



Journal of Coordination Chemistry

ISSN: 0095-8972 (Print) 1029-0389 (Online) Journal homepage: http://www.tandfonline.com/loi/gcoo20

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To cite this article: Yu Wu, Yun Huang, Yulan Wang, Xiang Zou, Jun Wang & Weiping Wu (2018): A regenerable zinc(II) coordination polymer as a dual-luminescent sensor for detection of $Cr_2O_7^{2-}$ and 2,4,6-trinitrophenol in aqueous phase, Journal of Coordination Chemistry, DOI: 10.1080/00958972.2018.1536784

To link to this article: https://doi.org/10.1080/00958972.2018.1536784



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Accepted author version posted online: 16 Oct 2018.



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A regenerable zinc(II) coordination polymer as a dual-luminescent sensor for detection of $\text{Cr}_2\text{O}_7^{2-}$ and 2,4,6-trinitrophenol in aqueous phase

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Developing a fast and sensitive method for the detection of 2,4,6-trinitrophenol (TNP) or $Cr_2O_7^{2-}$ in aqueous solution has received great attention. In this work, a regenerable fluorescent coordination polymer, $[Zn(L)(H_2L)]_n$ (1), has been constructed using a novel Schiff base ligand, N'-[(E)-(3,5-dibromo-2-hydroxyphenyl)methylene]isonicotinohydrazide (H₂L), and exploited as a dual detection probe for the selective sensing of $Cr_2O_7^{2-}$ and TNP in water media. Competitive fluorometric experiments involving mixtures of anions or nitro compounds demonstrated 1 as an efficient and selective sensor for both $Cr_2O_7^{2-}$ and TNP. The limits of detection for $Cr_2O_7^{2-}$ and 2,4,6-trinitrophenol in aqueous solutions were 11.4 and 1.19 µM, respectively. Moreover, 1 can detect TNP and $Cr_2O_7^{2-}$ in real water samples. All these features clearly demonstrate its great potential of practical TNP and $Cr_2O_7^{2-}$ detection in water media for public safety and security.

Keywords: Fluorescence sensing; Coordination polymer; 2,4,6-Trinitrophenol; Nicotinoylhydrazone complex

1. Introduction

With the acceleration of industrialization, huge volumes of effluents containing high concentrations of harmful ions and toxic organic pollutants have been discharged into bodies of water. Therefore, water contamination and environmental protection have become a global environmental issue [1-3]. Nitroaromatic compounds (NACs) not only as hazardous substances pose serious threats to homeland security but also as pollutants have an impact on environmental

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protection; thus, rapid and sensitive detection of nitroaromatic compounds has been of intense interest over the past few years [4-6]. Detection of $Cr_2O_7^{2-}$ ion is of vital importance because it can accumulate in living organisms and cause serious damage, such as cancer, deformity, and gene mutation to the human health [7]. The U.S. Environmental Protection Agency (EPA) has listed $Cr_2O_7^{2-}$ as one kind of priority pollutants in the USA [8]. On the other hand, rapid and selective detection of NACs such as 2,4,6-trinitrophenol (TNP) has also become a challenging issue in recent times, considering their serious threat towards water pollution and homeland security. TNP is not only a strong explosive but also used extensively in dyes, fireworks, and the pharmaceutical and leather industries [9, 10].

Coordination polymers (CPs) are an emerging class of promising materials constructed by the assembly of metal ions/clusters and organic ligands to generate multidimensional frameworks [11]. CPs in association with other important fluorescent sensors have undergone overwhelming development not only for their fascinating structures or topological networks but also for diverse applications in the areas of heterogeneous catalysis, gas storage, gas separation, drug delivery, and molecular sensing [12-17]. Currently, some sophisticated instrumental techniques such as gas chromatography and spectrophotometry could be used to detect $Cr_2O_7^{2-}/NACs$ accurately but unfortunately with a number of critical drawbacks such as time consumption, high cost, and requiring complex equipment and trained personnel [18-20]. Comparatively, based on the electron-deficient characteristic of NACs and the photoinduced electron transfer (PET) quenching mechanism, lanthanide and d¹⁰ metal node-based luminescent coordination polymers (LCPs) have been designed as efficient fluorescent chemosensors for the detection of NACs in the vapor/liquid phase with good sensitivity and ease of operation [21-28]. A few studies have also involved the sensing and detection of $Cr_2O_7^{2-}$ [29-31]. However, aqueous-phase detection of $Cr_2O_7^{2-}/TNP$ by LCPs is relatively limited in the literature, perhaps because of the chemical instability of LCPs in the respective analyte solutions [32-34]. In furtherance of our successive quest to devise new LCP sensor materials [35, 36], we here report a regenerable hydrazone-based Zn(II) coordination polymer as a dual detection fluorescent sensor

