Research paper

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A luminescent zinc(II) coordination polymer as a highly selective and sensitive chemosensor for Fe(III) cation and Cr(VI) anions detection in aqueous solution

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Abstract

А double-bent-mixed-ligand supported 2-periodic coordination polymer (CP) $\{[Zn_2(FDA)_2(4-abpt)_2(H_2O)_2]\}_n$ (1) has been synthesized from the unique combination of a bent furan-2,5-dicarboxylic acid (H₂FDA) ligand and a bent 4-amino-3,5-bis(4-pyridyl)-1,2,4-triazole (4-abpt) coligand. The CP 1 demonstrates readily dispersible two-dimensional (2D) 2-periodic layer structure and considerable chemostability in aqueous media. Luminescence titration experiments indicate that CP 1 can serve as chemosensors for sensitively and selectively detecting Fe^{3+} cation, CrO_4^{2-} and $Cr_2O_7^{2-}$ anions in water solution via an environmentally friendly manner. Besides, the luminescent selective quenching mechanism of CP 1 toward Fe^{3+} cation, CrO_4^{2-} and $Cr_2O_7^{2-}$ anions is comprehensively investigated in the light of absorption of the excitation energy of the host framework by individual analytes.

Keywords: a double-bent-mixed-ligand strategy; luminescence chemosensors; Zn(II) coordination polymer; Fe(III) cations recognition; Cr(VI) anions detection

Introduction

While sophisticated analytical instruments such as atomic absorption spectroscopy, mass spectrometry, inductively coupled plasma and chromatography have played an increasingly important role in the detection of hazardous substances,^[1-3] the use of simple, fast and readily available detection techniques continues to offer fascinating new approaches and at the same time offers deeper insight into the structural parameters and individual analytes in the detection process.^[4-6] Such a fact is especially true for luminescence detection techniques, which have been widely investigated for chemosensing applications. This is because in comparison with other analytical techniques, luminescence detection techniques are superior in simple operating procedures, excellent selectivity and sensitivity, low cost, online monitoring detection and high-efficiency response.^[7-9] Significantly, among the various candidate luminescence detection techniques, luminescence coordination polymers (LCPs) have attracted much attention.^[10-12] Specifically in sensing applications, LCPs have been proved to be optimal candidates as chemosensor for detecting explosives, corrosive gases, antibiotics, cancer markers, neurotransmitters, pH and so on because of their selective and sensitive response to the individual analytes.^[13-15] This superior performance in chemosensing applications may largely depend on their versatile components and highly tunable morphology. ^[16-18] More importantly, the excellent sensitivity, high selectivity and reusability of LPCs could also benefit their sensing applications in comparison with other the luminescence detection techniques.

Additionally, severe pollution caused by the abuse of hazardous chemicals has raised global concerns because the abused chemicals can seriously harm human health and severely contaminate natural environment and ecological systems. For instance, as an indispensable trace element, Fe^{3+} cations have played an important role in the oxygen-transfer and physiological processes and participated in the hemoglobin formation and the synthesis processes of DNA and RNA.^[19,20] However, the deficiency and excess of Fe^{3+} cations has lethal effects on organisms and could cause several adverse human health problems. Likewise, $CrO4^{2-}$ and Cr_2O7^{2-} anions are notorious chromium(VI) species because of their high toxicity, nonbiodegradablity and facile accumulation during the wide applications in industry, resulting in human lesion such as cancer and deformity.^[21,22]Thus, it is of significant importance to investigate an effective approach for detecting Fe^{3+} cations, CrO_4^{2-} and $Cr_2O_7^{2-}$ anions in aqueous media via highly sensitive, fast-responsive detection, of which LCPs are considered as optimized candidates to efficiently detect them.

