一个富路易斯碱位配合物的合成、结构及对痕量 Ag⁺的荧光检测

辛凌云[1]　李云平[1]　鞠丰阳[2]　李晓玲[1]　刘广臻[*,1]

([1] 洛阳师范学院化学化工学院，河南省功能导向多孔材料重点实验室，洛阳　471934)

([2] 洛阳师范学院食品与药品学院，洛阳　471934)

摘要： 通过溶剂热方法合成了一个由氢键拓展的携带路易斯碱位的三维超分子配位聚合物：$\{[Cd(HTZ\text{-}IP)(HPYTZ)(H_2O)_2]\cdot 5H_2O\}_n$ (HTZ-H₂IP=5-(5-四氮唑基)间苯二甲酸；HPYTZ=3,5-(4-吡啶基)-1,2,4-三唑]。X 射线单晶衍射结果表明，中心镉离子由含氮杂环羧酸配体和富氮辅助配体连接成"有悬挂手臂"的一维链，而链间则凭借配位水和 2 个配体的氢键作用拓展成三维超分子化合物。有趣的是配合物存在大量裸露的未配位的 N 原子，此 N 原子具有路易斯碱性质，能与路易斯酸性质的 Ag⁺有效结合，从而引起配合物的荧光猝灭。该性质能在无色溶液中有效检测 $10^{-4} \sim 10^{-6}$ mol·L⁻¹ 范围内的痕量 Ag⁺离子。

关键词： 溶剂热合成；配位聚合物；荧光；传感材料

Synthesis, Structure and Luminescent Detection for Trace Ag⁺ of a Coordination Polymer with Lewis Basic Sites

XIN Ling-Yun[1]　　LI Yun-Ping[1]　　JU Feng-Yang[2]　　LI Xiao-Ling[1]　　LIU Guang-Zhen[*,1]

([1]*College of Chemistry and Chemical Engineering, Henan Key Laboratory of Function-Oriented*

Porous Materials, Luoyang Normal University, Luoyang, Henan 471934, China)

([2]*School of Food and Drug, Luoyang Normal University, Luoyang, Henan 471934, China*)

Abstract: Hydrogen-bonded network with Lewis basic N sites have been obtained by the solvothermal reaction, named $\{[Cd(HTZ\text{-}IP)(HPYTZ)(H_2O)_2]\cdot 5H_2O\}_n$ (HTZ-H₂IP=5-(tetrazol-5-yl)isophthalic acid, HPYTZ=3,5-di(4-pyridyl)-1,2,4-triazolate ligand). The single-crystal X-ray diffraction analysis shows the adjacent Cd(Ⅱ) centers are bridged by HTZ-H₂IP ligand to form Cd carboxylate linear chains, while each HPYTZ molecule works as a terminal ligand with uncoordinated pyridine N atoms. The paralleled chains are connected by H-bonds between coordination H₂O and two ligands to produce its 3D supramolecular network. It is interesting that the network possess uncoordinated N atoms　(Lewis-base sites) existing a significant quenching effect to the luminescent intensity of complex by Ag⁺ ion. As a sensing material for Ag⁺, this coordinated polymer has features including simple preparation procedure, fast detection time, excellent selectivity for Ag⁺ in colorless solution, and high sensitivity with a detection range of $10^{-4} \sim 10^{-6}$ mol·L⁻¹ concentration limit . CCDC: 1528982.

Keywords: solvothermal reaction; coordination polymer; fluorescent property; sensing material

One of the premier performance metrics in chemical sensing applications is chemical selectivity, the ability to detect a given molecular species. When high selectivity is coupled with low detection limits and with signal transduction mechanisms that allow for facile device implementation, chemical sensing enables a range of applications in the defense, food packaging, and environmental monitoring sectors, among others[1-4].

The emergence of multifunctional coordinated polymers(CPs) materials is one of the most significant achievements in chemical sensing field over the past two decades[5-9]. The differential recognition/binding events with guest substrates confined by the tunable pore sizes and functionalized pore surfaces, which can be transduced into externally optical signals, have enabled the CPs to become a new type of sensing materials. In fact, some luminescent CPs materials have been realized for the sensing of ions and small molecules recently[10-12]. Particularly, some of those CPs show excellent luminescent sensing properties towards metal ions such as Al^{3+}, Cu^{2+}, Fe^{3+}. This is because that the Lewis basic coordination sites existing in the networks of CPs can interact with special metal ions, which may result in the changes in the luminescent intensity of the CPs-based material. Currently, some CPs bearing such sites have been reported, including Eu(Ⅲ)-CPs with many Lewis basic pyridine nitrogen atoms for sensing of Cu^{2+} ions[13-14], and Zn(Ⅱ)-CPs with uncoordinated Lewis-base sites showing excellent luminescence sensing of inorganic ions[15]. Of course, there are other approaches which can improve the sensing efficiency except for the retention of Lewis base sites within the CPs.