for selective and sensitive detection of $Cr_2O_7^{2-}$ as well as TNP. Thus, a novel one-dimensional coordination polymer, $[Zn(L)(H_2L)]_n$ (1), with excellent thermal and aqueous chemical stability has been synthesized and fully characterized. The intrinsic luminescence properties of this hydrazone-based LCP have been exploited for selective sensing of $Cr_2O_7^{2-}$ and TNP ignoring interferences from among a variety of anions and NACs, respectively. Furthermore, LCP 1 has been successfully applied to detect $Cr_2O_7^{2-}$ and TNP in environmental water samples.

2. Experimental

2.1. Materials and methods

Most reagent-grade starting materials, salicylaldehyde (98%), hydrobromic acid (40%), isonicotinic acid hydrazide (98%), zinc nitrate hexahydrate (99%), were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD and used without purification. All solvents were purchased from Chongqing Chuandong Chemical Co., LTD. Elemental analyses were obtained with an Elementar Vario EL cube analyzer. Powder X-ray diffraction (PXRD) measurements were collected on a Bruker AVANCE X-ray diffractometer with Cu-K α radiation ($\lambda = 1.5418$ Å) at 50 kV, 20 mA with a scanning rate of 5°/min and a step size of 0.02°. Fourier transform infrared (FT-IR) spectra were measured on KBr pellets using a Nicolet Impact 750 FTIR spectrometer from 400–4000 cm⁻¹. Thermogravimetric analysis was performed with an STA 409PC Luxx Netzsch instrument under N₂ atmosphere from room temperature to 950 °C at a heating rate of 10 °C/min. Photoluminescence (PL) spectra were recorded at room temperature utilizing an RF-5301PC spectrofluorophotometer. UV–vis spectra were obtained from a Shimadzu UV-2501PC UV-Vis recording spectrophotometer.

2.2. X-ray crystallography

The single crystal X-ray diffraction data were collected on a Bruker SMART APEX diffractometer that was equipped with graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å) by using an ω -scan technique. Data reduction included absorption corrections by the multiscan

method using SADABS [37]. The structure was solved and refined with SHELXTL package [38]. All hydrogens were generated geometrically and refined isotropically using the riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic details for **1** are listed in table 1, while selected bond dimensions for **1** are listed in table S1. CCDC number: 1835430.

2.3. Syntheses

2.3.1. Synthesis of N'-[(E)-(3,5-dibromo-2-hydroxyphenyl)methylene]isonicotinohydrazide (H_2L). An ethanol solution (30 mL) of 3,5-dibromosalicylaldehyde (10 mmol) and one drop of acetic acid were added with stirring to an ethanol solution (30 mL) of isonicotinic acid hydrazide (10 mmol). After stirring under reflux for 2 h, a yellow precipitate of H_2L was isolated by filtration and washed with ethanol and ether twice (scheme 1). ¹H NMR (600 MHz, DMSO-d₆): 12.78 (s, 1H, OH); 12.53 (s, 1H, NH, amide); 8.83 (s, 2H, aromatic); 8.57(s, 1H, -N=CH–, azomethine); 7.87–7.80 (m, 4H, aromatic). ¹³C NMR (150 MHz, DMSO-d₆): 165.4 (C=O), 160.3 (C-OH), 150.5 (C=N, pyridine), 146.7 (C=N, azomethine), 138.1, 131.2, 123.4, 122.6, 116.7, 113.5. IR (cm⁻¹): 3425(m), 3231(m), 1650(vs), 1514(m), 1341(m), 1237(v), 1176(v), 922(m), 810(m). Elemental analysis: C, 39.13; H, 2.27; N, 10.53. Found: C, 39.48; H, 2.14; N, 10.37.



