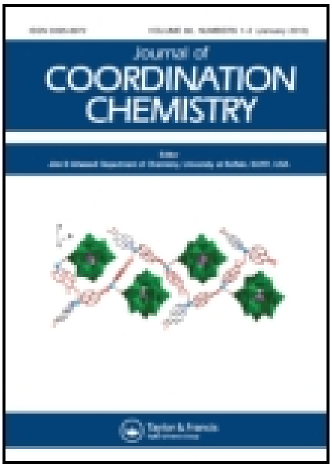
This article was downloaded by: [Institute Of Atmospheric Physics]
On: 09 December 2014, At: 15:37
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Click for updates

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis, crystal structure, and photophysical properties of a double open cubane-like Cd(II) complex based on 2-substituted-8-hydroxyquinoline

Guozan Yuan[ab], Kai Song[a], Lu-Lu Rong[a], Yinmin Tang[c] & Yanping Huo[c]

[a] School of Chemistry and Chemical Engineering, Anhui University of Technology, Maanshan, China

[b] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, PR China

[c] School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou, China

Accepted author version posted online: 01 Apr 2014.Published online: 29 Apr 2014.

To cite this article: Guozan Yuan, Kai Song, Lu-Lu Rong, Yinmin Tang & Yanping Huo (2014) Synthesis, crystal structure, and photophysical properties of a double open cubane-like Cd(II) complex based on 2-substituted-8-hydroxyquinoline, Journal of Coordination Chemistry, 67:7, 1141-1155, DOI: 10.1080/00958972.2014.910772

To link to this article: http://dx.doi.org/10.1080/00958972.2014.910772

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

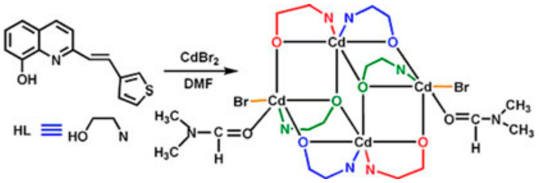
Journal of Coordination Chemistry, 2014
Vol. 67, No. 7, 1141–1155, http://dx.doi.org/10.1080/00958972.2014.910772

Synthesis, crystal structure, and photophysical properties of a double open cubane-like Cd(II) complex based on 2-substituted-8-hydroxyquinoline

GUOZAN YUAN*†‡, KAI SONG†, LU-LU RONG†, YINMIN TANG§ and YANPING HUO*§

†School of Chemistry and Chemical Engineering, Anhui University of Technology, Maanshan, China
‡State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, PR China
§School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou, China

(*Received 18 July 2013; accepted 1 February 2014*)



A 2-substituted-8-hydroxyquinoline (*E*)-2-[2-(3-thienyl)ethenyl]-8-quinolinol (HL) was synthesized and characterized by ESI-MS, NMR spectroscopy, and elemental analysis. Using solvothermal method, a tetranuclear complex $[Cd_4L_6Br_2]\cdot 6DMF$ (**1**) was fabricated by assembly of Cd(II) with HL. X-ray structural analysis shows that **1** exhibits a double open cubane-like core structure, which is bridged by six 8-hydroxyquinolinate-based ligands. The supramolecular structure of **1** features a 3-D porous solid constructed by aromatic stacking interactions, C–H$\cdots\pi$ interactions and C–H$\cdots$O hydrogen bonds. The assembly of cadmium salts and HL in solution was investigated by UV–vis and photoluminescence. We also studied the thermal stability and photophysical properties (fluorescent emission, lifetime, and quantum yield) of **1**. The results show that **1** emits yellow luminescence in the solid state.

Keywords: 8-Hydroxyquinoline; Tetranuclear complex; Crystal structure; Photophysical property

1. Introduction

Luminescent materials have attracted much attention owing to potential or real applications in many fields, including lighting, display, sensing, optical devices, etc. [1]. Many organic and inorganic luminescent compounds have been explored [2]. Generally, inorganic compounds have considerable thermal stability, high strength, and diverse coordination

---

*Corresponding authors. Email: guozan@ahut.edu.cn (G. Yuan); yphuo@gdut.edu.cn (Y. Huo) chemistry, while organic compounds are varied and easy to modify or process [3]. Since Tang and VanSlyke employed tris-(8-hydroxyquinoline)aluminum (Alq_3) as the emitting and electron-transporting material for fabrication of organic light-emitting diodes (OLEDs) [4], ligand-based fluorescent coordination compounds have attracted attention owing to applications, especially in modern electronics as materials to generate OLEDs [5–7]. The versatile physical and chemical properties, compositions, and processing techniques of the complexes offer a range of possibilities to fabricate luminescent materials. Although numerous metal–organic complexes have been synthesized, rational control in the synthesis of coordination compounds with self-assembly structures, and controllable luminescent properties has been a challenge [8]. Therefore, it is necessary to study the relationship between the structures and the components constructing the complexes.

Photophysical properties of organic chelate metal complexes based on 8-hydroxyquinoline in the solid state are dependent on the character of the metal ion, degree of aggregation, molecular, and supramolecular structures fabricated via noncovalent forces [9]. The zinc analog of Alq_3, bis(8-hydroxyquinoline) zinc(II) (Znq_2) complexes may be potential candidates to enhance electron-transporting properties for OLEDs [10]. Similar to zinc(II), cadmium(II) has a spectroscopically silent d^{10} electronic configuration. Meanwhile, owing to an ability to form bonds with different organic ligands simultaneously, a larger radius, as well as a wide variety of coordination modes and coordination numbers, many Cd(II) coordination polymers and multinuclear complexes based on disparate organic ligands have been explored. These Cd(II) complexes exhibit unique photophysical properties owing to different compositions and structures [11, 12]. For example, Cai group has reported that four multinuclear Cd(II) complexes with Schiff base ligands exhibit enhanced fluorescence intensities and a varying degree of blue shifts compared with free ligand due to the coordination of the metal centers to the ligands [11(a)]. Based on mixed bridging and chelating ligands, five Cd(II) complexes synthesized by Bu group display strong blue emissions in the solid state at room temperature [11(c)]. Some examples have shown that a strong conformational rigidity for supramolecular networks of Cd(II) complexes may lead to enhanced fluorescence intensities [12(a) and (d)]. However, the chemistry of metal–organic complexes with bidentate quinolinate derivatives, including related cadmium compounds, remains poorly explored [13], which significantly hampers the process of obtaining luminescent multinuclear metal complexes supported by quinoline derivatives.

In the course of our investigations on the relationship between structure (molecular or supramolecular structure) and photophysical properties of multinuclear 8-hydroxyquinolinate-based complexes [14], we report, herein, assembly of a double-open cubane-like complex by treating 2-substituted-8-hydroxyquinoline ligands with cadmium bromide. The aggregation behavior of Cd(II) ions and ligand in solution was investigated by UV–vis and photoluminescence (PL) spectra. In addition, we also study the thermal stability and fluorescent properties of the tetranuclear complex in the solid state.

