High Efficiency Electrochemiluminescence for Copper(II) and Cadmium(II) Pyrazolate Polymers

Feng-Zhen Hua

School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, China.

Chao Feng

School of Materials and Chemical Engineering, Bengbu University, Bengbu 233030, PR China.

Wei-Nan Xie

School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, China.

Yi-Ni Luo

Shiyan Hydrology and Water Resources Survey Bureau of Hubei Province, Shiyan 442000, China.

Ling-Mei Zhang

School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, China.

Hong Zhao (✉ zhaohong@seu.edu.cn)

School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, China.

<https://orcid.org/0000-0001-6596-6867>

Original Research Full Papers

Keywords: Pyrazole carboxylate, Crystal structure, Hirshfeld surface, Electrochemiluminescence

Posted Date: February 2nd, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-170561/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Version of Record: A version of this preprint was published at Journal of Inorganic and Organometallic Polymers and Materials on April 20th, 2021. See the published version at <https://doi.org/10.1007/s10904-021-01983-6>.

High efficiency electrochemiluminescence for copper(II) and cadmium(II) pyrazolate polymers

Feng-Zhen Hua^a, Chao Feng^b, Wei-Nan Xie^a, Yi-Ni Luo^c, Ling-Mei Zhang^a, Hong Zhao*^a

^a School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, China.

^b School of Materials and Chemical Engineering, Bengbu University, Bengbu 233030, PR China.

^c Shiyang Hydrology and Water Resources Survey Bureau of Hubei Province, Shiyang 442000, China.

Abstract Two new coordination polymers, namely, $[\text{Cu}_2(\text{L})_2(4,4'\text{-bpy})]_n$ (**1**) and $[\text{Cd}(\text{HL})\text{Cl}(1,10'\text{-phen})]_n$ (**2**) (H_2L = 1*H*-pyrazole-3-carboxylic acid, 4,4'-bpy = 4,4'-bipyridine, 1,10'-phen = 1,10-phenanthroline) have been synthesized *via* solvothermal method and were structurally characterized by single-crystal X-ray diffraction, FT-IR, elemental analysis and PXRD. The two complexes are both infinite 1D chain structures, in complex **1** the H_2L ligands are completely deprotonated and chelating the metal centers, while in complex **2**, H_2L ligands play a role in chelating-bridging the metal centers. What's more, the two complexes further extended to 3D supramolecular networks by hydrogen bonds and weak C–H $\cdots\pi$ interactions. The weak intermolecular interactions existed in the complexes structures were further studied by Hirshfeld surface analysis and 2D fingerprint plots. In addition, these two transition metal complexes exhibit high intense electrochemiluminescence (ECL) in N,N-dimethylformamide (DMF) and after ten circulations the ECL intensity still remains stable, which can be a useful guide for the construct of new polymers ECL materials.

Keywords Pyrazole carboxylate, Crystal structure, Hirshfeld surface, Electrochemiluminescence

1. Introduction

Coordination polymers (CPs) have attracted intense interest for their structural diversity and potential applications in many areas, such as gas adsorption/separation [1-3], catalysis [4], luminescence sensing [5, 6], battery [7- 9], supercapacitor [10, 11], and magnetism [12, 13]. The design and selection of organic ligands and metal ions are critical factors for the construction of CPs, due to the coordination mode of organic ligands and functional groups in them are directly affect the configuration and applications of the CPs. However, it is a great challenge to control the

^a School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, China.

^b School of Materials and Chemical Engineering, Bengbu University, Bengbu 233030, PR China.

^c Shiyang Hydrology and Water Resources Survey Bureau of Hubei Province, Shiyang 442000, China.

*Corresponding author: Hong Zhao

E-mail: zhaohong@seu.edu.cn

structures and construct the target molecules with desired properties [14], owing to temperature, pH value and solvent will also affect the structure of resulting crystals [15, 16].

Among the numerous organic ligands, pyrazole carboxylate ligands obtained widely concern due to possessing N-donors in pyrazole ring and O atoms on the carboxylate which can provide potential coordination nodes and can exhibit flexible chelating and bridging coordination modes [17, 18]. What's more, act as multiple proton donors, deprotonated ligands can increase the coordination site which can help to fabricate high-dimensional coordination polymers. Inspired by the afore-mentioned facts, our group has devoted ourselves to synthesis several intriguing coordination polymers based on pyrazole carboxylate ligands and have made some achievements [19-22].

