

Synthesis, Structure and Fluorescence of a New 1D Coordination Polymer Containing 1,2,4-Triazole-derived Macrocyclic [1₄] Heterophane

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The recent decades have witnessed the rapid development in the chemistry of macrocycles due to their applications in host-guest chemistry, molecular recognition and supramolecular chemistry.¹ The strategies in the design and synthesis of macrocyclic ligands aim at the improvements of the recognition and selective transport functions in self-organization and/or self-assembly processes.² A survey on the literatures reveals that there are two primary methods to synthesize macrocyclic ligands. One depends on the condensation of dialdehydes with diamines to form Schiff base macrocycles,³ involving fewer examples of a higher order [n+n] (n>2) macrocyclization.⁴ The other one follows convergent approach for the construction of macrocyclic [1₄] heterophanes, which contain a macrocycle fabricated by the linkage of four same and/or different heterocycles.⁵ Alcalde, E. and his coworkers introduced 1,2,4-triazole moieties into the macrocycles to successfully prepare and structurally characterize numerous [1₄] heterophanes, however no metal complexes have been reported to date.⁶ Torres *et al.* isolated some macrocyclic complexes containing triazole ring but none of them have been structurally characterized.⁷

The aim at the syntheses of 1,2,4-triazole-derived macrocycles is to incorporate 1,2,4-triazole moiety with macrocycle, thus to integrate the advantages of macrocycles and 1,2,4-triazole complexes,⁸ get greater stability, control of nuclearity and metal environments (such as geometry).⁹ A new [1₄] 1,2,4-triazole-derived heterophane complex [CdBr₂L]_n, where L is the macrocyclic ligand, was obtained from hydrothermal reaction with its crystal structure and fluorescence characterized.

Experimental Section

Materials and physical measurements. The reagents and solvents were used directly as supplied commercially without further purification. The IR spectrum was recorded on a Nicolet Magna 750 FT-IR spectrometer with KBr pellet in the range 4000-400 cm⁻¹. Elemental analysis was carried out on a Vario EL III elemental analyzer. The solid-state fluorescent excitation and emission spectra were performed on a FluoroMax-3 spectrophotometer at room temperature with excitation and emission slits at 5.0 nm, increment 1.0 nm and integration time 0.1 s.

Synthesis of [CdBr₂L]_n. CdBr₂·4H₂O (0.1 mmol, 33.4

mg), 1H-1,2,4-triazole (0.2 mmol, 13.8 mg), 3,5-bis(chloroethyl)-1,2,4-triazole (0.2 mmol, 38.9 mg) were mixed with 10 mL dry CH₃CN in a 25 mL Teflon-lined stainless-steel autoclave. The mixture was heated at 120 °C for 5 days in a furnace, and then naturally cooled to obtain colorless crystals. Yield based on Cd: 10.7 mg, 16.4%. Elemental analysis for C₁₆H₂₀Br₂CdN₁₂, Found (Calc.): C, 29.56 (29.45); H, 3.16 (3.09); N, 25.82 (25.75). IR data (in KBr, cm⁻¹): 3260 (br, s), 3131 (m), 3058 (m), 2952 (m), 1638 (s), 1569 (s), 1529 (m), 1476 (m), 1431 (m), 1367 (m), 1280 (w), 1182 (m), 1107 (w), 1023 (w), 978 (w), 863 (w), 793 (w), 768 (w), 749 (w), 679 (w), 597 (w), 516 (w).

X-ray crystallography. Data collection for the compound was performed on Rigaku Mercury CCD diffractometer equipped with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Intensity data were collected at 293(2) K, corrected for Lorentz and polarization effects as well as for absorption by the ω scan technique, and reduced using CrystalClear program.¹⁰ The structure was solved by direct method using SHELXTLTM package of crystallographic software¹¹ and refined by full-matrix least-squares technique on F^2 . All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to C and N atoms were located at geometrically calculated positions and refined with isotropic thermal parameters included in the final stage of the refinement on calculated positions bonded to their carrier atoms. Crystallographic data and the selected bond distance and angles for the title complex are respectively listed in Table 1 and 2.