2. Experimental

2.1. *General procedure*

All chemicals are commercially available and used without purification. Elemental analyses were performed with an EA1110 CHNS-0 CE elemental analyzer. IR (KBr pellet) spectra were recorded (400–4000 cm^{-1} region) on a Nicolet Magna 750 FT-IR spectrometer. Powder X-ray diffraction (PXRD) data were collected on a DMAX2500 diffractometer using

Cu-Kα radiation. The calculated PXRD patterns were produced using the SHELXTL-XPOW program and single crystal reflection data. All fluorescence measurements were carried out on a LS 50B Luminescence Spectrometer (Perkin-Elmer, Inc., USA). Room-temperature (RT) lifetime measurements were determined on a FSP920-combined time-resolved and steady-state fluorescence spectrometer (Edinburgh Instruments) equipped with a F900 microsecond flash lamp. All UV-vis absorption spectra were recorded on a Lambda 20 UV-vis Spectrometer (Perkin-Elmer, Inc., USA). ^{1}H and ^{13}C NMR experiments were carried out on a MERCURYplus 400 spectrometer operating at resonance frequencies of 100.63 MHz. Electrospray ionization mass spectra were recorded on a Finnigan LCQ mass spectrometer using dichloromethane–methanol as mobile phase.

2.2. *Synthesis of (E)-2-[2-(3-thienyl)ethenyl]-8-acetoxyquinoline*

To a solution of 8-hydroxyquinaldine (0.68 g, 4.28 mM) in acetic anhydride (5 mL), thiophene-3-carboxaldehyde (0.48 g, 4.28 mM) was added. The mixture was heated under reflux for 10 h. After cooling, it was subsequently poured into ice water (50 mL) and stirred overnight. The yellow solid obtained was filtered and washed with water. The solid residue was recrystallized from CH_2Cl_2 to afford (*E*)-2-[2-(3-thienyl)ethenyl]-8-acetoxyquinoline (0.96 g, 76%); m.p. 112.9–113.2 °C. MS, *m/z*: 296.29 $(M + H)^+$; ^{1}H NMR ($CDCl_3$, 400 MHz): 8.12 (d, *J* = 8.4 Hz, 1H), 7.47–7.64 (m, 2H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.52–7.34 (m, 5H), 7.20 (d, *J* = 16 Hz, 1H), 2.56 (s, 3H); IR (KBr): 3364, 1756, 1635, 1616, 1557, 696, 624 cm^{-1}; Anal. Calcd for $C_{17}H_{13}NO_2S$: C, 69.13; H, 4.44; N, 4.74. Found: C, 69.34; H, 4.24; N, 4.69.

2.3. *Synthesis of ligand HL: (E)-2-[2-(3-thienyl)ethenyl]-8-quinolinol*

A solution of acetoxyquinoline (0.80 g, 2.71 mM) in pyridine (10 mL) was refluxed for 3 h, and then water (20 mL) was added. The yellow solid obtained was filtered, washed with water, and dried *in vacuo* to give **2** (0.67 g, 97%). M.p. 106.5–107.2 °C. MS, *m/z*: 254.55 $(M + H)^+$; ^{1}H NMR (d_6-DMSO, 400 MHz): 9.53 (s, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 16 Hz, 1H), 7.75–7.58 (m, 3H), 7.55 (d, *J* = 4.8 Hz, 1H), 7.40–7.23 (m, 3H), 7.20 (d, *J* = 16 Hz, 1H), 7.06 (dd, *J* = 6.8 Hz, *J* = 1.6 Hz, 1H); IR (KBr): 3364, 1635, 1557, 1518, 718, 624 cm^{-1}; Anal. Calcd for $C_{15}H_{11}NOS$: C, 71.12; H, 4.38; N, 5.52. Found: C, 70.96; H, 4.32; N, 5.79.

2.4. *Synthesis of 1*

A mixture of $CdBr_2$ (2.7 mg, 0.02 mM), HL (2.9 mg, 0.01 mM), DMF (0.5 mL), and MeOH (2 mL) in a capped vial was heated at 80 °C for one day. Yellow block-like crystals of **1** were filtered, washed with MeOH, and dried at RT. Yield: 3.1 mg (73%). Elemental analysis data and IR of **1**: Anal (%). Calcd for $[Cd_4L_6Br_2]\cdot 6DMF$, $C_{108}H_{60}Br_2Cd_4N_{12}O_{12}S_6$: C, 51.48; H, 2.40; N, 6.67. Found: C, 51.32; H, 2.55; N, 6.53. IR (KBr pellet): 3437, 2350, 1654, 1624, 1600, 1553, 1501, 1446, 1412, 1385, 1371, 1339, 1308, 1268, 1101, 957, 866, 828, 775, 742, 618, 590, 573, 561, 524, 500, 489.

2.5. *X-ray crystallography*

Single-crystal X-ray diffraction (XRD) data for **1** were collected on a Bruker APEX area-detector X-ray diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å). The empirical absorption correction was applied using SADABS [15]. The structure was solved using direct methods and refined by full-matrix least-squares on F^2 SHELXTL97 [16]. Crystal data and details of the data collection are given in table 1, whereas selected bond distances and angles are presented in table 2. The CCDC number of **1** is 950215.

3. Results and discussion

3.1. *Synthesis considerations and spectroscopic characterization*

As outlined in scheme 1, HL was prepared from the cheap commercially available 8-hydroxyquinaldine in two steps in overall 74% yield and characterized by IR, ESI-MS, NMR spectroscopy, and elemental analysis. Single crystals of $[Cd_4L_6Br_2]\cdot 6DMF$ (**1**) were readily obtained in good yields by heating $CdBr_2\cdot 4H_2O$ and HL in a mixture of DMF and MeOH. The formulation was supported by microanalysis, IR, and single-crystal XRD. The reaction was originally accomplished in a 1 : 2 M ratio of Cd(II) and HL, but the products were not significantly affected by a change of the molar ratio. Moreover, when ethanol or isopropanol was used instead of methanol, the same products were obtained. Product **1** is, thus, a favorable species irrespective of the reactant molar ratios and concentrations and the organic solvents used.

Table 1. Crystal data and structure refinement for **1**.

Identification code	**1**
Empirical formula	$C_{108}H_{60}Br_2S_6N_{12}O_{12}Cd_4$
Formula weight	2561.79
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*P-1*
Unit cell dimensions	$a = 12.421(7)$ Å
	$b = 14.442(9)$ Å
	$c = 17.334(10)$ Å
	$\alpha = 69.0°$
	$\beta = 75.8°$
	$\gamma = 66.9°$
Volume (Å^3), Z	2651(3)
Density (Calcd) (mg m^{-3})	1.604
Absorption coefficient (mm^{-1})	1.729
$F(0\,0\,0)$	1288
θ Range for data collection (°)	2.32–25.00
Reflections collected	12,394
Independent reflections	9098 [R(int) = 0.2176]
Completeness to θ	25.24/94.9%
Data/restraints/parameters	9098/508/579
Goodness-of-fit on F^2	1.046
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0850$, $wR_2 = 0.2182$
R indices (all data)	$R_1 = 0.2489$, $wR_2 = 0.2874$
Largest diff. peak and hole (e Å^{-3})	2.257 and −1.550

Table 2. Selected bond lengths [Å] and angles [°] for **1**.

