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Diverse Cd(II) compounds based on *N*-benzoyl-*L*-glutamic acid and N-donor ligands: Structures and photoluminescent properties

Ning Ma, Wei-Ying Guo, Hui-Hua Song*, Hai-Tao Yu*

College of Chemistry and Material Sciences, Hebei Normal University, Shijiazhuang 050024, PR China

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ABSTRACT

Five new Cd(II) coordination polymers with *N*-benzoyl-*L*-glutamic acid (H_2bzgluO) and different N-donor ligands, [Cd(bzgluO)(2,2′-bipy)(H_2O)]$_n$ (**1**), [Cd(bzgluO)(2,4′-bipy)$_2$(H_2O)·3H_2O]$_n$ (**2**), [Cd(bzgluO)(phen)·H_2O]$_n$ (**3**), [Cd(bzgluO)(4,4′-bipy)(H_2O)]$_n$ (**4**), [Cd(bzgluO)(bpp)(H_2O)·2H_2O]$_n$ (**5**) were synthesized (2,2′-bipy = 2,2′-bipyridine, 2,4′-bipy = 2,4′-bipyridine, phen = 1,10-phenanthroline, 4,4′-bipy = 4,4′-bipyridine, bpp = 1,3-di(4-pyridyl)propane). Compounds **1**–**2** exhibit a 1D single-chain structure. Compound **1** generates a 2D supramolecular structure via π–π stacking and hydrogen bonding, 3D architecture of compound **2** is formed by hydrogen bonding. Compound **3** features a 1D double-chain structure, which are linked by π–π interactions into a 2D supramolecular layer. Compounds **4**-**5** display a 2D network structure. Neighboring layers of **4** are extended into a 3D supramolecular architecture through hydrogen bonding. The structural diversity of these compounds is attributed to the effect of ancillary N-donor ligands and coordination modes of H_2bzgluO. Luminescent properties of **1**–**5** were studied at room temperature. Circular dichroism of compounds **1**, **2** and **5** were investigated.

1. Introduction

Chiral coordination polymers have received extensive attention, not only because of their fascinating architectures and diverse topologies, but also for their unique applications in asymmetrical catalysis [1–3], enantioselective separation [4–6] and luminescence [7–10]. However, the formation of a desirable complex is depended on many complicated factors such as the solvent system, assistant ligands, andreaction temperature [11–14]. The most direct route is using chiral ligands to prepare chiral compounds [15–17]. The amino acid ligands, which are among the most important biological ligands, also hold both O- and N-donors (carboxylate and amino groups) and have rich coordination modes to metal atoms [18,19]. In addition, H-bonding and π–π stacking interactions also affect the results and they may further link low-dimensional entities into high-dimensional supramolecular structures [20–22]. We chose an amino acid derivative *N*-benzoyl-*L*-glutamic acid (H_2bzgluO) as a ligand because (I) the carboxylic group could adopt versatile and flexible coordination modes including monodentate, symmetric chelating, bidentate, and tridentate bridging to give high dimensional structures, (II) unlike amino acids, the H_2bzgluO possesses more functional groups, which can form noncovalent interactions and enrich the supramolecular interactions. To the best of our knowledge, reported complexes with *N*-benzoyl-*L*-glutamic acid are limited [23–26] and crystal data for these complexes are rare.

We are interested in two main facets of homochiral coordination networks based on H_2bzgluO. Firstly, N-donor ligands with different lengths and flexibility such as 2,2′-bipyridine, 2,4′-bipyridine, 1,10-phenanthroline, 4,4′-bipyridine and 1,3-di(4-pyridyl)propane were employed to enrich the versatility of the structures and we to gain a deeper insight into the influence of ligand length on the crystal structures [12,13]. Secondly, Cd(II) with a d^{10} configuration exhibits particular photoluminescent property and adopts a variety of coordination numbers forming four-coordinated, five-coordinated, six-coordinated, and seven-coordinated compounds [20,22,27].

Based on the above mentioned consideration, to investigate the effect of different N-donor ancillary ligands on the structural assembly and diversity, we synthesized five new compounds based on the H_2bzgluO ligand under different conditions, [Cd(bzgluO)(2,2′-bipy)(H_2O)]$_n$ (**1**), [Cd(bzgluO)(2,4′-bipy)$_2$(H_2O)·3H_2O]$_n$ (**2**), [Cd(bzgluO)(phen)·H_2O]$_n$ (**3**), [Cd(bzgluO)(4,4′-bipy)(H_2O)]$_n$ (**4**), [Cd(bzgluO)(bpp)(H_2O)·2H_2O]$_n$ (**5**). Herein, we report their syntheses, crystal structures, elemental analyses, infrared spectra (IR), thermogravimetric (TG) analyses, powder X-ray diffraction (PXRD), circular dichroism spectra (CD) and solid-state luminescent properties. Furthermore, the effects of N-donor ligands on the structures of the compounds have been discussed in detail.