Scheme 1. Synthesis scheme of 1.

2.3.2. Synthesis of $[Zn(L)(H_2L)]_n$ (1). A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.0297 g, 0.1 mmol), H_2L (0.0399 g, 0.1 mmol), DMF (3 mL) and methanol (3 mL) was stirred for 30 min in air. The resulting solution was placed in a Teflon-lined stainless steel vessel (25 ml) and heated to 105 °C

for 72 h. The solution was then cooled to room temperature at a rate of 5 °C h⁻¹. Yellow block crystals of **1**, {N'-[(E)-(3,5-dibromo-2-hydroxyphenyl)methylene]isonicotinohydrazide- κN } {N'-[(E)-(3,5-dibromo-2-hydroxyphenyl)methylene]isonicotinohydrazide- $\kappa^{3}O$,N,O'}-zinc(II) were obtained (yield 41% based on Zn). IR (cm⁻¹): 3437(vs); 1662(vs); 1597(vs); 1512(v); 1440(v); 1217(m); 1152(v); 1053(m); 857(m); 699(m). Elemental analysis: C, 36.21; H, 1.86; N, 9.75. Found: C, 36.56; H, 1.89; N, 9.50.

2.4. Sensing method

For the detection of $Cr_2O_7^{2-}$ and TNP, fluorimetric experiments were performed with 1 dispersed in aqueous solutions of sodium salts $(1 \times 10^{-2} \text{ M})$ or NACs $(1 \times 10^{-3} \text{ M})$. For detection and sensing studies, sixteen kinds of NaX (X = $CO_3^{2^-}$, NO_3^{-} , NO_2^{-} , F^- , $PO_4^{3^-}$, Ac^- , Cl^- , Br^- , $C_2O_4^{2^-}$, $SO_3^{2^-}$, I^- , WO_4^{2-} , SO_4^{2-} , HCO_3^{2-} , MnO_4^{-} and $Cr_2O_7^{2-}$) and different NACs, 4-nitrotoluene (4-NT), (2,4-DNT), 2,6-dinitrotoluene 2-nitrotoluene 2.4-dinitrotoluene (2,6-DNT), (2-NT), 1,3-dinitrobenzene (1,3-DNB) and TNP, were chosen. Before detection, 3 mg of 1 was finely ground and then added to a screw capped vial containing 3 mL of an aqueous solution of anions/nitroaromatics. The suspension was then ultrasonically agitated for 30 min and used for tests immediately. The luminescence quenching of each sample was recorded in the range of 400-650 nm upon excitation at 355 nm, and the fluorescence intensity at 476 nm was monitored. All of the titrations were repeated 3 times to get an average value of the detection results. The quenching efficiency was calculated as $[(I_0-I)/I_0] \times 100\%$, where I_0 and I are the fluorescence intensities before and after interaction with specific analyte.

3. Results and discussion

3.1. Crystal structure of $[Zn(L)(H_2L)]_n(1)$

Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the monoclinic crystal system with the $P2_1/c$ space group and features a one-dimensional chain structure. The results of crystallographic analysis revealed that the asymmetric unit of **1** contains two independent Zn(II)

