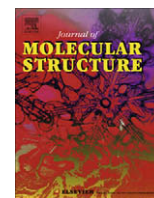


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Self-assembly of silver(I) coordination polymers from aminopyrimidyl derivatives and malonate acid: From 1D chain to 2D layer

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ABSTRACT

Two new silver(I) coordination polymers (CPs) of the formula $[Ag_2(dmapym)_4(mal)\cdot H_2O]_n$ (**1**) and $[Ag_3(apym)_3(mal)NO_3]_n$ (**2**) (dmapym = 2-amino-4,6-dimethylprimidine, apym = 2-aminopyrimidine, H_2mal = malonate) have been synthesized by reactions of $AgNO_3$ and 2-aminopyrimidyl ligands with malonate under the ammoniacal condition. Both complexes have been characterized by element analysis, IR and single-crystal X-ray diffraction. The monodentate dmapym and tridentate mal ligands link Ag(I) ions to give complex **1** a one-dimensional (1D) H-shaped chain structure. The complex **2** is a two-dimensional (2D) double sheet structure constructed by (4, 4) single sheet. Additionally, the hydrogen-bonding and C–H $\cdots\pi$ interactions also direct the self-assembly of supramolecular architectures. The photoluminescence properties of the **1** and **2** were investigated in the solid state at room temperature.

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1. Introduction

The crystal engineering of coordination networks based on multitopic organic ligands and metal centers has been extensively studied in recent years owing to their novel and diverse structural topologies as well as potential applications [1–13]. Although assembly of coordination polymers (CPs) is mainly directed by the inbeing of the metal ions and the predesigned organic ligands, it is also highly influenced by other factors such as the temperatures, the solvent systems, the counter ions with different bulk or coordination ability, the templates and metal/ligand ratio [14–30]. Parallel to the above aspects, the non-covalent forces such as hydrogen-bonding, $\pi\cdots\pi$ stacking, metal \cdots metal interactions based on d^{10} metal cations, metal $\cdots\pi$, C–H $\cdots\pi$ and anion $\cdots\pi$ interactions can also intensively impact the supramolecular topology and its dimensionality [31–37]. The aminopyrimidine contains three potential bonding sites with the capability of bridging at most three metal ions in chelating way, while the amino group can interact with guest molecules or counteranions through hydrogen bonds [38–40]. On the other hand, choosing malonate as auxiliary ligand is due to (i) the conformational freedom of the carbon skeleton, giving rise to various relative orientation of the two carboxylate moieties, (ii) the possibility to obtain mono- or di-anionic forms, (iii) the probability of triply coordinated oxygen atoms [7].

In our recent studies, 2-aminopyrimidine and its derivatives incorporating different dicarboxylates have been widely used to

construct a series of Ag(I) complexes [38,41–47]. As our continuous work, we introduced the versatile malonate as an auxiliary ligand to our previous systems and successfully obtained two new CPs with the dimensions spanning from 1D to 2D.

2. Experimental

2.1. Materials and physical measurements

All the reagents and solvents employed were commercially available and used as received without further purification. Infrared spectra were recorded on a Nicolet AVATAT FT-IR360 spectrometer as KBr pellets in the frequency range 4000–400 cm^{-1} . The elemental analyses (C, H, N contents) were determined on a CE instruments EA 1110 analyzer. Photoluminescence measurements were performed on a Hitachi F-4500 fluorescence spectrophotometer with solid powder on a 1 cm quartz round plate.

2.2. Synthesis of complex $[Ag_2(dmapym)_4(mal)\cdot H_2O]_n$ (**1**)

A mixture of $AgNO_3$ (167 mg, 1 mmol), dmapym (123 mg, 1 mmol) and H_2mal (104 mg, 1 mmol) were stirred in ethanol– H_2O mixed solvent (8 mL, v/v: 1/1). Then aqueous NH_3 solution (25%) was dropped into the mixture to give a clear solution under ultrasonic treatment. The resultant solution was allowed to evaporate slowly in darkness at room temperature for several days to give colorless crystals of **1** (yield, 76%). Anal. Calc. (found) for $Ag_2C_{27}H_{40}N_{12}O_5$: C, 39.14 (39.10); H, 4.87 (4.77); N, 20.29 (20.24)

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%. IR (KBr): $\nu(\text{cm}^{-1}) = 3430$ (s), 2914 (w), 2847 (w), 1625 (s), 1600 (s), 1466 (w), 1380 (m), 1118 (m), 790 (w).