Based on the reasons discussed above, we develop a luminescence detection approach based on LCPs to detect Fe³⁺ cations, CrO₄²⁻ and Cr₂O₇²⁻ anions in aqueous media rapidly and sensitively. Herein, a 2-periodic CP {[Zn₂(FDA)₂(4-abpt)₂(H₂O)₂]}_n (1) is designed *via* a double-bent-mixed-ligand strategy based on a bent dicarboxylic acid ligand and a bent pyridyl ligand (Scheme 1), which exhibits readily dispersible 2D *sql* layer structure and considerable chemostability in aqueous media. Moreover, luminescent exploration reveals that CP **1** represents superior luminescent properties, which can sensitively and selectively detect Fe³⁺ cations, CrO₄²⁻ and Cr₂O₇²⁻ anions in aqueous media. Further exploration of luminescence quenching mechanism toward Fe³⁺ cations, CrO₄²⁻ and Cr₂O₇²⁻ anions has been investigated by the UV-Vis spectral overlap experiment.



Scheme 1 Molecular structures of H₂FDA and 4-abpt.

Experimental Section

General Methods and Materials

All reagents and solvents were purchased from commercial sources and used as received without further purification. Elemental analyses of C, H and N were performed using a Perkin-Elmer 240 CHN elemental analyzer. IR spectra were recorded in the range 400–4000 cm⁻¹ with a Bruker Tensor 27 spectrometer on KBr disks. Powder X-ray diffraction measurements were carried out using a D/Max-2500 X-ray diffractometer with Cu/K α radiation. The luminescence spectrum was measured on a Varian Cary Eclipse Fluorescence spectrophotometer. UV/Vis spectra were recorded on a Agilent

Cary100 spectrophotometer.

Synthesis of 4-abpt. A mixture of 4-cyanopyridine (10 mmol, 1.04 g) and hydrazine monohydrate (80% 1.5 mL) in 2 mL C₂H₅OH was sealed in a 23 mL Teflon-lined stainless autoclave and heated at 120 °C for 3 days and subsequently cooled to room temperature at a rate of 1.25 °C h⁻¹. Colorless crystals of 4-abpt were collected by washing with C₂H₅OH, and dried in air. Yield: 86%. Anal. Calcd for C₁₂H₁₀N₆: C 60.50; N 35.27; H 4.23 Found: C 60.67; N 35.01; H 4.32%.

Synthesis of {[$Zn_2(FDA)_2(4-abpt)_2(H_2O)_2$]}_n (1). A mixture of H₂FDA (0.100 mmol, 0.0156 g), 4-abpt (0.100 mmol, 0.0368g) and Zn(NO₃)₂·6H₂O (0.100 mmol, 0.0297 g) in 4 mL DMA and 2 mL C₂H₅OH was sealed in a 23 mL Teflon-lined stainless autoclave and heated at 90 °C for 3 days and subsequently cooled to room temperature at a rate of 1.25 °C h⁻¹. Colorless block crystals of CP 1 were collected by washing with DMA several times and dried in air. Yield: 63% based on Zn. Anal. Calcd for C₃₆H₂₈N₁₂O₁₂Zn₂: C 45.44; N 17.66; H 2.97. Found: C 45.27; N 17.41; H 3.24%. IR (KBr, cm⁻¹): 3358w, 3118s, 2928w, 1610vs, 1359vs, 1210s, 1019m, 834m, 793m, 598m.

 Table 1 Crystal data and Structure Refinements for 4-abpt and 1.

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compound	4-abpt	1
formula	$C_{12}H_{10}N_{6}$	$C_{36}H_{28}N_{12}O_{12}Zn_2$
formula weight	238.25	951.50
temperature (K)	150(10)	150(10)
crystal system	monoclinic	orthorhombic
space group	$P2_{1}/c$	Aea2
<i>a</i> (Å)	13.1496(4)	14.8200(8)
b (Å)	7.0195(2)	32.601(3)
<i>c</i> (Å)	11.7924(4)	19.2529(12)
α (°)	90	90
β (°)	106.259(3)	90
γ (°)	90	90
$V(Å^3)$	1044.95(6)	9301.9(10)
Ζ	4	8
$D_c (\rm g cm^{-3})$	1.514	1.357
$\mu \text{ (mm}^{-1}\text{)}$	0.813	1.850
F(000)	496.0	3864.0
2θ range (°)	7.002 to 131.994	8.002 to 131.986
GOF on F^2	1.068	1.057
reflections collected / unique	2913/1801	6324 / 4252
R _{int}	0.0267	0.0813
$R_1,^a w R_2^b [I > 2\sigma(I)]$	0.0425, 0.1078	0.1340, 0.3285
R_1 , wR_2 (all data)	0.0470, 0.1140	0.1481, 0.3490

