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Three Novel Functional Cd^{II} Dicarboxylates with Nanometer Channels: Hydrothermal Synthesis, Crystal Structures, and Luminescence Properties

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Three novel functional transition-metal complexes with H_2A (H_2A = 9-ethylcarbazole-3,6-dicarboxylic acid), $Cd(HA)_2(H_2O)_2$ (**1**), $[Cd(A)(phen)]\cdot 1.5H_2O$ (**2**) (phen = 1,10-phenanthroline), and $Cd(HA)_2(bipy)$ (**3**) (bipy = 4,4′-bipyridine), have been successfully synthesized by a hydrothermal synthetic method and characterized by single-crystal X-ray diffraction, infrared spectroscopy, elemental analysis, thermogravimetric analysis, and photoluminescence. The results show that all of the complexes contain nanometer channels, while the coordination modes were changed by the addition of the mixed ligands. The 2D supramolecular open-framework **1** is constructed through hydrogen-bond and aromatic π–π interactions. 2D coordination polymer **2** is constructed by π–π interactions between adjacent metal-organic polymeric coordination chains. Interestingly, the 3D supramolecular architecture of **3** first formed 2D grid layers from 1D chains by intermolecular hydrogen bonds and then extended into a 3D structure through aromatic π–π interactions. Furthermore, strong emissions from these complexes were also changed by the coordination modes in the solid state. However, complexes **1**–**3** show high thermal stability.

Introduction

In recent years, metal complexes have been investigated in luminescent materials for potential applications as light-emitting diodes (LEDs).[1] Metal carboxylate supramolecular open frameworks as a kind of metal complex have been the focus of recent research interest because of their interesting supramolecular compositions and versatile framework topologies, as well as their potential as functional materials in gas storage,[2] ion recognition,[3] catalysis,[4] sensor technology,[5] and nanotechnology.[6] The aromatic multicarboxylate ligands, such as 1,3,5-benzenetricarboxylic acid and 1,2,4,5-benzenetetracarboxylic acid, have been extensively introduced in the preparations of metal-organic supramolecular open frameworks.[7] However, the small π-conjugation system inhibited their potential application in luminescent materials. It is popular to extend the π-conjunction system of some widely used fluorophore precursors, such as rhodamine,[8] xylene,[9] and so forth, to get new analogs, although their synthesis and further modification may be difficult and laborious. On the other hand, emission properties of many luminescent materials can be tuned by incorporating the functional ligands into a polymeric structure, such as an all-organic polymer, or into a mixed inorganic/organic polymer.[10] Carbazole has been extensively exploited as a convenient basic building block for the application of the electroluminescent (EL) device because of its good hole transporting and luminescent properties.[11] Modification of the carbazole on the 3- and 6-positions represents a possible approach for designing carbazole-based luminescent materials.

On the other hand, Cd^{II}-containing coordination compounds have received considerable interest recently because of their ability to form bonds with different donors, their large radius, their various coordination modes, and the special properties of the Cd^{II} ion. To date, four- to eight-coordinate Cd^{II} complexes and their potential applications in catalysis,[12] luminescent materials,[13] and NLO materials[14] have been explored. Also, a hydrothermal synthetic method has been demonstrated as an effective, simple, and environmentally friendly technique in crystal engineering.[15] Considering all these aspects, we used a functional organic ligand that we had established previously,[16] 9-ethylcarbazole-3,6-dicarboxylic acid (H_2A), and cadmium nitrate as building blocks. 2D supramolecular open-framework $[Cd(HA)_2(H_2O)_2]_n$ (**1**) was obtained using hydrothermal synthesis. The skilful combination of carboxylates, the other coligands, and metal ions may generate many interesting coordination architectures as well as different emission properties. Pyridine, Schiff base, and polyamine derivatives were widely used as coligands. However, the selection of the

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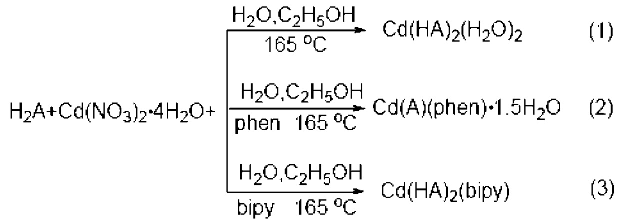
coligand remains a challenge for us because two different kinds of ligands must coexist and compete in coordinating to the same metal ion. In this paper, we introduced a luminescent rigid chelated ligand (phen) and a flexible bridge ligand (bipy) into the reaction system, obtaining 2D coordination polymer $\{[Cd(A)(phen)]\cdot 1.5H_2O\}_n$ (**2**) and 3D supramolecular open framework $[Cd(HA)_2(bipy)]_n$ (**3**) respectively. The emission wavelengths are tuned by changing coordination architectures.