2.3. Synthesis of complex $[\text{Ag}_3(\text{apym})_3(\text{mal})\text{NO}_3]_n$ (**2**)

The synthesis of **2** was similar to that of **1**, but with apym (95 mg, 1 mmol) in place of dmapym. Colorless crystals of **2** were obtained in 72% yield. They were washed with a small volume of cold ethanol and diethyl ether. Anal. Calc. (found) for $\text{Ag}_3\text{C}_{15}\text{H}_{17}\text{N}_{10}\text{O}_7$: C, 23.31 (23.28); H, 2.22 (2.27); N, 18.12 (18.20) %. IR (KBr): $\nu(\text{cm}^{-1}) = 3436$ (s), 2920 (w), 2844 (w), 1579 (s), 1380 (s), 1356 (s), 1115 (m), 1082 (m), 701 (w), 631 (w).

3. X-ray crystallography

Single crystals of the complexes **1** and **2** with appropriate dimensions were mounted on a glass fiber and used for data collection. Data were collected on a Bruker-AXS CCD diffractometer equipped with a graphite-monochromated $\text{MoK}\alpha$ radiation source ($\lambda = 0.71073 \text{ \AA}$) for **1** and **2**. All absorption corrections were performed with the SADABS program [48]. All the structures were solved by direct methods using SHELXS 97 [49] and refined by full-matrix least-squares techniques using SHELXL 97 [50]. Complex **2** crystallized in a chiral space group, $Pca2_1$, as determined by the systematic absences in the intensity data, intensity statistics, and the successful solution and refinement of the structures. The final absolute structure (Flack) parameter is 0.02(4), indicating the correct absolute structure and the absence of inversion twinning. The positions of the water H atoms were refined with the O–H bond length restrained to 0.85 Å. The crystallographic details of **1** and **2** are summarized in Table 1. Selected bond lengths and angles for **1** and **2** are collected in Table 2. The hydrogen bond geometries for **1** and **2** are shown in Table 3.

Table 1
Crystallographic data for complexes **1** and **2**.

	Complexes	
	1	2
Formula	$\text{Ag}_3\text{C}_{27}\text{H}_{40}\text{N}_{12}\text{O}_5$	$\text{Ag}_3\text{C}_{15}\text{H}_{17}\text{N}_{10}\text{O}_7$
M_r	828.45	773.00
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$Pca2_1$
a (Å)	7.5260(4)	13.325(3)
b (Å)	10.2052(5)	13.696(3)
c (Å)	21.5181(12)	12.507(3)
α (°)	94.565(4)	90
β (°)	92.406(4)	90
γ (°)	93.624(4)	90
Z	2	4
V (Å ³)	1642.31(15)	2282.6(8)
D_c (g cm ⁻³)	1.675	2.249
μ (mm ⁻¹)	1.249	2.609
$F(000)$	840	1496
No. of unique reflns.	6374	3353
No. of obsd. reflns. [$I > 2\sigma(I)$]	4138	2865
Parameters	423	316
GOF	1.053	1.014
Final R indices [$I > 2\sigma(I)$] ^{a,b}	$R_1 = 0.0601$, $wR_2 = 0.1042$	$R_1 = 0.0332$, $wR_2 = 0.0805$
R indices (all data)	$R_1 = 0.1383$, $wR_2 = 0.1485$	$R_1 = 0.0401$, $wR_2 = 0.0854$
Largest difference peak and hole (e Å ⁻³)	1.540 and -0.608	0.726 and -0.472

^a $R_1 = \sum \|F_o| - |F_c|\| / \sum |F_o|$.

^b $wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{0.5}$.

Table 2
Selected bond distances (Å) and angles (°) for **1** and **2**.

