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New 1-D and 3-D thiocyanatocadmates modified by various amine molecules and Cl⁻/CH₃COO⁻ ions: synthesis, structural characterization, thermal behavior and photoluminescence property

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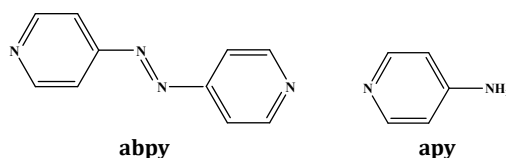
At the ambient conditions, the reactions of CdCl₂/Cd(CH₃COO)₂, SCN⁻ and various organic amine molecules in a strongly acidic solutions afforded five new thiocyanatocadmates as [H₂(abpy)][CdCl₂(SCN)₂] (abpy = azobispyridine) **1**, [H(apy)][Cd(SCN)₃] (apy = 4-aminopyridine) **2**, [H(ba)]₂[CdCl₂(SCN)₂] (ba = tert-butylamine) **3**, [H₂(tmen)][Cd₃Cl₆(SCN)₂] (tmen = *N,N,N',N'*-tetramethylethylenediamine) **4**, and [H(dba)]₂[Cd₂(CH₃COO)₂(SCN)₄] (dba = dibutylamine) **5**. Only in compound **2**, the CH₃COO⁻ ions for Cd(CH₃COO)₂ were completely displaced by SCN⁻, producing a chained thiocyanatocadmate [Cd(SCN)₃]⁻. In the other four compounds, the Cl⁻ or CH₃COO⁻ ions appeared in the final inorganic anion frameworks. In compound **1**, the Cl⁻ ions double bridge the Cd²⁺ centers into a one-dimensional (1-D) infinite chain, and the SCN⁻ group exists in a terminal form, whereas in compound **3**, the reverse situation is observed. Due to a *trans*-mode arrangement for two terminal Cl⁻ or SCN⁻ around each Cd²⁺ center, the inorganic anion chains in compounds **1** and **3** both show a linear shape. In compound **4**, Cd²⁺ and Cl⁻ first aggregate to form a 1-D endless chain with a composition of Cd₂Cl₆, which can be described as a linear arrangement of the open double cubanes. SCN⁻ serves as the second connector, propagating the Cd₂Cl₆ chain into a three-dimensional (3-D) network with the occluded H₂(tmen)²⁺ cations. In compound **5**, the SCN⁻ groups double bridge the Cd²⁺ centers into a 1-D zigzag-shape chain. The formation of the zigzag chain should derive from the chelation of the CH₃COO⁻ group to the Cd²⁺ center. The thermal behaviors and the photoluminescence properties for the title compounds were also investigated.

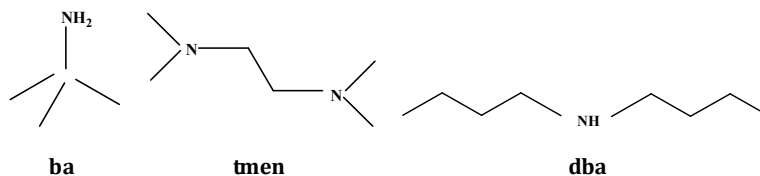
Introduction

As an important branch of hybrid organic-inorganic materials, the design and synthesis of novel organically templated halo(pseudohalo)metallates accepted a certain attention owing to their structural diversity,¹ and the potential applications in optics, electrical conductivity, and magnetism.² By employing various organic bases as the counteranions, a large number of novel halo(pseudohalo)metallates have been obtained over the last twenty years.³ For example, (i) Willett and his co-workers reported a series of organically templated halocuprates and halocadmates. Of those, some halocuprates exhibit the ferromagnetic properties due to the existence of the strong Cu(II)···Cu(II) interactions bridged by the Cl⁻ or Br⁻ ions,⁴ whereas some halocadmates show the ribbon structures with the different widths. These ribbons can be viewed as a slice of the 2-D CdX₂ sheet structure, namely the so-called dimensional reduction.⁵ Sometimes the ribbons can recombine into a new 2-D layer network, namely the so-called dimensional recombination;⁶ (ii) Mitzi and his co-workers

reported a series of organically templated haloplumbates(II) and halostannates(II) with the perovskite layer structures. Some of them were confirmed to be the remarkable candidate of the semiconducting materials.⁷ In any case, we must address that the structure of the as-synthesized halometallate is still unpredictable when a new organically templating agent is used, since the hybrid process is rather complicated, and dominated by many factors as the geometry of the metal ion, the coordination mode of the halogen or pseudohalogen ion, the form, size and the charge of the organic base, as well as the detailed experimental conditions.

The current investigation in our group is focused on the structural characterization of organically templated thiocyanatocadmates. Now, some interesting results have been obtained.⁸ For instance, (i) in compound $[\text{H}_2(4,4'\text{-dtdpy})][\text{Cd}_2(\text{SCN})_6]$ ($4,4'\text{-dtdpy} = 4,4'\text{-dithiodipyridine}$), two types of ribboned thiocyanatocadmates are observed in an identical compound;⁹ (ii) compound $[(\text{Hdabco})_2\text{Cd}_3(\text{SCN})_8]$ ($\text{dabco} = 1,4\text{-diazabicyclo}[2,2,2]\text{octane}$) is the first example of organically templated three-dimensional (3-D) thiocyanatocadmate;¹⁰ (iii) with $\text{H}(2,2'\text{-dtdpy})^+$ ($2,2'\text{-dtdpy} = 2,2'\text{-dithiodipyridine}$) as the templating agent, the inorganic anion $[\text{Cd}(\text{SCN})_3]^-$ exhibits a two-dimensional (2-D) honeycomb-like layer structure, in which the flexible feature of the 8-membered $\text{Cd}_2(\text{SCN})_2$ bop is discussed.⁹ On the other hand, we also found that CdCl_2 was used to react with SCN^- to prepare $\text{Cd}(\text{SCN})_2$ precursor, but sometimes the Cl^- ion could not be completely replaced by SCN^- , as a result it also appeared in the final inorganic anion framework.¹¹ That is to say, the thiocyanatocadmte framework can be modified by another kind of inorganic anion as the X^- ion. This not only enriches the thiocyanatocadmte framework structures, creating some new hybrid organic-inorganic materials, but also makes the compound produce some special property. For example, (i) due to the reservation of the Br^- ion, compound $[\text{H}_2(\text{bpip})][\text{Cd}_3\text{Br}(\text{SCN})_7]$ ($\text{bpip} = 1,2\text{-bis}(4\text{-piperidyl})\text{propane}$) crystallizes in a non-centric space group (C_c), which maybe makes this compound possess the second-order non-linear optical property;¹² (ii) in compound $[\text{H}_2(\text{dabco})]_2[\text{Cd}_3\text{Cl}_8(\text{SCN})_2] \cdot \text{H}_2\text{O}$, the reserved Cl^- ions first link the Cd^{2+} centers into a hexanuclear cluster. Then SCN^- acts as the second linker, extending the hexanuclear $\text{Cd}_6\text{Cl}_{16}^{4-}$ clusters into a one-dimensional (1-D) zigzag chain;¹³ (iii) compound $[\text{H}_2(\text{pip})]_4[\text{Cd}_3\text{Br}_8(\text{SCN})_2(\text{SO}_4)_2(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$ ($\text{pip} = \text{piperazine}$) shows a tube-like structure, in which Br^- and SO_4^{2-} were synchronously reserved.¹⁴ In this article, five new organic bases were selected to serve as the counteranions. The room-temperature reactions of $\text{CdCl}_2/\text{Cd}(\text{CH}_3\text{COO})_2$, SCN^- and various organic amine molecules in a strongly acidic solution were carried out, yielding five new thiocyanatocadmtes as $[\text{H}_2(\text{abpy})][\text{CdCl}_2(\text{SCN})_2]$ ($\text{abpy} = \text{azobispyridine}$) **1**, $[\text{H}(\text{apy})][\text{Cd}(\text{SCN})_3]$ ($\text{apy} = 4\text{-aminopyridine}$) **2**, $[\text{H}(\text{ba})]_2[\text{CdCl}_2(\text{SCN})_2]$ ($\text{ba} = \text{tert-butylamine}$) **3**, $[\text{H}_2(\text{tmen})][\text{Cd}_3\text{Cl}_6(\text{SCN})_2]$ ($\text{tmen} = N,N,N',N'\text{-tetramethylethylenediamine}$) **4**, and $[\text{H}(\text{dba})]_2[\text{Cd}_2(\text{CH}_3\text{COO})_2(\text{SCN})_4]$ ($\text{dba} = \text{dibutylamino}$) **5**. Note that only in compound **2**, the Cl^- ion was thoroughly displaced, whereas in the other four compounds, the Cl^- or CH_3COO^- ions appeared in the final inorganic anion frameworks. Scheme 1 illustrates the molecular structures of the organic bases in compounds **1-5**.