Electrochemiluminescence (ECL) is a special luminescence phenomenon, which combining the respective merits of electrochemistry and chemiluminescence [23, 24]. There are two fundamental mechanisms of ECL, one is annihilation ECL and the other is coreactant ECL, and the process of ECL including electrochemical excitation step and light radiation step [25]. Owing to its extremely low background noise, wide dynamic range and high sensitivity, ECL has been received considerable attention. As we known that, until now, most coordination polymers used as ECL luminophores contain Ru [26], Ir [27], and Re [28] precious metal, so it limited the application of these complexes due to high cost. As result, using transition metal complexes as ECL materials may be an alternative choice. What's more, researches in this area have also been reported before. Our group has been working on electroluminescence of complexes, especially pyrazole-based transition metal complexes [29, 30]. As our ongoing work, in this paper, Cu(II) and Cd(II) were chosen as the inorganic nodes to coordinate with 1*H*-pyrazole-3-carboxylic acid (H₂L) ligand and auxiliary ligand, and obtained two new complexes [Cu₂(L)₂(4,4'-bpy)]_n and [Cd(HL)Cl(1,10'-phen)]_n. The photoluminescence properties and ECL properties of complexes **1** and **2** have been investigated.

2. Experimental

2.1 Materials and Methods

All reagents were commercial grade materials and were used without purification. Elemental analyses were performed using a PerkinElmer Vario E1 microanalyzer. IR spectra were recorded on FRIR-8900 spectrophotometer (KBr pellet) from 4000 to 400 cm⁻¹. Thermogravimetric

analysis (TGA) measurements were carried out with SDT-600 from 50 to 800 °C at a rate of 20 °C min⁻¹ in N₂ atmosphere. Powder X-ray diffraction (PXRD) was collected on Ultima IV X-ray diffraction instrument.

2.2 Synthesis

2.2.1 Synthesis of [Cu₂(L)₂(4,4'-bpy)]_n (1)

1H-pyrazole-3-carboxylic acid (H₂L) (0.2 mmol, 0.0280 g) and 4,4'-bipyridine (0.2 mmol, 0.0312 g) were dissolved in 10.0 mL DMF, after that Cu(NO₃)₂·3H₂O (0.1 mmol, 0.0242 g) dissolved in 5.0 mL CH₃CN was added drop wise. After mixing for 30 min, the solution was put into a 25 mL Teflon-lined autoclave and then heated at 120 °C for 5 days and finally cooled to room temperature. Blue bulk crystals were obtained and washed with CH₃CN. (Yield: 65% based on H₂L). Elemental analysis calculated for C₉H₆CuN₃O₂: C, 42.89; H, 2.48; N, 16.73. Found: C, 42.95; H, 2.40; N, 16.69. IR (KBr, v/cm⁻¹): 3422 (w), 3053(w), 2988(w), 1614(s), 1536(w), 1492(w), 1456(w), 1419(w), 1343(s), 1261(m), 1222(m), 1144(m), 1072(m), 962(w), 854(w), 807(m), 779(m), 725(w), 644(m), 504(w).

2.2.2 Synthesis of [Cd(HL)Cl(1,10'-phen)]_n (2)

The mixture of H₂L (0.3 mmol, 0.0336 g), CdCl₂·6H₂O (0.1 mmol, 0.0228 g) in 8.0 mL DMF/H₂O(1:1 volume ratio) was stirred for 1h, after that 1,10'-phen (0.1 mmol, 0.0198 g) dissolved in 4.0 mL CH₃CN was added and continued stirring for 15 min, then was sealed in a 25 mL Teflon-lined autoclave, heated at 100 °C for 4 days and finally cooled to room temperature. Colorless needle-like crystals were obtained and washed with CH₃CN. (Yield: 60% based on H₂L¹). Elemental analysis calculated for C₁₆H₁₁CdClN₄O₂: C, 43.67; H, 2.69; N, 12.48. Found: C, 43.76; H, 2.52; N, 12.76. IR (KBr, v/cm⁻¹): 3212(m), 3097(m), 1617(w), 1588(s), 1515(w), 1481(m), 1450(w), 1424(w), 1371(s), 1249(w), 1193(m), 1111(w), 1060(w), 849(m), 812(m), 782(m), 638(w), 465(w).