Complex 1			
Ag1–N8	2.250(5)	Ag2–N6	2.294(6)
Ag1–N11	2.303(5)	Ag2–O4	2.341(5)
Ag1–O3	2.454(5)	Ag2–N2	2.354(6)
Ag1–O2	2.582(5)	Ag2 ⁱⁱ –O1	2.417(5)
N8–Ag1–N11	132.6(2)	N6–Ag2–O4	110.9(2)
N8–Ag1–O3	125.39(19)	N6–Ag2–N2	127.9(2)
N11–Ag1–O3	99.87(19)	O4–Ag2–N2	97.76(18)
N8–Ag1–O2	102.57(19)	N6–Ag2–O1 ⁱ	98.67(19)
N11–Ag1–O2	101.06(18)	O4–Ag2–O1 ⁱ	119.12(19)
O3–Ag1–O2	76.23(17)	N2–Ag2–O1 ⁱ	104.1(2)
Complex 2			
Ag1–N5	2.261(7)	Ag2–O3 ⁱⁱ	2.591(5)
Ag1–N2	2.273(6)	Ag2 ^v –N3	2.347(6)
Ag1–O7	2.639(7)	Ag3 ^{vi} –N8	2.272(6)
Ag1–O2 ^{viii}	2.651(5)	Ag3–O4	2.308(5)
Ag1–O4 ^{viii}	2.605(4)	Ag3–N9	2.323(6)
Ag2–N6	2.241(6)	Ag3–O1 ^{iv}	2.581(4)
Ag2–O2	2.264(4)	N3 ⁱ –Ag2–O3 ⁱⁱ	100.43(18)
N5–Ag1–N2	156.1(2)	N8 ⁱⁱⁱ –Ag3–O4	121.3(2)
N6–Ag2–O2	138.86(19)	N8 ⁱⁱⁱ –Ag3–N9	124.2(2)
N6–Ag2–N3 ⁱ	111.2(2)	O4–Ag3–N9	109.18(19)
O2–Ag2–N3 ⁱ	104.26(19)	N8 ⁱⁱⁱ –Ag3–O1 ^{iv}	105.25(17)
N6–Ag2–O3 ⁱⁱ	105.38(17)	O4–Ag3–O1 ^{iv}	90.34(15)
O2–Ag2–O3 ⁱⁱ	87.61(15)	N9–Ag3–O1 ^{iv}	96.19(17)

Compound **1**: Symmetry codes: (i) $x + 1, y, z$; (ii) $x - 1, y, z$.

Compound **2**: Symmetry codes: (i) $x, y, z + 1$; (ii) $x - 1/2, -y + 1, z$; (iii) $-x + 3/2, y, z + 1/2$; (iv) $x + 1/2, -y + 1, z$; (v) $x, y, z - 1$; (vi) $-x + 3/2, y, z - 1/2$; (viii) $x - 1/2, -y + 1, z - 1$.

Table 3
The hydrogen bond geometries for **1** and **2** (Å, °).

D–H...A	D–H	H...A	D...A	D–H...A
Complex 1				
N1–H1A...N3 ⁱⁱⁱ	0.88	2.29	3.151(8)	165
N1–H1B...O4	0.88	1.96	2.836(8)	174
O1 W–H1WA...O3 ⁱⁱ	0.85	1.82	2.649(7)	166
O1W–H1WB...O2	0.85	1.92	2.765(7)	172
N4–H4A...N12 ^{iv}	0.88	2.16	3.041(8)	178
N4–H4B...O1 ⁱ	0.88	2.01	2.827(8)	154
N7–H7A...N9 ^v	0.88	2.15	3.024(8)	171
N7–H7B...O1W ⁱ	0.88	1.96	2.801(7)	159
N10–H10A...O2	0.88	2.11	2.899(8)	150
N10–H10B...N5 ^{vi}	0.88	2.17	3.023(8)	162
Complex 2				
N1–H1A...O3 ^{vii}	0.86	2.09	2.935(8)	167
N1–H1B...O4 ^{viii}	0.86	1.98	2.831(8)	171
N4–H4B...O2 ^{viii}	0.86	1.97	2.813(7)	166
N4–H4C...O1	0.86	2.20	3.037(7)	166
N7–H7B...O1 ^{iv}	0.86	2.01	2.867(7)	174
N7–H7C...O3 ^{vi}	0.86	2.10	2.916(7)	159

Complex **1**: Symmetry codes: (i) $x + 1, y, z$; (ii) $x - 1, y, z$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $x + 1, y + 1, z$; (v) $-x + 1, -y + 2, -z$; (vi) $x - 1, y - 1, z$.