Cd(1)–O(2)#1	2.264(8)	Cd(1)–O(3)	2.280(7)
Cd(1)–N(12)	2.381(7)	Cd(1)–O(1)	2.374(7)
Cd(1)–O(4)	2.437(9)	Cd(1)–Br(1)	2.5810(19)
O(1)–Cd(2)	2.390(7)	O(1)–Cd(2)#1	2.337(8)
Cd(2)–O(2)	2.244(8)	Cd(2)–O(3)	2.265(7)
Cd(2)–N(3)	2.319(10)	Cd(2)–O(1)#1	2.337(8)
Cd(2)–N(2)	2.401(7)	O(2)–Cd(1)#1	2.264(8)
O(2)#1–Cd(1)–O(3)	90.6(3)	O(3)–Cd(2)–N(3)	73.0(3)
O(2)#1–Cd(1)–O(1)	74.5(2)	O(2)–Cd(2)–O(1)#1	75.6(2)
O(3)–Cd(1)–O(1)	78.3(3)	O(3)–Cd(2)–O(1)#1	97.8(3)
O(2)#1–Cd(1)–N(12)	144.3(3)	N(3)–Cd(2)–O(1)#1	104.0(3)
O(3)–Cd(1)–N(12)	86.9(3)	O(2)–Cd(2)–O(1)	92.9(3)
O(1)–Cd(1)–N(12)	70.2(3)	O(3)–Cd(2)–O(1)	78.3(3)
O(2)#1–Cd(1)–O(4)	89.5(3)	N(3)–Cd(2)–O(1)	151.2(3)
O(3)–Cd(1)–O(4)	155.3(3)	O(1)#1–Cd(2)–O(1)	80.0(2)
O(1)–Cd(1)–O(4)	77.9(3)	O(2)–Cd(2)–N(2)	71.4(3)
N(12)–Cd(1)–O(4)	78.7(3)	O(3)–Cd(2)–N(2)	113.5(3)
O(2)#1–Cd(1)–Br(1)	107.43(18)	N(3)–Cd(2)–N(2)	98.0(3)
O(3)–Cd(1)–Br(1)	111.7(2)	O(1)#1–Cd(2)–N(2)	145.9(3)
O(1)–Cd(1)–Br(1)	169.56(15)	O(1)–Cd(2)–N(2)	93.1(2)
N(12)–Cd(1)–Br(1)	106.5(3)	C(29)–S(2)–C(30)	96.0(9)
O(4)–Cd(1)–Br(1)	91.7(2)	C(16)–O(2)–Cd(2)	115.9(8)
C(1)–O(1)–Cd(2)#1	129.7(8)	C(16)–O(2)–Cd(1)#1	130.6(9)
C(1)–O(1)–Cd(1)	109.0(6)	Cd(2)–O(2)–Cd(1)#1	108.0(2)
Cd(2)#1–O(1)–Cd(1)	101.5(2)	C(24)–N(2)–Cd(2)	128.5(8)
C(1)–O(1)–Cd(2)	113.6(5)	C(21)–N(2)–Cd(2)	109.6(7)
Cd(2)#1–O(1)–Cd(2)	100.0(2)	C(31)–O(3)–Cd(2)	115.6(5)
Cd(1)–O(1)–Cd(2)	98.3(3)	C(31)–O(3)–Cd(1)	139.5(6)
C(54)–N(12)–Cd(1)	125.8(7)	Cd(2)–O(3)–Cd(1)	104.9(3)
C(47)–N(12)–Cd(1)	109.5(7)	C(39)–N(3)–Cd(2)	127.4(8)
O(2)–Cd(2)–O(3)	169.9(3)	C(36)–N(3)–Cd(2)	114.7(6)
O(2)–Cd(2)–N(3)	115.8(3)		

#1 $-x+1, -y+2, -z+1$.

3.2. *Coordination assembly in solution*

In order to investigate the coordination process of HL with Cd^{2+}, the reaction of HL with Cd^{2+} was monitored by UV–vis and fluorescence spectroscopic titration. The absorption bands of HL in MeOH dramatically change upon addition of Cd^{2+}. As depicted in figure 1, the band of **1** showed bathochromic shift from 300 to 305 nm. The absorbance at 338 nm decreases gradually and disappears in the presence of increasing amounts of Cd^{2+}. A new band at 425 nm may be attributed to charge transfer from metal to ligand. No differences were observed in the absorption spectra once a 2 : 3 M ratio of Cd(II) : **L** has been reached. Results from the UV–vis titrations were further corroborated by titrations followed by emission spectrum. As shown in figure 2, upon the addition Cd^{2+}, a new emission band with increasing intensity was found at 564 nm, while an emission band of ligand at 454 nm decreased simultaneously. Therefore, both UV–vis and emission spectra studies showed the formation of 2 : 3 ligand-to-metal complex in solution.

3.3. *^{1}H NMR and FT-IR spectra*

In the ^{1}H NMR spectrum of HL (figure S2, see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.910772), proton signals at 9.53, 8.24, 8.10, 7.75–7.58, 7.55, 7.40–7.23, 7.20, and 7.06 ppm can be easily assigned to corresponding hydrogens,

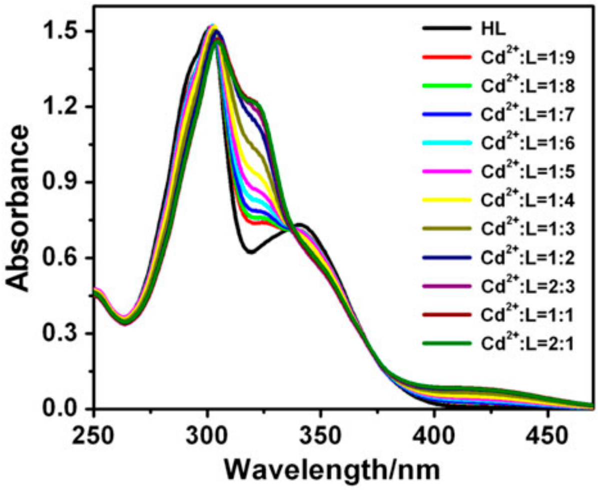


Figure 1. UV–vis titrations of HL (10 μM) in methanol with $CdBr_2$. Each spectrum was acquired 5 min after Cd^{2+} addition.