2.3 Single Crystal X-ray Crystallography

Single crystals of suitable size were placed on a Xcalibur, Atlas, Gemini ultra CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å), using the ω-θ scan mode in the ranges 3.4° ≤ θ ≤ 29.8° (1), 3.5° ≤ θ ≤ 25° (2). The structures were solved by direct methods using SHELXS-2014 and refined by full-matrix least-squares on F² using SHELXS-2014 [31, 32]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were positioned

geometrically and refined as riding. The measured crystallographic data are shown in Table 1. The relevant hydrogen bonding parameters were provided in Table 2.

(Insert here Table 1)

(Insert here Table 2)

3. Results and discussion

3.1 Crystal Structure Description

3.1.1 Description of $[Cu_2(L)_2(4,4'-bpy)]_n$ (**1**)

Single-Crystal X-ray diffraction analysis reveals that complex **1** crystallized in monoclinic system with a space group of $P2_1/c$. The asymmetric unit of **1** contains one Cu(II), one L^{2-} ligand and a half of 4,4'-bipyridine ligand. As depicted in Figure 1b, each Cu(II) center is four-coordinated by two N atoms from two independent L^{2-} ligands, another N atom from 4,4'-bipyridine ligand and a carboxylate O atom, forming a distorted tetrahedral **Cu(N3O)** which is consistent to those previously reported [33-35]. The Cu–N bond lengths vary from 1.948(8) to 1.996(8) Å, while Cu1–O1 bond length is 1.962(7) Å, which are all in the normal range. The L^{2-} ligand is completely deprotonated with three coordination atoms adopting monodentate and chelated modes, in the asymmetrical unit it adopts $\mu_2-\eta^1 : \eta^2$ coordination mode. In complex **1**, two Cu(II) metal centers were chelated by two L^{2-} ligands forming a dinuclear structure, while auxiliary 4,4'-bipyridine ligand plays a role in bridging the adjacent metal units, help expanding into a 1D chain. As shown in Figure 1c, a 2D layer structure is formed by hydrogen bonds C(5)–H(5)···O(1)ⁱ (Symmetry code: (i) 2–x, 1–y, –z) between the carboxylate oxygen (O1) and carbon (C5) atom from 4,4'-bipyridine. The 2D layers are further outspread to 3D networks by the intermolecular interaction C(2)ⁱⁱ–H(2)···Cg(3) (Symmetry code: (ii) x, 1/2 – y, – 1/2 + z) [C(2)/Cg(3) distance: 3.565 Å, Cg(3):N(3), N(2), C(6), C(7), C(8)].

(Insert here Figure 1)

3.1.2 Description of $[Cd(HL)Cl(1,10'-phen)]_n$ (**2**)

Complex **2** crystallized in monoclinic system with $P2_1/c$ space group and exhibits a 1D chain structure. Each crystallographic independence unit comprises one Cd (II), one HL^- ligand, one Cl^- anion, and one 1,10'-phen. Cd1 center is six-coordinated and it is in a distorted octahedral

environment with N1, N2 from the auxiliary 1,10'-phen ligand, O1A from a HL⁻ ligand, N3 and O2 from another HL⁻ ligand (Figure 2a). The bond lengths of Cd–O range from 2.256 to 2.516 Å. The Cd–N bond lengths are 2.354, 2.388, and 2.292 Å, respectively, which are longer than those in {[Cd₂(HL¹)(L⁴)₄(H₂O)₂](H₂O)}_∞ [36]. The bond angles surrounding the Cd(II) ion vary from 68.89(6) to 148.50(7)°. Each HL⁻ ligand connects two Cd atoms with one N atom and one carboxylate O atom chelating a Cd atom, and another carboxylate O atom links adjacent Cd atom to produce a 1D chain structure and the HL⁻ ligand in the asymmetrical unit adopt $\mu_2\text{-}\eta^1 : \eta^1 : \eta^1$ coordination mode. From Figure 2c, it is noteworthy that the polymeric chains are further assembled by interchain $\pi\cdots\pi$ packing interactions, resulting in a 2D crystal structure of **2**.

(Insert here Figure 2)

4 Hirshfeld Surface Analysis

(Insert here Figure 3)

(Insert here Figure 4)

The weak intermolecular interaction such as hydrogen bond, $\pi\cdots\pi$ stacking interactions and so on play a vital role in assembly of crystal structure. To study different types of intermolecular interactions existing in the crystal structure, a Hirshfeld surface analysis was carried out with Crystal Explorer program (Figure 3 and Figure 4) on their asymmetric units. Figure 3 demonstrated the Hirshfeld surface mapped over d_{norm} (−1.1281 to 0.9996); Shape Index(−1.0 to 1.0) and Curvedness(−4.0 to 4.0). The d_{norm} is a normalized distance and displays a surface with a red-white-blue colour: the red spots represent close-contacts in the crystal structure of the studied complexes, such as C–H $\cdots$ O interactions, the blue and white regions represent the weak intermolecular interaction, like C $\cdots$ H and H $\cdots$ H interaction [37]. The adjacent red / blue triangles on the shape-index of the Hirshfeld surface indicating the $\pi\cdots\pi$ stacking interactions.