Result and Discussion

Synthesis

The hydrothermal synthetic method is a useful way of growing complex crystals because of its effectiveness, simplicity, and environmental friendliness. Also, the formation of these complexes is greatly influenced by the base. We have tried NaOH, $Na_2C_2O_4$, pyridine, and triethylamine, and only $Na_2C_2O_4$ was successfully used in the formation of these compounds, suggesting that it is a compatible base for deprotonation of H_2A. The formations of **1**–**3** are shown in Scheme 1.



Scheme 1.

Description of Crystal Structure

$Cd(HA)_2(H_2O)_2$ (1)

Complex **1** crystallized with a monoclinic space group *C*2/*c*. The crystallographic analysis of complex **1** featured a 2D framework containing nanometer channels with a repeating unit $[Cd(HA)_2(H_2O)_2]_n$. The symmetric unit contains one cadmium atom, two H_2A groups, and two H_2O molecules. Part a of Figure 1 illustrates the ORTEP structure of compound **1**. Each cadmium ion is hexacoordinated by four O atoms [Cd(1)–O(1) 2.247(2) Å; Cd(1)–O(2) 2.489(2) Å; Cd(1)–O(1A) 2.247(2) Å; Cd(1)–O(2A) 2.489(2) Å] from two different H_2A ligands and two O atoms [Cd(1)–O(5) 2.187(3) Å; Cd(1)–O(5A) 2.187(3) Å] from two H_2O molecules and forms a distorted octahedral geometry. The dihedral angle of the two carbazole planes of H_2A is 83.57°. As for the H_2A ligand, it shed one proton and chelated to the cadmium atom while the other carboxylate group connected to the coordinated H_2O and carboxylate group of another H_2A by intermolecular hydrogen bonds (Figure 1, b). The C–O bond [C2AC–O3AC 1.306 Å] is much longer than the C=O bond [C2AC–O4AC 1.219 Å] in the carboxy group, so C2AC–O4AC can be assigned as a double bond and C2AC–O3AC as a single bond, and H is linked to O3AC. The O–H···O intermolecular hydrogen bond formed by the H_2A ligand and H_2O has a O···O distance of 2.659 Å (O–H–O 172.53°), while the other O–H···O intermolecular hydrogen bond formed by two H_2A ligands has a O···O distance of 2.686 Å (O–H–O 175.89°). Those units connected to each other and formed a 1D chain by intermolecular hydrogen bonds (O–H···O 2.712 Å, O–H–O 163.61°) (Figure 2). The 2D supramolecular open

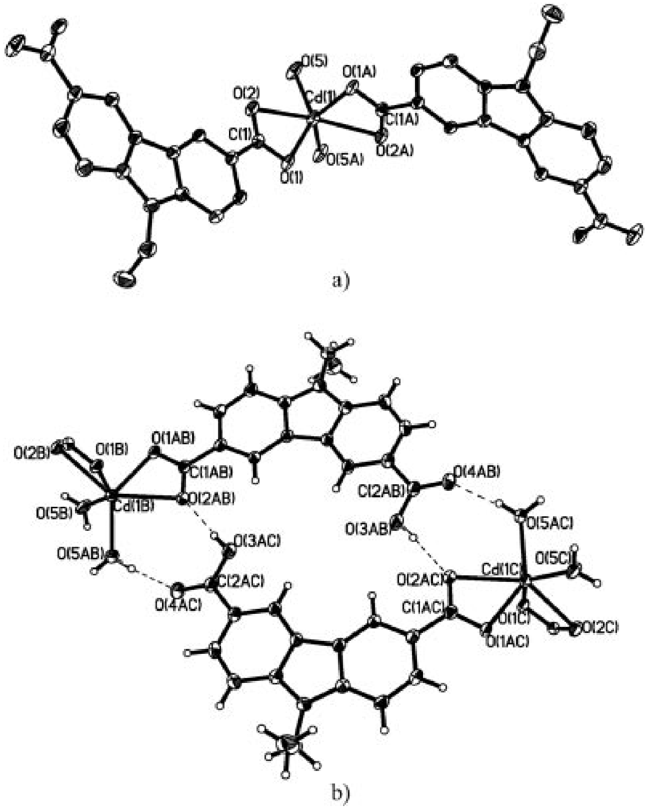


Figure 1. Perspective view of (a) the coordination environment of the cadmium atom in **1** and (b) the coordination mode of the H_2A ligand; all hydrogen atoms in (a) are omitted for clarity.