 $R_1^{a} = \sum (|F_0| - |F_c|) / \sum |F_0| \cdot {}^{b} w R_2 = \left[\sum \{ w(|F_0|^2 - |F_c|^2)^2 \} / \sum [w(|F_0|^2)^2] \right]^{1/2}$

X-ray Structure Determination. Data collections of 4-abpt and CP **1** were carried out using an Oxford Supernova diffractometer equipped with graphite-monochromated *Cu-Ka* radiation ($\lambda = 1.54178$ Å). The temperature was cooled by a cryoject controller attached to an Oxford Supernova diffractometer. Starting models for structure refinement were found using direct methods (*Olex2*,^[23] and *SHELXT-2014*^[24]). All non-hydrogen atoms were found from the different Fourier maps and refined by full-matrix least-squares techniques on *F*² using the *SHELXL-2014* programs.^[25] Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were placed in idealized positions and located in the difference Fourier map. CCDC 2002379 for 4-abpt and CCDC 2002381 for CP **1** contain the supplementary crystallographic data of this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif. The crystallographic data for 4-abpt and CP **1** are summarized in Table 1.

Luminescence Experiments. In a typical experiment, 5 mg CP 1 samples were powdered and

Journal Pre-proofs immersed in 2.5 mL MCl_x metal salts (10⁻² M) (M = Al³⁺, Ba²⁺, Ca²⁺, Cd²⁺, Co²⁺, Cu²⁺, Ni²⁺, Mg²⁺, Pd²⁺, Fe^{3+} and Cr^{3+}) aqueous solution with ultrasonication for 30 min to obtain the suspension of CP 1. Then, the obtained suspension was transferred to a quartz cuvette, and the photoluminescence spectra were recorded by a fluorescence spectrophotometer under excitation of 285 nm at room temperature.

As for the luminescence titration experiment, 5 mg crystalline powders CP 1 were dispersed in 2.5 mL water with ultrasonication for 30 min, forming stable suspensions. Then, the obtained suspension was transferred to a quartz cuvette, and 10⁻³ M MCl_x metal salts were added slowly, and the corresponding emission spectra were monitored.

As for the anti-interference ability of CP1, 5 mg of crystalline powders CP1 was dispersed in 2.5 mL of water, forming stable suspensions, then 100 μ L of the corresponding MCl_x metal salts (10⁻² M) were added to the suspension of CP 1, and the corresponding emission spectra were monitored. With the subsequent addition of 100 μ L FeCl₃ (10⁻² M) into the parallel tests, the corresponding emission spectra was monitored.

As for the luminescence quenching experiment of CrO_4^{2-} and $Cr_2O_7^{2-}$ anions, similar procedures have been performed as the luminescence quenching experiment of Fe^{3+} cation.

Results and Discussion

Description of the Crystal Structure



Scheme 2 Synthesis of 4-abpt crystals.

The solvothermal reaction of 4-cyanopyridine and excess hydrazine monohydrate in C_2H_5OH at 120 °C affords the crystals of 4-abpt (Scheme 2), which crystallize in the monoclinic system with space group $P2_1/c$ (Table 1). While the solvothermal treatment of $Zn(NO_3)_2$ 6H₂O, H₂FDA and 4-abpt at 90 °C for 3 days in a mixture solution of DMA and C₂H₅OH harvests colorless crystals of CP 1.