Scheme 1 Molecular structures of organic bases in compounds **1-5**.

Experimental

Materials and physical measurement

All chemicals are of reagent grade quality, obtained from commercial sources without further purification. Elemental analysis (C, H and N) was performed on a Perkin-Elmer 2400LS II elemental analyzer. Infrared (IR) spectrum was recorded on a Perkin Elmer Spectrum 1 spectrophotometer in 4000-400 cm^{-1} region using a powdered sample on a KBr plate. Powder X-ray diffraction (XRD) data were collected on a Rigaku/max-2550 diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). TG behavior was investigated on a Perkin-Elmer TGA-7 instrument with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ in air. Fluorescence spectrum was obtained on a LS 55 fluorescence/phosphorescence spectrophotometer at room temperature. Ultraviolet-visible (UV-vis) spectrum was obtained on a Rigaku-UV-3100 spectrophotometer.

Synthesis of 1-5

[H₂(abpy)][CdCl₂(SCN)₂] 1. A solution of abpy (184 mg, 1 mmol) in $\text{C}_2\text{H}_5\text{OH}$ (3 mL) was added slowly to an aqueous solution (5 mL) of a mixture of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (228 mg, 1 mmol) and NH_4SCN (152 mg, 2 mmol). A few drops of dilute H_2SO_4 were added to acidify the solution to $\text{pH} = 2$. The mixture was stirred for 48 hours, and then filtered. The light-yellow needle crystals of **1** were obtained after *ca.* 7 days of slow evaporation from the filtrate. Yield: *ca.* 25% based on Cd(II). Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{N}_6\text{S}_2\text{CdCl}_2$ **1**: C 29.67, H 2.48, N 17.30. Found: C 29.80, H 2.54, N 17.15%. IR (cm^{-1}): 2096 s, 1632 s, 1602 w, 1517 w, 1384 w, 1111 w, 804 m, 521 w.

[H(apy)][Cd(SCN)₃] 2. A solution of apy (94 mg, 1 mmol) in $\text{C}_2\text{H}_5\text{OH}$ (3 ml) was carefully layered over an aqueous solution (5 ml) of a mixture of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (267 mg, 1 mmol) and NH_4SCN (152 mg, 2 mmol). A few drops of dilute H_2SO_4 were added to acidify the solution to $\text{pH} = 2$. The colorless needle crystals of **2** were obtained after *ca.* 40 days of slow evaporation. Yield: *ca.* 30% based on Cd(II). Anal. Calcd for $\text{C}_8\text{H}_7\text{N}_5\text{S}_3\text{Cd}$ **2**: C 25.17, H 1.85, N 18.35. Found: C 25.02, H 1.83, N 18.21%. IR (cm^{-1}): 2107 s, 2082 s, 1647 m, 1585 m, 1529 m, 1398 w, 1201 m, 859 w, 765 m.

[H(ba)]₂[CdCl₂(SCN)₂] 3. A solution of ba-HCl (109 mg, 1 mmol) in CH_3OH (3 ml) was carefully layered over another CH_3OH solution (6 ml) of a mixture of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (228 mg, 1mmol) and NH_4SCN (152 mg, 2 mmol) ($\text{pH} = 4$). The colorless needle crystals of **3** were obtained after a month of slow evaporation. Yield: *ca.* 35% based on Cd(II). Anal. Calcd for $\text{C}_{10}\text{H}_{24}\text{N}_4\text{S}_2\text{CdCl}_2$ **3**: C 26.82, H 5.41, N 12.52. Found: C 26.60, H 5.45, N 12.49%. IR (cm^{-1}): 2082 s, 1602 m, 1575 m, 1502 m, 1470 m, 1404 m, 1378 m, 1299 m, 1207 m, 936 w, 759 w.

[H₂(tmen)][Cd₃Cl₆(SCN)₂] 4. A solution of tmen (0.1 ml) in $\text{C}_2\text{H}_5\text{OH}$ (3 ml) was carefully layered over an aqueous solution (5 ml) of a mixture of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (228 mg, 1 mmol) and NH_4SCN (152 mg, 2 mmol). A few drops of dilute H_2SO_4 were added to acidify the solution to $\text{pH} = 2$. The colorless needle crystals of **4** were obtained after *ca.* 45 days of slow evaporation. Yield: *ca.* 20% based on Cd(II). Anal. Calcd for $\text{C}_8\text{H}_{18}\text{N}_4\text{S}_2\text{Cd}_3\text{Cl}_6$

4: C 12.25, H 2.31, N 7.14. Found: C 12.24, H 2.19, N 7.05%. IR (cm⁻¹): 2108 s, 1970 m, 1453 m, 1386 m, 1359 w, 1287 w, 1140 w, 1116 m, 1044 w, 990 m, 960 m.

[H(dba)]₂[Cd₂(CH₃COO)₂(SCN)₄] 5. To a mixed solvent of methanol (10 ml), nitromethane (10 ml) and water (2 ml), Cd(CH₃COO)₂·2H₂O (801 mg, 3 mmol), NH₄SCN (152 mg, 2 mmol) and dba-HCl (165 mg, 1 mmol) were sequentially added. The mixture (pH = 4) was stirred for 48 hours, and then filtered. After complete evaporation of the solvent, the solid products were re-dissolved in 8 ml water. The light yellow block crystals of **5** were obtained after ca. 20 days of slow evaporation. Yield: ca. 15% based on Cd(II). Anal. Calcd for C₂₄H₄₆N₆O₄S₄Cd₂ **5**: C 34.49, H 5.55, N 10.06. Found: C 34.40, H 5.47, N 9.77%. IR (cm⁻¹): 2140 s, 2114 s, 1546 s, 1431 s, 1009 w, 950 w, 891 w, 739 w, 677 m, 615 w.

X-ray crystallography

The data were collected with Mo-K_α radiation ($\lambda = 0.71073 \text{ \AA}$) on a Siemens SMART CCD diffractometer for compounds **1**, **4** and **5**, and on a Rigaku R-Axis RAPID IP diffractometer for compounds **2** and **3**. With SHELXTL program, the structures of compounds **1**, **2**, **4** and **5** were solved using direct methods, while the structure of compound **3** was solved using heavy-atom methods.¹⁵ The non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement, and the other hydrogen atoms were treated using a riding model. The hydrogen atoms on N2 in compound **3** were obtained from the difference Fourier map. The hydrogen atoms on N3 in compound **2** were not located. The structures were then refined on F^2 using SHELXL-97.¹⁵ CCDC numbers are 1034206-1034208, 1038363, and 1034210 for compounds **1-5**, respectively. The crystallographic data for the title compounds are summarized in Table 1.

Table 1 Crystal data of **1-3**.

	1	2	3	4	5
Formula	C ₁₂ H ₁₀ N ₆ S ₂ CdCl ₂	C ₈ H ₇ N ₅ S ₃ Cd	C ₁₀ H ₂₄ N ₄ S ₂ CdCl ₂	C ₈ H ₁₈ N ₄ S ₂ Cd ₃ Cl ₆	C ₂₄ H ₄₆ N ₆ O ₄ S ₄ Cd ₂
<i>M</i>	485.71	381.77	447.75	784.33	835.71
<i>T</i> (K)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> 2/ <i>c</i>	<i>P</i> <i>n</i> <i>m</i> <i>a</i>	<i>P</i> -1	<i>C</i> 2/ <i>c</i>	<i>P</i> <i>n</i> <i>a</i> 2 ₁
<i>a</i> (Å)	14.1335(9)	10.450(2)	5.9343(12)	15.3979(8)	17.0284(14)
<i>b</i> (Å)	3.9687(3)	9.5557(19)	8.7361(17)	11.5941(8)	13.2610(8)
<i>c</i> (Å)	17.0383(12)	13.278(3)	10.178(2)	12.5879(8)	17.1968(9)
α (°)			107.00(3)		
β (°)	117.486(4)		105.40(3)	93.862(4)	
γ (°)			101.23(3)		
<i>V</i> (Å ³)	847.83(10)	1325.8(5)	464.76(16)	2242.1(2)	3883.3(4)
<i>Z</i>	2	4	1	4	4
<i>D</i> _c (g cm ⁻³)	1.903	1.913	1.600	2.324	1.429
μ (mm ⁻¹)	1.855	2.103	1.680	3.720	1.343
Reflections collected	4465	11969	4603	6105	21075
Unique reflections	1489	1611	2120	1969	6866
<i>R</i> _{int}	0.0208	0.0521	0.0271	0.0933	0.0380
Gof	1.171	1.112	1.187	1.187	1.091
<i>R</i> ₁ , <i>I</i> > 2 σ (<i>I</i>)	0.0192	0.0339	0.0315	0.0421	0.0324