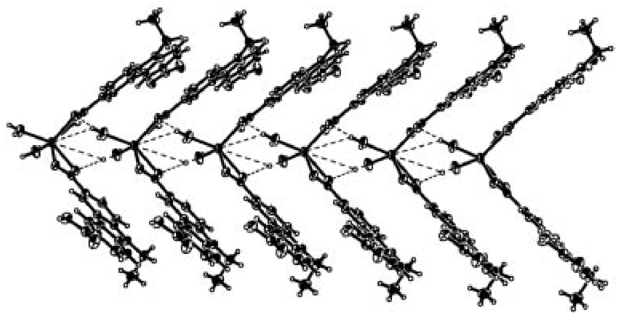


Figure 2. 1D structure of **1** along the *b* axis by intermolecular hydrogen bonds O–H···O.

framework contains 10.984 × 7.584 Å channels A formed by intermolecular hydrogen bonds and π–π interactions along the *b* axis with a distance of 3.41 Å (Figure 3).

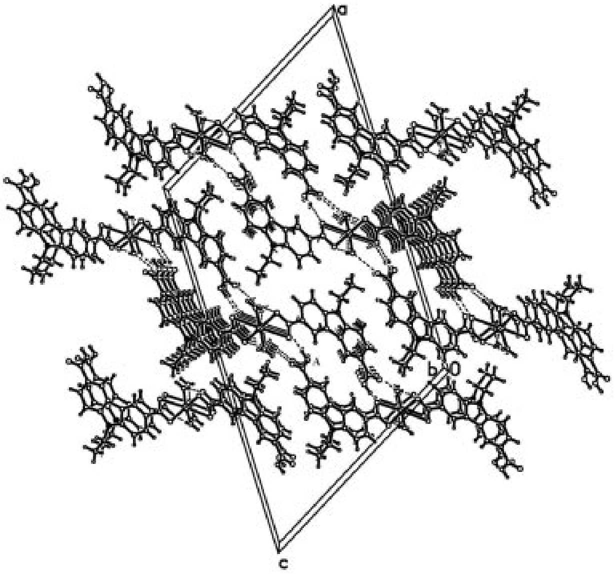


Figure 3. 2D structure containing nanometer channel A (10.984 × 7.584 Å) of **1** along the *a* axis by intermolecular hydrogen bonds O–H···O and π–π interactions.

[Cd(A)(phen)]·1.5H$_2$O (2)

Complex **2** crystallized in the monoclinic space group *P*2/*c* with a formula $\{[Cd(A)(phen)]\cdot 1.5H_2O\}_n$. The structure featured a 2D polymeric pattern containing nanometer channels. The asymmetric unit contains one cadmium atom, one H_2A group, and one phen molecule. Figure 4 illustrates the ORTEP structure of complex **2**. The cadmium atom is six-coordinate through coordination of one chelating carboxylate group [Cd(1)–O(1) 2.468(4) Å; Cd(1)–O(2) 2.315(3) Å], one chelating phen molecule [Cd(1)–N(2) 2.362(4) Å; Cd(1)–N(3) 2.372(4) Å], and two bridging carboxylate groups [Cd(1)–O(3A) 2.196(3) Å; Cd(1)–O(4B) 2.256(3) Å]. The coordination mode of H_2A is different from complex **1**. It shed two protons and chelated to the metal atom [O(1B)–C(13B)–O(2B) 120.1(4)°] through one of the carboxylate groups, while the other carboxylate group bridged to two metal atoms [O(4B)–C(14B)–O(3B) 125.0(4)°]. The basic units first formed rings and then formed a zigzag 1D chain (Figure 5) with the 73.57° dihedral angle of the ring planes. The phen molecules chelated to the metals from the two sides of the chains one by one. Two adjacent phen molecules connected to each other by π–π stacking interactions with a plane–plane distance of 3.38 Å. The 2D open framework contains 10.537 × 9.232 Å nanometer channel B formed by π–π interactions along the *b* axis with a distance of 3.48 Å (Figure 6). Two kinds of distorted guest water molecules filled the channels. One kind filled the channel in the form of a distorted single H_2O molecule (H–O–H 102.60°) by hydrogen bond (O–H···O 2.899 Å, O–H–O 128.47°) to the carboxylate group, while the other kind filled the channel in the form of distorted dimeric H_2O molecules (H–O–H 107.22°) by hydrogen bond (O–H···O 2.695 Å, O–H–O 132.46°) to the carboxylate group.