Complex **2**: Symmetry codes: (iv) $x + 1/2, -y + 1, z$; (vi) $-x + 3/2, y, z - 1/2$; (vii) $x - 1/2, -y + 1, z - 1$; (viii) $-x + 1/2, y, z - 1/2$.

4. Results and discussion

4.1. Syntheses and IR

The syntheses of complexes **1** and **2** are carried out in the darkness to avoid photodecomposition and summarized in Scheme S1. The formation of the products is not significantly affected by changes of the reaction mole ratio of organic ligands to metal ions and the resultant crystals are insoluble in water and common organic solvents. The infrared spectra and elemental analyses of **1** and **2** are fully consistent with their formations. Their IR spectra exhibit the absorptions in the range of ~ 3400 – 3296 cm^{-1} , corre-

sponding to the N–H stretching vibrations of the amino group. Strong characteristic bands of carboxylic groups are observed in the range of ~ 1630 – 1560 cm^{-1} for the asymmetric vibrations and ~ 1480 – 1350 cm^{-1} for symmetric vibrations, respectively. The absence of the characteristic bands at around $\sim 1700\text{ cm}^{-1}$ attributed to the carboxylic groups, indicating that the complete deprotonation of all carboxylate groups in **1** and **2** upon reaction with Ag(I) ions [51].

4.2. Crystal structures

4.2.1. Crystal structure of $[Ag_2(dmapym)_4(mal)\cdot H_2O]_n$ (**1**)

Complex **1** crystallizes in the triclinic space group $P\bar{1}$. It is a 1D CP with H-shaped chain structure. The asymmetric unit of **1** consists of two Ag(I) ions, four dmapym ligands, one mal anion and one lattice water molecule. Each Ag(I) ion in **1** is coordinated by two nitrogen atoms from two different dmapym ligands and two oxygen atoms from mal anions to form a distorted tetrahedral coordination geometry [average Ag–N = 2.30 and Ag–O = 2.45 Å] as shown in Fig. 1a. The distortion of the tetrahedron can be indicated by the calculated value of the τ_4 parameter introduced by Houser [52] to describe the geometry of a four-coordinate metal system, which are 0.72 for Ag1 and 0.80 for Ag2, respectively (for perfect tetrahedral geometry, $\tau_4 = 1$). The mal anions adopt μ_3 -mode to link Ag(I) ions to form 1D chains (Fig. 1b) in which the dmapym ligands adopt monodentate coordination mode to occupy the residual coordination sites. Due to the steric effect of substituent groups, dmapym ligands do not extend the 1D structure to the higher dimensions. In **1**, the mal simultaneously chelates one Ag(I) ion to form an envelope-like six-membered ring with RPA (Ring Puckering Analysis) parameters being $\theta = 94.9(5)^\circ$, $\phi = 342.0(6)^\circ$ and bridges two Ag(I) ions with a bidentate mode [53]. The closest

Ag...Ag distance in **1** is 5.88 Å indicating no evidence of stabilizing Ag(I)...Ag(I) interactions.

