具有荧光响应功能的分子四边形的组装

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摘要:由缩氨基脲和 2-喹啉醛合成了席夫碱配体 H_2L,并与过渡金属离子 Cd^{2+}组装得到了四边形配合物 CQ。用 X 射线衍射对配合物的晶体结构进行了测定,发现其具有 $I4_1/a$ 空间群。通过荧光测试发现该配合物在 CH_3CN 溶液中具有较强的荧光,加入间苯二甲酸、对苯二甲酸阴离子后荧光发生淬灭,而加入邻苯二甲酸阴离子荧光无变化,可以将邻苯二甲酸阴离子从其他 2 种二酸阴离子中区分出来。

关键词:镉离子;荧光;席夫碱配体;二酸阴离子
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Self-assembly of Fluorescent Molecular Squares

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Abstract: A novel Cd-based tetranuclear complex CQ ([$Cd_4H_2L_4$](NO_3)$_2$·14H_2O, where H_2L=bis[2-Quinoline methyl] carbohydrazone) has been synthesized via self-assembly. Single-crystal X-ray diffraction analysis shows that CQ is a molecular square, which crystallizes in an $I4_1/a$ space group. CQ shows a strong fluorescent emission band in CH_3CN solution. The fluorescent titration experiment shows the CQ has a fluorescent quenching effect toward *p*-phthalate and *m*-phthalate dicarboxylates, while silent for the *o*-phthalate one, suggesting it can be used as a fluorescent chemosensor for distinguishing *o*-phthalate from two other isomers of dicarboxylates. CCDC: 791184.

Key word: Cd^{2+} ions; luminescence; Schiff base ligand; dicarboxylates

0　Introduction

Supramolecular assembly of predesigned organic and inorganic building blocks is an excellent tool for constructing well-defined nanosize molecular cavities[1]. Synthetic strategies for constructing functional coordination cages with various structures and novel inclusion properties have been well established these years[2]. As the development of supramolecular chemistry, the major challenge goes beyond achieving a size- or a shape-selective dynamic molecular recognition and includes detecting and amplifying guest-bonding events to produce a measurable output[3]. Thus, a proper communication system that is able to transduce the recognition information into an easy-to-measure signal must be included in the overall molecular design[4].

Recently, the development of synthetic receptors able to bind anions selectively in a detectable fashion to an observer via changes in electrochemical response or in fluorescence intensity constitutes an important yet difficult task facing supramolecular chemists[5], since these species are not only strongly solvated in protonic

media but also characterized by multiple charges and complex shapes. Differentiation of geometric isomers (such as *ortho/meta/para* dicarboxylates) is, in general, a difficult task, because of their similar chemical and physical properties e.g. charge density and structural complexity[6-7].

In this paper, we report the synthesis and structure of a tetranuclear cadmium square via self-assembly. The ligand combining two quinoline groups into a semicarbazone group as an edge of a quadrilateral is used to design the well-programmed molecular square and addressed the problem of discriminating *o*-phthalate from *m*-phthalate and *p*-phthalate isomers by the molecular square. Each quinoline group acts as both fluorophore and binding site. On the other hand, urea and thiourea derivatives are well known as attractive building block in the construction of neutral hydrogen bonding receptors [8]. Hence, each ligand can provide two-armed N_2O tridentate coordinating site for the metal ion, which are simultaneously introduced as trigger sites to achieve efficient host-guest interactions, consequently yielding signal response[9]. In the presence of a specific anion as the conformational template, the hydrogen bonding interaction between the urea groups and the anion is expected and the fluorescent signal changes results[10-11].

1 Experimental

1.1 Materials and instrumentation

All the chemicals and solvents were of reagent grade quality obtained from commercial sources and used without further purification. The salts solutions of metal ions was $Cd(NO_3)_2 \cdot 4H_2O$. The elemental analyses of C, H and N were performed on a vario EL Ⅲ elemental analyzer. ^1H NMR spectra were measured on a BRUKER 400M spectrometer. ESI mass spectra were carried out on a HPLC-Q-Tof MS spectrometer using acetonitrile as mobile phase. UV-Vis spectra were measured on a HP 8453 spectrometer. The fluorescent spectra were measured on EDINBURGH FS920.

