyl)anthracene ligand and 4,4'-oxybis(benzoic acid) as organic linkers with Zn^{2+} ion to fabricate a new LMOF, $\{[Zn_3(bpanth)(oba)_3]\cdot 2DMF\}_n$ (bpanth = 9,10-bis(4-pyridyl)anthracene, H_2oba = 4,4'-oxybis(benzoic acid), denoted as **NUM-5**, the structure of which can be viewed as a three-dimensional (3D) network with one-dimensional (1D) triangular channels. Remarkably, **NUM-5** could maintain the crystallinity in several common solvents, especially in aqueous solution, providing the prerequisite for water-phase detection. In addition, **NUM-5** is highly fluorescent and exhibits selective and sensitive quenching response towards Cr^{VI} ($Cr_2O_7^{2-}$/CrO_4^{2-}) in aqueous solution, with a detection limit as low as 0.7 ppm for $Cr_2O_7^{2-}$, while 0.3 ppm for CrO_4^{2-}. Furthermore, this compound can also be easily and quickly regenerated, indicative of excellent recyclability.

Results and Discussion

Structural analysis

Single-crystal analysis reveals that **NUM-5** crystallizes in monoclinic system with space group *C2/c*. The asymmetric unit contains two Zn^{2+} cations (Zn1 and Zn2) in different coordination

---

[a] Z.-Q. Yao, G.-Y. Li, Dr. J. Xu, Prof. T.-L. Hu, Prof. X.-H. Bu
School of Materials Science and Engineering
National Institute for Advanced Materials
Tianjin Key Laboratory of Metal and Molecule-Based Material Chemistry
Nankai University
Tianjin 300350 (P. R. China)
E-mail: tlhu@nankai.edu.cn
buxh@nankai.edu.cn
[b] Prof. T.-L. Hu, Prof. X.-H. Bu
Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education)
Collaborative Innovation Center of Chemical Science and Engineering (Tianjin)
Tianjin 300071 (P. R. China)
[c] Prof. X.-H. Bu
College of Chemistry
Nankai University
Tianjin 300071 (P. R. China)
[†] These authors contributed equally.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.2017xxxxx.

environments, one bpanth ligand, three oba^{2-} ligands and two free DMF molecules (Figure S3). As shown in Figures 1a and 1b, Zn1 is octahedrally coordinated by six carboxylate oxygen atoms from six individual oba^{2-} ligands; Zn2 is five-coordinated by four oxygen atoms from three oba^{2-} ligands and one nitrogen atom from bpanth ligand, showing a tetragonal-pyramidal geometry. One Zn1 and two Zn2 ions form a unique tri-nuclear node as the secondary building unit (Figure 1c), $Zn_3O_{12}N_2$, which is further connected with six oba^{2-} ligands in different directions to generate a 3D network with 1D rhombic channels. In these channels, each Zn2 ion provides a coordination site to anchor bpanth ligand that has excellent luminescent property, generating a 3D framework with 1D triangular channels running along the *b* axis (Figure1e). We speculate that the specific bpanth ligands decorated with anthracene group in the channels play a role in the recognition process. In addition, PLATON analysis shows that the effective free volume of **NUM-5** is 34.6% of the crystal volume (2559.6 Å^3 out of the 7394.0 Å^3 unit cell volume) after squeezing DMF guest molecules.[42] From the topological viewpoint, when simplifying the tri-nuclear Zn as an 8-connected node (Figure 1d), the single 3D framework of **NUM-5** can then be viewed as an 8-connected ttd net with the point symbol of $\{4^{12}.5^8.6^7.7\}$ (Figure 1f).

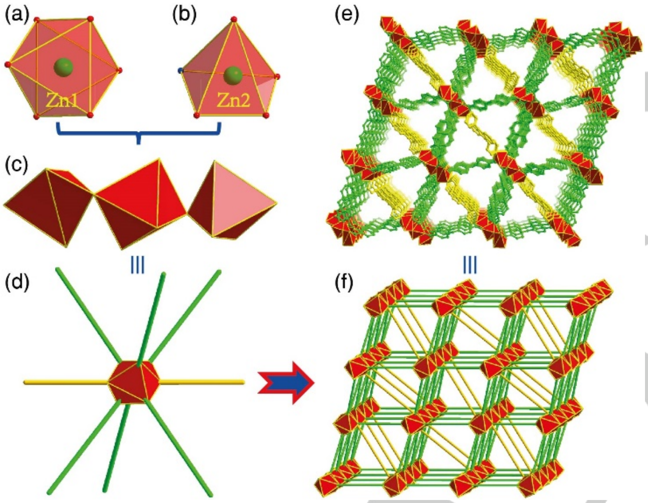


Figure 1. a)-b) Coordination environment of Zn^{2+} (Zn1 and Zn2) in **NUM-5**. c) Secondary building unit of tri-nuclear Zn_3 cluster. d) Tri-nuclear Zn_3 cluster viewed as an 8-connected node. e) Perspective view of 3D coordination framework of **NUM-5** along the *b*-axis (the bpanth ligands and oba^{2-} ligands are highlighted in yellow and green, respectively). f) ttd topology network of **NUM-5**.