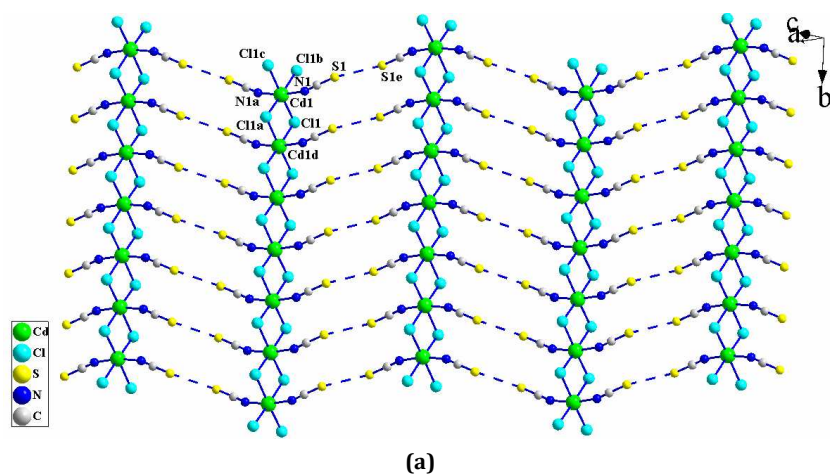
wR_2 , all data	0.0553	0.0794	0.0882	0.1028	0.0805
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Results and discussion

Synthetic analysis

All of the title compounds were obtained at the ambient conditions. The simple reactions of $\text{CdCl}_2/\text{Cd}(\text{CH}_3\text{COOH})_2$, SCN^- and organic bases in a $\text{H}_2\text{O}/\text{alcohol}$ solution produced the title compounds **1-5**. (i) All of the reactions are performed at a strongly acidic solution ($\text{pH} = 2$ for **1**, **2** and **4**; $\text{pH} = 4$ for **3** and **5**). On the one hand, the strongly acidic environment can assist the organic base to be completely protonated, as observed in compounds **1**, **3**, **4** and **5**. In compound **2**, apy shows an exception. Only the pyridyl N atom was protonated, while the amino N atom was not protonated. This may be associated with the inorganic anion effect. On the other hand, with the aid of the H^+ ion, the reactive precursors can be thoroughly dissolved by the solvent, which is helpful to the crystal growth and the increase of the yield. Sometimes even though in such a strongly acidic solution, the reactive precursors were still not completely dissolved. Two methods can solve this problem: filtering the undissolved substances, as observed when preparing compound **1**; adding the excessive solvent, as observed when preparing compound **5**. (ii) The reactions of $\text{CdCl}_2/\text{Cd}(\text{CH}_3\text{COO})_2$ with SCN^- in a molar ratio of 1:2 were carried out, but only in compound **2**, the CH_3COO^- ion was completely displaced by SCN^- , whereas in compounds **1**, **3**, **4** and **5**, the $\text{Cl}^-/\text{CH}_3\text{COO}^-$ ions still appeared in the resulting inorganic anion frameworks. This might be related to the organic amine cation. In the previous reports, the reservation of the halogen ions were frequently observed, but the CH_3COO^- ion was generally thorough replaced by SCN^- .⁸⁻¹⁴ (iii) The reactions of Cd^{2+} with SCN^- in a molar ratio of 1:2 were performed, but only in compounds **1**, **3** and **5**, the molar ratio of $\text{Cd}^{2+}:\text{SCN}^-$ is 1:2, while in compounds **2** and **4**, the molar ratios are 1:3 and 3:2, respectively. This should also be relevant with the organic amine cation. Maybe the reserved halogen ions should also be responsible for this.

Structural description



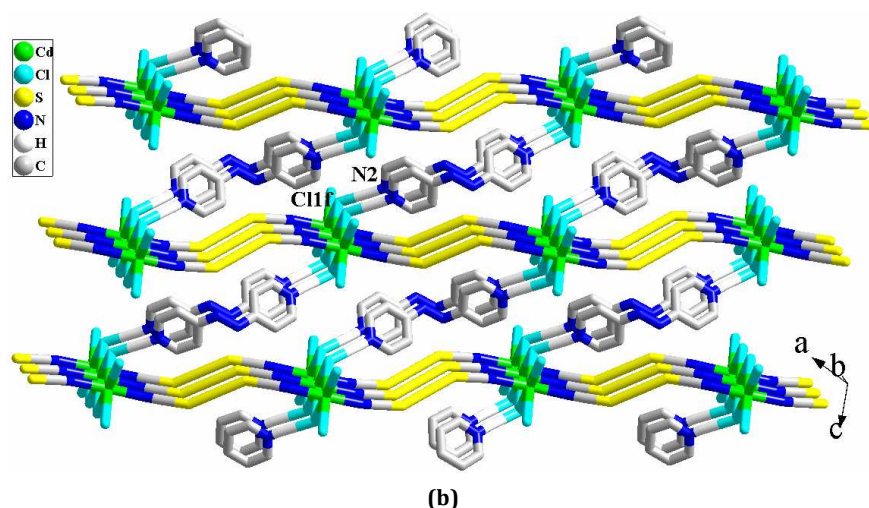
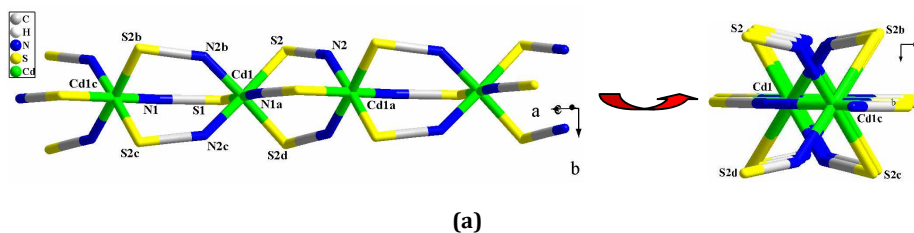


Fig. 1 2-D supramolecular layer (a) and 3-D supramolecular network (b) in **1** (a: $-x+1, y, -z+1/2$; b: $x, y+1, z$; c: $-x+1, y+1, -z+1/2$; d: $x, y-1, z$; e: $-x, -y+2, -z$; f: $x, -y+1, z+1/2$).

[H₂(abpy)][CdCl₂(SCN)₂] **1**. Compound **1** is a chained thiocyanatocadmate with H₂(abpy)²⁺ as the counteranion. The Cl⁻ ion is reserved in the final thiocyanatocadmate framework. The asymmetric unit for compound **1** is found to be composed of a half Cd²⁺ ion (Cd1), one Cl⁻ ion (Cl1), one SCN⁻ group (labeled as S₍₁₎C₍₁₎N₍₁₎) and a half H₂(abpy)²⁺ molecule, as shown in Fig. 1a, the octahedral Cd1 ion lies on an inversion center, surrounded by four Cl⁻ ions (Cl1, Cl1a, Cl1b, Cl1c) and two SCN⁻ N atom (N1, N1a). The Cd-Cl range and the Cd-N distance are 2.6773(6)-2.7817(6) Å and 2.218(2) Å, respectively. The Cl⁻ ion acts as the linker, double bridging the Cd²⁺ centers into 1-D infinite chain, extending along the *b*-axial direction. The 4-membered Cd₂Cl₂ ring in the chain is plane with a short Cd...Cd separation of 3.969 Å. SCN⁻ with the N atom as the donor serves as the terminal ligand. Due to a *trans*-mode arrangement for two SCN⁻ groups around each Cd²⁺ center, the CdCl₂ chain shows a linear shape, which is characterized by the Cd...Cd...Cd angle of 180°. Even though the SCN⁻ S atom is uncoordinate, there exists the weak S...S interaction between two neighboring SCN⁻ S atoms (S1...S1e = 3.751 Å). Via the weak S...S interactions, the adjacent [CdCl₂(SCN)₂]²⁻ chains are linked into a 2-D supramolecular sheet. Fig. 1b plots the projection of compound **1** in (010) direction. The diprotonated abpy molecules occupy the space between the 2-D supramolecular sheets. Via the N_{abpy}-H...Cl hydrogen-bonded interactions (N2...Cl1f = 3.162 Å), the abpy molecules propagate the 2-D supramolecular sheets into a 3-D supramolecular network.