The 2D fingerprint plots clearly show the quantitative of different types of intermolecular interaction. In complex **1**, the maximum contribution in the 2D fingerprint plot is from H $\cdots$ H contacts(25.1%), which is reflected in the middle of the 2D fingerprint plot. The next is C $\cdots$ H contacts(18.7%) which result from the presence of C–H $\cdots\pi$ interactions. In complex **2**, the highest interatomic contact contribution is between hydrogen atoms, H $\cdots$ H contacts(26.3%). The contribution of Cl $\cdots$ H/H $\cdots$ Cl contacts is 16.2%, its 2D fingerprint plots present two sharp spikes

pointing towards the lower left, the above sharp spike corresponds to the donor of the hydrogen bond and the other is acceptor, which is accordance with the C–H $\cdots$ Cl hydrogen bond. The proportions of C $\cdots$ H/H $\cdots$ C, N $\cdots$ H/H $\cdots$ N, Cd $\cdots$ O/O $\cdots$ Cd is 24.7%, 6.5%, 4.7% of the total area of the Hirshfeld surfaces respectively (seen in Figure S3).

5 PXRD and TG analyses

(Insert here Figure 5)

In order to confirm the phase purities of complexes **1** and **2**, powder X-ray diffraction experiments have been performed (Figure S1). It is obvious that the experimental PXRD patterns are in accordance with the simulated ones, indicating samples crystallize in the pure phase. The thermogravimetric analysis (TGA) under a nitrogen atmosphere increasing from 25 to 800 °C with a rate of 10 °C /min were carried out in a platinum crucible to investigate the thermal behaviors of complexes **1** and **2**. The TG curves are shown in Figure 5. For complex **1**, no obvious weight loss can be observed up to 250 °C, after that it begins to break down, at 250-320 °C the weight loss of 47.9% (calculated: 44.52%) which can be described to the decomposition of a L²⁻ ligand in complex **1**. Complex **2** was stable up to 320 °C, the first mass loss occurred in 350 °C and showed about 13.28% weight loss that can be assigned to the loss of Cl atom, calc. 15.35%, while the weight loss of 38.18% (calc. 45.14%) at 480 °C can be ascribed to the removal of the 1, 10'-phen ring. Based on the starting decomposition temperatures, it showed that complex **2** is relatively stable.

6 ECL properties of 1–2

(Insert here Figure 6)

The ECL properties of pure complex **1** and complex **2** (the phase purity of **1-2** has been checked by PXRD) were assessed in DMF solution and the results were showed in Figure 6. Cyclic voltammetry (CV) was studied to investigation the redox properties of **1-2**. All experiments used a standard three-electrode cell and the results are depicted in Figure 6a, when 0.1 mol / L K₂S₂O₄ has been added into the solution, an oxidation peak in the cathodic current at -1.2 V for complex **1** and -1.4 V for complex **2**, a reduction peak in the cathodic current are all at -2.0 V.

For complexes **1** and **2** the maximum luminous intensity are about 1870 and 1286 a.u.. After ten circulations, the ECL intensity still remain stable, it can be arise from the complexes did not

collapse during tests. Compared with complex **2**, complex **1** has higher the maximum luminous intensity. Taken $\text{Ru}(\text{bpy})_3^{3+}$ as the standard for ECL efficiency [38], resulting in ECL yields of 0.42 and 0.29. It is tentatively suggested that the introduction of Cu(II) and Cd(II) ions could strengthen the spin-orbit coupling effect and enhance the ECL emission [21]. Compared to Cu(II) complexes [39] and Cd(II) complexes [40] reported before, the two complexes exhibit a stronger ECL emission and higher stability, and this result maybe help us to construct new ECL materials.