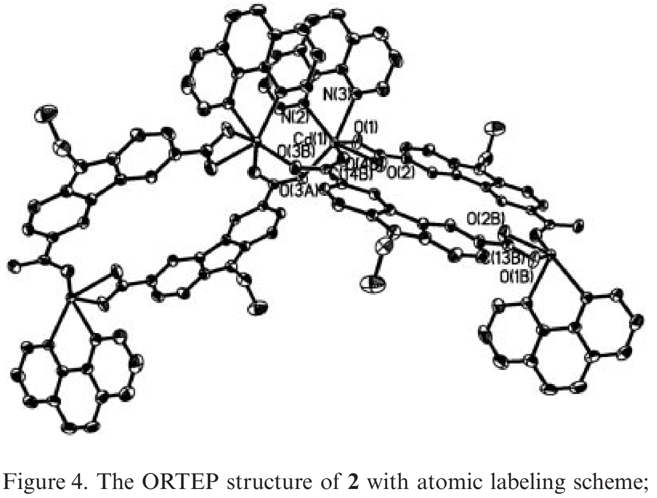


Figure 4. The ORTEP structure of **2** with atomic labeling scheme; all hydrogen atoms are omitted for clarity.

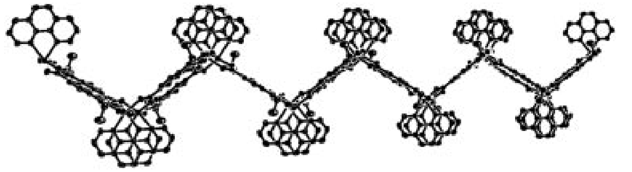


Figure 5. 1D zigzag chains of **2** formed by the basic units; all hydrogen atoms are omitted for clarity.

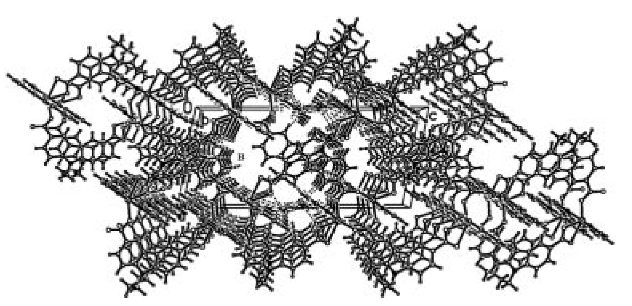


Figure 6. 2D structure containing nanometer channel B (10.537 × 9.232 Å) of **2** along the *b* axis by π–π interactions.

Cd(HA)$_2$(bipy) (3)

Complex **3** (Figure 7) crystallized with a monoclinic space group *C*2/*c* with the formula $[Cd(HA)_2(bipy)]_n$. X-ray crystallographic analysis reveals that complex **3** is 3D open framework with nanometer channels. The symmetric unit contains one cadmium atom, two H_2A groups, and two pyridine groups. The cadmium atom adopts a distorted octahedral geometry by coordinating to four oxygen atoms [Cd(1C)–O(1AC) 2.303(5) Å; Cd(1C)–O(2AC) 2.490(6) Å; Cd(1C)–O(1C) 2.303(5) Å; Cd(1C)–O(2C) 2.490(6) Å] of two chelating H_2A ligands and two nitrogen atoms [Cd(1C)–N(2C) 2.218(8) Å; Cd(1C)–N(3C) 2.299(9) Å] of two different bipyridines. These basic units form a 1D chain. The coordination mode of H_2A ligand is the same as that of complex **1**. It shed one proton and chelated to the cadmium atom through one of the carboxylate groups while the other carboxylate group connected to the chelated carboxylate group by a hydrogen bond (O–H···O 2.583 Å, O–H–O 170.37°), combining the 1D chains into the 2D grid layer (Figure 8 and Figure 9). The C–O bond (C16A–O3A 1.324 Å) is much longer than the C=O bond (C16A–O4A 1.228 Å) in the carboxy group, so C16A–O4A can be assigned as a double bond and C16A–O3A as a single bond, and the hydrogen atom is linked to O3A. 2D grid layers were extended along the *a* axis and formed a 3D supramolecular framework with 9.437 × 7.620 Å nanometer channel C by π–π interactions with a distance of 3.47 Å (Figure 10).