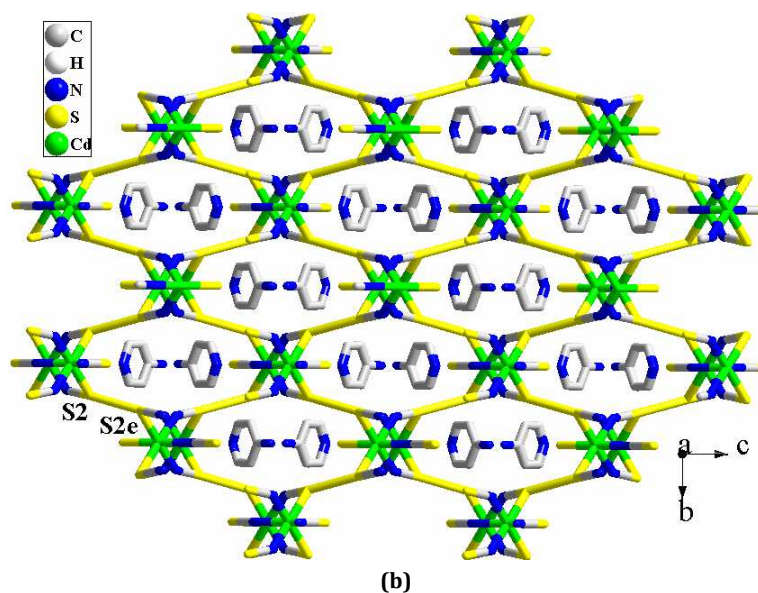


Fig. 2 1-D chain (a) and 3-D supramolecular network with occluded H(apy)⁺ cations (b) for **2** (a: $x+1/2$, $y, -z+1/2$; b: $x-1/2, -y+1/2, -z+1/2$; c: $x-1/2, y, -z+1/2$; d: $x, y+1/2, z$; e: $-x+3, -y+1, -z+1$).

[H(apy)][Cd(SCN)₃] **2**. Compound **2** is a H(apy)⁺-templated chained thiocyanatocadmate. CH₃COO⁻ is completely displaced by SCN⁻. The asymmetric unit for compound **2** is found to be composed of a half Cd²⁺ ion (Cd1), a half apy molecule and two types of SCN⁻ groups (SCN I labeled as S₍₁₎C₍₁₎N₍₁₎, occupancy ratio: 0.5 for each atom; SCN II labeled as S₍₂₎C₍₂₎N₍₂₎). The apy molecule should exist in a monoprotonated form, rather than the expected diprotonated form, in order to balance the charge of the inorganic anion. Two N atoms are both located at the special position, indicating that the pyridyl N atom has been protonated, while the amino N atom has not been protonated. Fig. 2a plots the 1-D chain structure of compound **2**. The crystallographically unique Cd1 center in the chain is in an octahedral site, completed by three SCN⁻ S atoms (S1, S2, S2d) and three SCN⁻ N atoms (N1a, N2b, N2c). The Cd-N_{μ-1,3-SCN} distances (2.296(3)-2.364(2) Å) are slightly longer than that of the Cd-N_{μ-3-SCN} observed in compound **1**. The Cd-S range is 2.6986(11)-2.7233(8) Å. Both SCN I and SCN II adopt a double-bridged mode, using N and S as the donors. The SCN⁻ groups triple bridge the Cd²⁺ centers to form a 1-D endless chain, running down the *a*-axial direction. The Cd...Cd...Cd angle of 151 ° implies that the chain shows a zigzag shape. Fig. 2a right plots the projection of the chain in *bc* plane. The symmetry-related S2 atoms are distributed around the chains. As shown in Fig. 2b, via the weak S...S interactions (S2...S2e = 3.421 Å), each [Cd(SCN)₃]⁻ chain interacts with the neighboring four [Cd(SCN)₃]⁻ chains. In this kind of linking way, compound **2** self-assembles into a 3-D supramolecular network with the 1-D channels. The apy molecules as the guest species occupy the space of the channels, stabilizing the 3-D supramolecular network structure of compound **2**.

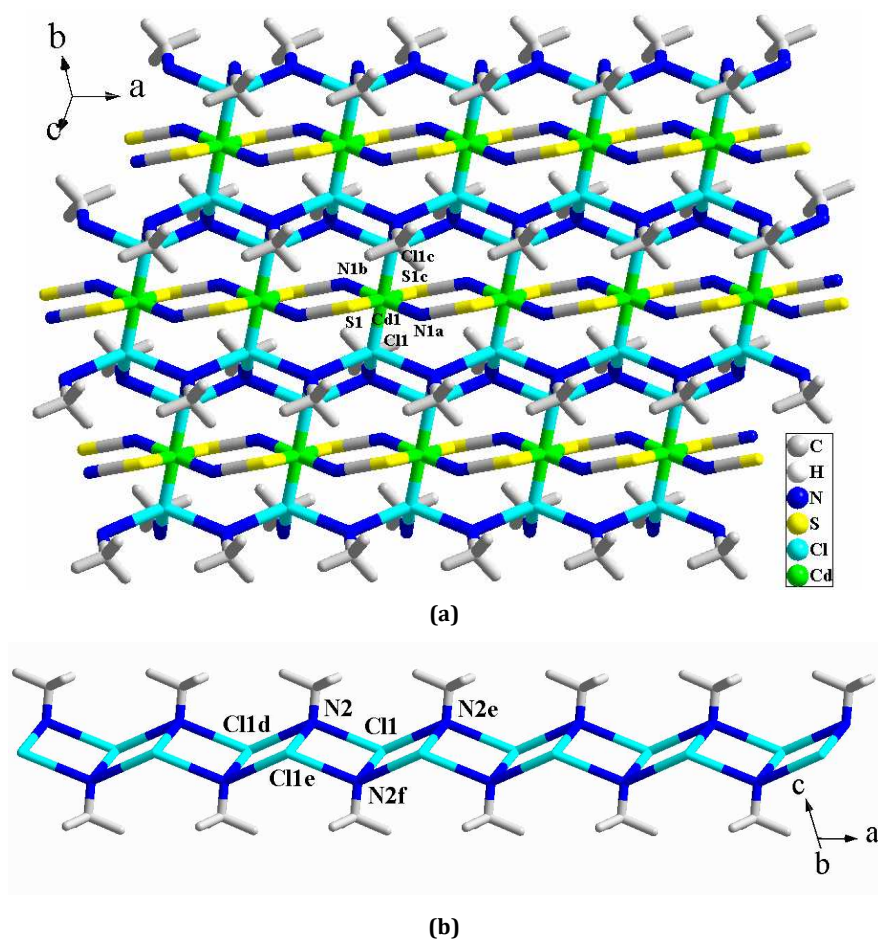


Fig. 3 2-D supramolecular layer (a) and 1-D staircase-like chain (b) in **3** (a: $-x+2, -y+1, -z$; b: $x-1, y, z$; c: $-x+1, -y+1, -z$; d: $x+1, y, z$; e: $-x+2, -y+2, z$).

[H(ba)]₂[CdCl₂(SCN)₂] **3**. Compound **3** is a chained thiocyanatocadmium with H(ba)⁺ as the countercation. The Cl⁻ ion is observed in the final inorganic anion framework. The asymmetric unit for compound **3** is found to be composed of a half Cd²⁺ ion (Cd1), one Cl⁻ ion (Cl1), one SCN⁻ group (labeled as S₍₁₎C₍₁₎N₍₁₎) and one H(ba)⁺ molecule. Templated by H(ba)⁺, the inorganic anion [CdCl₂(SCN)₂]²⁻ also exhibits a 1-D chain structure, as shown in Fig. 3a. Since the inorganic anion has the same composition as that of compound **1**, some structural similarities have been observed: (i) the octahedral Cd1 is located at an inversion center; (ii) two terminal ligands around each Cd center array in a *trans* mode (iii) the chain shows a linear shape (Cd...Cd...Cd = 179 °). There also exist some structural differences: (i) the SCN⁻ group adopts a double-bridged mode; (ii) the Cl⁻ ion acts as the terminal ligand, so the Cd-Cl distance of 2.6595(11) Å is slight short; (iii) the μ -1,3-mode SCN⁻ groups double bridge the Cd²⁺ centers into this 1-D chain, so the Cd-N distance of 2.326(3) Å and the Cd...Cd separation of 5.934 Å are somewhat long; (iv) the 8-membered Cd₂(SCN)₂ loop is non-planar with a larger mean deviation (0.2118 Å) from the least-squares plane; (v) the octahedral Cd1 center is completed by two SCN⁻ S atoms (S1, S1c), two SCN⁻ N atoms (N1a, N1b) and two Cl⁻ atoms (Cl1, Cl1c). The H(ba)⁺ molecules occupy the space between the chains. Each H(ba)⁺ N atom forms the hydrogen bonds to the adjacent three Cl⁻ ions (N2...Cl1 = 3.233 Å, N2...Cl1d = 3.277 Å, N2...Cl1e = 3.271 Å), whereas each terminal Cl⁻ ion forms the hydrogen bonds to the neighboring three H(ba)⁺ N atoms. Via the N-H...Cl interactions, compound **3** self-assembles into a 2-D supramolecular layer network. As shown in Fig. 3b, the terminal Cl⁻

ions and the $\text{H}(\text{ba})^+$ molecules form a staircase-like supramolecular chain, stabilizing the 2-D supramolecular layer. In the staircase chain, each Cl^- or N is involved in a tetrahedral geometry.