7 Conclusion

In summary, two coordination polymers, $[\text{Cu}_2(\text{L})_2(4,4'\text{-bpy})]_n$ (**1**) and $[\text{Cd}(\text{HL})\text{Cl}(1,10'\text{-phen})]_n$ (**2**) ($\text{H}_2\text{L} = 1H\text{-pyrazole-3-carboxylic acid}$) have been successfully prepared by adding different auxiliary ligands. Complexes **1** and **2** are both 1D chain structures, in complex **1** the H_2L ligands chelate the metal center as a monomolecular structure with binuclear, and 4,4'-bipyridine link adjacent metal units to form a 1D chain structure, while in complex **2**, the auxiliary ligands chelating the metal center and H_2L ligands chelating-bridging the metal center to help build an infinite 1D chain structure. The quantitative of the intermolecular interactions in complexes were studied by Hirshfeld surface analysis. Additionally, we further studied the ECL properties of pure complex **1** and complex **2**, the results exhibit that the two complexes possess higher ECL emission and higher stability than that reported before, which may offer new ECL materials.

8 Supplementary Material

Crystallographic data for the structures in this work have been deposited to the Cambridge Crystallographic Data Centre, CCDC **1941495** and **2036652**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Acknowledgements

This work is financially supported by the Starting Research Fund of Bengbu University (BBXY2018KYQD15).

Reference

- 1 M.L. Foo, R. Matsuda, and S. Kitagawa, *Chem. Mater.* **26**, 310–322 (2014).
- 2 J. R. Li, Y. G. Ma, C. M. McCarthy, J. Sculley, J. Yu, H. K. Jeong, P.B. Balbuena, H.C. Zhou, *Coord. Chem. Rev.* **255**, 1791–1823 (2011).
- 3 R. Ali Shokuhi, C. Aref, *J. Inorg. Organomet. Polym. Mater.* **27**, 1826–1834 (2017).
- 4 M. Yoon, R. Srirambalaji, K. Kim, *Chem. Rev.* **112**, 1196–1231 (2012).
- 5 Y. T. Yan, J. Liu, G. P. Yang, F. Zhang, Y. K. Fan, W. Y. Zhamg, Y. Y. Wang, *CrystEngComm.* **20**, 477–486 (2018).
- 6 X. H. Zhou, H. H. Li, H. P. Xiao, L. Li, Q. Zhao, T. Yang, J. L. Zuo, W. Huang, *Dalton Trans.* **42**, 5718–5723 (2013).
- 7 T. Li, Y. L. Bai, Y. Wang, H. Xu, H. Jin, *Coord. Chem. Rev.* **410**, 213221 (2020).
- 8 G. C. Sun, L. L. Yu, Y. Hu, H. R. Sha, B. L. Li, H. J. Liu, Q. Liu, *Cryst. Growth Des.* **19**, 6503–6510 (2019).
- 9 J. Xu, C. Yang, Y. F. Xue, C. Wang, J. Y. Cao, Z. D. Chen, *Electrochimica Acta.* **211**, 595–602 (2016).
- 10 Y. Xu, Q. Li, H. G. Xue, H. Pang, *Coord. Chem. Rev.* **376**, 292–318 (2018).
- 11 C. Feng, C. P. Lv, H. Zhao, Z. Q. Li, W. N. Xie, L. N. Sun, Y. C. Wang, *Cryst. Growth Des.* **20**, 5682–5687 (2020).
- 12 H. Y. Dai, C. J. Wang, Y. Y. Tang, Y. Tong, K. L. Mao, Z. B. Zhang, X. L. Zhou, *J. Inorg. Organomet. Polym. Mater.* **27**, 80–86 (2017).
- 13 H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, *Science.* **341**, 1–12 (2013).
- 14 S. J. Bora, R. Paul, A. Dutta, S. Goswami, A. K. Guha, A. J. Thakur, *Dalton Trans.* **49**, 5454–5462 (2020).
- 15 P. Gao, Y. Y. Bing, M. Hu, *Inorg. Chem. Commun.* **59**, 28-31(2015).
- 16 S. H. Zhang, R. X. Zhao, G. Li, H. Y. Zhang, C. L. Zhang, G. Muller, *RSC Adv.* **4**, 54837–54846 (2014).
- 17 C. Pettinari, A. Tăbăcaru, S. Galli, *Coord. Chem. Rev.* **307**, 1–31 (2016).
- 18 G. N. Liu, W. J. Zhu, Y. N. Chu, C. C. Li, *Inorg. Chim. Acta.* **425**, 28–35 (2015).
- 19 C. Feng, C.P. Lv, Z. Q. Li, H. Zhao, H. H. Huang, *J Solid State Chem.* **265**, 244–247 (2018).
- 20 C. Feng, Y. H. Ma, D. Zhang, X. J. Li, H. Zhao, *Dalton Trans.* **45**, 5081–5091 (2016).