Results and Discussion

Description of crystal structure. The title compound features a 1D coordination chain, whose asymmetric unit contains two Cd(II) centers of half occupancy, two Br⁻, and one macrocyclic ligand L. Cd1 and Cd2 are located in inverse centers, whose coordination spheres both are octahedral geometries with their equatorial planes occupied by four nitrogen atoms from two L ligands with Cd-N distances locating in a narrow scope between 2.418(4) and 2.560(4) Å, and the two apical positions by two Br⁻ (Figure 1) with distances ranging from 2.6379(7) to 2.7084(6) Å. L ligands alternately bond Cd1 and Cd2 centers in centrosymmetric mode to form a linear -Cd1-L-Cd2-L- chain.

Table 1. Crystallographic and refinement data

Empirical formula	C ₁₆ H ₂₀ Br ₂ CdN ₁₂
Color and Habit	colorless block
Crystal Size (mm)	0.213 × 0.119 × 0.115
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	10.500(2)
<i>b</i> (Å)	13.361(3)
<i>c</i> (Å)	14.973(3)
β (°)	99.153(3)
<i>V</i> (Å ³)	2073.8(7)
<i>Z</i>	4
<i>F</i> _w	652.66
<i>D</i> _{calcd} (Mgm ⁻³)	2.090
μ (mm ⁻¹)	4.940
<i>F</i> (000)	1272
θ (°)	2.49 to 28.43
Reflections measured	12165
Index ranges of measured data	-14 ≤ <i>h</i> ≤ 9, -17 ≤ <i>k</i> ≤ 13, -19 ≤ <i>l</i> ≤ 20
Independent reflections	5088 (<i>R</i> _{int} = 0.0556)
Observed Reflection [<i>I</i> > 2σ(<i>I</i>)]	2917
Parameter/Restraints/Data(obs.)	283 / 0 / 2917
Final <i>aR</i> ₁ , <i>bwR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0603, 0.1371
<i>R</i> ₁ , <i>wR</i> ₂ indices (all)	0.1069, 0.1525
<i>S</i>	1.033
(Δ/ σ) _{max/min}	0.001, 0.000
(Δρ) _{max/min} (eÅ ⁻³)	1.678, -1.544

$$^a R_1 = (\sum |F_o| - |F_c|) / \sum |F_o|, ^b wR_2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum (w|F_o|^2)]^{1/2}$$

There are totally twelve N-donor sites from four 1,2,4-triazole rings in one L ligand. While only 2-positioned nitrogen atoms in the four 1,2,4-triazole rings were chosen to participate in the coordination. Generally, referred to the literatures, the metal centers incorporate with macrocyclic

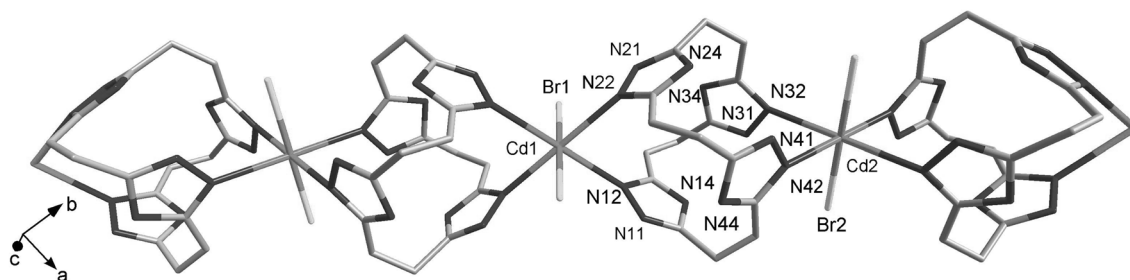
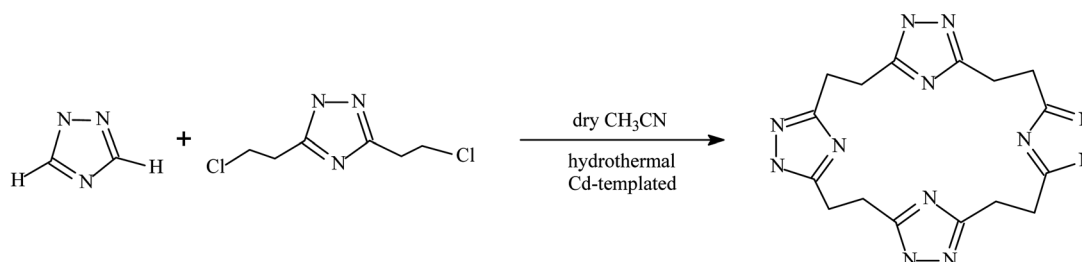
Table 2. Selected bond distances (Å) and angles (°)