Single-crystal X-ray diffraction study revealed that CP 1 crystallized in the orthorhombic system with space group Aea2 (Table 1). Each asymmetric unit is composed of two crystallographically independent Zn(II) ions, two FDA²⁻ ligands, two 4-abpt ligands and two water molecules, of which partial Zn(II) ions, FDA²⁻ ligands and 4-abpt ligands are disordered (Figure 1a). Each Zn²⁺ ion is hexacoordinated by three oxygen atoms from two FDA²⁻ ligands, one oxygen atom from water molecule and two nitrogen atoms from two 4-abpt ligands, generating a distorted distorted octahedral {ZnN2O4} coordination geometries. The Zn–O bond distances range from 2.041 (8) to 2.405(5) Å and the Zn–N bond distances are in the range of 2.126 (9) to 2.164 (5) Å, which are comparable to those distances reported for Zn-based CPs^[26-28]. And each FDA²⁻ ligand with the (η^2) - (η^1) - μ_2 coordination mode, supported by the infrared spectra (Figure S1 of the supporting information) connects with two separate Zn^{2+} ions. As a result, a 2D sql 2-periodic layer structure is formed due to the partial disordered structure of the asymmetric unit (Figure 1b and Figure 1c), which stacks along the b-axis in an -AABB- fashion (Figure 1d). The consecutive 2-periodic layer structures can be bridged together via direct inter-layer hydrogen bonds involving the coordinated water molecules of one layer and carboxylate groups as well as the oxygen atoms of furan groups of a neighboring layer (O11-H11E...O9, O11-H11F...O6, O11-H11F...O8, O12A-H12A...O5, O12A-H12B...O2, O12A-H12C...O2, O12A-H12C...O3 and O12A-H12D...O5) (Table S1 of the supporting information), which support the 3D supermolecular structure of CP 1.



Figure 1. (a) The asymmetric unit in CP **1** (thermal ellipsoids are drawn at the 30% probability level). All hydrogen atoms were omitted for clarity. [Symmetry code: (#) 3/2-X, Y, 1/2+Z; (##) 1+X, +Y, +Z]; (b) 2D 2-periodic layer structure of CP **1** (part of disordered molecules were omitted for clarity); (c) The 2-periodic *sql* square grid of CP **1**. (d) Overrall packing of the structure of CP **1**. All hydrogen atoms were omitted for clarity;

Powder X-ray Diffraction (PXRD) Measurement

The crystalline phase purity of CP **1** has been performed at room temperature and confirmed by comparing the simulated PXRD pattern from the single crystal data with the experimental pattern. The current result indicates one crystalline phase is present in sample CP **1** (Figure S2 of the supporting information). The slight difference may be derived from the variation of preferred orientation of CP **1**. Moreover, when samples CP **1** were dispersed in 10^{-2} M Fe³⁺ cations, CrO_4^{2-} and $Cr_2O_7^{2-}$ anions of aqueous solution, the PXRD patterns are consistent with the simulated pattern, which suggest the structure of CP **1** is undecomposed and can be stable in Fe³⁺ cations, CrO_4^{2-} and $Cr_2O_7^{2-}$ anions.

Thermogravimetric (TG) Measurement

The thermal stability of sample CP 1 has been performed under an N₂ atmosphere in the temperature

range of 25 - 800 °C (Figure S3 of the supporting information). The curve shows a steady plateau from room temperature to 140 °C, indicating that there are no free solvent molecules in CP **1**. Then, a weight loss of *ca.* 4.26% (calcd. 3.78%) before 270 °C is observed, indicative of the removal of two coordinated water molecules. As the temperature is raised, the whole structure begins to decompose.

Luminescence Measurement

The luminescence measurements of H₂FDA, 4-abpt and CP **1** have been performed in the solid state at room temperature. Upon excitation at 300 nm, the luminescence emission band of H₂FDA and 4-abpt shows a main emission peak with the maximum value of 365 nm and 378 nm, respectively. This luminescence phenomenon could be ascribed to ligand-to-lignand charge transfer transition ($\pi^* \rightarrow \pi$ or $\pi^* \rightarrow n$). Compared to H₂FDA and 4-abpt ligands, a strong luminescence emission at 380 nm is observed upon the excitation of 285 nm (Figure S4 of the supporting information), resulting in a red shift of 15 nm and 2 nm, respectively. Such luminescence emission phenomenon could be attributed to neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) due to the fact of the difficulty of being oxidized or reduced regarding as Zn²⁺ ions d¹⁰ configuration. Therefore, the luminescence emission band of CP **1** could be reasonably speculated to the mixed contribution of the intra-ligand charge transfer transition of π -electron-rich linkers and ligand-to-lignand charge transfer transition ($\pi^* \rightarrow \pi$ or $\pi^* \rightarrow n$) of the organic ligands.^[29]

It is well-known that much work has been devoted to developing luminescence detection approaches based on LCPs because of their superior performance for the effective response and sensing of hazardous analytes such as toxic anions and cations.^[30-33] Of particular concern to the Zn-based LCPs are the favorable advantage in sensing applications. In this contribution, CP **1** is exploited as the luminescence chemosensor to recognize Fe^{3+} cations, CrO_4^{2-} and $Cr_2O_7^{2-}$ anions via the luminescence quenching effects.