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* Corresponding authors.
E-mail addresses: songhuihua@mail.hebtu.edu.cn (H.-H. Song), haitaoyu@mail.hebtu.edu.cn (H.-T. Yu).

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2. Experimental section

2.1. Materials and methods

All reagents and solvents for syntheses were purchased from commercial sources and were used as received without further purification (Table S1, Supplementary information). Element analyses (C, H and N) were performed on an Elemental Vario EL elemental analyzer. Infrared (IR) spectra were (KBr pellets) measured on a FTIR-8900 spectrometer from 4000 to 400 cm^{-1}. Thermogravimetric analyses (TGA) were carried out on a simultaneous STA 449F3/TENSOR 27 thermal analyzer under nitrogen with a heating rate of 10 °C min^{-1} from room temperature to 800 °C. The PXRD patterns were checked at room temperature. Fluorescence spectra were recorded on a Hitachi F-4500 luminescence spectrometer.

2.2. Synthesis of [Cd(bzgluO)(2,2′-bipy)(H_2O)]$_n$ (*1*)

A solution of H_2bzgluO (0.0251 g, 0.1 mmol) and Cd(OAc)$_2\cdot 2H_2O$ (0.0266 g, 0.1 mmol) in H_2O (8 mL) was stirred for 10 min. Then, a solution of 2,2′-bipy (0.0156 g, 0.1 mmol) in EtOH (8 mL) was added. The solution was adjusted to pH=5.1 with addition of a dilute aqueous 1 mol/L NaOH solution.The mixture was stirred for 15 minutes at room temperature and then filtered. The filtrate was slow evaporated at room temperature for 7 days or so to deposit colorless rod-shaped crystals of compound **1**. Yield: ~52% (based on Cd). Anal. calc. for $C_{22}H_{21}CdN_3O_6$ (%): C, 48.13; H, 3.86; N, 7.57. Found: C, 49.31; H, 3.95; N, 7.84. IR (KBr, cm^{-1}) ν: 3309(b), 3072(w), 1634(m), 1584(s), 1543(s), 1477(w), 1442(m), 1395(s), 1343(w), 1321(m), 1306(w), 1194(w), 1163(w), 1094(w), 1016(w), 860(w), 826(w), 773(m), 725(m), 650(w), 521(w), 416 (w).

2.3. Synthesis of [Cd(bzgluO)(2,4′-bipy)$_2$(H_2O)·3H_2O]$_n$ (*2*)

The preparation of **2** was similar with that of **1** except that Cd(OAc)$_2\cdot 2H_2O$ and 2,2′-bipy were replaced by Cd(NO$_3$)$_2\cdot 4H_2O$ and 2,4′-bipy. The colorless rod-shaped transparent crystals **2**, suitable for X-ray analysis were obtained by filtration. Yield: ~31% (based on Cd). Anal. calc. for $C_{32}H_{32}CdN_5O_9$ (%): C, 51.47; H, 4.69; N, 9.42. Found: C, 51.52; H, 4.73; N, 9.39. IR (KBr, cm^{-1}) ν: 3428(b), 3134(b), 1643(s), 1611(s), 1464(m), 1402(s), 1288(w), 1223(w), 1159 (w), 1065(w), 1013(w), 934(w), 878(w), 841(w), 772(s), 721(w), 642(w), 615(w), 565(w), 539(w), 443(w).

2.4. Synthesis of Cd(bzgluO)(phen)·H_2O]$_n$ (*3*)

A mixture of Cd(OAc)$_2\cdot 2H_2O$ (0.0532 g, 0.2 mmol), H_2bzgluO (0.0502 g, 0.2 mmol), phen (0.0396 g, 0.2 mmol) and H_2O (10 mL) as starting materials were sealed in 23 mL Teflon-lined stainless steel reactor and heated to 140 °C for 7 days and then slowly cooled to room temperature. Colorless block-shaped crystals of compound **3** were obtained after the reactor was cooled to room temperature from reaction temperature. Yield: ~65% (based on Cd). Anal. calc. for $C_{24}H_{21}CdN_3O_6$ (%): C, 51.67; H, 3.77; N, 7.47. Found: C, 51.49; H, 3.78; N, 7.51. IR (KBr, cm^{-1}) ν: 3447(b), 3358(s), 1649(s), 1566(s), 1516(s), 1485(s), 1400(s), 1339(m), 1292(m), 1269 (w), 1179(w), 1143(w), 970(w), 916(w), 853(m), 799(w), 781(m), 731(m), 711(s), 652(m), 579(w), 520(w).