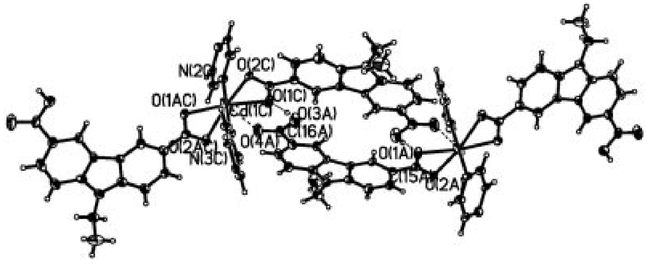


Figure 7. The ORTEP structure of **3** with atomic labeling scheme.

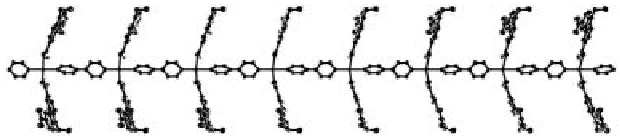


Figure 8. 1D chains of **3** formed by the basic units; all hydrogen atoms are omitted for clarity.

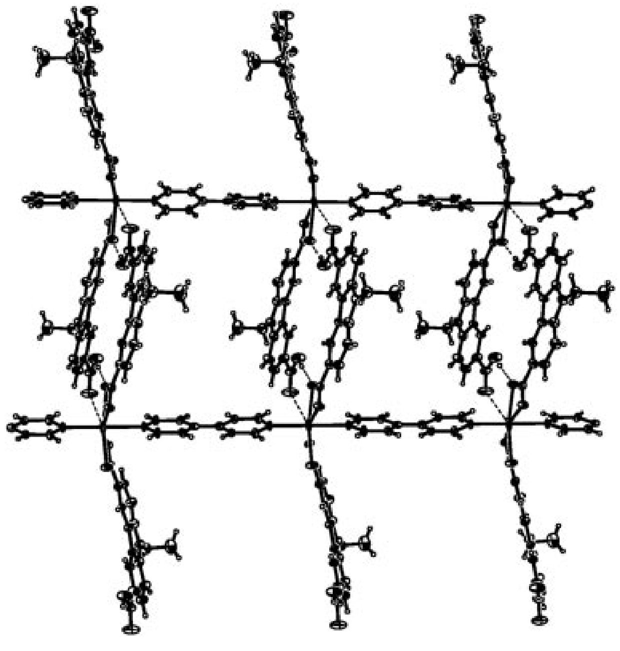


Figure 9. 2D grid layer based on 1D chains formed by intermolecular hydrogen bonds O–H···O.

Traditionally, flexible carboxylate ligands are able to produce more unique frameworks with aesthetic and useful properties than the rigid carboxylate ligands because of their flexibility and conformational freedom. However, in complexes **1**–**3**, the coordination modes were changed by the addition of the other ligand. With the exception of the different coordination mode in these complexes, many O–H···O hydrogen bonding interactions were observed in the crystal structure. Generally, the carboxylate groups are the main part of hydrogen-bonded networks. The hydrogen bonds of complex **1** are more numerous and more complicated than the others, because of the coordinated water. These strong O–H···O hydrogen bonds play an important role in the formation of the 2D or 3D supramolecular open frameworks containing nanometer channels. It should also be noted that, in comparison with **1** and **3**, the H_2A ligand in **2** shed all the protons, which suggests that phen may potentially act as a base for deprotonation of H_2A. All of the nanometer channels had similar dimensions, which may be due to the formation of these channels by two H_2A ligands. The small difference in size is a result of the different coordination modes and distorted stacking of aromatic rings.