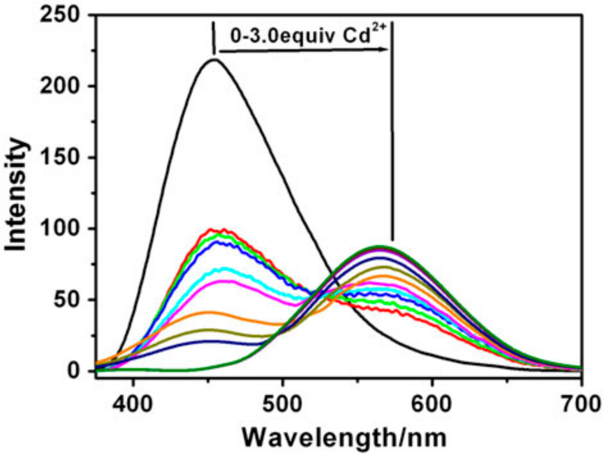


Figure 2. Fluorescence emission changes of HL (20 μM) in methanol with $CdBr_2$. Each spectrum was acquired 5 min after Cd^{2+} addition.

respectively, which indicate the presence of the hydroxyquinoline and vinylene. Compared to that of the (*E*)-2-[2-(3-thienyl)ethenyl]-8-acetoxyquinoline (figure S1), the proton signal at 2.56 ppm corresponding to MeO–proton of the quinoline is not observed in the ^{1}H NMR spectrum of HL. The proton signal at 9.53 ppm corresponds to HO–proton of the quinoline. Two doublets at 8.10 and 7.20 ppm with a coupling constant = 16 Hz indicate the presence of *trans*-configuration in the vinylene units. In the IR spectrum of **1** (figure S3), the peak at 1654 cm^{-1} is assigned to the C=O stretch of coordinated DMF. A sharp peak at 742 cm^{-1} can be assigned to the out-of-plane bending mode of the *trans*-vinylene groups, suggesting that the generated double bond is mainly in the *trans*-configuration [14(d)]. The absorption at 1624 cm^{-1} is assigned to the C=C stretch. In **1**, coordination of Cd^{2+} to HL is substantiated by weak bands at 590–489 cm^{-1} [12(c)].

3.4. *Structural description*

A single-crystal XRD study reveals that **1** crystallizes in the triclinic space group *P-1* (2). The asymmetric unit of **1** consists of two Cd(II) ions, three ligands HL, one coordinated DMF, one coordinated bromine atom, and two DMF molecules (figure 3). The coordination environment of Cd^{2+} ions in **1** is shown in figure 4, and there are two crystallographically independent Cd(II) ions. Cd1 adopts octahedral geometry with the equatorial plane occupied by NO_2 donors of two HL and one coordinated bromide, and the apical positions by one quinolinate O and one oxygen of DMF. Cd2 ions on the center of the tetranuclear unit are also sixcoordinate, resulting in octahedral geometry with the equatorial plane occupied by the NO_3 donors of three ligands, and the apical positions by one phenol oxygen and one pyridyl nitrogen of two ligands, respectively. The bond lengths and angles around Cd(II) are 2.319(10)–2.401(7) Å for Cd–N, 2.244(8)–2.437(9) Å for Cd–O, 74.5(2)°–169.9(3)° for O–Cd–O, 70.2(3)°–151.2(3)° for O–Cd–N, and 98.0(3)° for N–Cd–N, respectively. However, six oxygens of six HL link two Cd1 ions and two Cd2 ions into a double-open cubane-like unit (Cd_4O_6). The distances of adjacent Cd centers in the centrosymmetric tetranuclear (binuclear of binuclear) unit are 3.6042(22), 3.6480(17), and 3.6213(18) Å, respectively (figure 4). Only one cadmium(II) complex having a face-sharing double-cubane structure was reported previously, and **1** is a second example [17]. Additionally, this peculiar coordination would be achieved by stabilization due to the π-system spreading over the whole structure of the ligand as well as intra-molecular hydrogen bonds between phenolato oxygen and the C–H of ethenyl (C–H···O: 3.8413(21) Å) (figure 5).

Through C–H···π inter-molecular interactions (between C–H group of the coordinated DMF molecules and pyridine ring of adjacent ligand, 3.7143(23) Å), the tetranuclear Cd(II) units are linked into a 2-D network in the *ab* plane (figure 6), which are further assembled

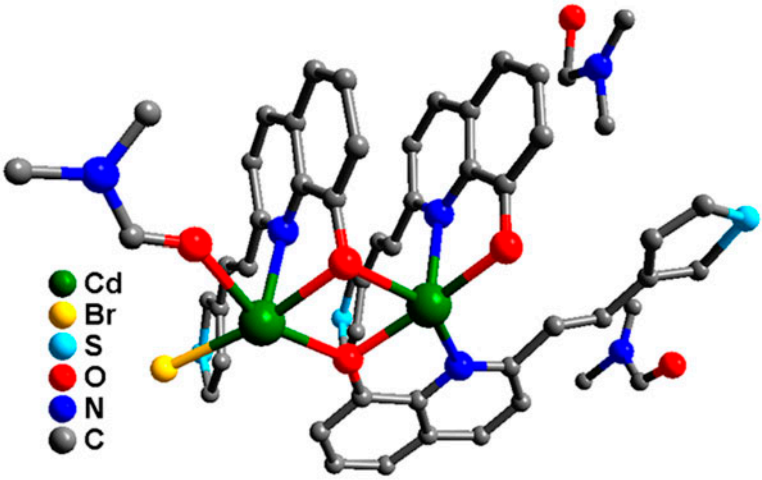


Figure 3. Views of the asymmetric unit in **1** (hydrogens omitted for clarity).

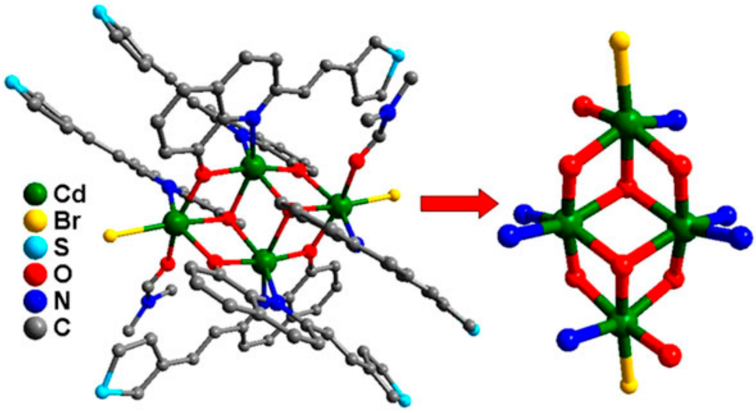


Figure 4. Views of the coordination geometries of Cd(II) in **1** (hydrogens omitted for clarity).