Stability characterization of NUM-5

In order to inspect the thermal stability of **NUM-5**, thermogravimetric analysis (TGA) and powder X-ray diffraction (PXRD) were then carried out. The TGA analysis of the freshly prepared **NUM-5** reveals a weight loss of 12.4% from 87 to 200 ˚C, corresponding to the loss of free DMF molecules in channels (calculated value of 10.1%) and the framework was not collapsed until 350 ˚C (Figure S6). The PXRD pattern of the as-synthesized **NUM-5** matches well with the simulated result from single-crystal data, indicating the phase purity (Figure S5). On the other hand, in order to explore its solvent stability, we immersed the fresh sample of **NUM-5** in several common solvents (CH_3CN, EtOH, AcOEt, THF, H_2O, $CHCl_3$, MeOH, DMF, DMAC, acetone) for 24 h and found that all the PXRD patterns matched well with that of the as-synthesized sample, indicating that this compound has good resistance against a wide range of solvents (Figure 2a). More strikingly, **NUM-5** could maintain the single crystallinity in water for 1 week, even in pH =3 to pH = 11 aqueous solution for 1 day, as revealed by the PXRD patterns in Figure 2b. These results indicate that the sample is also intact in acid aqueous solutions. Evidently, such an excellent solvent stability of **NUM-5** makes it more feasible in practical applications.

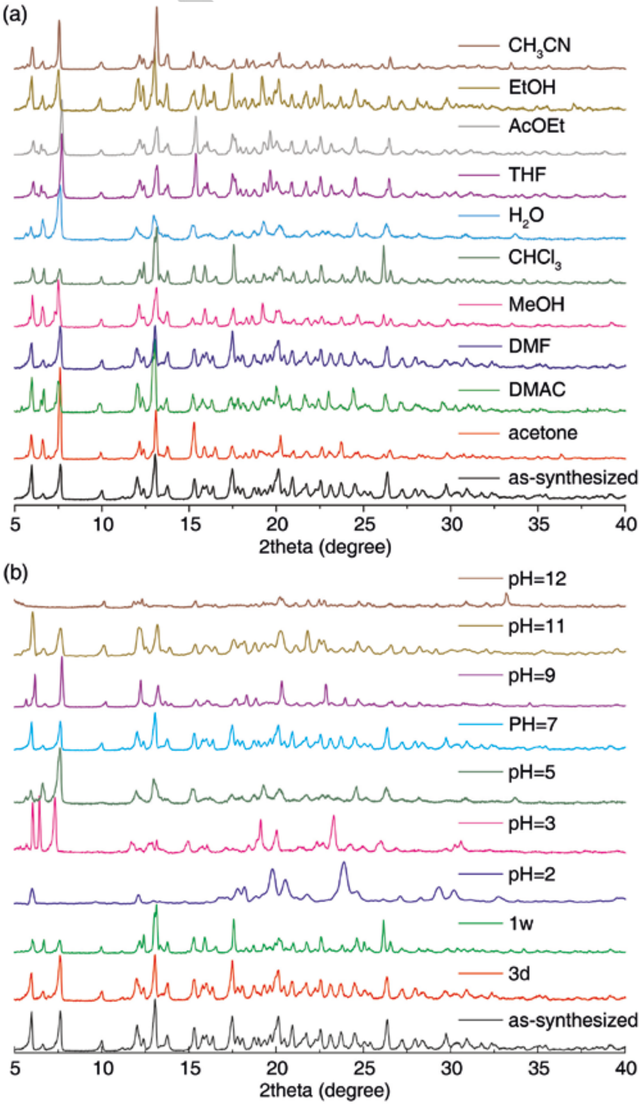


Figure 2. a) PXRD patterns of **NUM-5** immersed in different solvents for 24 h. b) PXRD patterns of **NUM-5** immersed in aqueous solutions (pH = 2-12) for 1 d and in water at pH = 7 for 3 days (red) and 1 week (green) at room temperature.

Luminescent properties and detection of Cr^{VI}

Next, we investigated the solid-state luminescent properties of **NUM-5** at room temperature. As shown in Figure S7, under UV light (365 nm) irradiation, **NUM-5** exhibits bright cyan light emission with the maximum around 460 nm, which red-shifts about 10 nm relative to that of the bpanth ligand. Thus, the luminescence of **NUM-5** should originate from intra-ligand emission and the observed slight emission shift is due to the interaction between the organic linkers and d^{10} metal ions.[17] Furthermore, **NUM-5** also exhibits much stronger emission compared to bpanth ligand in aqueous solution due to the better disperse efficiency (Figure S8). Considering the excellent luminescent property as well as the good stability in aqueous solution, employing **NUM-5** as a fluorescent sensor for detecting Cr^{VI} in aqueous solution seems to be feasible and promising.

In order to explore the sensing property of **NUM-5** towards Cr^{VI}, we separately added several sodium salt aqueous solutions (F^-, Cl^-, Br^-, I^-, OAc^-, NO_3^-, SO_4^{2-}, ClO_4^-, MoO_4^{2-}, WO_4^{2-}, CrO_4^{2-}, $Cr_2O_7^{2-}$) with the concentration of 2.5×10^{-3} mol L^{-1} to the aqueous suspension of **NUM-5**. As shown in Figure 3a, only the additions of CrO_4^{2-} and $Cr_2O_7^{2-}$ led to significant turn-off quenching with the quenching percentage being 98.3% and 99.3%, respectively. In contrast, the other anions displayed slight or no discernible effect under the same conditions. Beneficially, the fluorescence quenching of **NUM-5** in response to the presence of CrO_4^{2-} or $Cr_2O_7^{2}$ could be observed by the naked eyes under UV light (Figure 3b), even when the concentration of Cr^{VI} ($Cr_2O_7^{2-}$/CrO_4^{2-}) is as low as 1×10^{-5} mol L^{-1} (Figure S9). Thus, all these results suggest **NUM-5** to be a qualified fluorescent sensor highly selective to Cr^{VI} ($Cr_2O_7^{2-}$/CrO_4^{2-}) among other common anions.