1.2 Synthesis of the ligand H_2L

10 drops of acetic acid were added to a methanol (50 mL) solution of 2-quinoline carboxaldehyde (0.690

g, 4.4 mmol) with semicarbazone (0.180 g, 2 mmol). After refluxed for 6 h, a white floccule was collected by filtration, washed with methanol, and dried in vacuo. Yield: 0.56g, 76%. ^1H NMR (400 MHz, DMSO-d$_6$, ppm) δ: 11.34 (s, 2H), 8.45 (d, 4H), 8.32 (s, 2H), 8.03(d, 4H), 7.82 (m, 2H), 7.65 (m, 2H). Element analysis Calcd. for $C_{21}H_{16}N_6O$ (%): C 68.45; H, 4.38; N, 22.81. Found (%): C, 68.81; H, 4.83; N, 22.36 (Scheme 1).
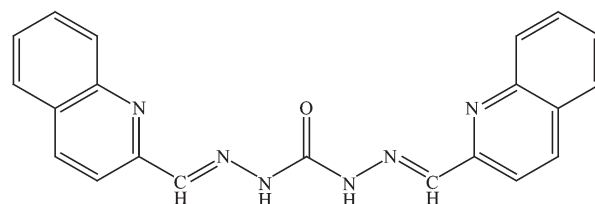
Scheme 1　Chemical structure of H_2L

1.3 Preparation of compound CQ

The solution of $Cd(NO_3)_2 \cdot 4H_2O$ (0.031 g, 0.1 mmol) in 10 mL methanol was added to a suspension of H_2L (0.038 g, 0.1 mmol) in 10 mL methanol. Red block single crystals of CQ suitable for X-ray crystallographic analyses were carried out from evaporating the mixture for one week and collected by filtration, washed with methanol, and dried in vacuum. Yield: 30%. Element analysis Calcd. for $C_{84}H_{86}Cd_4N_{26}O_{24}$(%): C, 43.99; H, 3.78; N, 15.88. Found(%): C, 44.35; H, 3.56 N, 16.21. ESI of CQ in a CH_3CN solution exhibits the intense peak at m/z =638.72 and m/z =644.72 with the isotopic distribution patterns separated by 0.33±0.01, which could be assigned to the species of $[Cd_4H_3L_4]^{3+}$ and $[Cd_4H_3L_4 \cdot H_2O]^{3+}$, respectively, indicating the stability of Cd-based molecular square in solution.

1.4 Structure determination

Suitable crystals were selected for single-crystal X-ray diffraction structural analysis and the data were collected on a Bruker SMART APEX CCD diffracto-meter with graphite-monochromatized Mo $K\alpha$ radiation (λ =0.071 073 nm), using the SMART and SAINT prog-rams[12]. The structures were solved by direct method and refined on F^2 by full-matrix least-squares methods with SHELXTL version 5.1[13]. Crytsal data of CQ: $C_{84}H_{86}Cd_4N_{26}O_{24}$, M_r=2 293.39, Tetragonal, space group $I4_1/a$, red block, a=2.912 67(9) nm, c=1.226 80(7) nm, V = 10.407 7(7) nm^3, Z=4, T=180 K. 4 004 unique reflec-

tions (R_{int}=0.067 5). Final R_1 (with I>2σ(I))=0.068 6, wR_2 (all data)=0.177 9, for 2θ=48.5°. Except the slovent molecules and the counter aion, anisotropic thermal parameters were refined for non-hydrogen atoms, hydrogen atoms were localized in their calculation positions and refined by using the riding model. The solvent water oxygen atoms were added with hydrogen atoms which were found from the difference Fourier maps and then fixed with the O⋯H distances of 0.096 nm and H⋯H distances of 1.52, isotropic parameters of these hydrogen atoms were fixed as 1.5 times the isotropic parameters of the oxygen atom it was attached.

CCDC: 791184.

2　Results and discussion

2.1　Structure feature

The structure analysis shows that CQ is a centrosymmetry neutral tetranuclear Cd(Ⅱ) square, which is crystallized in centrosymmetric $I4_1/a$ space group of tetragonal crystal system. In this square four Cd(Ⅱ) ions occupy the corners of the molecular square, and each ligand acts as the bridge between two metal ions to form an edge (Fig.1). Each Cd(Ⅱ) ion is therefore octahedrally coordinated by the carbonyl oxygen atoms, the quinoline and imine nitrogen atoms from two ligands in the mer-configuration, and the dihedral angle between the two chelating planes around each Cd(Ⅱ) center ranges from 85° to 92°. With the two chelating units at the para positions of the urea spacer, the ligand displays a nearly linear configuration leading to a relatively large and planar molecular square. The presence of two counteranions for each CQ molecule