ions (Zn1, Zn2), two deprotonated L^{2-} ligands, and two free base H₂L ligands. As illustrated in figure 1a and scheme S1, both Zn1 and Zn2 are five-coordinate; the specific geometries of the Zn ions were measured according to the τ_5 parameter proposed by Addison, for Zn1, $\tau_5 = 0.353$; for Zn2, $\tau_5 = 0.302$. Since the τ_5 parameter are both closer to 0 than 1, the geometries of Zn1 as well as Zn2 are distorted square pyramidal. For Zn1, two phenoxo oxygen atoms, O(1) and O(2), and one imine nitrogen atom N(3) of the deprotonated di-Schiff base with the help of one N(4)nitrogen atom of the pyridyl ring from an adjacent bridging ligand constitute the equatorial plane, whereas another nitrogen atom N(10) from the monodentate free base H₂L occupied the axial location. Interestingly, the hydrazone H₂L acts as chelating, bridging and monodentate ligand in the formation of one-dimensional polymeric chains, which is rarely seen in reported literatures. Similar to Zn1, three ONO-donor pockets (O3, O4, N6) of ligand and N(1) form the equatorial plane, with the axial position occupied by N(7). In the equatorial plane the Zn-O and Zn-N distances are similar, being in the range of 2.000(4)-2.085(4) Å, while the axially coordinating Zn-N bond distances are comparatively longer at 2.106(7) and 2.131(6) Å, respectively. The deviations of the coordinating atoms, N(1) and N(4), from the mean plane are 1.055 Å and 1.138 Å. It is noteworthy that the salicyloyl-O of the H₂L ligand enolizes during complexation and deprotonates to bond through the carbonylate-O, which is also observed in other reports [39]. It is interesting to compare the structure of LCP 1 with the reported [Zn(o-phen)LCu(OAc)], which differs in the structure of Schiff base ligand but also forms a five-coordinate square pyramidal geometry with a N₃O₂ coordination sphere for the zinc ion [40]. While Zn-N bond lengths of LCP 1 are a little longer than those of [Zn(o-phen)LCu(OAc)], Zn-O bond lengths and bond angles [X-Zn-X (X = N, O)] are close to each other. In LCP 1, the Zn(II) ions are infinitely connected by hydrazone ligands to generate a 1D chain (figure 1b). Furthermore, each hydrazone ligand serves as a bridging ligand to connect two Zn(II) centers into supramolecular structures and the two-dimensional supramolecular sheet structure of the complex is constructed by π - π stacking interactions (3.4700 Å) with a slip-angle of 4.76°, as shown in figure 1c.

3.2. FT-IR and TGA analysis of 1

As the FT-IR spectrum shows (figure S1), v(O-H) is observed at 3431 cm⁻¹ and v(N-H) is observed at 3220 cm⁻¹ in the IR spectrum of CP **1**, confirming the existence of uncoordinated OH and NH groups from the assistant Schiff base ligand. The appearance of a new v(C-O) band in **1** in the range of 1370-1360 cm⁻¹ definitely suggests bonding of the ligand to the zinc ion through the phenolate-O. The newly-emerged bands in the 760-700 cm⁻¹ and 570-510 cm⁻¹ ranges have been tentatively assigned to v(Zn-O) and v(Zn-N).

TGA was carried out to ascertain the thermal stability of LCP **1** (figure **S**2). The TGA curve shows no obvious weight loss until 410 °C, indicating its excellent thermal stability. The weight loss of the monodentate coordinating H_2L molecule is observed in the range of 410-440 °C (observed, 44.2%; calculated, 46.3%). Subsequently, the decomposition of the chelating Schiff base ligand starts and finally the coordination polymer is converted into metal oxide, estimated to be ZnO (observed, 16.8%; calculated, 18.1%).

3.3. Fluorescence properties

The solid-state luminescence properties of **1** and the free Schiff base were first characterized at room temperature. As figure S3 revealed, **1** exhibited a maximum emission peak at 485 nm upon excitation at 355 nm, with a slight blue shift compared to the free Schiff base ($\lambda_{em} = 493$ nm). The emission peaks of both can be attributed to π^* - π or π^* -n transitions. As shown in figure S4, the luminescence performance of **1** dispersed in commonly used solvents were extensively examined, including DMF, DMA, DCM, THF, DMSO, acetonitrile, methanol, ethanol, toluene, 1,4-dioxane, acetone and nitrobenzene. The PL spectra of emulsions of **1** in different solvents exhibited broad peaks with emission maxima ranging from 465 nm to 486 nm, with the highest luminescence intensity of **1** in the case of water dispersion and the lowest one in the case of nitrobenzene, *i.e.*, nitrobenzene showed the highest fluorescence quenching. The interactions between the coordination polymer and organic solvent molecules may be the reason for the observed fluorescence quenching effect. Upon excitation, energy transfer from the nearly

coplanar Schiff base ligand to the nitrobenzene might take place, resulting in the observed fluorescence quenching [41-43]. Interestingly, **1** showed the strongest luminescence when dispersed in water, which inspired us to check its aqueous stability. The aqueous chemical stability of LCP **1** was investigated as follows: soaking LCP **1** in water at room temperature for several days, after which the material was centrifuged and removed from the emulsion, washed thoroughly with distilled water and diethyl ether, and dried under vacuum for PXRD test. As the PXRD patterns demonstrated (figure S5), the crystalline structure integrity was perfectly preserved. It is also found that the fluorescence emission from **1** (figure S6) is very stable in aqueous emulsion as verified by a day-to-day fluorescence measurement, indicating its wonderful aqueous stability, which in turn confirms the application of LCP **1** as a promising candidate in the aqueous detection of analytes.