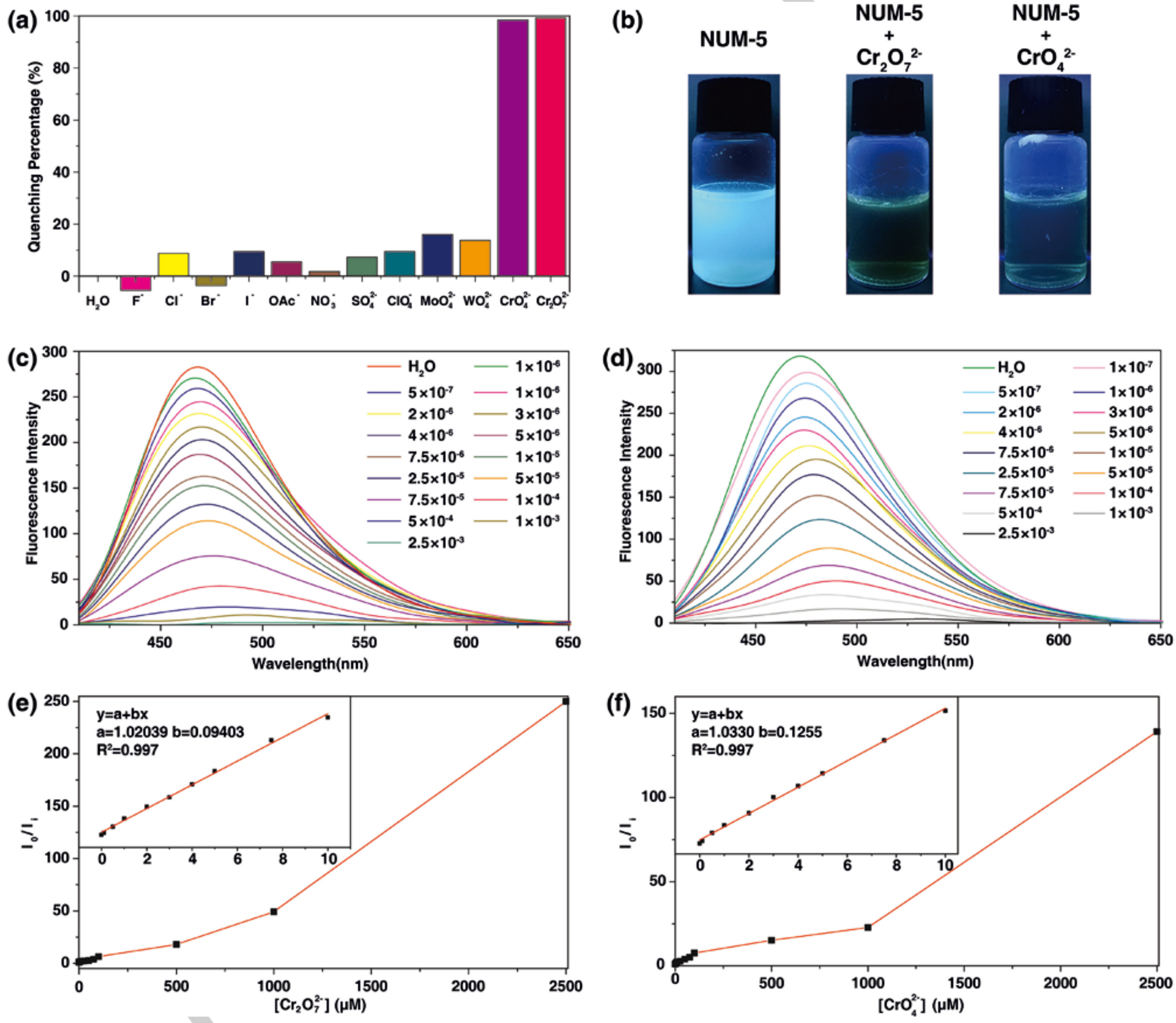


Figure 3. a) Anions (2.5×10^{-3} mol L^{-1}) selectivity of **NUM-5** in aqueous solution. b) Fluorescence color changes of **NUM-5** aqueous solution (3 mg/10 mL, 10 mL) before and after adding $Cr_2O_7^{2-}$ or CrO_4^{2-} (2.5×10^{-3} mol L^{-1}) under 365 nm UV light. c)-d) Fluorescence quenching effect of **NUM-5** towards different concentrations of $Cr_2O_7^{2-}$ or CrO_4^{2-} (0-2.5 mM) in aqueous solution (λ_{ex} = 390 nm). e)-f) Stern-Volmer plot of I_0/I vs. the concentration of $Cr_2O_7^{2-}$ or CrO_4^{2-} in **NUM-5** aqueous solution (Inset figure: enlarged view of a selected area).

We also carried out the titration experiments to further assess the sensing ability of **NUM-5** against Cr^{VI} ($Cr_2O_7^{2-}$/CrO_4^{2-}). As shown in Figures 3c and 3d, the emission intensity of **NUM-5** in aqueous solution gradually decreased with the increasing concentration of $Cr_2O_7^{2-}$ (or CrO_4^{2-}) from 0 to 2.5 × 10^{-3} mol L^{-1}. When the concentration of Cr^{VI} approached 2.5 × 10^{-3} mol L^{-1}, the fluorescence signal of **NUM-5** was almost completely quenched. The quenching degree can be quantitatively evaluated by $K_{sv.}$ (i.e., quenching effect constant) using the Stern-Volmer equation: $I_0/I = 1 + K_{sv}[G]$. Herein, I_0 and I are the fluorescence intensities of **NUM-5** before and after adding Cr^{VI} ($Cr_2O_7^{2-}$/CrO4^{2-}), while [G] represents the corresponding concentration. Figures 3e and 3f show that the ratio I_0/I increases in direct proportion to increasing concentration of either $Cr_2O_7^{2-}$ or CrO_4^{2-}, with the K_{sv} values calculated to be 9.4 × 10^4 M (R^2 = 0.997) and 1.24 × 10^5 M (R^2 = 0.997), respectively. In addition, the detection limits of $Cr_2O_7^{2-}$ and CrO_4^{2-} are about 0.7 ppm and 0.3 ppm, respectively (Figure S10), based on the well-established formula.[43] It is noteworthy that in the light of literatures, there have been only a small number of MOF-based fluorescent probes that can detect $Cr_2O_7^{2-}$ and CrO_4^{2-} ions simultaneously in aqueous solution,[45,47] compared to which **NUM-5** possesses the lowest detection limit that is very close to the standard established by WHO.[44-46] In conclusion, the above-demonstrated results strongly suggest that **NUM-5** qualifies as a chemosensor for Cr^{VI} ($Cr_2O_7^{2-}$/CrO_4^{2-}) in aqueous solution with high sensitivity.