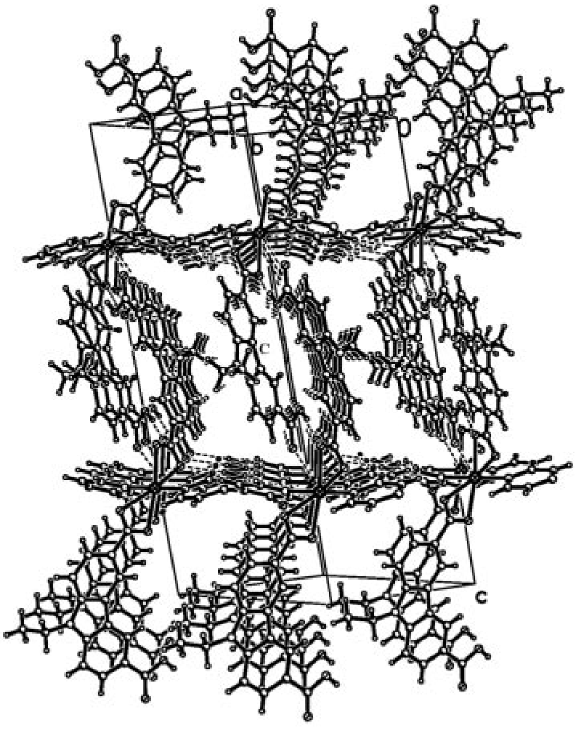


Figure 10. 3D structure containing nanometer channel C (9.437 × 7.620 Å) of **3**.

Thermogravimetric Analysis

Thermogravimetric analyses (TGA) of complexes **1**–**3** were performed on single crystal samples in the range of 20–650 °C under nitrogen. Complexes **1**–**3** exhibit high thermal stability. For complex **1**, the first weight loss occurred in stages starting at 164 °C and completing at 227 °C, corresponding to the loss of two coordinated water molecules. The anhydrous complex suffered from serious mass loss upon heating to 277 °C, attributable to decomposition of the organic composition. For complex **2**, the first major weight loss from 77 °C to 140 °C corresponded to the loss of guest water molecules. The main structure decomposed at 404 °C, exhibiting high thermal stability. Complex **3** also exhibits high thermal stability, as there is no weight loss below 361 °C.

Fluorescent Properties

Fluorescent transition-metal complexes containing rigid multichromophoric ligands with a large π-conjugation system have been studied intensively because of their potential use. On the other hand, to extend the π-conjugation only by synthesis and modification of organic composition may be difficult and tedious. Synthesis of inorganic/organic coordination complexes by using functional ligands gained from simplified synthetic approaches, some coligands, and transition-metal centers can be a useful method to obtain new photoluminescent materials. The luminescent properties of the free ligand H_2A and complexes **1**–**3** were investigated in solid state at room temperature (Figure 11). The nanosecond range of lifetime in the solid state at room temperature reveals that the emission is fluorescent in nature. The emission for free H_2A ligand is at 422 nm (λ_{exc} = 269 nm), which can be assigned to the $\pi^* \rightarrow \pi$ transition of the carbazole moiety.[17] Complex **1** exhibits a broad emission band with the maximal emission at 453 nm (λ_{exc} = 268 nm), which is 31 nm red-shifted compared to the free ligand. These emissions may be attributed to ligand-to-ligand charge transfer (LLCT).[18] The shoulder at 390 and 369 nm may be assigned to the excimer emission of the ligand because of the interaction between the molecules.[19] The emission of complex **2** is at 492 nm (λ_{exc} = 269 nm), which is red-shifted 70 nm compared to the free ligand; it can be assigned to the ligand-to-metal charge transfer (LMCT).[18] Generally, the intraligand and fluorescence emission is determined by the energy gap between π and π* molecular orbitals of the free ligand, which is simply related to the extent of π conjugation in the system.[20] Complex **3** exhibits strong emission at 396 nm (λ_{exc} = 270 nm), which can be assigned to the intraligand fluorescent emission of coordinated H_2A ligands. It is 26 nm blue-shifted compared to the free ligand and 57 nm blue-shifted compared to complex **1**, which may be due to the increase of the π–π stacking distance of the ligands [3.41 Å for **1**; 3.48 Å (H_2A), 3.38 Å (phen) for **2**; and 3.47 Å for **3**].

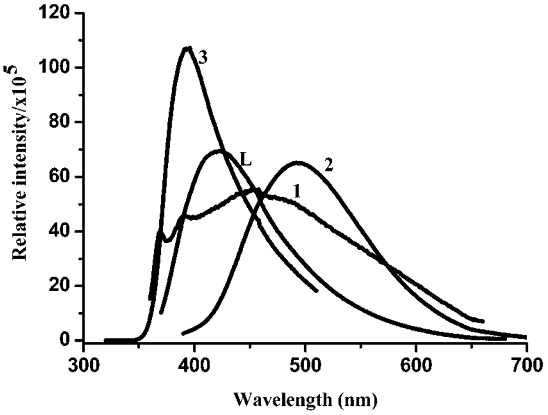


Figure 11. Photoluminescent spectra of H_2A and complexes **1**–**3** in the solid state at room temperature.