Cd1-N22 = 2.511(4)	Cd1-N12 = 2.533(4)
Cd1-Br1 = 2.6379(7)	Cd2-N42 = 2.418(4)
Cd2-N32 = 2.560(4)	Cd2-Br2 = 2.7084(6);
N22-Cd1-N12 = 80.67(13)	N22-Cd1-N12A = 99.33(13)
N22-Cd1-Br1 = 88.67(8)	N22A-Cd1-Br1 = 91.33(8)
N12-Cd1-Br1 = 90.17(9)	N12A-Cd1-Br1 = 89.83(9)
N42B-Cd2-N32 = 97.65(13)	N42-Cd2-N32 = 82.35(13)
N42-Cd2-Br2B = 87.64(9)	N32-Cd2-Br2B = 91.45(9)
N42B-Cd2-Br2 = 87.64(9)	N42-Cd2-Br2 = 92.36(9)
N32-Cd2-Br2 = 88.55(9)	

Symmetry code: *A* = -*x*, -*y*, -*z*+2; *B* = -*x*+1, -*y*+1, -*z*+2.

ligands always in the inner of the cycles,¹² thus to form compounds with more coordination bonds between metals and ligands. However, in this work, Cd atoms abnormally link L outside of the macrocycle, which may be related with the metal-templating role of Cd atoms in the ring closure (Scheme 1), namely, the coordination of Cd atoms to triazole ring is possibly simultaneous with the ring closure. The reaction mechanism is still in investigation. Interestingly, it is noteworthy that there exists two sets of the chains along the *a*+*b* and *a*-*b* vectors (Figure 2). The two sets of the linear chains are further connected by the weak hydrogen bondings N41-H...Br1 (3.172(4) Å) into a 3D supramolecular framework (Figure 3). Furthermore, the minimum distance of C5 between the centroid of triazole ring (N41) being 3.337 Å, indicates the existence of *T*... π stacking interaction C5-H... π , which further strengthens the structure.

It is worthy noting that, in our systematic experiments, numerous experiments to obtain coordination complexes only gave powder samples, which may be related with the nature of the ligand and accord with the absence of the

**Figure 1.** The 1D coordination chain containing the [1₄] heterophane.**Scheme 1.** The synthetic route of the macrocyclic ligand L.

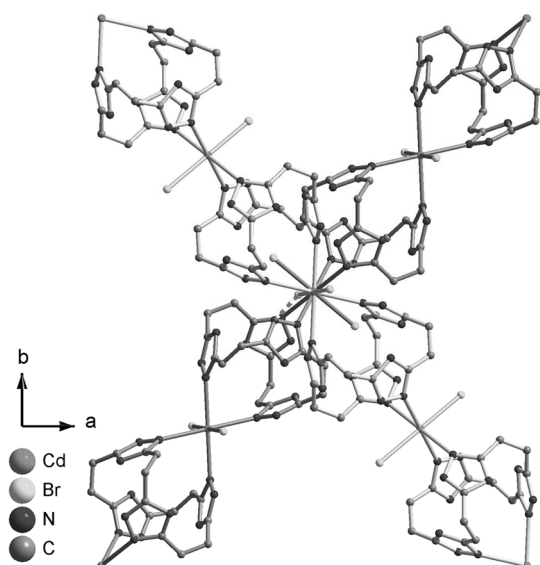


Figure 2. Two sets of 1D chains along the $a+b$ and $a-b$ vectors.