However, chemosensors feasible in practical applications require not only high sensitivity and selectivity, but also good anti-interference ability, recyclability and response rate. For **NUM-5**, the fluorescence intensity was acutely quenched in the presence of CrO_4^{2-} or $Cr_2O_7^{2-}$, while no obvious change was observed when the competitive anions (F^-, Cl^-, Br^-, I^-, OAc^-, NO_3^-, SO_4^{2-}, ClO_4^-, MoO_4^{2-}, WO_4^{2-}) were added into the solution (Figures 4a and 4b). Furthermore, the quenching degree of **NUM-5** was almost not decreased during five consecutive cycles, for either CrO_4^{2-} or $Cr_2O_7^{2-}$(Figures 4c and 4d), and the PXRD patterns illustrate that the structure of **NUM-5** was well maintained (Figure S11). More strikingly, after adding Cr^{VI} ($Cr_2O_7^{2-}$/CrO_4^{2-}) ions (2.5 × 10^{-3} mol L^{-1}), the fluorescence intensity of **NUM-5** quenched immediately and reached to minimum in 30s, which indicates the fast response rate (Figure S12). Consequently, these results support that **NUM-5** has good anti-interference ability, recyclability and fast response rate, thus promising for sensing Cr^{VI} anions in real environments.

Mechanism for sensing Cr^{VI}

In order to explore the possible mechanism of the fluorescent quenching of **NUM-5** induced by Cr^{VI} ($Cr_2O_7^{2-}$/CrO_4^{2-}), PXRD experiments were first carried out. The patterns in Figure S11 confirmed that the sample of **NUM-5** maintained the crystallinity after titration and cyclic experiments. Hence, the fluorescence

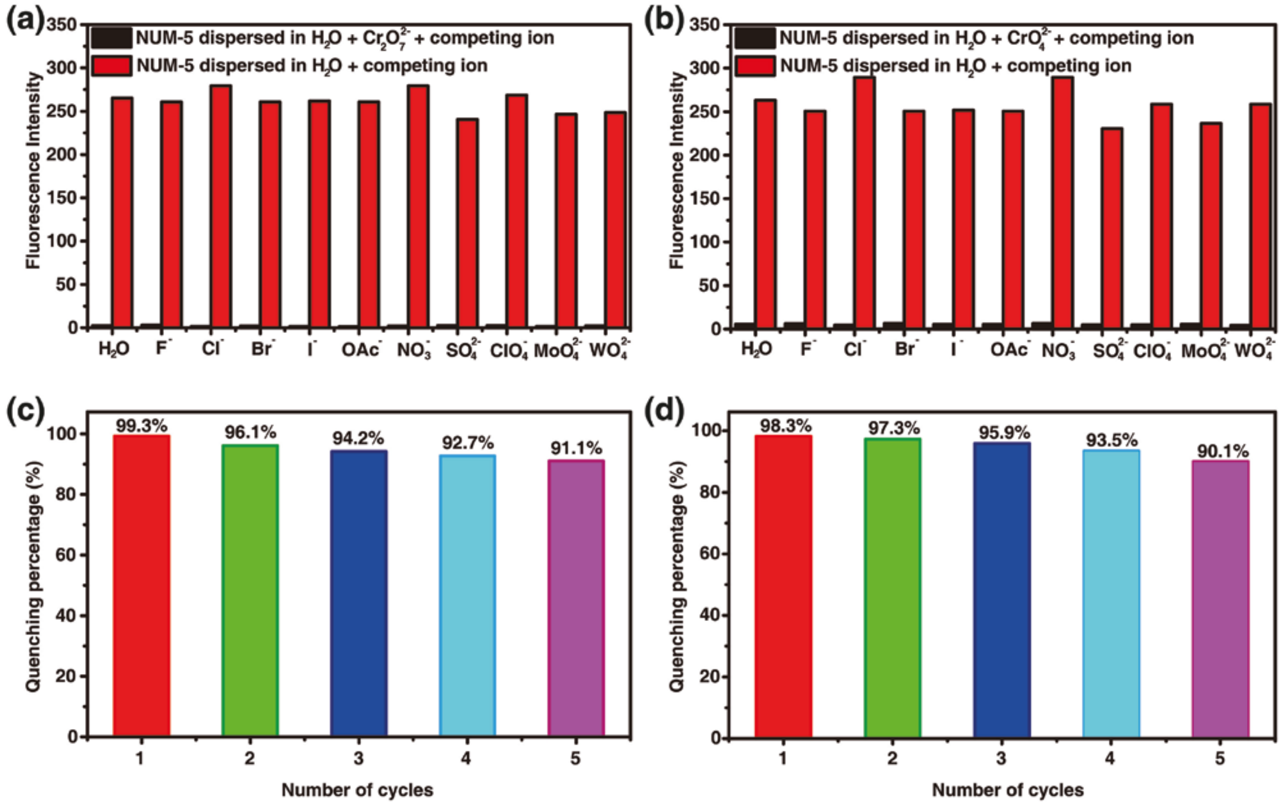


Figure 4. a)-b) Fluorescence spectra of **NUM-5** dispersed in aqueous solutions upon addition of 1 × 10^{-2} mol L^{-1} selected anions (red) and subsequent addition of $Cr_2O_7^{2-}$ or CrO_4^{2-} ion (black). c)-d) Recyclability of **NUM-5** for $Cr_2O_7^{2-}$ or CrO_4^{2-} detection in aqueous solution.