Conclusions

In this work, three supramolecular networks with strong luminescence as well as high thermal stability were obtained by hydrothermal synthesis. All of them contain nanometer channels formed by hydrogen bonds and π–π stacking. We have started to alter the luminescent properties and coordination modes by transforming the mixed ligands. This should lead to new, tunable, fluorescent materials. A novel 2D supramolecular network based on H_2A ligand and $Cd(NO_3)_2 \cdot 4H_2O$ has been obtained by hydrothermal synthesis. When the phen molecule was added, the coordination mode was changed and a 2D coordination polymer was obtained. When phen was changed into bipy, a 3D supramolecular network was obtained. The maximum emission wavelengths of complexes **1**–**3** are 453, 492, and 396 nm, respectively. In addition to their strong emissions and reasonable thermal stability, they are almost insoluble in common polar and nonpolar solvents such as ethanol, chloroform, acetone, acetonitrile, benzene, and water. In conclusion, these compounds may be good candidates as advanced materials for light-emitting diode devices. The paper also shows that transforming the mixed ligands is an excellent way of changing the coordination modes and luminescent properties.

Experimental Section

General Remarks: All chemicals and solvents were dried and purified by the usual methods. Elemental analysis data (C,H,N) were obtained using a Perkin–Elmer 240 analyzer. IR spectra were recorded with a Nicolet FTIR 170SX instrument (KBr discs) in the region of 4000–400 cm^{-1}. The luminescent spectra were measured on power samples at room temperature (room temp.) using a model Perkin–Elmer LS55 fluorescence spectrophotometer. TGA analyses were recorded with a Perkin–Elmer Pris-1 DMDA-V1 analyzer in nitrogen at a heating rate of 5 °C min^{-1}.

9-Ethylcarbazole-3,6-dicarboxylic Acid: The H_2A ligand was synthesized using the established literature procedure.[16]

Compound 1: Complex **1** was synthesized using the established literature procedure.[16]

Compound 2: A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.117 g, 0.38 mmol), phen (0.0760 g, 0.38 mmol), H_2A (0.0530 g, 0.19 mmol), $Na_2C_2O_4$ (0.0251 g (0.19 mmol), H_2O (15 mL), and 15 drops of C_2H_5OH was placed in a 25-mL Teflon-lined stainless steel vessel and then heated to 165 °C for 3 d and the reactant was cooled at a rate of 5 °C min^{-1}. The yellow crystals were obtained with a yield of 0.0780 g (70.2%) based on H_2A. $C_{28}H_{22}CdN_3O_{5.50}$ (600.89): calcd. C 55.97, H 3.69, N 6.99; found C 55.85, H 3.65, N 7.03. It is difficult to obtain reliable elemental analytical data because of the sensitivity of the analyzer. IR (KBr): $\tilde{\nu}$ = 3409 (m), 3066 (m), 2930

Table 1. Crystallographic data for compounds **1**–**3**.

	1	**2**	**3**
Empirical formula	$C_{32}H_{28}CdN_2O_{10}$	$C_{28}H_{22}CdN_3O_{5.50}$	$C_{42}H_{32}CdN_4O_8$
Formula mass	712.96	600.89	833.12
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c*	*P*2/*c*	*C*2/*c*
Crystal size [mm]	0.41 × 0.34 × 0.19	0.26 × 0.11 × 0.08	0.43 × 0.35 × 0.22
a [Å]	31.464(5)	10.533(8)	12.284(3)
b [Å]	5.1789(7)	10.138(8)	11.609(3)
c [Å]	20.453(3)	23.817(18)	26.995(4)
β [°]	119.320(2)	100.324(13)	102.322(3)
V [Å^3]	2905.8(7)	2502(3)	3761.0(14)
Z	4	4	4
D_{calcd} [Mg m^{-3}]	1.630	1.595	1.471
μ [mm^{-1}]	0.816	0.920	0.640
F (000)	1448	1212	1696
θ range [°]	1.48–25.10	2.01–5.01	2.44–25.01
Collected reflections	7161	11395	8513
Unique reflections	2573	4368	3037
Parameters	214	339	251
Goodness-of-fit on F^2	0.997	1.002	1.022
R_1, wR_2 [$I > 2\sigma(I)$]	0.0343, 0.0898	0.0404, 0.0971	0.0931, 0.2217
R_1, wR_2 [all data]	0.0387, 0.0928	0.0720, 0.1077	0.1358, 0.2498
Max., min. $\Delta\rho$ [e Å^{-3}]	0.641, –0.593	1.070, –0.608	1.106, –1.071

(m), 1599 (vs), 1547 (s), 1460 (m), 1383 (vs), 1308 (s), 1265 (m), 1230 (m), 1142 (m), 849 (m), 779 (s), 720 (s), 665 (m) cm^{-1}.