In order to obtain such sensing material, we present a synthetic strategy to create multi-functional CPs by employing polydentate N-heterocyclic carboxylate or dipyridyl-type ligands, such as 5-(tetrazol-5-yl)-isophthalic acid and 3,5-di(4-pyridyl)-1,2,4-triazolate ligand, which has multiple coordination sites involving polyzole nitrogen atoms, pyridyl nitrogen atoms and carboxylate oxygen atoms. All of them are good bridging ligands for constructing multi-functional CPs.

Especially, the polyzole-based ligands has attracted much attention because its abundant nitrogen electron-donating atoms tend to leave uncoordinated nitrogen atoms (receptor) combined metal cation. Once the analyte is recognized by the receptor, the fluorescence signals can be observed in the form of quenching or enhancement in the fluorescence maxima due to either electron transfer (ET), charge transfer (CT), or energy transfer (ET) processes[16-18].

Herein, we present a hydrogen-bonded supramolecular network with exposed Lewis basic nitrogen atoms ({[Cd(HTZ-IP)(HPYTZ)(H₂O)₂]·6H₂O}ₙ), hydrothermally prepared by a mixed-ligand strategy with the combination of a rigid 5-(tetrazol-5-yl)isophthalic acid (HTZ-H₂IP) and 3,5-di(4-pyridyl)-1,2,4-triazolate ligand (HPYTZ). Importantly, we have demonstrated that the infinite CPs is capable of detecting Ag^+ in colorless solution. As a sensing material for Ag^+, this CPs has features including simple preparation procedure, fast detection time, excellent selectivity for Ag^+, and high sensitivity with a detection range of $10^{-4}\sim10^{-6}$ $mol\cdot L^{-1}$ concentration limit.

1　Experimental

1.1　Materials and methods

All reagents used in these syntheses were of analytical grade and used as purchased without further purification. Elemental analyses (C, H, N) were performed on a Flash EA 2000 elemental analyzer. Infrared spectra were recorded on a Nicolet 6700 FT-IR spectrophotometer over a range of 4 000~600 cm⁻¹. The thermo-gravimetric analyses (TGA) were performed on a SⅡ EXStar6000 TG/DTA6300 analyzer in flowing N₂ with a heating rate of 10 ℃·min⁻¹. The powder X-ray diffraction (PXRD) patterns were recorded with a Bruker AXS D8 Advance diffractometer using monochromated Cu $K\alpha$ radiation (λ=0.154 18 nm; generator current: 40 mA; generator voltage: 40 kV; scanning scope: 2θ=5°~50°). Luminescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer at room temperature.

1.2　Preparation of complex

A mixture of HTZ-H₂IP (0.1 mmol, 23.4 mg),

HPYTZ (0.1 mmol, 22.3 mg), Cd (OAC)$_2$·2H$_2$O (0.1 mmol, 26.7 mg), N,N'-dimethylformamide (DMF, 1.0 mL), and H$_2$O (5.0 mL) was placed in a 23 mL Teflon liner stainless steel reactor. The vessel was heated to 120 ℃ for 4 days, and then cooled to room temperature at a rate of 5 ℃·h^{-1}. Colorless crystals were obtained, and further crystals were filtered off, washed with mother liquid, and dried under ambient conditions. Yield: 35%. Anal. Calcd. for C$_{21}$H$_{27}$N$_9$O$_{11}$Cd(%): C 36.35, H 3.92, N 18.17; Found (%): C 36.52, H 4.02, N 18.06. IR (cm^{-1}): 3 315m, 1 597s, 1 565vs, 1 559s, 1 507m, 1 493m, 1 426m, 1 395vs, 1 301w, 1 292m, 1 216m, 1 148m, 1 015m, 982m, 893m, 862m, 849s, 749m, 724s, 706m, 685m.