intensity reduction was not due to the decomposition of crystalline structures.[41] Then, we examined the filtrate of **NUM-5** with Cr^{VI} ($Cr_2O_7^{2-}$/CrO_4^{2-}) in titration experiments by ICP analysis and solid-state fluorescence spectra measurement. The results show that only a little amount of $Cr_2O_7^{2-}$ (CrO_4^{2-}) ions in solution can be immobilized into the channels of **NUM-5** (Table S3) and this part of Cr^{VI} ($Cr_2O_7^{2-}$/CrO_4^{2-}) has little quenching effect to the fluorescence intensity of **NUM-5** (Figure S13). Therefore, in this system, the adsorption amount of target anions is also not the determining factor for the observed fluorescence quenching behavior.[48] The luminescence lifetimes of **NUM-5** before and after being immersed in Cr^{VI} ($Cr_2O_7^{2-}$/CrO_4^{2-}) aqueous solutions are same, which indicated that there was no coordination effect between Cr^{VI} ions and **NUM-5** (Figure S14). Notably, as shown by Figure S15, the UV/Vis absorption bands of **NUM-5** and Cr^{VI} anions ($Cr_2O_7^{2-}$/CrO_4^{2-}) strongly overlapped, far exceeding other tested anions. Thus, the Cr^{VI} ($Cr_2O_7^{2-}$/CrO_4^{2-}) ions in aqueous solution compete and hinder the absorption of excitation energy, accounting for the selective fluorescence quenching response of **NUM-5**.[49,50] Apart from this, it is evident that the broad absorption bands of Cr^{VI} ($Cr_2O_7^{2-}$/CrO_4^{2-}) from 250 to 525 nm also cover a large part of the emission band of **NUM-5** (400-650 nm), while in the same wavelength range no overlap between the emission band of **NUM-5** and the absorption bands of other anions was observed (Figure S16). Thus, the resonance energy transfer from the MOF (**NUM-5)** to the analyte (Cr^{VI}) might take place and lead to the fluorescence quenching.[45] Based on these pieces of evidence, we suggest that both competitive absorption and resonance energy transfer are responsible for the fluorescence quenching response of **NUM-5** to Cr^{VI} anions (Figure 5), as reported in other previous studies.[40,50,51]

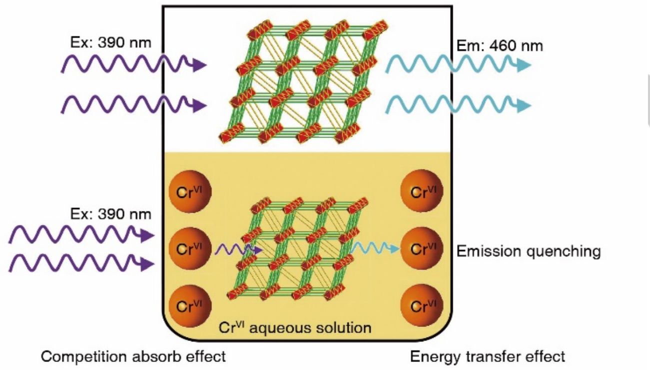


Figure 5. The possible quenching mechanism for detecting Cr^{VI} by **NUM-5**.

Conclusions

In summary, a new luminescent Zn(II)-MOF (**NUM-5**) based on anthracene-contained ligand has been rationally constructed. The results of fluorescence titration, anti-interference, and cyclic experiments indicate that this compound can be used as an excellent probe for sensing Cr^{VI} ($Cr_2O_7^{2-}$/CrO_4^{2-}) in aqueous solution with high sensitivity, selectivity and anti-interference ability. Moreover, **NUM-5** can be simply regenerated, indicating its excellent recyclability. Further detailed analyses reveal that the fluorescence quenching response of **NUM-5** actually originates from the synergistic effect of competitive absorption and resonance energy transfer from MOF to Cr^{VI}. Notably, the detection limits of **NUM-5** for sensing Cr^{VI} can reach 0.7 and 0.3 ppm, for $Cr_2O_7^{2-}$ and CrO_4^{2-}, respectively. All the results suggest that **NUM-5**, as an efficient fluorescent probe, holds promise in the practical application for sensing Cr^{VI} ($Cr_2O_7^{2-}$/CrO_4^{2-}) in aqueous solution.

Experimental Section

Materials and Methods: All the reagents and solvents for the synthesis were purchased from commercial sources and used as received, except for 9,10-bis(4-pyridyl)anthracene ligand, which was synthesized by using a previous procedure.[52] All solvents were analytical grade and without further purification. ^{1}H NMR spectrum was recorded on a Mercury Vx-300 spectrometer at 300 MHz in $CDCl_3$. Mass spectrum was tested on an Agilent 6520 Q-TOF LC/MS in CH_2Cl_2. Elemental analysis (C, H and N) was performed on a vario EL CUBE. IR spectrum was measured on a FTS6000 (Bio-rad) FT-IR spectrometer using KBr pellets in the 4000-400 cm^{-1} range. Thermogravimetric analysis (TGA) was carried out on a Rigaku standard TG-DTA analyzer with a heating rate of 10 ˚C·min^{-1}, with an empty Al_2O_3 crucible used as a reference. The room-temperature powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku D/Max-2500 diffractometer at 60 kV, 300 mA with a Cu-target tube and a graphite monochromator. All fluorescent measurements were performed on a Varian Cary Eclipse fluorescence spectrometer equipped with a plotter unit.