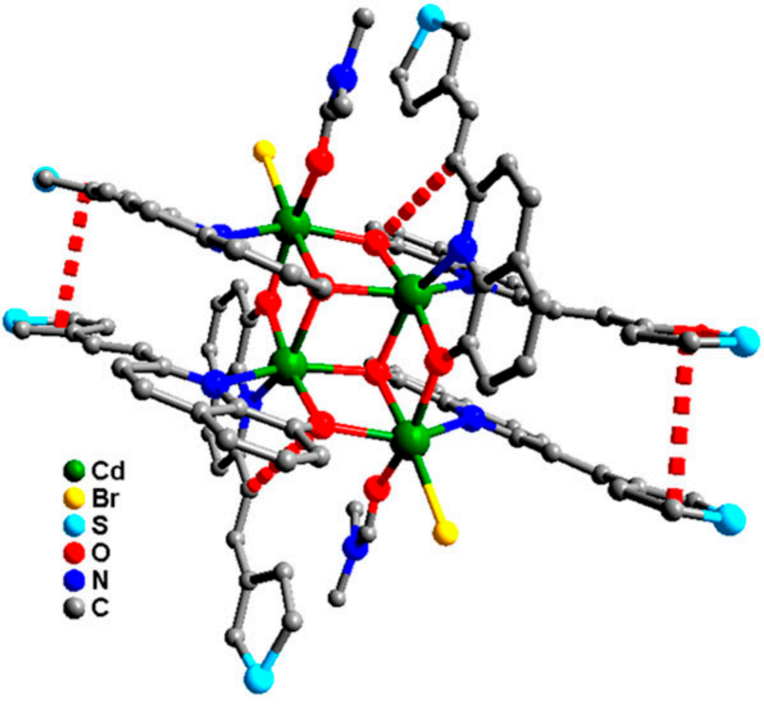


Figure 5. Perspective views of intra-molecular C–H···O hydrogen bondings and $\pi\cdots\pi$ stacking in **1** (hydrogens omitted for clarity).

into a 3-D supramolecular structure (figure 8) by two kinds of noncovalent forces (figure 7; C–H···O, 3.3302(21) Å; C–H···π, 3.927(20) Å). A space-filling model of **1** viewed along the *a* axis indicates open channels with dimensions of 7.4 × 5.2 Å. Calculations using

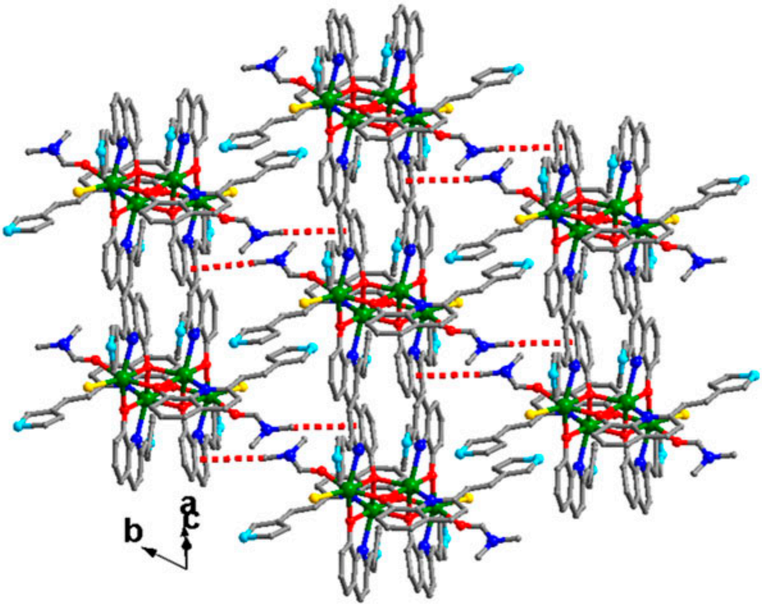


Figure 6. 2-D supramolecular structure of **1** mediated by C–H···π interaction (red-dashed lines), see http://dx.doi.org/10.1080/00958972.2014.910772 for color version.

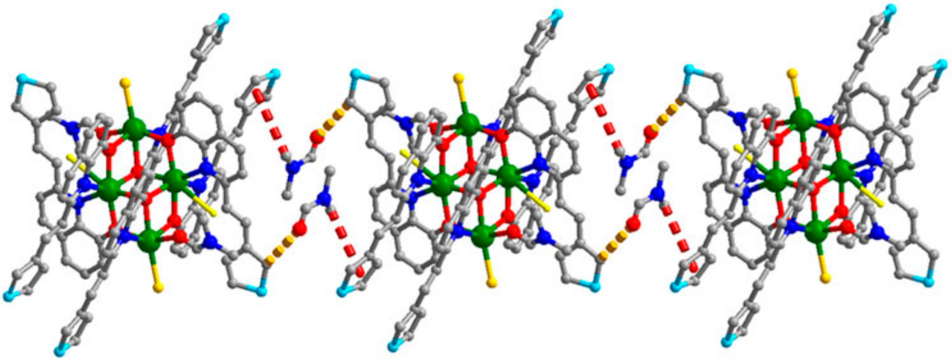


Figure 7. View of 1-D chain fabricated via C–H···O hydrogen bondings and C–H···π interactions in **1**.

PLATON software indicated that **1** has 20.6% of its total volume occupied by DMF molecules (figure 9).

A tetranuclear Cd(II) complex based on 2-substituted-8-hydroxyquinoline was synthesized via solvothermal method. The different intra- and inter-molecular forces in **1** play a vital role in fabrication of the 3-D porous material. Non-covalent interactions are of particular significance in many areas of modern chemistry, especially in the field of supramolecular chemistry and materials design [18]. Therefore, other quinolinates with different substituents (such as –F, –Cl, –CN, and –NO_2) will be prepared to fabricate multinuclear Cd(II) optical materials in our further study. These functional groups may lead to different

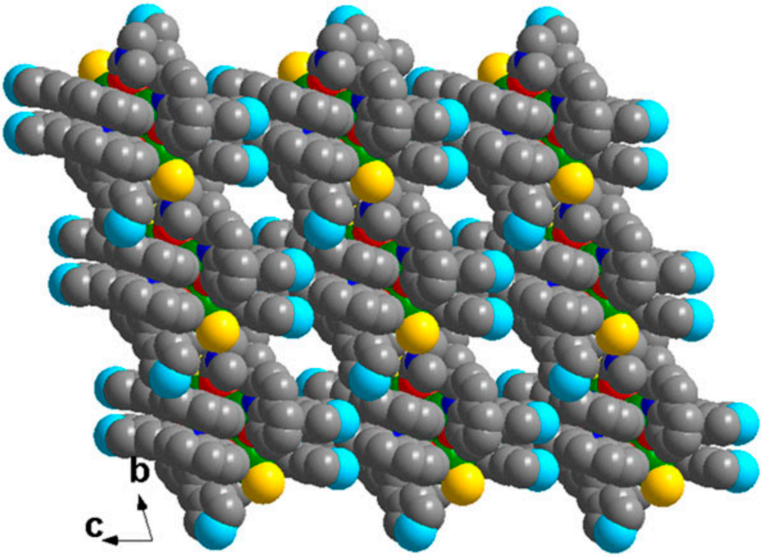


Figure 8. View of the porous 3-D lamellar structure of **1** along the *a* axis.