Fe³⁺ Cations Recognition

The 5 mg tiny samples of CP 1 were dispersed into 10⁻² M cations (AlCl₃, BaCl₂, CaCl₂, CdCl₂,

CoCl₂, CuCl₂, NiCl₂, MgCl₂, PdCl₂, FeCl₃ and CrCl₃) of 2.5 mL water solution by 30 min ultrasonic process, forming suspension solutions. As demonstrated in Figure 2a, different cations have significant influences on the luminescence intensities of the CP **1** suspension, along with the slightly red-shifted or blue-shifted luminescence peaks due to the contribution of the interaction between the guest cations and the host skeletons of CP **1**. Particularly, Fe³⁺ cations have the most significant influences on the luminescence intensities, demonstrating the most noticeable turn-off quenching effect, and the luminescence of CP **1** is totally quenched. Compared with the phenomenon of Fe³⁺ cations on the influences of CP **1**, other cations have a moderate effect on the luminescence of CP **1**. This fact suggests CP **1** could be qualified as a promising luminescence chemosensor for selective Fe³⁺ cations detection. To evaluate the anti-interference sensing ability of CP **1**, the competing experiments have been performed (Figure 2b and Figure S5-S15 of the supporting information). The experimental results reveal that CP **1** shows visible luminescent quenching effects in the case of Fe³⁺ cations as well as outstanding selectivity to Fe³⁺ cations.



Figure 2. (a) The luminescence of CP **1** dispersed in different cations; (b) The luminescence intensity (348 nm) of CP **1** dispersed in H₂O with the addition of different competing cations (green) and subsequent addition of Fe³⁺ cations (purple); (c) The luminescence of CP **1** dispersed in H₂O with different concentration of Fe³⁺ cations; (d) The linear

correlation between the luminescence of CP $\mathbf{1}$ and the low concentration of Fe³⁺ cations.

To further explore the sensing sensitivity and better understand the quenching effects of Fe^{3+} cations, the titration experiments have been carried out. As expected, the luminescence behaviour of CP 1 is in accordance with the concentration of Fe^{3+} cations (Figure 2c). The luminescence curve shows the luminescence changes of the intensities in different degrees could be clearly present and the existence of turn-off quenching phenomenon simultaneously became remarkable. Moreover, the intensities could gradually decrease with the increasing concentration of Fe^{3+} cations, endowing CP 1 with the capacity of the quantitative detection of Fe^{3+} cations. The relationship between the luminescence intensities and the concentration of Fe^{3+} cations is illustrated in Figure 2d and Figure S16 of the supporting information. A best fit of I_0 / I vs the low concentration of Fe³⁺ cations is evaluated based on the equation of $I_0 / I =$ $0.98596 + K_{sv}$ [Fe³⁺ cations] with the correlation coefficient of 0.9989, where the values of I_0 and Irepresent the initial and ultimate luminescence intensity of CP 1. [Fe³⁺ cations] is the molarity of the corresponding anions (mM) and K_{sv} stands for the quenching constant (M⁻¹), respectively. The result shows a linear correlation of luminescence quenching and the low concentration of Fe³⁺ cations and is in close proximity to the Stern–Volmer (SV) equation: $I_0 / I = 1 + K_{sv}[Fe^{3+} \text{ cations}]$. The K_{sv} value is quantitatively calculated to be 1.23×10^4 M⁻¹ by the linear regression of the curve, indicating the significant quenching efficiency of CP 1. The detection limit for Fe³⁺ cations can be calculated by using $3 \delta / k$, in which δ is standard error and k is slope according to the SV equation with a value of 12.4 μ M for CP 1, further indicative of an excellent sensitivity for sensing Fe^{3+} cations. The superior K_{sv} value and low detection limit of CP 1 qualifies CP 1 as a high-efficiency luminescence chemosensor for quantitative Fe³⁺ cations detection. Furthermore, the recyclable performance demonstrates the negligible changes of luminescence intensity after four cycles, revealing the high recyclability of CP 1 for Fe³⁺ cations detection (Figure S17 of the supporting information).