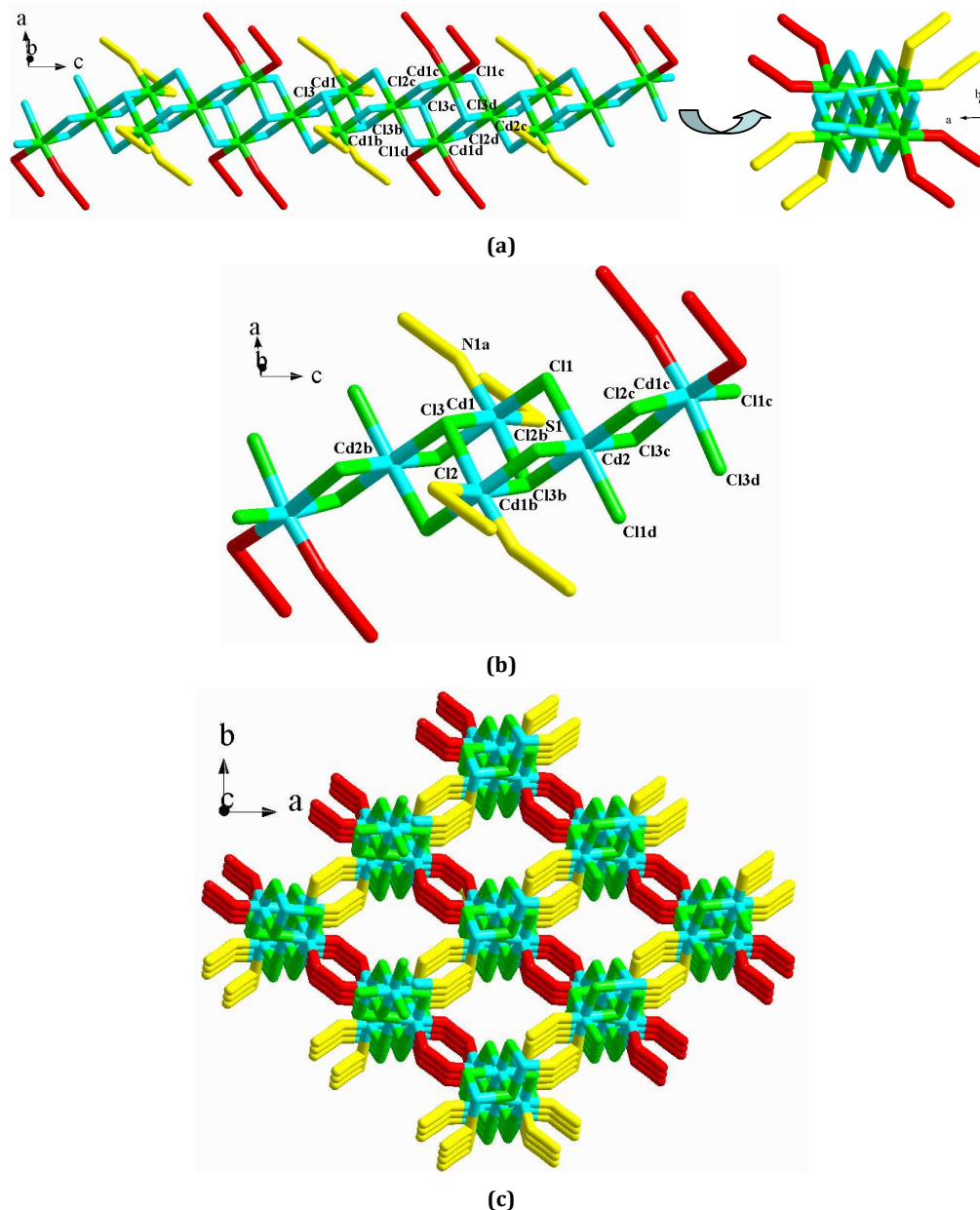
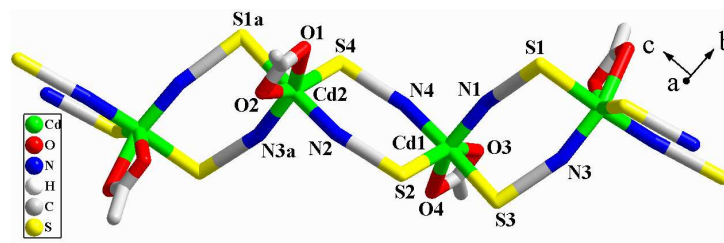


Fig. 4 $[\text{Cd}_2\text{Cl}_6\text{SCN}_2]^{2-}$ chain (a), hexanuclear cluster (b), and 3-D network (c) in **4** (a: $-x+1/2, -y+1/2, -z$; b: $-x, -y+1, -z$; c: $x, -y+1, z+1/2$; d: $-x, y, -z+1/2$)

$[\text{H}_2(\text{tmen})][\text{Cd}_3\text{Cl}_6(\text{SCN})_2]$ 4. Compound **4** is a 3-D thiocyanatocadmate with the occluded $\text{H}_2(\text{tmen})^{2+}$ cations. The Cl^- ions are not only reserved, but also form a 1-D infinite chain with the Cd^{2+} ions. The asymmetric unit for compound **4** is found to be composed of two types of Cd^{2+} ions (Cd1, Cd2; occupancy ratio: 1 for Cd1, 0.5 for Cd2), three types Cl^- ions (Cl1, Cl2, Cl3), one SCN^- group (labeled as $\text{S}_{(1)}\text{C}_{(1)}\text{N}_{(1)}$), and a half $\text{H}_2(\text{tmen})^{2+}$ molecule. In order to understand the formation of the 3-D network of compound **4**, the concept of the dimensional reduction and recombination should be introduced. Fig. 4a shows a chain

structure formed by Cd^{2+} , Cl^- and SCN^- . Note that the Cd-Cl chain is not a slice of the 2-D CdCl_2 layer, but the hexanuclear Cd-Cl cluster observed in this chain should originate from the 2-D CdCl_2 layer (see Fig. 4b). So the formation of the 3-D network of compound **4** maybe undergo the following several processes (i) with $\text{H}_2(\text{tmen})^{2+}$ as the so-called scissors, the 2-D CdCl_2 sheet is cut into a hexacluster Cd-Cl cluster with a composition of $\text{Cd}_6\text{Cl}_{24}^{12-}$; (ii) via the interactions between Cd1d and Cl3c, Cd1d and Cl3d, and Cd2c and Cl3d, the hexanuclear $\text{Cd}_6\text{Cl}_{24}^{12-}$ clusters recombine into a new Cd-Cl chain with a composition of $\text{Cd}_3\text{Cl}_6^{2-}$, running down the *c*-axial direction. Meanwhile, Cl1d bonds to Cd1d, and Cl1c bonds to Cd2c. In the 2-D CdCl_2 layer, Cd1d interacts with Cl2c, and Cd1c interacts with Cl2d; (iii) the SCN^- groups just replace the terminal Cl⁻ ions, forming the title $\text{Cd}_3\text{Cl}_6(\text{SCN})_2^{2-}$ chain; (iv) the double-bridged SCN^- groups act as the second connectors, linking the Cd_3Cl_6 chains into the 3-D network of compound **4** (see Fig. 4c). We must stress that the recombination of the $\text{Cd}_6\text{Cl}_{24}^{12-}$ clusters plays a crucial role in the formation of the 3-D network of compound **4**. In compound **4**, the Cd_2Cl_6 chain can also be regarded as a linear arrangement of the open double cubanes by sharing a corner (also see Fig. 4a). The recombination alters the arranging way of the neighboring open double cubanes: the centric planar Cd_2Cl_2 units are near vertical with a dihedral angle of 70.7° . In the 2-D CdCl_2 layer, they are parallel to each other. Since some open double cubanes change the arrangement way, each Cd_2Cl_6 chain has a chance to interact with the adjacent four Cd_2Cl_6 chains via SCN^- as the connectors, finally form a 3-D network of compound **4** with the occluded $\text{H}_2(\text{tmen})^{2+}$ cations. Without the occurrence of the recombination, maybe compound **4** only possesses a 2-D layer structure. In the Cd_2Cl_6 chain, the double-bridged Cl1 and Cl2 are distributed on the outside, while the triple-bridged Cl3 are distributed on the inside. Cd1 and Cd2 are still in the octahedral sites: Cd1 is coordinate with four Cl⁻ ions (Cl1, Cl2, Cl3, Cl3b), one SCN^- S atom (S1) and one SCN^- N atom (N1a), while Cd2 is surrounded by six Cl⁻ ions (Cl1, Cl1d, Cl2b, Cl3b, Cl2c, Cl3c). The Cd-Cl bond lengths basically obey the rule below: $d(\text{Cd-Cl}_{\text{triple-bridged}}) > d(\text{Cd-Cl}_{\text{double-bridged}})$. The Cd1-S1 and Cd1-N1a distances of 2.6565(12) Å and 2.291(4) Å are comparable with those observed in compound **3**. The shortest Cd...Cd contact distance is Cd1...Cd2 = 3.8705(4) Å.