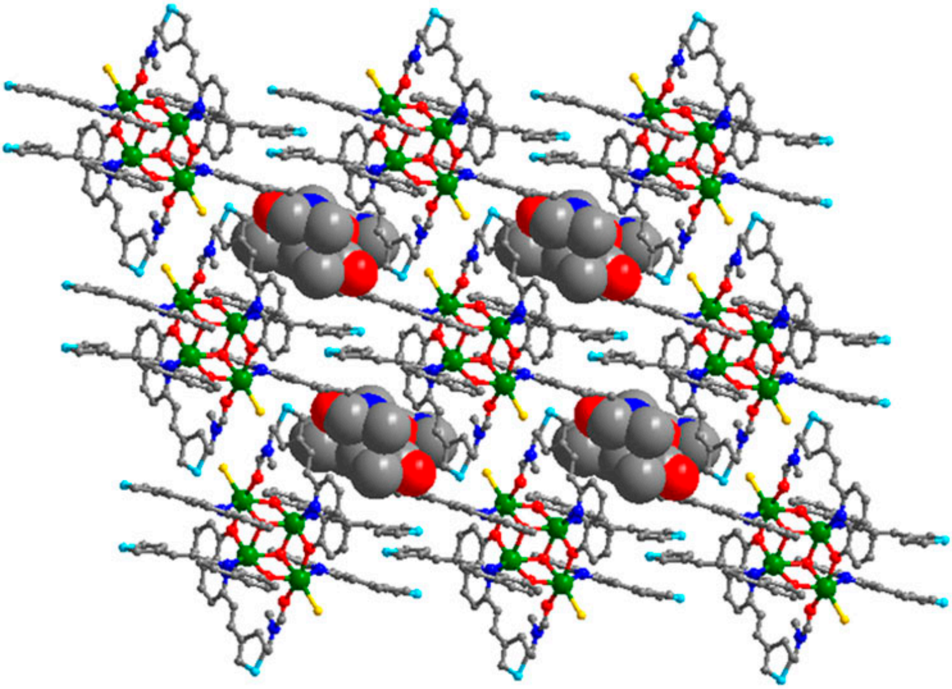


Figure 9. View of the arrangement of DMF molecules (space-filling mode) in the channels of **1**.

intermolecular interactions (such as hydrogen bonding and halogen-related interactions) in the solid state. Our goal is to achieve control over the supramolecular structures and thereby the physical properties on the new materials via multiple non-covalent interactions [14(c)].

3.5. *Thermal stability*

The product was also characterized by PXRD. As shown in figure 10, the PXRD pattern is consistent with the results simulated from single crystal data, illuminating the high purity of the as-synthesized sample. To investigate its thermal stability, thermogravimetric analysis (TGA) of **1** was carried out from 35 to 850 °C under a flow of nitrogen with heating rate of 20 °C min^{-1} (figure 11). There is no obvious weight loss until 64 °C. On further heating, the complexes begin to decompose due to the DMF molecules in the channels of **1**. The weight loss of 17.5% from 64 to 406 °C corresponds to the loss of two coordinated DMF molecules (Calcd: 17.4%). The organic groups start to decompose gradually above 408 °C. From TGA results, the tetranuclear complex forms stable six-membered chelate rings, which may be attributed to the fact that M–N and M–O bonds are highly polarized [19]. Together with the results of the elemental analyses, we conclude that the synthesized bulk material of **1** have high purity.

3.6. *Photoluminescent properties in the solid state*

The fluorescent properties of HL and **1** were investigated in the solid state at room temperature (figure 12). **1** exhibits intense PL with the emission maximum at 556 nm upon excitation at 350 nm. Compared with free HL (Em: 468 and 540 nm), the bright and extensive yellow emissions of **1** predominantly originate from metal-to-ligand charge transfer transition. However, the corresponding **1** exhibits a red shift compared with free HL. The results may be attributed to the following two reasons: the introduction of metal ions enhances the mobility of the electron transfer in backbone and decreases the electron transition energy of intra-ligand charge transfer due to backcoupling π-bond between the metal and the ligand.

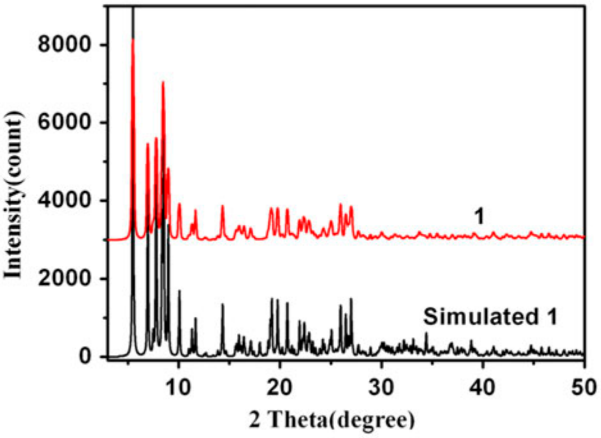


Figure 10. PXRD patterns of **1**.

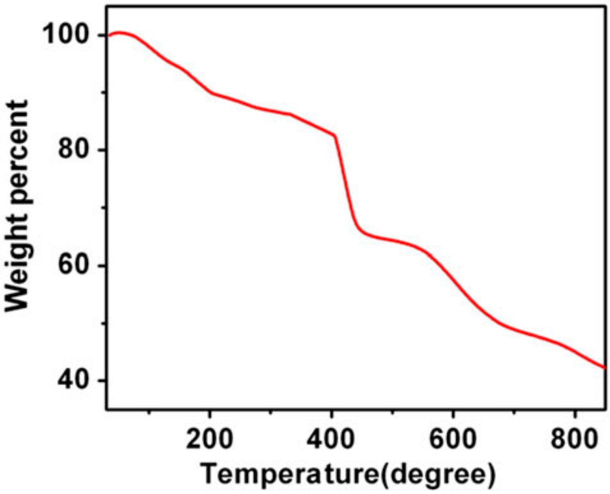


Figure 11. TGA curves of **1**.

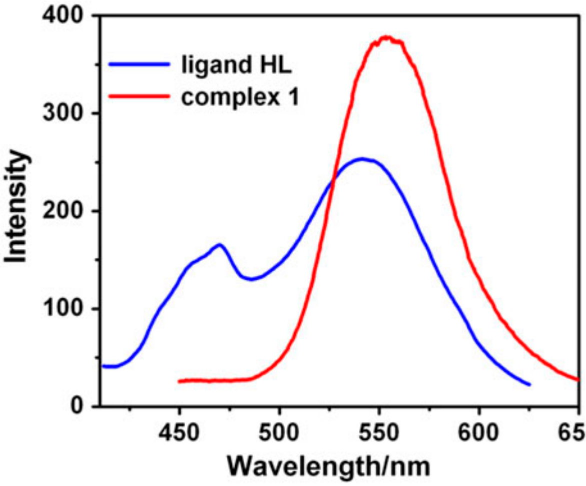


Figure 12. Emission spectra of **1** in the solid state.

The five-membered chelate rings formed between NO donors and Cd(II) center increases the π–π^* conjugation length and the conformational coplanarity, and thereby reduces the energy gap between the π and π^* molecular orbital of the ligand [14].