In addition, the lattice water molecule as donor interacts with oxygen atoms of mal to form a puckering eight-membered ring with O1W...O_{mal} distances of 2.765(7) and 2.649(7) Å. Meanwhile, lattice water molecule as acceptor interacts with nitrogen atoms of dmapym to form intra-chain hydrogen bonds (Fig. 1b). The inter-chain C_{methyl}–H... π _{dmapym} interactions [C6–H6C...Cg1^{vii}: $d_{H...Cg} = 2.94\text{ Å}$, $d_{C...Cg} = 3.597(9)\text{ Å}$ and $\theta = 125^\circ$; C12–H12B...Cg1^{viii}: $d_{H...Cg} = 2.84\text{ Å}$, $d_{C...Cg} = 3.736(10)\text{ Å}$ and $\theta = 152^\circ$; C17–H17B...Cg2^{ix}: $d_{H...Cg} = 2.85\text{ Å}$, $d_{C...Cg} = 3.537(8)\text{ Å}$ and $\theta = 128^\circ$; Cg1 and Cg2 are centroids of ring N2/C1/N3/C4/C3/C2 and N8/C13/N9/C16/C15/C14; θ is the angle of C...H...Cg, Fig. S2] and inter-chain self-complementary N–H...N hydrogen bonds of two pyrimidine moieties (Fig. 2) act as a “glue” to reinforce the resulting 3D supra-molecular framework (Fig. S1). (Symmetry code: (vii) $2 - x, 1 - y, 1 - z$; (viii) $-x + 1, -y + 2, 1 - z$; (ix) $-x, -y + 2, -z$.)

4.2.2. Crystal structure of $[Ag_3(apym)_3(mal)NO_3]_n$ (**2**)

X-ray single-crystal analysis reveals that **2** crystallizes in the orthorhombic chiral space group $Pca2_1$ with the asymmetric unit containing three crystallographically unique Ag(I) ions, one deprotonated malonate ligand, three apym ligands and one coordinated nitrate anion (Fig. 3a). In complex **2**, Ag1 adopts a [AgN₂O₃] distorted square pyramidal geometry in which two nitrogen atoms from two different apym ligands, one oxygen atom from mal and one oxygen from nitrate anion build the base of pyramid and the other one oxygen atom from the same mal occupies the vertex of the pyramid. The distortion of square pyramid can be indicated by the calculated value of the τ_5 factor [54], which is 0.16 in **2** (the τ_5 value for ideal square pyramid is 0). Both Ag2 and Ag3 adopt distorted tetrahedral geometries ($\tau_4 = 0.78$ and 0.81 for Ag2 and Ag3, respectively), completed by two nitrogen atoms from two different bridging apym ligands and two oxygen atoms from two different mal anions. The largest angle around Ag2 and Ag3 are opened up to 138.86(19) and 124.2(2)°, respectively, from the ideal tetrahedral angle, while the remaining angles are in the range of 87.61(15)–111.22(2)° and 90.34(15)–124.2(2)° for Ag2 and Ag3, respectively. The Ag–O and Ag–N distances range from 2.241(6) to 2.651(5) Å and 2.261(7) to 2.347(6) Å, respectively, which are all within the normal ranges observed in O-containing and N-containing Ag(I) complexes [55–62]. In complex **2**, mal anion shows simultaneously bidentate chelating through O2 and O4 towards Ag1 to form a six-membered ring with twist-boat conformation indicated by RPA [$\theta = 86.9(7)^\circ$, $\phi = 275.8(6)^\circ$] and μ_2 -bridging coordination modes. As with **1** there is no evidence of any Ag(I)...Ag(I) interactions, the closest Ag...Ag distance is 3.56 Å between the two adjacent Ag(I) ions in **2**.

In the whole view, the apym ligands with bidentate fashion link the Ag(I) ions to form zig-zag chains which are further extended to a 2D irregular (4, 4) single sheet by mal ligands along *ac* plane (Fig. 3b). Due to the multidirectional linkage ability of mal, the adjacent 2D sheets are interlinked to form a 2D double sheet structure through mal ligands (Fig. 3c). Moreover, hydrogen-bonding exists in the adjacent apym and mal ligands (Fig. S3). The D...A (donor...acceptor) distances fall in the range of 2.813(7)–3.037(7) Å. The amino group and acceptor O atoms from mal ligands form two different hydrogen bonds motifs: $R_4^3(10)$ and $R_4^3(12)$ [63], which involve the N4, N7, O1, O2, O3 and N1, N7, O1, O3, O4 atoms, respectively.

