Fresh hetero-metallic compound as luminescent sensor for detection of CS$_2$ and inhibitory activity on children diabetes

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Abstract
The combination of the dicarboxylate ligand of 2-aminoterephthalic acid (H$_2$L), Cd(NO$_3$)$_2$·4H$_2$O, and KNO$_3$ under hydrothermal condition formed a fresh hetero-metallic coordination polymer, namely, [CdK$_2$(L)$_2$(H$_2$O)$_4$]$_n$ (1). The compound exhibited a high luminescence intensity at normal environment as well as high sensitivity and selectivity in the measurement of CS$_2$. The effect of the fresh compound on childhood diabetes was investigated. A blood glucose monitor was utilized to assess the blood glucose level of the body after the addition of the compound. Moreover, the relative expression level of the insulin recipient on hepatocytes was assessed by real time RT-PCR.

Keywords Hetero-metallic compound · Luminescence sensor · Children diabetes

Introduction
With the progress of society, the living conditions of humans have gradually improved, and their lifestyle has changed rapidly. The morbidity of diabetes in immature individuals and adults is increasing [1]. It shows significant regional differences; the incidence rate of diabetes in children in Southeast Asia is the lowest, and that in Southeast Asia is significantly higher than that in the US and Europe [2]. Children aged 10 to 14 years are most likely to suffer from diabetes and should be given special attention.

Carbon disulfide is widely utilized in the manufacture of cellophane, vulcanized rubber, pesticides, viscose fibers, and carbon tetrachloride due to its colorless and volatile properties [3]. Once the human body is exposed to high concentration of toxic carbon disulfide, coronary artery and atherosclerosis may occur [4]. In this regard, a simple and high sensitive alternative to carbon disulfide as detection material should be developed. In recent years, fresh multifunctional crystalline metal–organic frameworks (MOF) have made significant technological progress [5–8]. At present, a variety of MOFs with obvious luminous intensity have been discovered and used to detect toxic heavy metal ions, volatile organic solvents, and nitroaromatic dynamites [9–12]. MOF detection based on luminous intensity has higher sensitivity, simpler procedure, and more obvious results than transition detection technology [13]. Creating MOF with high thermal stability and luminous intensity for detection of toxic substances remains challenging. Polycarboxylic acid ligands are used to manufacture MOF due to their diverse metal coordination patterns with metal cations [14–16]. Pairing metal cations with polycarboxylic acid ligands can simply form rod-shaped substructures [17, 18]. The reasonable superposition of this structure can lead to a more stable MOF frame. In the present study, 2-aminoterephthalic acid was used as an organic ligand to link to K(II) and Cd(II) ions and obtain fresh hetero-metallic compound, namely, [CdK$_2$(L)$_2$(H$_2$O)$_4$]$_n$ (1). The compound displayed high sensitivity and selectivity for CS$_2$ probe. The effect of the compound on children’s diabetes was analyzed, and the underlying mechanism was investigated.
Experimental

Materials and instrumentation

All experimental materials were purchased from the manufacturer and used without additional treatment. Elemental analyses (carbon, hydrogen, and nitrogen) were conducted on elemental Vario EL III analyzer. Powder X-ray diffraction analysis was performed using PANalytical X’Pert Pro powder diffractometer with Cu/Kα radiation (λ = 1.54056 Å) with a step length of 0.05°. Thermogravimetric analysis was implemented by a NETSCHZ STA-449 C thermoanalyzer at the warming ratio of 10 °C/minute under atmosphere condition ranging from 30 to 800 °C. The luminescent functions of 1, phen, and H2L were detected using Edinburgh Analytical instrument FLS920.

Synthesis of compound [CdK2(L)(H2O)]4n (1)

In brief, 0.100 mmol Cd(NO3)2·4H2O was mixed with 0.1 mmol KNO3, 0.100 mmol H2L, 0.20 mmol NaHCO3, and 10.0 mL of H2O. The mixture was kept in a 25.0 mL Teflon-lined huge-tensity holder at 150 °C for 3 h. After decreasing to normal temperature at 2 °C/minute, yellow bulk crystals of 1 were produced in 38% yield based on H2L. Calculated for C16H12CdK2N2O10 (Mr is 582.89), carbon is 32.94%; hydrogen is 2.06%; nitrogen is 4.8%. Found: carbon is 32.97%; hydrogen is 2.03%; nitrogen is 4.83%.

X-ray crystallography

Single-crystal detection of 1 was implemented using the program designed for Oxford Xcalibur 3 diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293(2) K. The conformation of 1 was detected through dual-direct technique and elucidated by full-matrix least square method referring to SHELXL-2014 software [19]. Table 1 shows the crystal parameters of the compound. Table S1 presents the bond length and angle of the compound.