To further understand the fluorescent properties of **1**, its fluorescence lifetime and quantum yield were investigated in the solid state. The average lifetime (figure 13) was determined by allowing α_i and τ_i to vary, and then convoluting equation (1) with the instrument response function. The data were successfully modeled using double exponentials, and the average lifetime was determined using equation (2). In both equations t is time, τ is lifetime, and α is a pre-exponential factor [20]. The average lifetime of **1** is 2.93 ns. Absolute

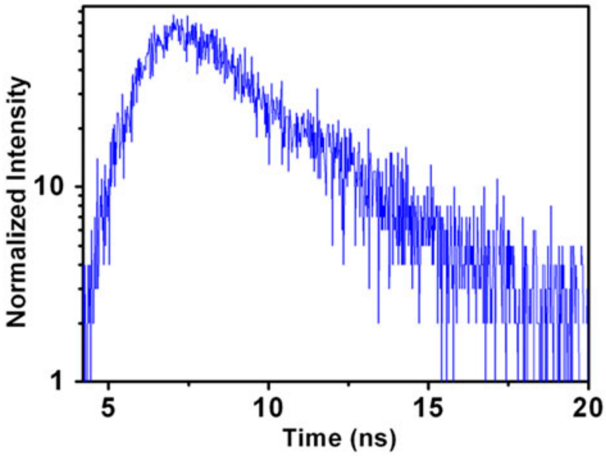
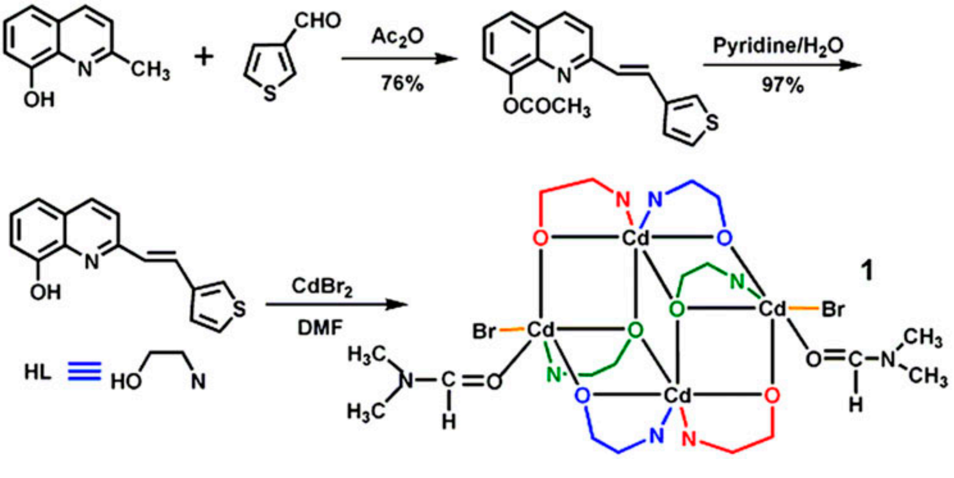


Figure 13. Fluorescence decay curves of **1** in the solid state.



Scheme 1. Synthesis of HL and **1**.

quantum yield of **1** is 2.10%. However, the photophysical properties of **1** are comparable with those found in multinuclear coordination compounds [21].

$$I(t) = \sum_{i=1}^{n} \alpha_i \exp(-t/\tau_i) \tag{1}$$

$$\tau_{\mathrm{avg}} = \frac{\alpha_1 {\tau_1}^2 + \alpha_2 {\tau_2}^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2} \tag{2}$$

4. Conclusion

In the present work, a tetranuclear complex $[Cd_4L_6Br_2]\cdot 6DMF$ was fabricated by self-assembly of Cd(II) ions with 2-substituted-8-hydroxyquinoline. The supramolecular structure of **1** features a 3-D porous solid constructed by aromatic stacking interactions, C–H···π interactions, and non-classical C–H···O hydrogen bonds. The aggregation behaviors of cadmium salts and HL in solution were investigated with UV–vis and PL. The luminescence of **1** shows that the material emits yellow luminescence at 556 nm (λ_{em}, max) in the solid state. The fluorescence lifetime and quantum yield were 2.93 ns and 2.10%, respectively. With knowledge of single-crystal structures, the present research holds promise in the development of multinuclear Cd(II) optical materials, and may contribute to understanding of structure–property relationships.

Supplementary material

CCDC 950215 contains detailed information of the crystallographic data for this paper and these data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Funding

This work was financially supported by the National Natural Science Foundation of China [grant number 21201002], [grant number 21172047]; Anhui Provincial Natural Science Foundation [grant number 1308085QB22]; Provincial natural science research program of higher education institutions of Anhui province [grant number KJ2013Z028]; the Foundation of State Key Laboratory of Structural Chemistry [project number 20130016]; National Training Programs of Innovation and Entrepreneurship for Undergraduates [grant number 201210360087].

References

[1] (a) S.V. Eliseeva, J.C.G. Bünzli. *Chem. Soc. Rev.*, **39**, 189 (2010); (b) K. Binnemans. *Chem. Rev.*, **109**, 4283 (2009); (c) S.H. Hwang, C.N. Moorefield, G.R. Newkome. *Chem. Soc. Rev.*, **37**, 2543 (2008); (d) L.D. Carlos, R.A.S. Ferreira, V. de Zea Bermudez, B. Julián-López, P. Escribano. *Chem. Soc. Rev.*, **40**, 536 (2011).

[2] (a) R. Exelby, R. Grinter. *Chem. Rev.*, **65**, 247 (1965), and references therein; (b) Y. Han, W. Jia, W. Yu, G. Jin. *Chem. Soc. Rev.*, **38,** 3419 (2009); (c) Y. Han, H. Li, G. Jin. *Chem. Commun.*, **46**, 6879 (2010).

[3] (a) M. Wang, G. Xu, Z. Zhang, G. Guo. *Chem. Commun.*, **46**, 361 (2010); (b) T. Yamase. *Chem. Rev.*, **98**, 307 (1998); (c) T. He, J. Yao. *Prog. Mater. Sci.*, **51**, 810 (2006), and references therein; (d) K. Liu, W. Shi, P. Cheng. *Dalton Trans.*, 8475 (2011).

[4] C.W. Tang, S.A. VanSlyke. *Appl. Phys. Lett.*, **51**, 913 (1987).

[5] (a) C.H. Chen, J. Shi. *Coord. Chem. Rev.*, **171**, 161 (1998); (b) M. Brinkmann, G. Gadret, M. Muccini, C. Taliani, N. Masciocchi, A. Sironi. *J. Am. Chem. Soc.*, **122**, 5147 (2000); (c) A.P. Kulkarni, C.J. Tonzola, A. Babel, S.A. Jenekhe. *Chem. Mater.*, **16**, 4556 (2004); (d) C. Pérez-Bolívar, S. Takizawa, G. Nishimura, V.A. Montes, P. Anzenbacher Jr. *Chem. Eur. J.*, **17**, 9076 (2011).