1.3　X-ray crystallography

　　Suitable single crystals of complex were mounted on a Bruker Smart APEX Ⅱ CCD diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation (λ =0.071 073 nm) by using φ-ω scan technique at room temperature. Semi-empirical absorption corrections were applied using SADABS[19]. The structures were solved using direct method and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions and refined isotropically with a riding model except for those bound to water molecules, which were initially located in a difference Fourier map and included in the final refinement by use of geometrical restraints with the O-

H distances being fixed at 0.085 nm and U_{iso} (H) equivalent to 1.5 times of U_{eq}(O). All calculations were performed using the SHELXTL-97 program package[20-21]. Some disordered solvent H$_2$O molecules in complex are squeezed by PLATON/SQUEEZE program[22]. The details of the structure solutions and final refinements for the complex are summarized in Table 1. Selected bond distances and angles are listed in Table S1.

　　CCDC: 1528982.

2　Results and discussion

2.1　Synthesis and IR characterization

　　Hydrothermal method has been proven to be a powerful approach for the preparation of sparingly soluble organic-inorganic hybrid material[23-24]. However, the given crystal growth is influenced by various hydrothermal parameters such as the pH value, temperature, the molar ratio of the reactant and reactant solvent[25-26]. The reactions of melt salt with HTZ-H$_2$IP and HPYTZ in molar ratio of 1∶1∶1 at the reaction medium of DMF and H$_2$O mixture (V_{DMF}:V_{H_2O} =1∶5) gave rise to the homogeneous single crystals suitable for X-ray diffraction analysis. The broad bands in the area of 3 400~3 200 cm^{-1} in the compound belong to the O-H stretching modes within coordinated and guest water molecules. Furthermore, the IR spectrum shows the sharp characteristic bands of dicarboxylate groups in the usual region at ~1 600 and ~1 500 cm^{-1} for the asymmetric stretching and at ~1 400 cm^{-1} for

Table 1　Crystal and structure refinement data for the complex

Formula	C$_{21}$H$_{27}$CdN$_9$O$_{11}$	F(000)	1 208
Formula weight	693.89	GOF	1.051
Temperature / K	296(2)	R_1 [$I>2\sigma(I)$]	0.033 3
Crystal system	Monoclinic	wR_2 [$I>2\sigma(I)$]	0.081 6
Space group	$P2_1/c$	R_1 (all data)	0.041 8
a / nm	1.003 06(6)	wR_2 (all data)	0.084 6
b / nm	2.160 02(13)	θ range / (°)	1.87~25.1
c / nm	1.345 20(8)	Reflection collected, unique	17 086, 4 853
β / (°)	110.068(10)	R_{int}	0.047 1
Volume / nm^3	2.737 6(3)	Completeness to θ / %	100
Z	4	Data, restraint, parameter	4 853, 0, 334
D_c / (g·cm^{-3})	1.465	$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / (e·nm^{-3})	622, −549
μ / mm^{-1}	0.848		

the symmetric stretching.

2.2 Structural description of {[Cd(HTZ-IP) (HPYTZ)(H₂O)₂]·5H₂O}ₙ

Single-crystal X-ray analysis reveals that the complex displays a hydrogen-bonded supramolecular network with the exposed uncoordinated N atoms. The asymmetric unit contains one Cd(II) atom, one HPYTZ molecule, one double-deprotonated HTZ-IP anion, two coordinated H₂O and five disordered guest H₂O molecule confirmed by TGA and Elemental analyses. Cd(II) ion adopts a highly distorted $CdNO_5$ octahedral geometry formed by three carboxylate O atoms belonging to two different HTZ-IP anion (Co-O 0.219 2(2)~ 0.250 5(3) nm), two coordinated water molecule (Co-O_w 0.236 4(3) and 0.237 8(2) nm), and one nitrogen atom from HPYTZ ligand (Co-N 0.228 0(3) nm), as shown in Fig.1(a).