4.3. Photoluminescence properties

The solid-state photoluminescence data for free ligands and complexes **1** and **2** at room temperature are shown in Fig. 4, respectively. Complexes **1** and **2** exhibit photoluminescence with

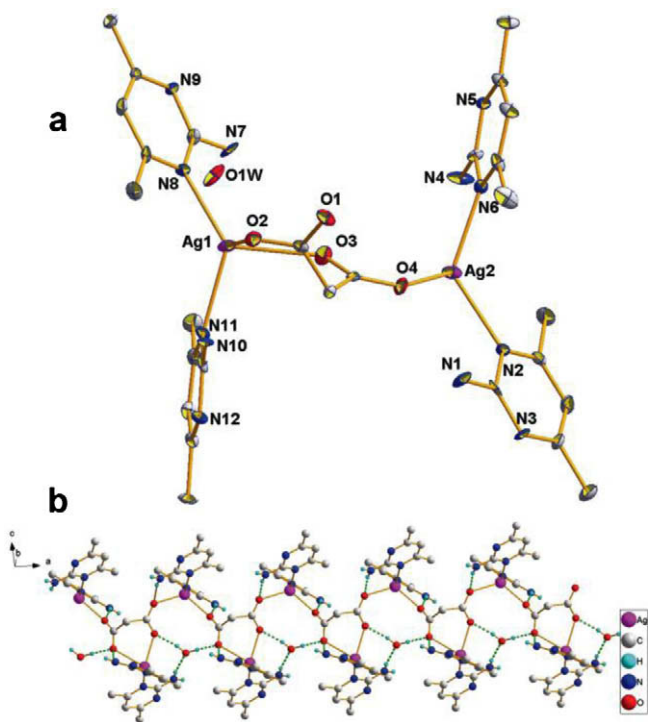


Fig. 1. (a) The coordination environments of the Ag(I) ions and the linkage modes of ligands in **1** with 30% thermal ellipsoid probability hydrogen atoms are omitted for clarity. (b) The 1D H-shaped chain incorporating intra-chain hydrogen bonds (green dashed lines). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

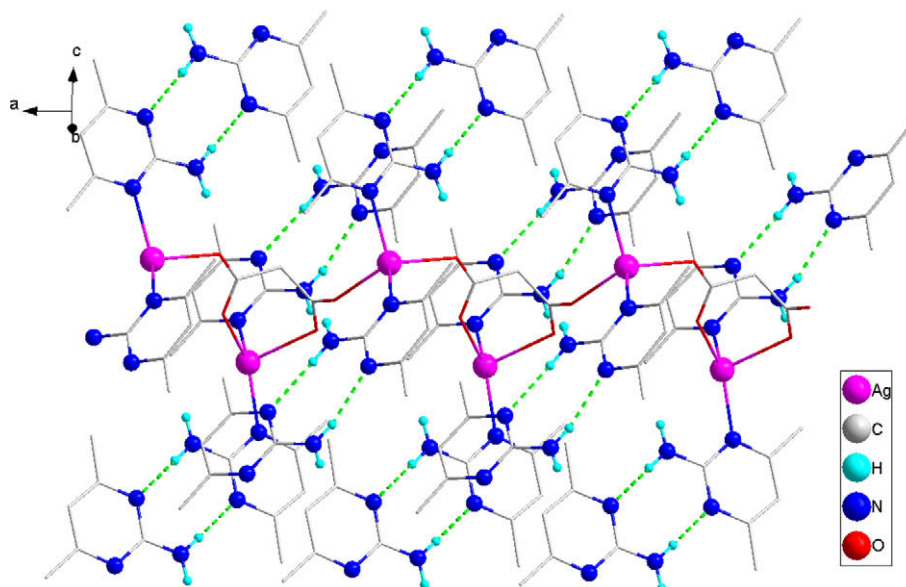


Fig. 2. Inter-chain self-complementary N–H...N hydrogen bonds highlighted with green dashed lines, water molecules are omitted for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