3.4. Fluorescence studies for $Cr_2O_7^{2-}$ detection

Because of the strong luminescence property and excellent chemical stability of **1**, we sought to explore its application in monitoring $Cr_2O_7^{2-}$ ion in water through fluorescence sensing. As depicted in figure 2a, among the various anions chosen for detection in water by **1**, the existence of $Cr_2O_7^{2-}$ leads to almost complete luminescence quenching, and MnO_4^- makes the luminescence intensity slightly decrease, while other anions have no obvious effect on the luminescence intensity. Considering the fact that mixed anions coexisted in the wastewater, the distinguishing quenching effect between $Cr_2O_7^{2-}$ and other anions encouraged us to investigate the potential application of **1** to selective sensing $Cr_2O_7^{2-}$ by fluorescence quenching. Thus, competitive experiments were conducted by addition of 1.5 mL of $Cr_2O_7^{2-}$ (2×10^{-2} M) to 1.5 mL of aqueous solutions of other interfering anions (2×10^{-2} M). As shown in figure 2b, the fluorescence quenching effect of $Cr_2O_7^{2-}$ on **1** was hardly influenced by other anions. These results definitely indicate that **1** could be successfully used for selective probing $Cr_2O_7^{2-}$ in water from among the above-mentioned anionic series.

Moreover, the fluorometric titration of varying concentrations of aqueous $Cr_2O_7^{2-}$ $(1-500\times10^{-5} \text{ M})$ against 1 dispersed in water was carried out to test the sensitivity and quenching efficiency of 1 toward $Cr_2O_7^{2-}$. As shown in figure 2c, the emission intensity located at 476 nm gradually decreased with incremental concentration of $Cr_2O_7^{2-}$ aqueous solution. The quenching efficiency was estimated by fitting the fluorescence intensity ratio versus concentration of $Cr_2O_7^{2-}$ data to the Stern–Volmer (SV) equation, $I_0/I = 1 + K_{SV}[Q]$, where, I_0 and I are the emission intensities of the aqueous suspension of 1 before and after interacting with the aqueous solution of $Cr_2O_7^{2-}$, respectively, [Q] is the molar concentration of $Cr_2O_7^{2-}$, and K_{SV} is the quenching constant. As demonstrated in figure 2d, the SV plot was nearly linear over the added $Cr_2O_7^{2-}$ concentration range (0-100×10⁻⁵ M), and the calculated quenching constant value is K_{SV} = 1.897×10^3 M⁻¹ with a linear fit coefficient value of 0.9907. The limit of detection (LOD) was calculated to be 1.1417×10^{-5} M on the basis of $3\sigma/m$ [27]. It is noteworthy that aqueous-phase detection of $Cr_2O_7^{2-}$ by LCPs has rarely been reported. Important reports on aqueous-phase detection of $Cr_2O_7^{2-}$ by LCPs are listed in table S2. Evidently, the K_{SV} of LCP **1** is comparable to those of known MOF-based sensors for aqueous $Cr_2O_7^{2-}$ ion detection and LOD value in the present investigation is also comparable to previous reports.

3.5. Fluorescence studies for TNP detection

The strong luminescence of **1** in water suspension and its noticeable fluorescence quenching upon exposing to nitrobenzene prompted us to investigate its sensing performance towards nitroaromatic compounds in aqueous media, which has vital importance in environmental and security issues. Several electron-deficient NACs were chosen as detection analytes and dispersed in water with a constant concentration of 5×10^{-4} M, including 4-nitrotoluene (4-NT), 2-nitrotoluene (2-NT), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 1,3-dinitrobenzene (1,3-DNB) and TNP. As revealed in figure 3a, **1** exhibited fast and high luminescence quenching efficiency for TNP and significant quenching of up to 67.5% was observed, whereas for the other NACs, it showed comparatively negligible quenching effects.