square suggests the four ligands lost six protons in virtue of coordination to metal ions[14-15]. As a result, all the bond distances within two arms are intermediate between the normal single bond and double bond, further indicating extensive delocalization over the entire molecular skeleton. Neighboring Cd[Ⅱ] ions are bridged by the single oxygen atoms of the ligand "edges" with M⋯M separations of approximately 0.425 nm and M-O-M angles of about 130°. There are four urea groups in the tetranuclear complex CQ which located within the square, providing static, geometric, coordinative, and functional properties to the square-like complex, which are important for the recognition of carboxylate derivatives, such as dicarboxylates[16-18].
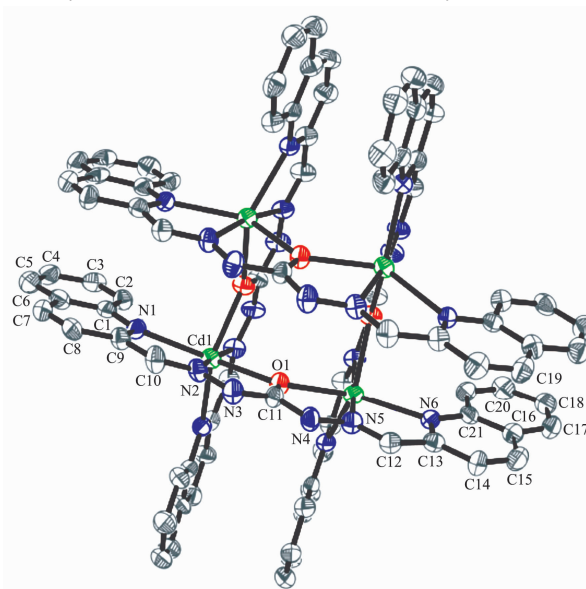
Displacement ellipsoild are drawn at the 30% probability level, hydrogen atoms, solvent molecules and counter anion are omitted for clarity

Fig.1　Molecular structure of the molecular square CQ

Table 1　Selected bond distance (nm) and angle (°)

Cd(1)-N(2)	0.227 4(6)	Cd(1)-N(5A)	0.228 7(6)	Cd(1)-O(1)	0.234 6(5)
Cd(1)-O(1A)	0.234 6(5)	Cd(1)-N(1)	0.235 1(6)	Cd(1)-N(6A)	0.238 0(6)
C(11)-O(1)	0.128 7(8)	C(11)-N(3)	0.134 4(9)	C(11)-N(4)	0.135 4(9)
N(2)-Cd(1)-N(5A)	171.2(2)	N(2)-Cd(1)-O(1A)	108.8(2)	N(5A)-Cd(1)-O(1A)	68.3(2)
N(2)-Cd(1)-O(1)	68.2(2)	N(5A)-Cd(1)-O(1)	103.3(2)	O(1)-Cd(1)-O(1A)	90.4(2)
N(2)-Cd(1)-N(1)	71.5(2)	N(5A)-Cd(1)-N(1)	116.5(2)	O(1A)-Cd(1)-N(1)	93.9(2)
O(1)-Cd(1)-N(1)	138.6(2)	N(2)-Cd(1)-N(6A)	110.6(2),	N(5A)-Cd(1)-N(6A)	71.1(2)
O(1A)-Cd(1)-N(6A)	139.1(2)	O(1)-Cd(1)-N(6A)	94.1(2)	N(1)-Cd(1)-N(6A)	108.6(2)

Symmetry code A: −y+5/4, x+1/4, −z−7/4.

2.2 Fluorescence feature

Fluorescence spectrum of CQ in the CH₃CN solution shows a strong emission band at 620 nm attributing to the Cd-quinoline group (excitation at 468 nm) (Fig.2). Upon addition of an *o*-phthalate ion in the form of tetrabutylammonium (TBA) salt[19], the emission intensity decreases slightly, and no significant shift of the wavelength is found when excited at 468 nm. But upon the addition of *m*- or *p*-phthalate ions, the intensity of the emission band at 620 nm decreases drastically. The observed fluorescent quenching could be attributed to the typical guest-induced PET process [20]. Upon coordination of the anion with the sensor, the hydrogen bonds between the anion and urea cause a decrease in the oxidation potential of the urea receptor, which triggers the PET from urea to coordinate to the relatively electron deficient Cd-quinoline fluorophore, leading to the enhancement of a PET effect, thus causing the fluorescence to be "switched-off".
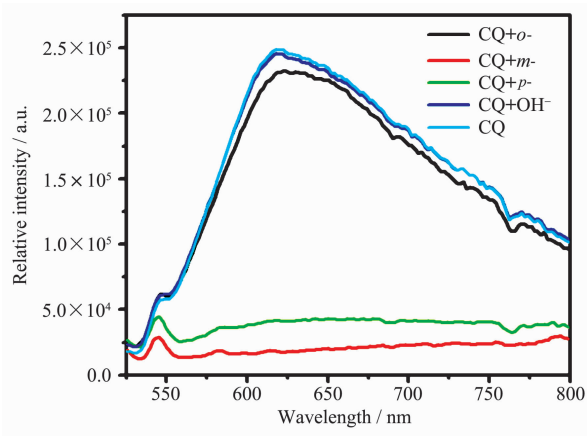