Both carboxylate groups of the HTZ-H₂IP ligand bridge the adjacent Cd(II) centers by a monodentate bridging and a bidentate chelating mode to form Cd carboxylate linear chains running along the crystallographic a axis, while each HPYTZ molecule works as a terminal ligand with uncoordinated pyridine N atoms (Fig.1b). The mono-coordinated HPYTZ ligands are pendant and decorate the chain from one side. The paralleled chains are connected by H-bonds between coordinated H₂O and triazolate N atom of HPYTZ molecule (O(5W)−H(1W)···N(7); d(O5···N7)=0.288 8 nm; ∠O−H···N7=173.59°) to develop the 2D thick-layer, containing circular channels with free aperture about 0.504 nm×0.605 nm (the short distance not including the van der Waals radii), as shown in Fig. S1. The adjacent thick-layers are adhered together by further H-bonds between coordination H₂O and carboxylate O atoms (O(6W)−H(3W)···O(4); d(O6···O4)= 0.283 3 nm; ∠O−H···O4=164.22°) producing its entire hydrogen-bonded supramolecular network (Fig.1c and Fig.1d) with little aperture about 0.377 nm×0.496 nm
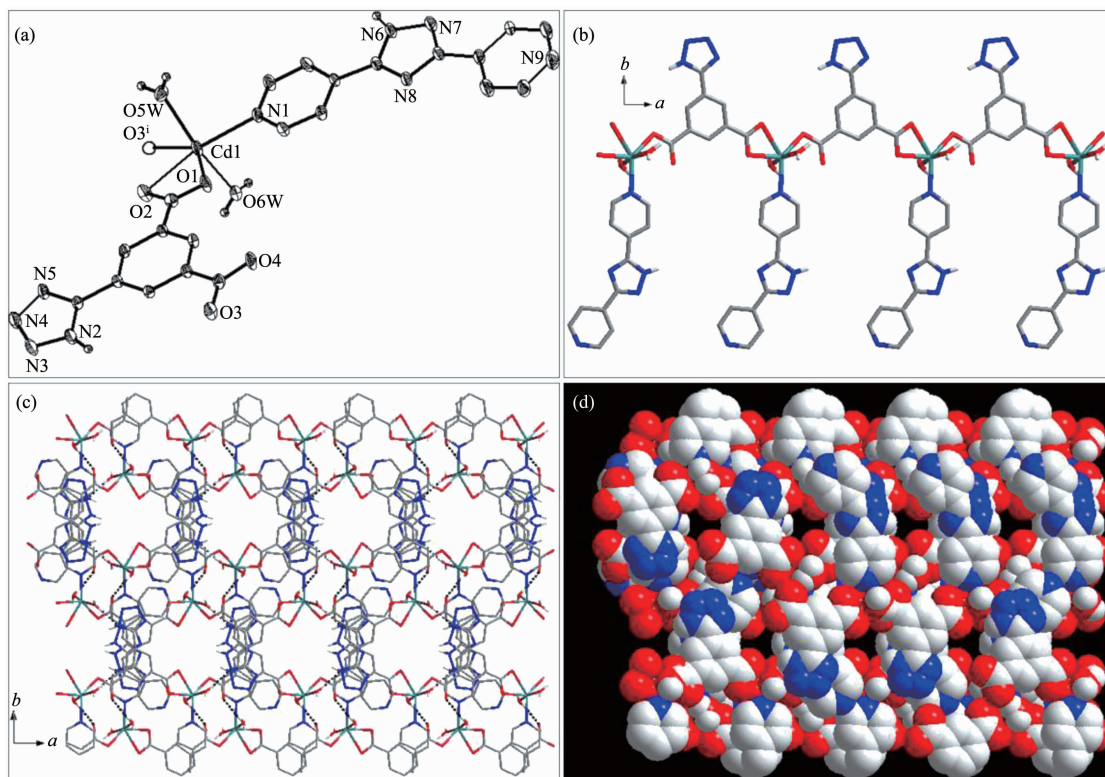
Symmetry codes: ⁱ 1+x, −1+y, z; Displacement ellipsoids are drawn at the 30% probability level and all hydrogen atoms of carbon atoms are omitted for clarity

Fig.1　(a) View of coordination environment of Cd(II); (b) View of a 1D chain featuring HTZ-IP-bridged CdO_5N octahedral; (c) Side view of a 3D supramolecular network consisting of 1D polymeric chains cohered by H-bonds; (d) Packing view of the supramolecular network

(the short $H\cdots H$ and $O\cdots O$ distance), as shown in Fig.S2.

2.3 TGA and PXRD analysis

Thermogravimetric analysis (TGA) were conducted to determine the thermal stability of the complex. TGA reveals that the removal of guest water molecules starts at room temperature (Fig.2a). The first weight loss of the complex is ~18.76% from room temperature to ~150 ℃, corresponding to the elimination of five guest water molecules and two coordinated water molecules per formula unit (Calcd. 18.17%). The residual solid starts to decompose at 250 ℃, and complete decomposition finishes at about 540 ℃. The

final residual species holds a weight of 18.13% of the total sample, and seems to be CdO (Calcd. 18.50%).