The quenching percentages were calculated using the formula $[(I_0-I)/I_0] \times 100\%$ and found roughly to be in the following order: TNP > 1, 3-DNB > 2,6-DNT \approx 4-NT > 2,4-DNT > 2-NT. As high selectivity is crucial for most probes to be applied in real sample detection, the fluorescence quenching of **1** by TNP in the coexistence of other nitroaromatic compounds were systematically studied. As figure 3b depicts, no significant changes of fluorescence intensity were observed in the experiments in which other nitroaromatic compounds were simultaneously added into the TNP-containing systems, demonstrating the excellent selectivity of **1** towards TNP.

Fluorescence quenching titration with varying concentrations of TNP were conducted with an excitation wavelength of 355 nm at room temperature. Upon incremental addition of TNP in the concentration range of $5-50 \times 10^{-5}$ M to an aqueous suspension of 1, the observed fluorescence quenching percentage was 24.4, 34.3, 41.9, 47.9, 52.9, 56.9, 60.4, 63.3, 65.8 and 67.9%, respectively (figure 3c). The photoluminescence quenching efficiency can be quantitatively calculated according to the SV equation. As shown in figure 3d, TNP displays a good linear SV relationship ($R^2 = 0.9976$) in the concentration range of 5-50×10⁻⁵ M and the calculated quenching constant value is $K_{SV} = 4.111 \times 10^3 \text{ M}^{-1}$. As seen in table S2, the K_{SV} of **1** is comparable to those of reported MOF-based sensors. The LOD was calculated to be as low as 1.19 μ M on the basis of $3\sigma/m$ [27]. As is well known, fast and simple regeneration methods are crucially important on the recyclable performance of luminescent sensor in terms of application in real sample detection. Hence, we immersed 1 in an aqueous solution of 10^{-2} M TNP or Na₂Cr₂O₇ for 30 min to form inclusions of 1@TNP or 1@Cr₂O₇²⁻, after which the solid was separated by centrifugation and washed several times with distilled water and diethyl ether. After three cycles of repeated fluorescence measurements, the luminescence intensity of the recycled sample was consistent with the original one, showing the satisfying recyclable performance of **1** (figure 4). Next, the possible mechanism that the introduction of $Cr_2O_7^{2-}/TNP$ decreased luminescence intensity is discussed. Based on previous literature studies [44], energy loss caused by the collision between luminescent coordination polymers and analytes during the energy transferring process usually results in fluorescence quenching of luminescent sensors. The

UV-Vis spectra of $Cr_2O_7^{2^-}$ and TNP solutions show absorption at about 370 nm for $Cr_2O_7^{2^-}$ and 380 nm for TNP (figure S7). The strongest excitation wavelength of **1** locates at 355 nm; as a result, TNP and $Cr_2O_7^{2^-}$ in the solution can significantly absorb the energy of the excited light, resulting in luminescence decrease of **1**. The collision between the TNP/ $Cr_2O_7^{2^-}$ analytes and **1** in association with the adsorption of TNP/ $Cr_2O_7^{2^-}$ in the UV-Vis region reduce energy of the transmission process and contribute to luminescence quenching.

3.6. Sensing of TNP/ $Cr_2O_7^{2-}$ in real water samples

For the sake of investigating the TNP/Cr₂O₇²⁻ sensing behaviors of **1** in real water samples, a total of eight water samples were collected, including four samples of the same type (tap or river water). The concentrations of TNP/Cr₂O₇²⁻ found and the recovery percentages in the environmental water samples are displayed in table 2. The recovery percentages of TNP/Cr₂O₇²⁻ were in the range of 90.85-99.12% for all the samples and the RSD values were in the range of 2.51-5.57 (RSD = (SD/mean value) × 100). The good recovery percentages and low RSD values obviously imply that the probe can provide adequate recoveries and good analytical precisions for real water samples.