- 21 H. Zhao, Z. J. Chu, G. Y. Gao, H. H. Huang, Z. R. Qu, *Polyhedron*. **83**, 143–149 (2014).
- 22 C. Feng, X. J. Li, H. Zhao, D. Zhang, *J. Iran. Chem. Soc.* **13**, 823–830 (2016).
- 23 Z. F. Ding, B. M. Quinn, S. K. Haram, L. E. Pell, B. A. Korgel, A. J. Bard, *Science*. **296**, 1293–1297 (2002).
- 24 L. Z. Hu, G. B. Xu, *Chem. Soc. Rev.* **39**, 3275–3304 (2010).
- 25 B. M. Huang, X. B. Zhou, Z. H. Xue, X. Q. Lu, *Trends Anal. Chem.* **51**, 107–116 (2013).
- 26 A. N. Khramov, M. M. Collinson, *Anal. Chem.* **72**, 2943–2948 (2000).
- 27 I. S. Shin, Y. T. Kang, J. K. Lee, H. Kin, T. H. Kim, J. S. Kim, *Analyst*. **136**, 2151–2155 (2011).
- 28 Q. H. Wei, F. N. Xiao, L. J. Han, S. L. Zeng, Y. N. Duan, G. N. Chen, *Dalton Trans.* **40**, 5078–5085 (2011).
- 29 F. Chao, H. Zhao, Z. Q. Li, *J Solid State Chem.* **285**, 841–844 (2018).
- 30 W. N. Xie, F. Z. Hua, C. Feng, Y. H. Jiang, H. Zhao, *Inorg. Chem. Commun.* **119**, 108124 (2020).
- 31 Li Wang, Xiao-Yan Li, Qing Zhao, Li-Hong Li and Wen-Kui Dong, *RSC Adv.* **7**, 48730 (2017).
- 32 S. R. Balaji, T. Balu, T. R. Rajasekaran, *Mater. Res. Express.* **5**, 026205 (2018).
- 33 M. L. Cheng, M. N. Qin, L. Sun, L. Liu, Q. Liu, X. Y. Tang, *Dalton Trans.* **49**, 7758–7765 (2020).
- 34 S. Y. Shaban, M. M. Ibrahim, F. I. Elshami, R. V. Eldik, *Inorg. Chim. Acta.* **486**, 608–616 (2019).
- 35 F. Alessandra, G. Julieta, D. Vadim, Z. Sandro, Q. Silvio, G. Nicolae, *Inorg. Chim. Acta.* **353**, 336–343 (2003).
- 36 C. S. Liu, X. S. Shi, J. R. Li, J. J. Wang, X. H. Bu, *Cryst. Growth Des.* **6**, 656–663 (2006).
- 37 M. A. Spackman, J. J. McKinnon, *CrystEngComm.* **4**, 378–392 (2002).
- 38 M. M. Richter, *Chem. Rev.* **104**, 3003–3036 (2004).
- 39 D. D. Li, X. S. Sun, N. Q. Shao, G. C. Zhang, S. L. Li, Y. P. Tian, *Polyhedron*. **93**, 17–22 (2015).
- 40 Z. H. Chen, S. H. Zhang, S. M. Zhang, Q. C. Sun, Y. Xiao, K. Wang, *ChemPlusChem.* **84**, 190–202 (2019).

Figures

Figure 1

(a) The coordination environment of Cu (II) in 1 with thermal ellipse at the 30% probability level (symmetry code: (i) $-x + 1, -y + 1, -z$). (b) The coordination environment of Cu (II) in 1. (c) 3D framework of complex 1

Figure 2

(a) The coordination environment of Cd (II) in 2. (b) The 1D chain structure of complex 2. (c) Two-dimensional structure of complex 2.

Figure 3

Hirshfeld surfaces mapped with d_{norm} , shape index and curvedness for complexes 1-2

Figure 4

The 2D fingerprint plots of complexes 1-2

Figure 5

Thermogravimetric analysis of complexes 1-2.

Figure 6

(a)Cyclic voltammetry curve of complexes 1-2.(b)Electrochemiluminescence for 1-2.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Table1.docx](#)
- [Table2.docx](#)
- [SupportingInformation.docx](#)