Crystal Structure Determination: X-ray single-crystal diffraction data for **NUM-5** was collected on a Rigaku SCX-mini diffractometer at 293(2) K with Mo-Ka radiation (λ = 0.71073 Å) in ω scan mode. The program SAINT[53] was used for the integration of the diffraction profiles. All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL (semiempirical absorption corrections were applied using the SADABS program).[54] Metal atoms were located from the E-maps and other non-hydrogen atoms were located from the successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. Hydrogen atoms of the ligands were generated theoretically on the specific atoms and refined isotropically with fixed thermal factors. Hydrogen atoms of the DMF molecules were added by difference Fourier maps and refined with constraints. Detailed crystallographic data is summarized in Table S1. The selected bond lengths and angles are given in Table S2. CCDC 1482730 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Synthesis of Bpanth Ligand:[52,55-56] 9,10-Dibromoanthracene (2.00 g, 5.95 mmol), 4-pyridylboronic acid (2.40 g, 17.80 mmol), and K_2CO_3 (11.60 g, 35.50 mmol) were added to a mixture of dry PhMe/DMF (300 mL, v:v = 1:1), which had been degassed with Ar for 15 min. Next, $Pd(PPh_3)_4$ (0.68 g, 0.59 mmol) was added to the reaction mixture and the solution was heated to 130 ˚C under Ar for 48 h. Then, the reaction mixture was cooled to room temperature and the palladium catalyst was filtered off using Celite. The organic phase was concentrated under vacuum and then dissolved in CH_2Cl_2 followed by extracting with H_2O three times. Concentrated HCl was added dropwise (pH = 2-3) to the organic layer, which caused the desired product to precipitate from solution. The precipitate was collected by filtration and then dissolved in H_2O. Finally, NaOH (aq., 10 M) was added dropwise to the water layer until the pH was ~ 8-9, which resulted in precipitation of pure product. Yield: 1.4g (70%). Data for bpanth: MS: *m/z* (%): 333.1387 $[M+H]^+$ ^{1}H NMR (300MHz, $CDCl_3$): δ=8.87 (d, *J*=6.0 Hz, 4H; ArH), 7.61 (m, 4H, ArH), 7.44 (d, *J*=6.0 Hz,4H;ArH), 7.40 ppm (m, 4H, ArH). MS and ^{1}H NMR spectra of bpanth were shown in Figure S1 and Figure S2, respectively.

Synthesis of NUM-5: $Zn(NO_3)_2{\cdot}6H_2O$ (30.00 mg, 0.10 mmol), bpanth (16.60 mg, 0.05 mmol), and 4,4'-oxybis(benzoic acid) (H_2oba) (16.60 mg, 0.10 mmol) were dissolved in 3 mL N,N'-dimethylformamide (DMF), and stirred for 30 min. The resulting solution was then sealed, and heated to 100 ˚C and kept for 3d. After cooling down to room temperature, orange chrysanthemum petal-shaped crystals were obtained (yield ca. 53.8 %, based on bpanth). EA Calcd (%) for $C_{72}H_{54}Zn_3N_4O_{17}$: C 59.12, H 3.77, N 3.88; Found: C 58.83, H 3.68, N 3.68. FT-IR (cm^{-1}, KBr): 3321w, 3065s, 2932s, 1923m, 1662s, 1606vs, 1562vs, 1500s, 1409vs, 1302m, 1163vs, 1099s, 1017m, 877vs, 777vs, 701m, 658s, 532m.

Fluorescence Titration Experiments: Fluorescence titrations were performed on a Varian Cary Eclipse fluorescence spectrometer using a 1 cm path length quartz fluorescence cell. Titrations were carried out by placing the aqueous suspensions of **NUM-5** (3 mg/10 mL) into the 4 mL cuvette and adding increasing amounts of Cr^{VI} ($Cr_2O_7^{2-}$ or CrO_4^{2-}) (0-2.5 × 10^{-3} mol L^{-1}) using a microsyringe. The aqueous suspensions of **NUM-5** was excited at 390 nm, and the emission spectra were recorded in the range 400-650 nm. After each addition, an equilibration time of 8-10 min was allowed before the fluorescence intensity was recorded. Statistical analysis of the data was carried out using Origin 8.0.

Acknowledgements

This work was financially supported by the NSFC (21371102, 21531005, 21673120 and 21771113), and the NSF of Tianjin (16JCZDJC36900 and 15JCZDJC38800).

Keywords: Luminescent metal-organic-framework • water-phase stability • chemosensor • water system • hexavalent chromium