(a)

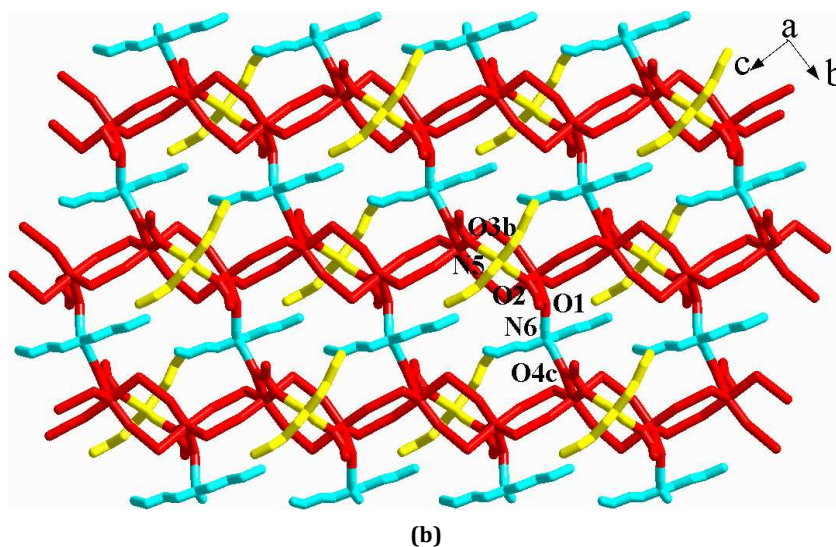


Fig. 5 1-D chain structure (a) and 2-D supramolecular layer network (b) for **5** (a: $-x-3/2, y-1/2, z+1/2$; b: $-x-3/2, y-1/2, z+1/2$; c: $-x-3/2, y+1/2, z+1/2$).

[H(dba)]₂[Cd₂(CH₃COO)₂(SCN)₄] **5**. Compound **5** is a chained thiocyanatocadmate with H(dba)⁺ as the counteranion. Interestingly, the CH₃COO⁻ ion appeared in the final thiocyanatocadmate framework. The asymmetric unit for compound **5** is found to be composed of two types of Cd²⁺ ions (Cd1, Cd2), four types of SCN⁻ groups (SCN I labeled as S₍₁₎C₍₁₎N₍₁₎, SCN II labeled as S₍₂₎C₍₂₎N₍₂₎, SCN III labeled as S₍₃₎C₍₃₎N₍₃₎, SCN IV labeled as S₍₄₎C₍₄₎N₍₄₎), two types of CH₃COO⁻ ions (CH₃COO I, CH₃COO II) and two types of H(dba)⁺ molecules (dba I, dba II). As shown in Fig. 5a, all of the SCN⁻ groups adopt a μ -1,3 mode, double bridging the Cd(II) centers into a 1-D endless chain, running down the *c*-axial direction. Due to the chelation of the CH₃COO⁻ ion to the Cd(II) center, the chain shows a zigzag shape, which is characterized by the Cd...Cd...Cd angle of *ca.* 140°. SCN I and SCN III link two Cd(II) centers into a 8-membered loop (loop I), while SCN II and SCN IV link two Cd(II) centers into another 8-membered loop (loop II). Two types of loops show some differences: (i) the loop II is almost planar with a quite small mean deviation of 0.0113 Å, while the loop I is non-planar with a larger mean deviation of 0.3080 Å; (ii) the Cd...Cd separation of 5.742 Å in loop I is slight shorter than that in loop II (5.832 Å). Along the extending direction of the chain, two types Cd₂(SCN)₂ loops array in an alternate way. As shown in Fig. 5b, the larger mean deviation for loop I may be due to the hydrogen-bonded interactions of the dba I N atom (yellow) with two CH₃COO⁻ O atoms (N5...O2 = 2.784 Å, N5...O3b = 2.795 Å). The dba II molecules (blue) occupy the space between the chains. Via the N-H...O interactions (N6...O1 = 2.825 Å, N6...O4c = 2.723 Å), the dba II molecules propagate the 1-D chains into a 2-D supramolecular layer network. Each Cd(II) with an octahedral geometry is coordinate with two SCN⁻ S atoms, two SCN⁻ N atoms and two CH₃COO⁻ O atoms. The Cd-N, Cd-S, and Cd-O ranges are 2.232(5)-2.291(7) Å, 2.6020(16)-2.770(2) Å, and 2.333(4)-2.433(4) Å, respectively.

Structural discussion

We employed five organic bases to serve as the counteranions, obtaining five new chained and 3-D thiocyanatocadmates with the different structures. The role of the organic base has been extensively studied in the past reports, namely by the form, size and the charge, the organic base imparts the structure of the inorganic anion.¹⁻⁷ Here we want to address that the hydrogen-bonded interactions between the organic base and the inorganic anion can not be ignorant: these weak interactions also have an effect on the structure of

the inorganic anion. As observed in compound **3**, only the Cl⁻ ions exist in a terminal form, they form a stable staircase-like supramolecular chain with the -NH₃⁺ ions. Here the -NH₃⁺ ion determines the existing form of the Cl⁻ ion; (ii) through these weak interactions, the low-D inorganic anions are propagated into diverse high-D supramolecular networks, as found in compounds **1**, **3** and **5**. The weak S...S interaction between the SCN⁻ groups can not be ignorant, either. It plays a key role in the formation of the stable supramolecular network.¹⁶ As observed in compound **2**, the N_{apy}-H...S_{SCN} and/or N_{apy}-H...N_{SCN} interactions do not form, but via the S...S interactions, the inorganic anions are extended into a 3-D supramolecular network. In compounds **1**, **3** and **4**, the Cl⁻ ions appeared in the final inorganic anion frameworks. This means that the reaction of CdCl₂ with SCN⁻ is not a simple replacement. On the one hand, the reservation of the Cl⁻ ions should be related to the hydrogen-bonded interaction. This has been mentioned above. On the other hand, the concept of the dimensional reduction should be introduced to understand the reaction between CdCl₂ and SCN⁻.^{1c,5,6} In the reaction, the role of the organic base should be considered. Here the organic base acts as the so-called scissors, first cutting the 2-D CdCl₂ into a cluster or ribbon. Once an oligomer forms, generally the SCN⁻ groups only displace the Cl⁻ ions on the outside. So some Cl⁻ ions on the inside were reserved in the final inorganic anion, which enriches the thiocyanatocamate framework structures. The most important role for SCN⁻ is to serve as the second linker, extending those chlorocadmate oligomers into a high-D network, as observed in compound **4**, and several reported compounds as [H₂(dabco)]₂[Cd₃Cl₈(SCN)₂·H₂O], [H₂(pip)][CdCl₃(SCN)]·2H₂O¹³ and [CdI(SCN)L] (L = SC(-OC₂H₅)=NH₂).¹⁴ In addition, the introduction of the concept of the dimensional recombination can better understand the formation of the 3-D network structure of compound **4**.