Fig.2 Selectivity experiment of CQ (50 μmol·L⁻¹) toward OH⁻ and the three forms of dicarboxylate (1 equiv) in CH₃CN, λ_{ex}=468 nm, λ_{em}=620 nm

Upon the addition of *m*- or *p*-phthalate ions to the CH₃CN solution of CQ, the intensity of the emission band at 620 nm decreases similarly (Fig.3,4). The luminescent titrations with the two isomeric phthalates suggest the formation of 2:1 stoichiometry host-guest interacted as the titration curve shows a steady and smooth decrease until a plateau is reached with 0.5 equiv of the *p*-, and *m*-phthalate anions, respectively. However, upon the addition of equivalent OH⁻ anions,

the emission intensity decreases slightly (Fig.2). Although we don′t have any further proof to confirm the interaction of hydrogen bond between anion and the square, the receptor CQ has high selectivity toward the *o*-phthalate anion over the other two isomers of dicarboxylates. Based on the luminescent titrations, it is suggested that there are two square bind one *m*-phthalate or *p*-phthalate anion, the two COO⁻ in the *m*- or *p*-phthalate anion combine the urea groups of two squares tightly and cause the decrease of the fluorescence drastically (Scheme 2), but the fluorescence decreases slightly with the addition of *o*-phthalate anion because the angle of two COO⁻ is too narrow to form tightly hydrogen bond with both squares.

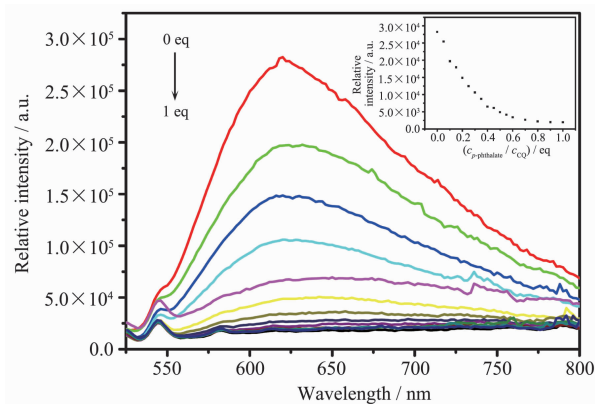Fig.3 Fluorescent response of CQ (50 μmol·L⁻¹) upon addition of *p*-phthalate dicarboxylate in CH₃CN, the insert picture shows the fluorescence titration profile around 620 nm with the excitation wavelength of 468 nm

Fig.4 Fluorescent response of CQ (50 μmol·L⁻¹) upon addition of *m*-phthalate dicarboxylate in CH₃CN, the inset picture shows the fluorescence titration profile around 620 nm with the excitation wavelength of 468 nm
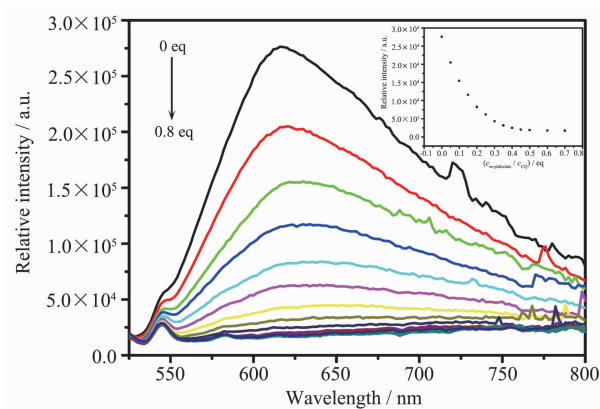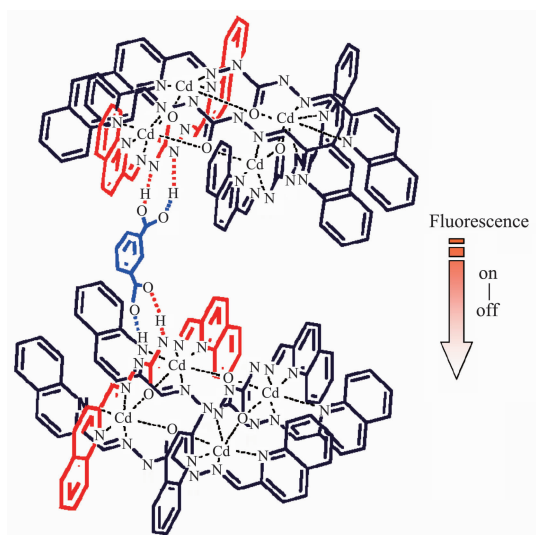
Scheme 2　Possible recognition pattern between the *m*-(or *p*-) phthalate anion and the molecular square CQ

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