[1] A. Levina, P. A. Lay, *Coord. Chem. Rev.* **2005**, *249*, 281-298.
[2] M. Reynolds, L. Stoddard, I. Bespalov, A. Zhitkovich, *Nucleic Acids Res.* **2007**, *35*, 465-476.
[3] A. Zhitkovich, *Chem. Res. Toxicol.* **2005**, *18*, 3-11.
[4] P. K. Lee, S. Yu, H. J. Chang, H. Y. Cho, M. J. Kang, B. G. Chae, *Sci. Rep.* **2016**, *6*, 36088.
[5] Y. Zhang, Q. Wang, J. N. Lu, Q. Wang, Y. Q. Cong, *Chemosphere* **2016**, *162*, 55-63.
[6] A. V. Desai, B. Manna, A. Karmakar, A. Sahu, S. K. Ghosh, *Angew. Chem. Int. Ed.* **2016**, *55*, 7811-7815.
[7] U. Araujo-Barbosa, E. Peña-Vazquez, M. C. Barciela-Alonso, S. L. C. Ferreira, A. M. P. dos Santos, P. Bermejo-Barrera, *Talanta* **2017**, *170*, 523-529.
[8] T. J. Jiang, M. Yang, S. S. Li, M. J. Ma, N. J. Zhao, Z. Guo, J. H. Liu, X. J. Huang, *Anal. Chem.* **2017**, *89*, 5557-5564.
[9] X. J. Gong, Y. Liu, Z. H. Yang, S. M. Shuang, Z. Y. Zhang, C. Dong, *Anal. Chim. Acta* **2017**, *968*, 85-96.
[10] P. J. Li, Y. Y. Hong, H. T. Feng, S. F. Y. Li, *J. Mater. Chem. B* **2017**, *5*, 2979-2988.
[11] L. J. Zhu, X. Peng, H. T. Li, Y. Y. Zhang, S. Z. Yao, *Sensor. Actuat. B*, **2017**, *238*, 196-203.
[12] B. B. Campos, M. Algarra, B. Alonso, C. M. Casado, J. Jiménez-Jiménez, E. Rodríguez-Castellón, J. C. G. E. da Silva, *Talanta* **2015**, *144*, 862-867.
[13] M. Zheng, Z. G. Xie, D. Qu, D. Li, P. Du, X. B. Jing, Z. C. Sun, *ACS Appl. Mater. Inter.* **2013**, *5*, 13242-13247.
[14] M. A. Shenashen, A. Shahat, S. A. El-Safty, *J. Hazard. Mater.* **2013**, *244-245*, 726-735.
[15] M. C. So, G. P. Wiederrecht, J. E. Mondloch, J. T. Hupp, O. K. Farha, *Chem. Commun.*, **2015**, *51*, 3501-3510.
[16] M. D. Allendorf, C. A. Bauer, R. K. Bhaktaa, R. J. T. Houk, *Chem. Soc. Rev.*, **2009**, *38*, 1330-1352.
[17] Z. C. Hu, B. J. Deibert, J. Li, *Chem. Soc. Rev.* **2014**, *43*, 5815-5840.
[18] Z. Hu, W. P. Lustig, J. Zhang, C. Zheng, H. Wang, S. J. Teat, Q. Gong, N. D. Rudd, J. Li, *J. Am. Chem. Soc.* **2015**, *137*, 16209-16215.
[19] L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne, J. T. Hupp, *Chem. Rev.* **2012**, *112*, 1105-1125.
[20] Q. Zhang, J. Su, D. Feng, Z. Wei, X. Zou, H. C. Zhou, *J. Am. Chem. Soc.* **2015**, *137*, 10064-10067.
[21] Z. Wei, Z. Y. Gu, R. K. Arvapally, Y. P. Chen, R. N. McDougald, J. F. Ivy, A. A. Yakovenko, D. Feng, M. A. Omary, H. C. Zhou, *J. Am. Chem. Soc.* **2014**, *136*, 8269-8276.
[22] Y. B. He, W. Zhou, G. D. Qian, B. Chen, *Chem. Soc. Rev.* **2014**, *43*, 5657-5678.
[23] W. P. Lustig, S. Mukherjee, N. D. Rudd, A. V. Desai, J. Li, S. K. Ghosh, *Chem. Soc. Rev.* **2017**, *46*, 3242-3285.
[24] W. Cho, H. J. Lee, G. Choi, S. Choi, M. Oh, *J. Am. Chem. Soc.* **2014**, *136*, 12201-12204.
[25] B. Wang, X. L. Lv, D. W. Feng, L. H. Xie, J. Zhang, M. Li, Y. B. Xie, J. R. Li, H. C. Zhou, *J. Am. Chem. Soc.* **2016**, *138*, 6204-6216.
[26] J. Yang, Y. Dai, X. Y. Zhu, Z. Wang, Y. S. Li, Q. X. Zhuang, J. L. Shi, J. L. Gu, *J. Mater. Chem. A* **2015**, *3*, 7445-7452.
[27] J. H. Wang, M. Li, D. Li, *Chem. Sci.* **2013**, *4*, 1793-1801.
[28] S. Y. Zhang, W. Shi, P. Cheng, M. J. Zaworotko, *J. Am. Chem. Soc.* **2015**, *137*, 12203-12206.
[29] Y. Fang, W. Liu, S. J. Teat, G. Dey, Z. Shen, L. An, D. Yu, L. Wang, D. M. O'Carroll, J. Li, *Adv. Funct. Mater.* **2017**, *27*, 1603444.
[30] Y. J. Cui, T. Song, J. C. Yu, Y. Yang, Z. Y. Wang, G. D. Qian, *Adv. Funct. Mater.* **2015**, *25*, 4796-4802.
[31] Z. S. Dou, J. C. Yu, Y. J. Cui, Y. Yang, Z. Y. Wang, D. R. Yang, G. D. Qian, *J. Am. Chem. Soc.* **2014**, *136*, 5527-5530.
[32] W. X. Ni, M. Li, J. Zheng, S. Z. Zhan, Y. M. Qiu, S. W. Ng, D. Li, *Angew. Chem. Int. Ed.* 2013, 52, 13472-13476.
[33] J. Zhang, D. Jia, M. G. Humphrey, S. Meng, M. J. Zaworotko, M. P. Cifuentesb, C. Zhang, *Chem. Commun.* **2016**, *52*, 3797-3800.
[34] M. Usman, S. Mendiratta, S. Batjargal, G. Haider, M. Hayashi, N. R. Gade, J. W. Chen, Y. F. Chen, K. L. Lu, *ACS Appl. Mater. Inter.* **2015**, *7*, 22767-22774.
[35] P. Deria, J. Yu, T. Smith, R. P. Balaraman, *J. Am. Chem. Soc.* **2017**, *139*, 5973-5983.
[36] V. Stavila, A. A. Talin, M. D. Allendorf, *Chem. Soc. Rev.* **2014**, *43*, 5994-6010.
[37] Y. X. Guo, X. Feng, T. Y. Han, S. Wang, Z. G. Lin, Y. P. Dong, B. Wang, *J. Am. Chem. Soc.* **2014**, *136*, 15485-15488.
[38] G. F. Ji, J. J. Liu, X. C. Gao, W. Sun, J. Z. Wang, S. L. Zhao, Z. L. Liu, *J. Mater. Chem. A* **2017**, *5*, 10200-10205.
[39] Q. Zhang, J. C. Yu, J. F. Cai, L. Zhang, Y. J. Cui, Y. Yang, B. Chen, G. D. Qian, *Chem. Commun.* **2015**, *51*, 14732-14734.
[40] F. Y. Yi, J. P. Li, D. Wu, Z. M. Sun, *Chem. Eur. J.* **2015**, *21*, 11475-11482.
[41] W. Liu, X. Huang, C. Xu, C. Y. Chen, L. Z. Yang, W. Dou, W. M. Chen, H. Yang, W. S. Liu, *Chem. Eur. J.* **2016**, *22*, 18769-18776.
[42] A. L. Spek, *J. Appl. Cryst.* **2003**, *36*, 7-13.