CrO₄²⁻ and Cr₂O₇²⁻ anions Detection

Likewise, the influences of different anions (KCl, KBr, KF, KI, KNO₃, KSCN, K₂SO₄, K₂CO₃, K₂MoO₄, K₂WO₄, K₂Cr₂O₇, K₂CrO₄ and K₃PO₄) on the luminescence intensities of CP **1** have been

explored (Figure 3). The result proves that different anions have significant influences on the luminescence signal of CP 1. The luminescence signal can completely disappear in the presence of CrO_4^{2-} and $Cr_2O_7^{2-}$ anions, whereas the luminescence signal can negligibly change in the presence of other anions. The completely quenched luminescence signal in the case of CrO_4^{2-} and $Cr_2O_7^{2-}$ anions for CP 1 indicates CP 1 can also be exploited as a possible luminescence chemosensor for selectively sensing CrO_4^{2-} and $Cr_2O_7^{2-}$ anions. The anti-interference sensing ability experiments also show CrO_4^{2-} and $Cr_2O_7^{2-}$ anions can dramatically quench the luminescence signal, while other anions can scarcely influence the luminescence intensities of CP 1, further indicative of the superior selectivity to CrO_4^{2-} and $Cr_2O_7^{2-}$ anions (Figure 4a-4b and Figure S18-S28 of the supporting information). The sensitivity ability of CP 1 has been demonstrated by the titration experiments (Figure 4c-4d). It turns out that significant luminescence quenching variation is implemented with the gradual addition of CrO₄²⁻ and $Cr_2O_7^{2-}$ anions, indicating CP 1 has the capacity of the quantitative detection of CrO_4^{2-} and $Cr_2O_7^{2-}$ anions. The relationship between the luminescence intensities and the concentration of CrO4²⁻ and $Cr_2O_7^{2-}$ anions is illustrated in Figure 4e-4f and Figure S29-30 of the supporting information. Similarity with the case of Fe³⁺ cations, the best fit of $I_0 / I vs$ the low concentration of Cr₂O₇²⁻ anions and CrO₄²⁻ anions could also be calculated based on the equations of $I_0 / I = 0.99179 + K_{sv} [CrO_4^{2-} anions]$ with the correlation coefficient of 0.9949 and $I_0 / I = 0.98469 + K_{sv} [Cr_2O_7^{2-} anions]$ with the correlation coefficient of 0.9913, respectively. The fitting result shows a linear correlation of luminescence quenching and the low concentration of $Cr_2O_7^{2-}$ anions and CrO_4^{2-} anions, which is in close proximity to the SV equation: $I_0 / I = 1 + K_{sv}[Cr(VI) \text{ anions}]$. Accordingly, the K_{sv} values can be quantitatively calculated to be 7.20×10^3 M⁻¹ for CrO₄²⁻ anions and 7.92×10^3 M⁻¹ for Cr₂O₇²⁻ anions and the detection limits are as low as 101 μ M for CrO₄²⁻ anions and 120 μ M for Cr₂O₇²⁻ anions, which further indicate that CP 1 serves as selective and sensitive chemosensors for sensing CrO_4^{2-} anions and $Cr_2O_7^{2-}$ anions in aqueous solution. Moreover, the recyclable performance demonstrates the negligible changes of luminescence intensity after four cycles, revealing the high recyclability of CP 1 for sensing CrO_4^{2-}

anions and $Cr_2O_7^{2-}$ anions (Figure S17 of the supporting information).

Comparatively, the superior K_{sv} value and low detection limit for Fe³⁺ cations of CP **1** is superior to the values of Cr(VI) anions and previous reports (Table S2 of the supporting information). The phenomenon of the superior sensitivity determination is likely to be caused by the fact that the amino and triazolyl nitrogen atoms are anchored in the skeleton. Additionally, it should be noted that the K_{sv} value and detection limit is comparable or superior to the reported LCPs as luminescence chemosensors to recognize Fe³⁺ cations and Cr(VI) anions in aqueous solution.^[34-36] Such fact clearly indicates the high selectivity and superior sensitivity of CP **1** for sensing Fe³⁺ cations and Cr(VI) anions in aqueous solution.