4. Conclusion

Using a newly-synthesized Schiff base ligand, N'-[(E)-(3,5-dibromo-2-hydroxyphenyl)methylene]isonicotinohydrazide, one novel luminescent CP **1** has been designed and synthesized which is well suitable for the selective and sensitive detection of both $Cr_2O_7^{2-}$ and TNP in aqueous solution through fluorescence quenching, and is scarcely affected by other possible coexistent interfering species. Most importantly, **1** exhibited exceptional thermal and chemical stability in aqueous solutions, and its fluorescence could be recycled by a fast and simple method. Notably, the K_{SV} value as well as LOD of **1** towards $Cr_2O_7^{2-}$ and TNP are comparable to those reported for MOF materials to date. The limits of detection of **1** towards $Cr_2O_7^{2-}$ and TNP in aqueous solutions can reach as low as 11.4 and 1.19 μ M, respectively. Given

the satisfied performance of **1** toward the detection of $Cr_2O_7^{2-}$ and TNP in real water samples, we believe that our work will trigger substantial research interest in the field of MOF based $Cr_2O_7^{2-}$ and TNP sensors in water media.

Acknowledgements

The authors acknowledge financial assistance from National Natural Science Foundation of China (Nos. 21501124 and 41603124), the program of Science and Technology Department of Sichuan Province (Nos. 2016JY0048, 2016GZ0172 and 2017JY0194), the Education Committee of Sichuan Province (Nos. 18ZB0425 and 18ZA0337), the Start-up Foundation of Sichuan University of Science & Engineering (No. 2017RCL02), and Student's Platform for Innovation and Entrepreneurship Training Program in Sichuan Province (201710622066).

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Figure 1. (a) The coordination environment of Zn(II) in 1; thermal ellipsoids are drawn at the 30% probability level and hydrogens are omitted for clarity; (b) view of the 1D chain along the *a*-axis; (c) view of the 2D layer constructed by π - π interactions from adjacent chains.



Figure 2. (a) Fluorescence response of **1** to various anions in the water; (b) the selective detection of $Cr_2O_7^{2-}$ on **1** in the presence of interfering anions in the water; (c) emission spectra of **1** in different concentrations of $Cr_2O_7^{2-}$ anion in the water (excited at 355 nm); (d) the Stern-Volmer plot of **1** in the presence of different $Cr_2O_7^{2-}$ concentrations.

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Figure 3. (a) Fluorescence response of 1 to various nitroaromatics in the water; (b) fluorescence quenching of 1 in the water upon addition of TNP and other nitroaromatic compounds; (c) emission spectra of 1 in different concentrations of TNP in the water (excited at 355 nm); (d) the Stern-Volmer plot of 1 versus different TNP concentrations.

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Figure 4. The luminescence intensity of three recycles for 1 towards TNP (a) and $Cr_2O_7^{2-}$ (b), respectively.

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Formula	$C_{52}H_{32}Br_8N_{12}O_8Zn_2$
Formula weight	1722.92
Crystal system	Monoclinic
Space group	P21/c
Crystal color	Yellow
<i>a</i> [Å]	15.1794(16)
<i>b</i> [Å]	12.6165(13)
<i>c</i> [Å]	40.257(4)
α [°]	90.00
β [°]	2.724(2)
γ [°]	90.00
V [Å ³]	7700.9(14)
Z	4
Dc, g/cm ³	1.486
μ , mm ⁻¹	4.822
F(000)	3328
θ Range, deg	2.30-20.23
Reflections collected	13552/6157
Goodness-of-fit on F^2	1.069
$R_1, wR_2 (I > 2\sigma(I))^*$	0.0627, 0.1293
R_1 , wR_2 (all data)**	0.1377, 0.1483
$*R_1 = \sum (F_0 - F_c) / \sum (F_0); **wR_2 = \{\sum$	$[w(F_{o}^{2} - F_{c}^{2})^{2}]/\sum (F_{o}^{2})^{2}\}^{1/2}$

Table 1. Crystal data and structure refinement information for **1**.

Samples	Tap water		River water					
	μM)	Detected values ^a (µM)	Recovery (%)	Detected values ^a (µM)	Recovery (%)			
$Cr_2O_7^{2-}$	20	18.96±4.53	94.80	18.74±5.57	93.68			
	40	39.38±5.12	98.46	36.34±4.69	90.85			
TNP	20	19.07±4.74	95.34	19.82±3.42	99.12			
	40	38.56±2.51	96.40	37.03±5.02	92.58			
^a Detected values ± RSD (n=3)								
		Ś						

Table 2. Detection performance of **1** for $Cr_2O_7^{2-}/TNP$ in real water samples.

Graphical abstract