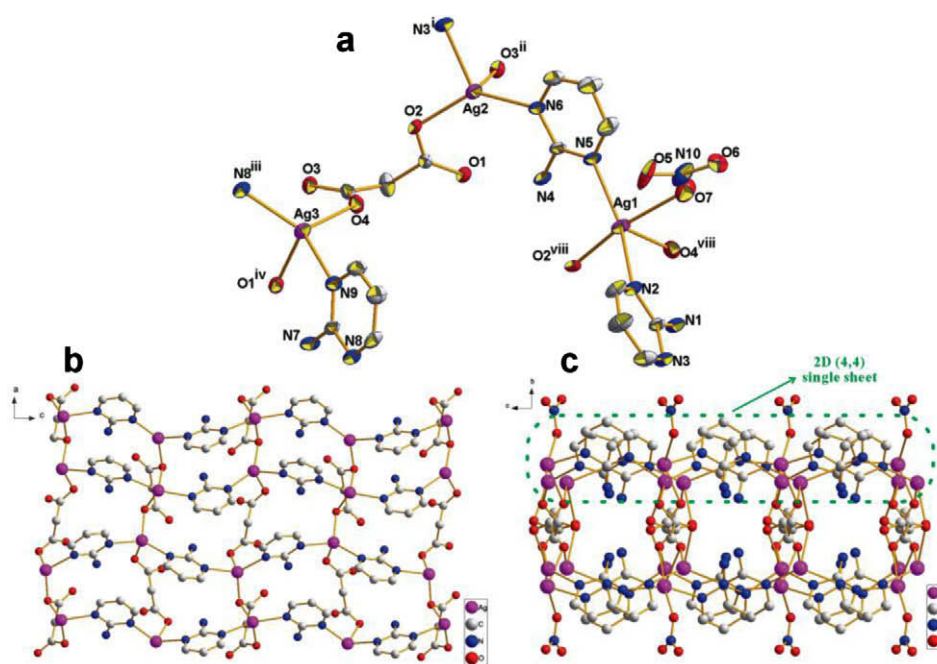


Fig. 3. (a) The coordination environments of the Ag(I) ions and the linkage modes of ligands in **2** with 30% thermal ellipsoid probability. Hydrogen atoms are omitted for clarity. (b) The 2D (4, 4) net incorporating 1D zig-zag chains in **2**. (c) The 2D double sheet structure (symmetry codes: (i) $x, y, z + 1$; (ii) $x - 1/2, -y + 1, z$; (iii) $-x + 3/2, y, z + 1/2$; (iv) $x + 1/2, -y + 1, z$; (viii) $x - 1/2, -y + 1, z - 1$).

emission maxima at 353 and 367 nm, respectively, upon excitation at 320 nm at room temperature. To understand the nature of the emission bands, we analyzed the photoluminescence properties of the corresponding free ligands and found that free apym and dmapym ligands do not emit any photoluminescence in the range 400–800 nm. The fluorescent emissions of **1** and **2** are similar to that of N-donor ligands and should be assigned to intraligand transition of coordinated N-donor ligands. The shifted emissions and enhancement of luminescence of **1** and **2** were attributed to ligand coordination to the metal center, which effectively increases the rigidity of the ligand and reduces the loss of energy by radiationless decay. Those complexes may be excellent candidates for

photoactive materials and for thermally stable and solvent-resistant blue fluorescent material.

5. Conclusions

In our study, we assembled various 2-aminopyrimidyl derivations and versatile malonate with AgNO_3 under the ammoniacal condition and successfully obtain two new silver(I) CPs with interesting structures spanning from 1D to 2D motifs. The investigation of the crystallographic data of **1** and **2** evidently shows that the overall architecture of the crystals is mainly controlled by the nat-

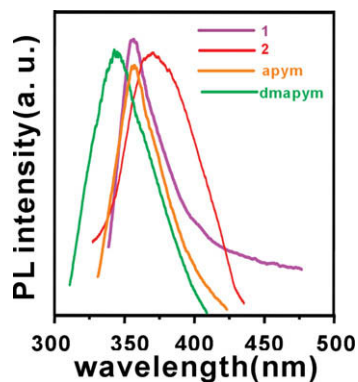


Fig. 4. Emission spectra of the ligands and complexes **1** and **2**.

ure of the different substituted 2-aminopyrimidine ligands, *i.e.* steric and electronic effect of ligands, and the different coordination modes of malonate ligand.

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Appendix A. Supplementary data

CCDC 747011 and 747009 contain the supplementary crystallographic data for **1** and **2**, respectively, in this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB 21EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2010.02.062.

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