Figure 3. The luminescence of CP 1 dispersed in different anions.



Figure 4. (a) The luminescence intensity (348 nm) of CP 1 dispersed in H₂O with the addition of different competing anions (green) and subsequent addition of $Cr_2O_7^{2-}$ anions (purple); (b) The luminescence intensity (348 nm) of CP 1 dispersed in H₂O with the addition of different competing anions (green) and subsequent addition of CrO_4^{2-} anions (purple); (c) The luminescence of CP 1 dispersed in H₂O with different concentration of $Cr_2O_7^{2-}$ anions; (d) The luminescence of CP 1 dispersed in H₂O with different concentration of CrO_4^{2-} anions; (e) The linear correlation between the luminescence of CP 1 and the low concentration of $Cr_2O_7^{2-}$ anions; (f) The linear correlation between the luminescence of CP 1 and the low concentration of CrO_4^{2-} anions; (f) The linear correlation between the luminescence of CP 1 and the low concentration of CrO_4^{2-} anions; (f) The linear correlation between the luminescence of CP 1 and the low concentration of CrO_4^{2-} anions; (f) The linear correlation between the luminescence of CP 1 and the low concentration of CrO_4^{2-} anions; (f) The linear correlation between the luminescence of CP 1 and the low concentration of CrO_4^{2-} anions; (f) The linear correlation between the luminescence of CP 1 and the low concentration of CrO_4^{2-} anions; (f) The linear correlation between the luminescence of CP 1 and the low concentration of CrO_4^{2-} anions; (f) The linear correlation between the luminescence of CP 1 and the low concentration of CrO_4^{2-} anions.

Quenching Mechanism

The possible luminescent turn-off sensing mechanism of CP **1** caused by Fe³⁺ cations and Cr(VI) anions has been investigated. The PXRD patterns before and after the sensing performance reveal that CP **1** is still intact, excluding the structural collapse of the framework during the sensing process. Additionally, there is almost no obvious overlap between the absorption spectra of Fe³⁺ cations, Cr(VI)

anions and the emission spectrum of CP 1, also excluding the luminescence resonance energy transfer (FRET) process between the donor of CP 1 and the Fe³⁺ cations, Cr(VI) anions acceptor. However, UV–visible absorption spectroscopy of Fe³⁺ cations and Cr(VI) anions have an effective overlap with the excitation spectrum of CP 1 (Figure S31 in the Supporting information), clearly indicating the fact that Fe³⁺ cations and Cr(VI) anions could absorb the energy of the irradiated light of CP 1 and weaken the effective energy transfer from the organic ligands to the central Zn²⁺ ions. This may be the reason for the luminescence quenching phenomenon with the increase of Fe³⁺ cations and Cr(VI) anions and promote the sensing performance of CP 1.

Conclusion

In summary, a 2-periodic 2D *sql* CP with a considerable chemostability in aqueous media is designed *via* a double-bent-mixed-ligand strategy. The result of the luminescence performance demonstrates CP **1** has the promisingly potential capacity to be used as an efficient luminescence turn-off chemosensor for quantitatively sensing Fe^{3+} cations and Cr(VI) anions with superior selectivity and advantageous sensitivity. Further analysis of luminescence quenching mechanism interprets the competitive absorption between the Fe^{3+} cations or Cr(VI) anions and CP **1** may dominates the luminescence quenching response of CP **1** based on the UV-Vis spectral overlap experiments. All evidence support the fact that a facile access to synthesize luminescence chemosensors for the practical application in sensing Fe^{3+} cations and Cr(VI) anions in aqueous solution have been realized. And the result promotes us a new horizon for exploiting superior chemosensor materials for hazardous analytes recognition.

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Research Highlights

- 4 a 2-periodic *sql* coordination polymer is designed *via* a double-bent-mixed-ligand strategy.
- This coordination polymer can sensitively and selectively detects Fe^{3+} cations, CrO_4^{2-} and $Cr_2O_7^{2-}$ anions in aqueous media.

The luminescence quenching mechanism has been investigated by the UV-Vis spectral overlap experiment.



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