In order to further prove the purity of super-molecular structure, the washed and dried complex is sufficiently ground, and then examined by powder X-ray diffraction (PXRD), as shown in Fig.2b. The result shows the complex still has good crystallinity, because all major peaks in experimental PXRD match quite well that of simulated, indicating the reasonable crystalline phase purity. However, the difference in intensity may be due to the preferred orientation of the microcrystalline powder samples.
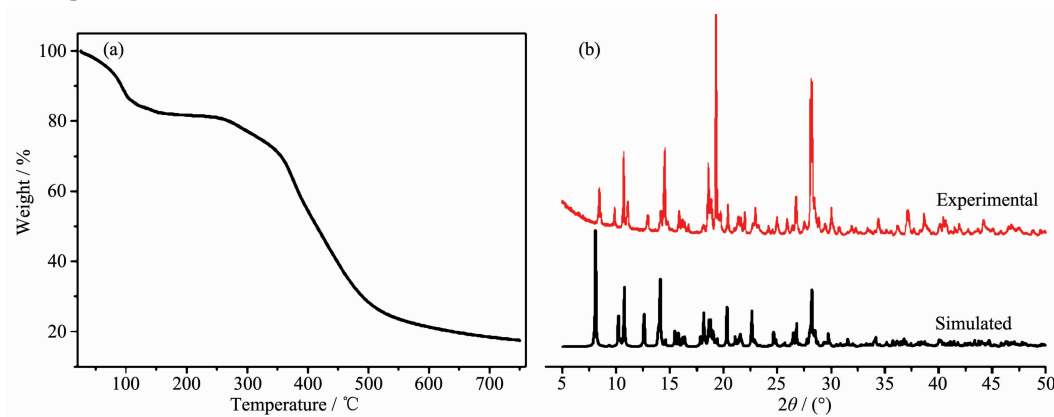

Fig.2　TGA curve (a) and PXRD patterns (b) of the complex

2.4 Luminescent detection for trace Ag^+

The photoluminescent properties of compound in the solid state at room temperature showed an intensity emission band at 436 nm with excitation wavelength of 371 nm (Fig.S3), while an intensity emission band at 422 nm was observed in aqueous solution. Along with its existence of the free Lewis basic sites (uncoordinated N atoms) promoted us to investigate its potential application in the detection of common metal ions. Because these free Lewis basic sites could be available for interactions with the Lewis acid species like metal ions.

In order to examine the ability of selective sensing of metal ions, the complex is sufficiently ground, and then dispersed by ultrasonic in aqueous solution containing 0.01 mol·L^{-1} of nitrate salts of Na^+, Ag^+, K^+, Ba^{2+}, Zn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, Fe^{3+}, Al^{3+}, Cd^{2+}, Hg^{2+}, Ca^{2+}, Mn^{2+} and Mg^{2+} for 2 h. It is

shown that most of the ions make no significant effect to the luminescent intensities of complex, except that there exist quenching effect to the luminescent intensities of complex including colorless Ag^+ ion and colored Fe^{2+}, Fe^{3+} and Ni^{2+} ions. So, only the influence of colorless ions on luminescent detection of Ag^+ ion were investigated in this work, considering the colored ions are visible to the naked eye. As presented in Fig. 3a, the complex may act as a high-performance luminescence sensor for detecting Ag^+ ion in colorless solution. In order to elucidate the possible mechanism for such luminescence quenching, powder XRD was employed to monitor the structure changes by Ag^+ solution treatment. The powder XRD patterns of the complex immersed in Ag^+ solution for 2 h have obvious change comparing with that of pristine complex, as shown in Fig.S4. That implies a new kind of structure may form relying on interaction between Lewis basic
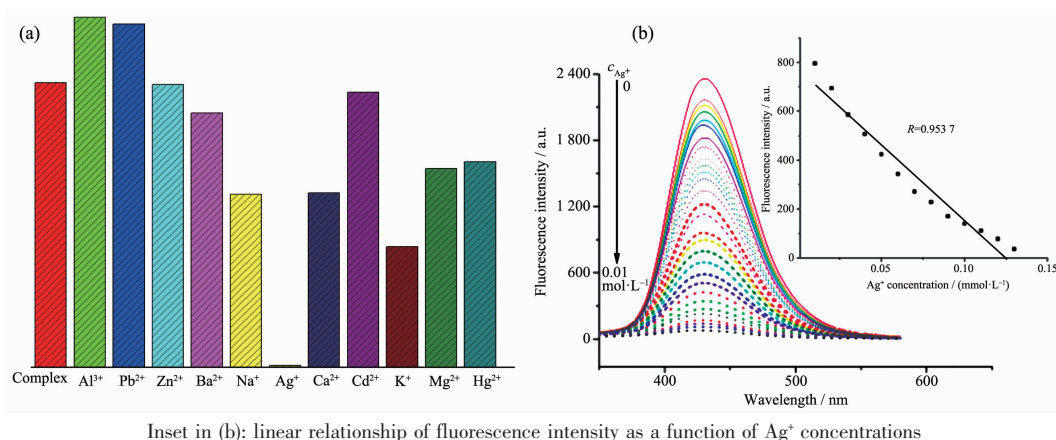
Inset in (b): linear relationship of fluorescence intensity as a function of Ag⁺ concentrations