Sensing experiments

Compound 1 (4 mg) was added to 4 mL of diverse solvent of DMF (N,N-dimethylformamide, THF (tetrahydrofuran), CS2,MeOH, EtOH, H2O, EG (ethylene glycol), DMA, (N,N-dimethylacetamide), CH3CN, and acetone. The mixtures were ultrasonically treated for 5 min. A 1 cm-wide quartz cell was used for fluorescence probe. Titration studies were carried out by gradually adding CS2 to the DMF solvent.

Blood glucose measurement

A blood glucose monitor was used to estimate the blood glucose content in human before the experiment and after using the mixture. All operations were completed according to the manufacturer’s proposal with minor adjustments. Fifty Balb/c rats (aged 3 weeks, weighing 13–16 g) were acquired from the Creature Study Centre of Nanjing University (Nanjing, China) and maintained at strict environment of 45% humidity and 20–25 °C. Diabetic rat models were established by feeding mice with high-fat diet. When blood glucose ≥ 16.7 mmol, it was considered to be a normal model. The compound was then added at 1, 2, and 5 mg/kg. Under the injection, the liver organs of the animals were taken and all the RNA of the tissues was picked up.

Table 1 Crystallographic parameters of compound

| Formula          | C16H12CdK2N2O10 |
|------------------|------------------|
| Fw               | 582.89           |
| Crystal system   | tetragonal       |
| Space group      | I4_1/acd         |
| a (Å)            | 21.298(2)        |
| b (Å)            | 21.298(2)        |
| c (Å)            | 12.211(2)        |
| α(°)             | 90               |
| β(°)             | 90               |
| γ(°)             | 90               |
| Volume (Å³)      | 5538.8(1)        |
| Z                | 8                |
| Density (calculated) | 1.398        |
| Abs. coeff. (mm⁻¹) | 1.732        |
| Total relections | 9168             |
| Unique relections| 1576             |
| Goodness of fit on F² | 1.111        |
| Final R indices [I > 2σ(I)] | R = 0.0807, wR² = 0.2286 |
| R (all data)     | R = 0.1031, wR² = 0.2518 |
| CCDC             | 2,082,357        |
Results and discussion

Crystal structure of compound 1

Based on the X-ray crystallographic detection, compound 1 shows a 3D hetero-metallic structure that forming crystal in the tetragonal $I4_1/acd$ space group. Every asymmetric part of 1 contains half $L^2^−$ ligand, half K(I) ion, a single forth Cd(II) ion, and a single-coordinated H2O molecule. The Cd1 ion links with 8 O atoms on four carboxylate groups of four separated $L^2^−$ ligands, forming a twisted tetragonal...
antiprism, and the K1 ion links with a single-terminal H2O ligand and three carboxylate O atoms on three diverse L2– ligands prior to constructing a twisted tetrahedron (Fig. 1). The Cd-O bond length is between 2.336(4) and 2.517(5) Å, and the K-O bond length is between 2.692(5) and 2.708(5) Å. Every L2– ligand applies a (µ2-µ2)-(µ2-µ2)-µ6 coordination pattern bridging with double Cd(II) ions and 4 K(I) ions (Figure S1). For the conformation of I, every {CdO8} polyhedron offers four edges with four contiguous {KO4} tetrahedrons; every {KO4} tetrahedron offers double edges with double contiguous {CdO8} polyhedrons. These bonding points connect the polyhedrons into a 1D chain expanding along the crystallographic b-direction (Fig. 2a). These unlimited one-dimensional chains are bridged via the L2– ligands, constructing a 3D heterometallic conformation (Fig. 2b). Based on the estimation with PLATON, the conformation of I had 25.5% dissolvant accessible volume (1391.8 Å³ gross accessible volume/5538.8 Å³ every cell volume).

Powder X-ray diffraction pattern (PXRD) and thermogravimetric analysis (TGA)

The PXRD patterns simulated are shown in Figure S2a. According to previous studies, the experimental and simulated graphs are consistent, and the bulk sample represents the single-crystal structure of I. The TGA curve of I is shown in Figure S2b. The double-stage mass reduction procedure. The initial mass reduction is 12.31% at 72 and 112 °C to evaporate the coordinated H2O molecules (calcd: 20.35%), and Phase I occurred within 300–410 °C with a mass reduction of 49.48% that may be due to the disassembly of the organic ligand (calcd: forty-nine point 5%).