Characterization

Fig. S1 plots the IR spectra of compounds **1-5**. Based on the IR spectra, we can preliminarily know the existing form of the SCN⁻ group in the compound, bridging or terminal.¹⁷ The peaks appear at 2107 cm⁻¹ for **2**, 2108 cm⁻¹ for **4**, as well as 2140 and 2114 cm⁻¹ for **5**, being larger than 2100 cm⁻¹, indicate that there exist the bridging SCN⁻ groups in these three compounds. The maximum at 2096 cm⁻¹ (< 2100 cm⁻¹) implies a terminal mode for SCN⁻ in compound **1**. But meanwhile, several exceptions still appear. In compound **3**, the ν(CN) peak appears at 2082 cm⁻¹, but X-ray single-crystal diffraction analysis reveals that SCN⁻ shows a bridging mode. In compound **2**, a peak at 2082 cm⁻¹ is also observed, but there is no terminal SCN⁻ group in this compound. In the other reported compounds, the exceptions have also been observed.⁸⁻¹⁴

The TG behaviors of compounds **1-3** were investigated. Fig. S2 gives the temperature vs. weight-loss curves. Compound **1** possesses the better thermal stability, and can be thermal stable up to ca. 210 °C. Compound **1** underwent the two steps of weight loss. The first step of weight loss occurred in the temperature of 210 - 470 °C, corresponding to the sublimation of the double salt [H₂(abpy)]Cl(SCN) (Calcd: 57.6%; Found: ca. 57%). After the first step of weight loss, the product is CdCl₂·Cd(SCN)₂. The final residue was proved to be CdS (Calcd: 14.9%, Found: ca. 15.5%), implying that in the second step, CdCl₂ completely evaporated, and Cd(SCN)₂ synchronously transformed into CdS. Compound **2** possesses the similar thermal stability to compound **1**, and can be thermal stable up to ca. 230 °C. Upon heating, compound **2** also underwent the two steps of weight loss. Ca. 40% weight loss for the first step should be assigned to the department of [H(apy)](SCN), since the calculated value of 40.2 is well comparable with that observed. The final residue was confirmed to be CdS (Calcd: 37.7%, Found: 36.5%), indicating that the CN⁻ group lost in the second step. Compound **3** also underwent two steps of weight loss. The first step of ca. 59.3% weight loss might be attributed to the removal of the double salt [H(ba)]₂Cl_{0.65}(SCN)_{1.35} (Calcd: 59.4%), rather than [H(ba)]₂Cl(SCN) (Calcd: 57.5%). So after the first step of weight loss, the intermediates is CdCl_{1.35}(SCN)_{0.65}. At ca. 550 °C, the

second step of weight loss occurred, corresponding to the thorough evaporation of CdCl_2 in the intermediates. The final remaining was CdS (Calcd: 12.0%, Found: ca. 12%). If the intermediates is $\text{CdCl}(\text{SCN})$, the final residue content is 17.2%, obviously higher than that observed.

Fig. S3 presents the experimental and simulated powder XRD patterns of **1-5**. The experimental powder XRD pattern for each compound is in accord with the simulated one generated on the basis of structural data, confirming that the as-synthesized product is pure phase.

Photoluminescence property

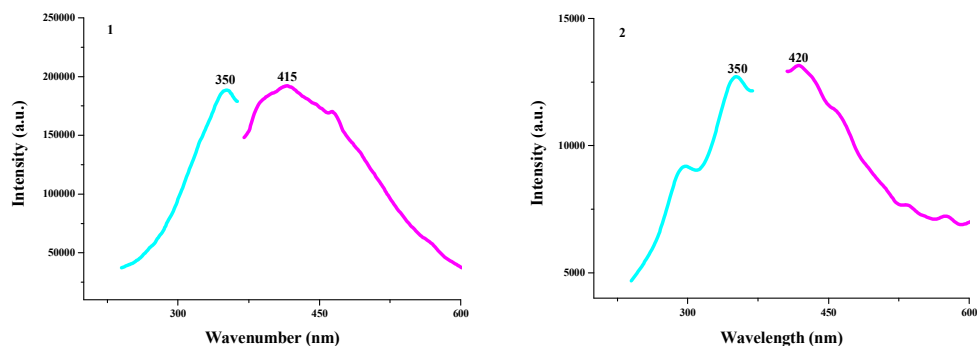


Fig. 6 Photoluminescence excitation (blue) and emission spectra (pink) of **1** and **2**.

The photoluminescence properties of the title compounds were investigated. Fig. 6 illustrates the related excitation and emission spectra. Obviously, compounds **1** and **2** possess the photoluminescence properties. Upon excitation ($\lambda_{\text{ex}} = 350 \text{ nm}$ for **1** and **2**), both compounds emit blue light with the similar maximums at 415 nm for **1**, and 420 nm for **2**. But the emission intensities for two compounds show the difference. The emission intensity for compound **1** is by far stronger than that of compound **2**. In order to understand the emission mechanism of both compounds, the photoluminescence behaviors of two organic bases abpy and apy were also investigated. As shown in Fig. S4, when excited at 340 nm, the organic molecules abpy and apy both emit the extremely weak blue light with the similar maximums at 463 nm for abpy, and 461 nm for apy, respectively.¹⁹ Even though the blue shift by ca. 40 nm occurs, the emissions of compounds **1** and **2** should still be attributed to the ligand-centered electronic excitations. The blue-shift might be due to the hybrid. Moreover, the emission intensities for compounds **1** and **2** are obviously stronger than that of the corresponding organic ligand, which might also be due to the hybrid. The title compounds **3-5** do not emit light. In order to understand the emission behaviors of compounds **1-5**, (i) the UV-vis spectra of compounds **3-5** were measured (see Fig. S5), and (ii) the diagrams of energy levels of compounds **1** and **3** as the representatives were drawn according to the photoluminescence spectra of **1** and the UV-vis spectrum of **3** (see Fig. S6).²⁰ In the UV-vis spectra of compounds **3-5**, the peaks appear at 240 nm for **3**, 230 nm for **4**, and 245 nm for **5**, which should be assigned to the $n \rightarrow \pi^*$ transition of the amine cation. As shown in Fig. S6(a), when excited at 350 nm, the electron transfers from the ground-state E_0 to the excited-state E_2 . Then it nonradiatively decays to the excited-state energy level E_1 , from which the electron returns back to the ground-state E_0 with the light energy emission (415 nm). The similar situation occurs for compound **2**. So compounds **1** and **2** emit light. However, the difference is observed for compounds **3-5**. As shown in Fig. S6(b), upon excitation, the electron transfers from the ground-state E_0 to the excited-state E_1 (240 nm). Then from the excited-state energy level to the ground-state energy level, the electron decays in a nonradiative form.

So compounds **3-5** do not emit light. The occurrence of this situation might be due to two reasons: (i) organic aliphatic amine molecules themselves do not emit light due to the lack of the conjugated structure in the molecules; (ii) the organic aliphatic amines in compounds **3-5** do not induce the inorganic anions to emit light. The decay curve for compound **1** fit into a double exponential function, and the lifetimes were calculated to be $\tau_1 = 0.50$ ns and $\tau_2 = 3.67$ ns, respectively. The luminescence lifetime for compound **2** was calculated to be $\tau_1 = 0.28$ ns and $\tau_2 = 3.36$ ns, respectively (see Fig. 7).

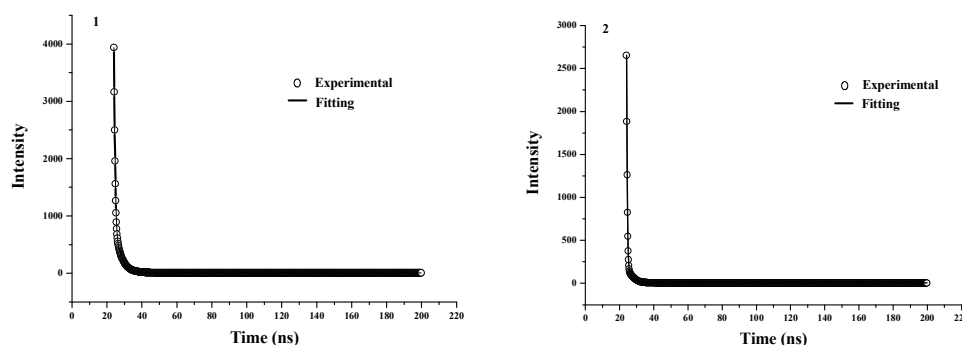


Fig. 7 Decay curves of **1** and **2**.