Compound 3: The same synthesis procedure was used as for **2** except that phen was replaced by bipy. Yellow crystalline products were collected with a yield of 0.0950 g (60.3%) based on H_2A. $C_{42}H_{32}CdN_4O_8$ (833.12): calcd. C 60.55, H 3.87, N 6.72; found C 60.43, H 3.89, N 6.75. IR (KBr): $\tilde{\nu}$ = 3413 (m), 3056 (m), 2972 (m), 1699 (s), 1600 (vs), 1529 (s), 1486 (s), 1388 (vs), 1353 (s), 1305 (s), 1238 (s), 1150 (m), 814 (m), 775 (m), 648 (m), 510 (m) cm^{-1}.

Table 2. Selected bond lengths [Å] and angles [°] for **1**–**3**.

1			
Cd(1)–O(1)	2.247(2)	O(1A)–Cd(1)–O(2A)	54.92(7)
Cd(1)–O(2)	2.489(2)	O(5)–Cd(1)–O(1A)	100.18(10)
Cd(1)–O(5)	2.187(3)	O(5)–Cd(1)–O(2)	84.76(8)
Cd(1)–O(1A)	2.247(2)	O(1)–Cd(1)–O(2)	54.92(7)
Cd(1)–O(2A)	2.489(2)	O(5A)–Cd(1)–O(1)	100.18(10)
Cd(1)–O(5A)	2.187(3)	O(5A)–Cd(1)–O(2A)	84.76(8)
2			
Cd(1)–O(1)	2.468(4)	O(2)–Cd(1)–O(1)	54.35(11)
Cd(1)–O(2)	2.315(3)	N(3)–Cd(1)–O(1)	93.06(12)
Cd(1)–O(3A)	2.196(3)	N(2)–Cd(1)–N(3)	70.56(14)
Cd(1)–O(4B)	2.256(3)	O(3A)–Cd(1)–N(2)	92.00(13)
Cd(1)–N(2)	2.362(4)	O(3A)–Cd(1)–O(4B)	98.29(13)
Cd(1)–N(3)	2.372(4)	O(4B)–Cd(1)–O(2)	88.30(12)
		O(1B)–C(13B)–O(2B)	120.1(4)
		O(4B)–C(14B)–O(3B)	125.0(4)
3			
Cd(1C)–O(1AC)	2.303(5)	O(1AC)–Cd(1C)–O(2AC)	54.46(19)
–O(2AC)	2.490(6)	N(2C)–Cd(1C)–O(2C)	97.41(14)
Cd(1C)–O(1C)	2.303(5)	N(2C)–Cd(1C)–O(1AC)	95.60(18)
Cd(1C)–O(2C)	2.490(6)	O(1C)–Cd(1C)–O(2C)	54.46(19)
Cd(1C)–N(2C)	2.218(8)	N(3C)–Cd(1C)–O(2AC)	82.59(14)
Cd(1C)–N(3C)	2.299(9)	N(3C)–Cd(1C)–O(1C)	84.40(18)
		O(3A)–C(16A)–O(4A)	121.7(8)
		O(1A)–C(15A)–O(2A)	121.0(7)

Single-Crystal Structure Determination: Data collection was performed at 298 K for **2** and **3** and 293 K for **1** using a Siemens Smart CCD area detector diffractometer with Mo-K_α radiation with an ω-scan mode (λ = 0.71073 Å). The structure was solved with direct methods using the SHELXTL program and refined anisotropically with SHELXTL using full-matrix least-squares procedure. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added theoretically and not refined. The crystallographic data for **1**–**3** are listed in Table 1, and selected bond lengths and angles for **1**–**3** are presented in Table 2.

CCDC-278329 (for $[Cd(HA)_2(H_2O)_2]$), -299277 (for $[Cd(A)(phen)]\cdot1.5H_2O$), and -299279 (for $[Cd(HA)_2(bipy)]$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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