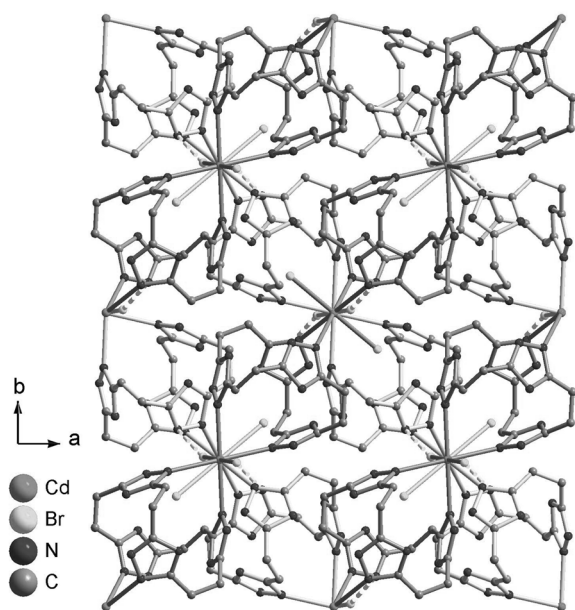


Figure 3. The 3D supramolecular architecture based on the 1D chains linked by hydrogen bondings.

complex containing [14] heterophanes. Only crystal or crystal-like samples were produced in low ratios of metal to the precursors (1:2:2 and 1:1:1). It may come from the reasons: *i*) the higher ratios of Cd to the two precursors (2:1:1~8:1:1 with a step of 1) produce more insoluble resultants; *ii*) the transition metal centers are a very important factor in the synthesis of macrocyclic as templating agents to orient the reacting groups of the reactants into the desired conformation for optimum ring closure in template reactions.^{12a,12c,12d,13} More metal centers have higher possibilities to react with the reactants of 1,2,4-triazole, the resulting complexes may block the metal-template role in the formation of the desired ring closure. Thus we also hope to learn if other metal atoms have similar roles as Cd centers.

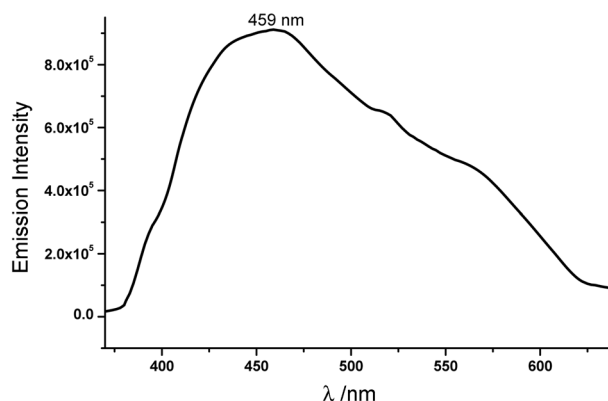


Figure 4. The solid-state electronic emission spectrum of the title compound ($\lambda_{\text{ex}} = 362 \text{ nm}$) recorded at room temperature.

Fluorescence. Among the design strategies for heterocycle-based organic blue emission molecular materials, introducing a heterocycle into a molecular structure is an efficient way to obtain excellent organic blue emission molecular materials. π -deficient and π -excessive heterocycles may respectively act as efficient acceptor and donor moieties.¹⁴ 1,2,4-Triazole ring, a 6-electrons π -excessive system, has potential applications to achieve the heterocycle-based organic blue emission molecular materials.

The fluorescent property of the title compound was explored in the solid state at room temperature. It can be observed that an intense blue fluorescence with a broad emission peak at *ca.* 459 nm was produced on the excitation at 362 nm (Figure 4). Compared to the fluorescence of other 1,2,4-triazole complexes with withdrawing electron groups, the blue emission peak may be assigned to $\pi \cdots \pi^*$ intra-ligand transition of L.¹⁵ though the emission peak locates in the region of blue ray (435–480 nm), the compound can not be regarded as a good candidate for organic blue emission materials because of its broad emission. However, further systematic explorations of the effects of metal centers on the structure, properties and the formation of macrocyclic ligand call our endeavor.

Supplementary material. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-681971). The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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