2.5. Synthesis of [Cd(bzgluO)(4,4′-bipy)(H_2O)]$_n$ (*4*)

A mixture of Cd(OAc)$_2\cdot 2H_2O$ (0.0266 g, 0.1 mmol), H_2bzgluO (0.0251 g, 0.1 mmol), 4,4′-bipy (0.0156 g, 0.1 mmol), and H_2O (10 mL) as starting materials were sealed in 23 mL Teflon-lined stainless steel reactor and heated to 120 °C for 7 days and then slowly cooled to room temperature. Colorless block-shaped crystals of compound **4** were obtained after the reactor was cooled to room temperature from reaction temperature. Yield: ~44% (based on Cd). Anal. calc. for $C_{22}H_{21}CdN_3O_6$ (%): C, 49.31; H, 3.95; N, 7.84. Found: C, 49.09; H, 3.90; N, 7.85. IR (KBr, cm^{-1}) ν: 3258(b), 1653(s), 1605(s), 1578(s), 1541(s), 1412(m), 1360(w), 1327(m), 1290(w), 1221(m), 1148(w), 1067(w), 1009(w), 958(w), 866(w), 808(m), 741 (w), 694(w), 629(m), 590(w), 488(w).

2.6. Synthesis of [Cd(bzgluO)(bpp)(H_2O)·2H_2O]$_n$ (*5*)

A solution of H_2bzgluO (0.0125 g, 0.05 mmol) and Cd(OAc)$_2\cdot 2H_2O$ (0.0133 g, 0.05 mmol) in H_2O (10 mL) was stirred for 10 minutes. Then, a solution of bpp (0.0099 g, 0.05 mmol) in EtOH (10 mL) was added. The solution was adjusted to pH=4.8 with addition of a dilute aqueous 1 mol/L NaOH solution. The mixture was stirred for 15 minutes at room temperature and then filtered. The filtrate was slow evaporated at room temperature for 7 days or so to deposit colorless needle-shaped crystals of compound **5**. Yield: ~52% (based on Cd). Anal. calc. for $C_{25}H_{31}CdN_3O_8$ (%): C, 49.76; H, 4.93; N, 6.92. Found: C, 49.64; H, 4.50; N, 6.94. IR (KBr, cm^{-1}) ν: 3402(b), 3244(s), 1638(s), 1613(s), 1576(b), 1487(w), 1425(s), 1350(w), 1325(m), 1300(w), 1225(w), 1101(w), 1071(w), 1015(w), 960(w), 812(w), 716(m), 613(w), 575(w), 515(w), 403(w).

2.7. X-ray crystal structure determinations

Suitable single crystals for title compounds were selected for X-ray diffraction analyses. Crystallographic data were collected at 100 K on a Bruker SMART-CCD diffractometer with graphite monochrome Mo-Kα radiation (λ=0.71073 Å). All structures were solved through direct methods using the program SHELXTL-97 and refined using SHELXL-97. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 using SHELXL-97 [28]. The hydrogen atoms were included at their calculated positions. The Flack parameters of compounds **1**, **2** and **5** are close to zero. The assignment of the absolute structures for was confirmed by the refinement of the Flack parameter to values of −0.034(16), −0.054(19), −0.04(3), respectively [20,27,29]. Further crystallographic data and experimental details for structural analyses of complexes **1**–**5** are summarized in Table 1. The selected bond lengths and angles of **1**–**5** are given in Table S2.

3. Results and discussion

3.1. Crystal structure of complex [Cd(bzgluO)(2,2′-bipy)(H_2O)]$_n$ (*1*)

The crystallographic analysis reveals that complex **1** crystallizes in the orthorhombic space group $P2_12_12_1$ and features a 1D infinite chain. The asymmetry units are made up of one Cd(II) ion, one bzgluO^{2-} ligand, one 2,2′-bipy ligand and one coordinated water, as shown in Fig. 1a. The Cd(II) ion is six-coordinated by three carboxylate oxygen atoms (O2, O3, O6$^{\#1}$) from two different bzgluO^{2-} anions, two pyridyl nitrogen atoms (N2, N3) and water (O5), forming a distorted octahedral geometry. The O3, O6$^{\#1}$, O5 and N2 atoms form the equatorial plane, while the N3 atom and O2 are located in the axial position. The Cd–O bond lengths are in the range of 2.2010(16) Å to 2.5034(18) Å, the Cd–N distances are 2.319(2) Å and 2.332(2) Å, respectively.

Each bzgluO^{2-} anion adopts the μ_2-κ°O:κ^1O:κ^1O:κ^1O tridentate coordination mode (one carboxylic oxygen atom from the α-carboxyl group and two oxygen atoms from the γ-carboxyl group) (Scheme 1a), bridging two Cd(II) ions to form a 1D infinite linear single-chain of Zn–O–C rods with an adjacent Cd–Cd