Fig.3　(a) Luminescent intensities of the complex at 422 nm treated with different metal ions (0.01 mol·L⁻¹) in water at ambient temperature; (b) Fluorescence responses of complex for the determination of Ag⁺ in water

N sites of the complex and Ag⁺. However, the IR characteristic peak of the complex immersed in Ag⁺ solution for 2 h are similar to that of pristine complex (Fig.S5), suggesting that the main framework of complex does not change although the photoluminescence is mostly quenched. So, the quenching effect can be largely ascribed to between the receptor unit (uncoordinated N atom of ligand) and analyte (Ag⁺), which may cause the electrons of ligands to transfer from complex to Ag⁺ ions, resulting in the above-mentioned luminescent decay.

Furthermore, the quenching effect of complex was examined as a function of $AgNO_3$ concentration in the range of 0~0.01 mol·L⁻¹. The solid samples were immersed in different concentrations of $AgNO_3$ for 2 h, and then their luminescence intensity at 422 nm was recorded. When Ag⁺ concentration increased from 0 to 0.01 mol·L⁻¹, the fluorescence intensity of complex continuously decreased (Fig.3b). Ag⁺ concentrations are proportional to the fluorescence intensity of complex in the range of 10^{-4}~10^{-6} mol·L⁻¹ (Inset in Fig.3b). This concentration limit can detect trace Ag⁺ in the colorless solution, which is at the level of the reported fluorescence probes for Ag⁺[27-30].

Along with the sensitivity requirement, high selectivity is crucial in most scenarios, especially in real sample detections. Therefore, the selectivity of the complex in FL sensing system was estimated and shown in Fig.S6. Besides Ag⁺, the effects of other ten kinds of colorless cations, including colorless Na⁺, K⁺,

Ba^{2+}, Zn^{2+}, Pb^{2+}, Al^{3+}, Cd^{2+}, Hg^{2+}, Ca^{2+} and Mg^{2+} at the same concentration of Ag⁺, on the FL response of complex containing 0.01 mol·L⁻¹ Ag⁺ at the same time were investigated. We can find that the FL intensities are significantly quenched by 0.01 mol·L⁻¹ Ag⁺, whereas almost no additional inhibition of the FL intensities happens in the presence of Na⁺, Pb^{2+}, Cd^{2+} and Ca^{2+} ions, and only little enhancement of the FL intensities happens in the presence of K⁺, Ba^{2+}, Zn^{2+}, Al^{3+}, Hg^{2+} and Mg^{2+} ions. Apparently, the result clearly indicates that the FL sensing system exhibits high selectivity for Ag⁺ in the colorless solution.

3　Conclusions

In summary, a hydrogen-bonded supramolecular network with exposed nitrogen atoms is prepared by the cooperation of cadmium acetate with 5-(tetrazol-5-yl)isophthalic acid and nitrogen-rich co-ligand. It is noted that the material may not only accomplish an effective and reliable quantitative testing method for pure Ag⁺ ion with a detection range of 10^{-4}~10^{-6} mol·L⁻¹ concentration limit, but also display selective sensing of Ag⁺ ion in colorless solution. As a sensing material for Ag⁺, this compound has distinct features of simple preparation procedure and fast detection time. Although the selectivity of luminescence sensing for Ag⁺ ion need to be further improved, these results show that the Lewis base sites existing in CPs-based materials are quite critical in such fluorescence response process, which provides an insight into the

development of new multifunctional CPs-based materials with potential applications in the luminescence sensor.

Supporting information is available at http://www.wjhxxb.cn

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