[43] P. Y. Wu, Y. H. Liu, Y. Liu, J. R. Wang, Y. Li, W. Liu, J. Wang, *Inorg. Chem.* **2015**, *54*, 11046-11048.

[44] W. Liu, Y. L. Wang, Z. L. Bai, Y. X. Li, Y. X. Wang, L. H. Chen, L. Xu, J. Diwu, Z. F. Chai, S. Wang, *ACS Appl. Mater. Inter.* **2017**, *9*, 16448-16457.

[45] S. G. Chen, Z. Z. Shi, L. Qin, H. L. Jia, H. G. Zheng, *Cryst. Growth Des.* **2017**, *17*, 67-72.

[46] R. C. Gao, F. S. Guo, N. N. Bai, Y. L. Wu, F. Yang, J. Y. Liang, Z. J. Li, Y. Y. Wang, *Inorg. Chem.* **2016**, *55*, 11323-11330.

[47] C. S. Cao, H. C. Hu, H. Xu, W. Z. Qiao, B. Zhao, *CrystEngComm* **2016**, *18*, 4445-4451.

[48] X. L. Zhao, D. Tian, Q. Gao, H. W. Sun, J. Xu, X. H. Bu, *Dalton Trans.* **2016**, *45*, 1040-1046.

[49] J. L. Chen, F. Y. Yi, H. Yu, S. H. Jiao, G. S. Pang, Z. M. Sun, *Chem. Commun.* **2014**, *50*, 10506-10509.

[50] Y. Li, H. Song, Q. Chen, K. Liu, F. Y. Zhao, W. J. Ruan, Z. Chang, *J. Mater. Chem. A* **2014**, *2*, 9469-9473.

[51] W. Sun, J. Wang, G. Zhang, Z. Liu, *RSC Adv.* **2014**, *4*, 55252-55255.

[52] X. J. Cui, A. N. Khlobystov, X. Y. Chen, D. H. Marsh, A. J. Blake, W. Lewis, N. R. Champness, C. J. Roberts, M. Schröder, *Chem. Eur. J.* **2009**, *15*, 8861-8873.

[53] Bruker AXS, *SAINT Software Reference Manual*, Madison, WI, **1998**.

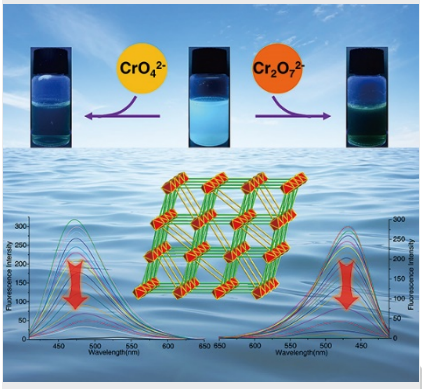
[54] G. M. Sheldrick, *SHELXTL NT Version 5.1. Program for Solution and Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, **1997**.

[55] G. Marin, M. Andruh, A. M. Madalan, A. J. Blake, C. Wilson, N. R. Champness, M. Schröder, *Cryst. Growth. Des.* **2008**, *8*, 964-975.

[56] J. C. Barnes, M. Juríček, N. L. Strutt, M. Frasconi, S. Sampath, M. A. Giesener, P. L. McGrier, C. J. Bruns, C. L. Stern, A. A. Sarjeant, J. F. Stoddart, *J. Am. Chem. Soc.* **2013**, *135*, 183-192.

FULL PAPER

A novel luminescent Zn(II)-MOF, (**NUM-5**) has been successfully assembled and investigated as a regenerable luminescent sensor with excellent sensitivity, selectivity and fast luminescence quenching response to Cr^{VI}-anions in aqueous solution. The experiments exhibit **NUM-5** can be a great candidate for quantitatively detecting Cr^{VI}-anions in aqueous solution.



Zhao-Quan Yao,† Guang-Yu Li,† Jian Xu, Tong-Liang Hu, and Xian-He Bu**

Page No. – Page No.

A Water-Stable Luminescent Zn(II) Metal-Organic Framework as Chemosensor for High-Efficiency Detection of Cr^{VI}-Anions ($Cr_2O_7^{2-}$ and CrO_4^{2-}) in Aqueous Solution