Photoluminescent sensing properties of I

The solid luminescence pattern of I and unlimited H2L were assessed at normal temperature (Figure S3). Compound I has high luminous intensity, and the center of the emission band is 456 nm (λex is 350 nm). The emission band of free H2L is located at 436 nm (λex is 340 nm), leading to intraligand π*→π electronic migration transitions. According to a previous article [20], the luminescence principle of I was temporarily considered to be caused by charge movement in the ligand. In contrast to the unlimited H2L ligand, the apparent red-shift at 20 nm can be influenced by the coordination of the L2– ligand to the central metal cation.

Compound I has high luminous intensity and heat resistance and thus can be used to explore sensing characteristics for diverse dissolvent molecules. The luminescence intensity of I dissolved in diverse solvents increases at normal temperature. As shown in Fig. 3a, the luminous intensity of I is basically not affected in solvents such as MeOH, DMA, EtOH, DMF, and H2O. In solvents, such as acetone, EG, CH3CN, and THF, the luminous intensity of I decreases by 27.5–51.6%, which is significantly affected. When I detects CS2, it is almost completely quenched. According to the above experiments, the compound has huge selectivity for CS2. Based on the titration experiment of adding 10 ppm CS2 successively, the sensitivity of I to CS2 was further studied. Based on the patterns in Fig. 4b, after adding CS2, the luminous intensity of I slowly decreased. When the concentration of CS2 reaches 110 ppm, the luminescence of I was near totally extinguished, and the extinction efficiency reaches 95.92%. In addition, the detection range of I to CS2 was evaluated with 3σ/k (k means slope, σ means standard) by linear matching in the content scope of 0 to 60 ppm; the quantity for the detection range for CS2 is assessed approximately as 0.113 ppm (Figure S4). Hence, compound I has huge detection sensitivity to CS2. Under the detection of CS2, the PXRD experiment shows that the main framework of I does not change (Figure S2a). Therefore, when compound I was used to detect CS2a, it has the characteristics of stable framework, huge selectivity and huge sensitivity.
Compound obviously inhibited the relative expression of the insulin receptor on liver cells. The fresh compound evidently decreased the blood glucose level in a consumption-dependent and time-growth manner. Because the insulin receptor on the liver tissues control the human’s main blood glucose levels, real time RT-PCR was performed and used to determine the quantity of the insulin receptor on the liver tissues was evaluated. Figure 5 shows the relative expression of the insulin receptor on the liver tissues of the control model and was higher than that in the animal model. After adding fresh compound, the quantity of insulin receptors on hepatocytes increased obviously. The inhibitory effect of the fresh compound on blood glucose was positively correlated with the amount and time of addition.

Compound significantly reduced the body blood glucose levels of dose and time dependently. A compound with creative framework was created, and its inhibitory effect on blood glucose was measured by blood glucose monitor to treat childhood diabetes. Figure 4 shows that the blood glucose level in the model group is higher than that in the control group (with P < 0.005. After adding compounds at the content of one, 2 and 5 mg/kg, the blood glucose levels in diabetic mice decreased in a dose-dependent and time-growth manner. The experiments manifested that the compound can be effectively used for treatment of children with diabetes.
Conclusions

A fresh heterometallic compound of $[\text{CdK}_2 \text{L}_2 \text{H}_2 \text{O}]_n$ (I) was formed under hydrothermal condition. Crystallography was assessed by single-crystal framework analysis. A 3D structure with 25.5% solvent-accessible volume was used. The analysis of the luminescence sensing performance of I showed that it can sense CS$_2$ with high selectivity and sensitivity at normal environment. The compound also decreased the blood glucose level in a consumption-dependent and time-growth manner. Furthermore, the real-time RT-PCR showed that the relative expression of the insulin receptor on hepatocytes.

Supplementary information The online version contains supplementary material available at https://doi.org/10.1007/s10895-022-02943-0.

Author contribution Wen-Hui Sun carried out the experiments, analyzed the data and wrote the draft of this manuscript; Bing Ye designed the whole experiments and revised the draft.

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Availability of data and material Selected bond lengths ($A$, and angles ($^\circ$) for I (Table S1); The coordination mode of L$^{2-}$ ligand in I (Fig. S1); PXRD patterns of I (Fig. S2). The luminescent emission spectra of I and free H$_2$L ligand at room temperature (Fig. S3). The detection limit of I toward CS$_2$ (Fig. S4), the information could be found in the supporting information file.

Code Availability Not applicable.

Declarations

Conflict of interest All authors declare that there is no conflict of interest regarding the publication of this paper.

Ethics approval All the preformation conducted in this present research was approved by the Animal Ethics Committee of Qilu Children’s Hospital of Shandong University.

Consent to participate Not applicable.

Consent for publication Written informed consent for publication was obtained from all participants.

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