[6] (a) G. Yu, S. Yin, Y. Liu, Z. Shuai, D. Zhu. *J. Am. Chem. Soc.*, **125**, 14816 (2003); (b) H. Xu, Z.F. Xu, Z.Y. Yue, P.F. Yan, B. Wang, L.W. Jia, G.M. Li, W.B. Sun, J.W. Zhang. *J. Phys. Chem. C*, **112**, 15517 (2008); (c) H.J. Son, W.S. Han, J.Y. Chun, B.K. Kang, S.N. Kwon, J. Ko, S.J. Han, C. Lee, S.J. Kim, S.O. Kang. *Inorg. Chem.*, **47**, 5666 (2008); (d) T. Kawamoto, M. Nishiwaki, Y. Tsunekawa, K. Nozaki, T. Konno. *Inorg. Chem.*, **47**, 3095 (2008); (e) F.D. Souza, E. Maligaspe, M.E. Zandler, N.K. Subbaiyan, K. Ohkubo, S. Fukuzumi. *J. Am. Chem. Soc.*, **130**, 16959 (2008); (f) C. Deraeve, A. Maraval, L. Vendier, V. Faugeroux, M. Pitié, B. Meunier. *Eur. J. Inorg. Chem.*, 5622 (2008).

[7] (a) C.S.B. Gomes, P.T. Gomes, M.T. Duarte, R.E. Di Paolo, A.L. Maçanita, M.J. Calhorda. *Inorg. Chem.*, **48**, 11176 (2009); (b) A.O. Eseola, W. Li, R. Gao, M. Zhang, X. Hao, T. Liang, N.O. Obl-Egbedi, W.H. Sun.

Inorg. Chem., **48**, 9133 (2009); (c) Q. Chu, D.A. Medvetz, M.J. Panzner, Y. Pang. *Dalton Trans.*, 5254 (2010).

[8] (a) Y. Cui, Y. Yue, G. Qian, B. Chen. *Chem. Rev.*, **112**, 1126 (2012); (b) W. Xuan, M. Zhang, Y. Liu, Z. Chen, Y. Cui. *J. Am. Chem. Soc.*, **134**, 6904 (2012); (c) W. Xuan, C. Zhu, Y. Liu, Y. Cui. *Chem. Soc. Rev.*, **41**, 1677 (2012); (d) G. Yuan, C. Zhu, Y. Liu, W. Xuan, Y. Cui. *J. Am. Chem. Soc.*, **131**, 10452 (2009); (e) H.C. Fang, J.Q. Zhu, L.J. Zhou, H.Y. Jia, S.S. Li, X. Gong, S.B. Li, Y.P. Cai, P.K. Thallapally, J. Liu, G.J. Exarhos. *Cryst. Growth Des.*, **10**, 3277 (2010); (f) Z. Gu, H. Fang, P. Yin, L. Tong, Y. Ying, S. Hu, W. Li, Y. Cai. *Cryst. Growth Des.*, **11**, 2220 (2011).

[9] (a) M. Cöle, R.E. Dinnebier, W. Brütting. *Chem. Commun.*, 2908 (2002); (b) H. Bi, H. Zhang, Y. Zhang, H. Gao, Z. Su, Y. Wang. *Adv. Mater.*, **22**, 1631 (2010).

[10] (a) Q.L. Huang, J.F. Li, T.J. Marks. *J. Appl. Phys.*, **101**, 093101 (2007); (b) L.S. Sapochak, F.E. Benincasa, R.S. Schofield, J.L. Baker, K.K.C. Riccio, D. Fogarty, H. Kohlmann, K.F. Ferris, P.E. Burrows. *J. Am. Chem. Soc.*, **124**, 6119 (2002).

[11] (a) X. Gong, Y. Ge, M. Fang, Z. Gu, S. Zheng, W. Li, S. Hu, S. Li, Y. Cai. *CrystEngComm.*, **13**, 6911 (2011); (b) N. Kundu, S.M.T. Abtab, S. Kundu, A. Endo, S.J. Teat, M. Chaudhury. *Inorg. Chem.*, **51**, 2652 (2012); (c) C. Liu, X. Shi, J. Li, J. Wang, X. Bu. *Cryst. Growth Des.*, **6**, 656 (2006).

[12] (a) L.N. Yang, Y.X. Zhi, J.H. Hei, J. Li, F.X. Zhang, S.Y. Gao. *J. Coord. Chem.*, **64**, 2912 (2011); (b) J.Q. Liu. *J. Coord. Chem.*, **64**, 1503 (2011); (c) M. Zhang, D.M. Xian, N. Zhang, Z.L. You. *J. Coord. Chem.*, **65**, 1837 (2012); (d) G. Li, C. Wang, X. Zhang. *J. Coord. Chem.*, **66**, 1107 (2013).

[13] (a) M. Albrecht, M. Fiege, O. Osetska. *Coord. Chem. Rev.*, **252**, 812 (2008); (b) K. Sokołowski, I. Justyniak, W. Śliwiński, K. Sołtys, A. Tulewicz, A. Kornowicz, R. Moszyński, J. Lipkowski, J. Lewiński. *Chem. Eur. J.*, **18**, 5637 (2012).

[14] (a) G. Yuan, Y. Huo, X. Nie, X. Fang, S. Zhu. *Tetrahedron*, **68**, 8018 (2012); (b) G. Yuan, Y. Huo, L. Rong, X. Nie, X. Fang. *Inorg. Chem. Commun.*, **23**, 90 (2012); (c) G. Yuan, Y. Huo, X. Nie, H. Jiang, B. Liu, X. Fang, F. Zhao. *Dalton Trans.*, 2921 (2013); (d) Y. Huo, S. Zhu, S. Hu. *Tetrahedron*, **66**, 8635 (2010).

[15] G.M. Sheldrick. *SADABS, Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany (1996).

[16] G.M. Sheldrick. *SHELXTL97, Program for Crystal Structure Refinement*, University of Göttingen, Germany (1997).

[17] B. Machura, I. Nawrot, K. Michalik. *Polyhedron*, **31**, 548 (2012).

[18] (a) R. Desiraju. *Nature*, **412**, 397 (2001); (b) B. Moulton, M.J. Zaworotko. *Curr. Opin. Solid State Mater. Sci.*, **6**, 117 (2002).

[19] Q. Wu, M. Esteghamatian, N.X. Hu, Z.D. Popovic. *Chem. Mater.*, **12**, 79 (2000).

[20] D. Selmarten, M. Jones, G. Rumbles, P. Yu, J. Nedeljkovic, S. Shaheen. *J. Phys. Chem. B*, **109**, 15927 (2005).

[21] (a) N. Kundu, S.M.T. Abtab, S. Kundu, A. Endo, S.J. Teat, M. Chaudhury. *Inorg. Chem.*, **51**, 2652 (2012); (b) M.J. Romero, R. Pedrido, A.M. González-Noya, M. Maneiro, M.I. Fernández-García, G. Zaragozac, M.R. Bermejo. *Dalton Trans.*, 10832 (2012).