During the past several years, we have reported a series of new thiocyanatocadmates. Of those, some of them have been verified to possess the photoluminescence properties in the solid state. Generally, they emit the high-energy blue or violet light. For example, compounds $[\text{H}_2(\text{pdma})][\text{Cd}_2(\text{SCN})_4(\text{SO}_4)]$ (pdma = 1,4-phenylenedimethanamine),^{8a} $[\text{H}_2(\text{bpyp})][\text{CdBr}_2(\text{SCN})_2]$ (bpyp = 1,2-bis(4-pyridyl)propane),¹⁰ $[(\text{Hbim})_2\text{CdCl}_2(\text{SCN})_2]$ (bim = 2,2'-biimidazole), and $[\text{H}_2(\text{pip})][\text{Cd}(\text{SCN})_4]$ ¹¹ all emit blue light, and the maximums appear around 460 nm; compound $[\text{H}_2(\text{bim})][\text{Cd}(\text{SCN})_2(\text{H}_2\text{O})_2]\text{SO}_4$ ^{8a} also emits blue light, but the maximum is at *ca.* 420 nm; compounds $[\text{H}_2(\text{pympip})]_2[\text{Cd}_2(\text{SCN})_4(\text{SO}_4)_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$ (pympip = 1-(2-pyrimidyl)piperazine)^{8a} and $[\text{H}_2(\text{bpip})][\text{Cd}_3\text{Br}(\text{SCN})_7]$ ¹² emit violet light, and the maximums appear around 390 nm. Only an unpublished compound $[\text{H}_2(\text{bpe})][\text{CdBr}_2(\text{SCN})_2]$ (bpe = 1,2-bis(4-piperidyl)ethane)¹⁸ shows an exception, emitting green light with the maximum at 495 nm. Although the hybrid has occurred, those blue or violet light emissions including the title compounds **1** and **2** are basically attributed to the charge transfers within the organic molecules, since the free organic molecules in the solid state exhibit the similar emissions to the corresponding hybrids. Sometimes a slight blue shift or red shift is observed, exemplified by compounds **1** and **2**. In compound $[\text{H}_2(\text{bpip})][\text{Cd}_3\text{Br}(\text{SCN})_7]$, an even larger red-shift by *ca.* 80 nm is observed. This emission was tentatively assigned to the charge transfer between $[\text{H}_2(\text{bpip})]^{2+}$ and SCN^-/Br^- with the hydrogen bond as the bridge for electronic transition. Now maybe this emission can also be attributed to the charge transfer associated with the organic molecule. The green-light emission for compound $[\text{H}_2(\text{bpe})][\text{CdBr}_2(\text{SCN})_2]$ should be assigned to the Br-to- Cd^{2+} charge transfer, because a similar emission was observed in the emission spectrum of CdBr_2 ($\lambda_{\text{em}} = 434$ nm for bpe). It is noteworthy that in the emission spectrum of CdBr_2 , the maximum is centered at 520 nm, and the peak at 495 nm is only a shoulder. But after a hybrid, the peak at 520 nm quenches, and the peak at 495 nm significantly enhances, dominating green-light emission of compound $[\text{H}_2(\text{bpe})][\text{CdBr}_2(\text{SCN})_2]$. Actually, a majority of reported thiocyanatocadmates with the aromatic amine cations do not emit light, which might be relevant to the close packing of the molecules as well as the excited state inter/intramolecular proton transfer (EXIPT).^{8-14,21}

Based on the photoluminescence behaviors of the title compounds and the previous related reports, we can know that: (i) most thiocyanatocadmates do not emit light, and only limited examples possess the photoluminescence properties; (ii) the thiocyanatocadmates generally emit the high-energy blue or violet light; (iii) the violet- or blue-light emissions derive from the ligand-centered electronic excitations; (iv) due to the hybrid, the emission intensity maybe significantly enhances; (v) also due to the hybrid, a red- or blue-shift generally occurs. Sometimes the larger shift is observed.

Conclusion

In summary, we selected five organic bases to serve as the counteranions, preparing five new thiocyanatocadmates. Synthetically, the strongly acidic environments not only ensure the organic bases to be thoroughly protonated, but also assist the reactive precursors to be completely dissolved by the solvent molecule. Structurally, the Cl^- or CH_3COO^- ions were found to appear in the final inorganic anion frameworks in the title four compounds. That is to say, besides the organic base molecules, the thiocyanatocadmates framework can be further modified by another inorganic anion as the X^- or CH_3COO^- ion. This also indicates that the reaction of CdCl_2 with SCN^- is not just a simple displacement. The reservation of the Cl^- ion might be associated from two reasons: (i) the hydrogen-bonded interactions between the amine cation and the inorganic anion framework; (ii) the organic base participated in the reaction of CdCl_2 with SCN^- . Based on the concept of the dimensional reduction, the organic base acts as a scissors, cutting first the 2-D CdCl_2 layer into an oligomer (ribbon or cluster). While SCN^- can only displace the Cl^- ions on the outside of the oligomer. The important role for SCN^- is to serve as the second connector, propagating these oligomers into a new infinite network. The introduction of the concept of the dimensional recombination provides an approach to better understand the formation of the 3-D network structure of compound **4**. The TG analysis indicates that this kind of material generally underwent the following weight-loss procedures upon heating: the loss of the amine molecule in a halide or/and pseudohalide form, the evaporation of CdCl_2 , and the loss of CN^- for SCN^- . The title compounds **1** and **2** emit blue light, which are assigned to the ligand-centered electronic excitations.

Acknowledgements

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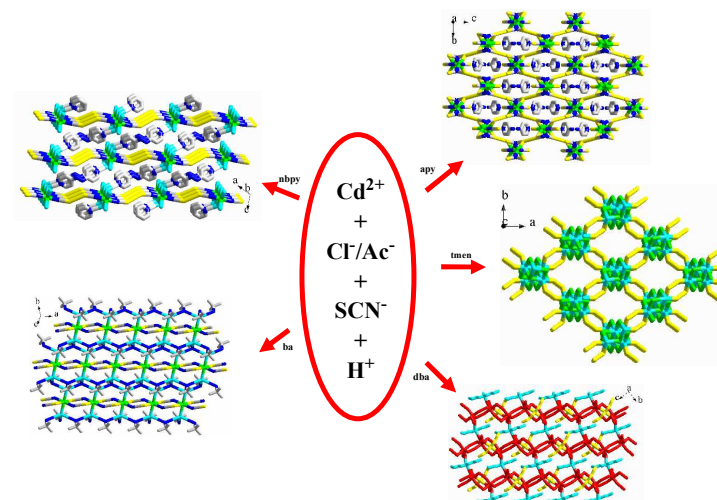
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New 1-D and 3-D thiocyanatocadmates modified by various amine molecules and Cl⁻/CH₃COO⁻ ions: synthesis, structural characterization, thermal behavior and photoluminescence property

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At the ambient conditions, the reactions of CdCl₂/Cd(CH₃COO)₂, SCN⁻ and various organic amine molecules in a strongly acidic solutions afforded five new thiocyanatocadmates as [H₂(abpy)][CdCl₂(SCN)₂] (abpy = azobispyridine) **1**, [H(apy)][Cd(SCN)₃] (apy = 4-aminopyridine) **2**, [H(ba)]₂[CdCl₂(SCN)₂] (ba = tert-butylamine) **3**, [H₂(tmen)][Cd₃Cl₆(SCN)₂] (tmen = *N,N,N',N'*-tetramethylethylenediamine) **4**, and [H(dba)]₂[Cd₂(CH₃COO)₂(SCN)₄] (dba = dibutylamine) **5**. Only in compound **2**, the CH₃COO⁻ ions for Cd(CH₃COO)₂ were completely displaced by SCN⁻, producing a chained thiocyanatocadmate [Cd(SCN)₃]. In the other four compounds, the Cl⁻ or CH₃COO⁻ ions appeared in the final inorganic anion frameworks. In compound **1**, the Cl⁻ ions double bridge the Cd²⁺ centers into a one-dimensional (1-D) infinite chain, and the SCN⁻ group exists in a terminal form, whereas in compound **3**, the reverse situation is observed. Due to a *trans*-mode arrangement for two terminal Cl⁻ or SCN⁻ around each Cd²⁺ center, the inorganic anion chains in compounds **1** and **3** both show a linear shape. In compound **4**, Cd²⁺ and Cl⁻ first aggregate to form a 1-D endless chain with a composition of Cd₃Cl₆, which can be described as a linear arrangement of the open double cubanes. SCN⁻ serves as the second connector, propagating the Cd₃Cl₆ chain into a three-dimensional (3-D) network with the occluded H₂(tmen)²⁺ cations. In compound **5**, the SCN⁻ groups double bridge the Cd²⁺ centers into a 1-D zigzag-shape chain. The formation of the zigzag chain should derive from the chelation of the CH₃COO⁻ group to the Cd²⁺ center. The thermal behaviors and the photoluminescence properties for the title compounds were also investigated.