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## Assembly of silver(I) coordination polymers incorporating pyromellitic acid and N-heterocyclic ligands

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### ABSTRACT

Five mixed ligands coordination polymers  $[Ag_4(apym)_2(pma)\cdot(H_2O)_2]_n$  (**1**),  $\{[Ag_4(dmapym)_4(pma)\cdot(H_2O)_2]\cdot(H_2O)_6\}_n$  (**2**),  $[Ag_2(apyz)_2(H_2pma)\cdot(H_2O)_4]_n$  (**3**),  $\{[Ag_4(apyz)_2(pma)\cdot(H_2O)_2]\cdot(H_2O)_2\}_n$  (**4**) and  $[Ag_4(NH_3)_8(pma)\cdot(H_2O)_6]_n$  (**5**) (*apym* = 2-aminopyrimidine, *dmapym* = 4, 6-dimethyl-2-aminopyrimidine, *apyz* = 2-aminopyrazine, *H<sub>4</sub>pma* = pyromellitic acid) were synthesized and characterized. For **1** and **2**, as the substituents change from H to methyl, the dimensions of **1–2** decrease from three-dimension (3D) to one-dimension (1D) due to the steric effect of methyl groups. For **3** and **4**, as the ratios of  $Ag_2O/apyz/pma$  vary from 1:1:1 to 2:1:1, the structure of **3** is a 1D ladder structure built from  $Ag-apyz$  double chains and *pma* anions, while the structure of **4** is a two-dimension (2D) grid. As excess ammonia is added to above four reaction systems, the structure of **5** contains unprecedented  $\{[Ag(NH_3)_2]^+\}_n$  chains and *pma* anions. The substituent on the pyrimidyl ring, ratios of reactants, solvent systems and ligand isomers intensively influence the coordination environments of metal ion and the coordination modes of the carboxyl group, and thus determine the structures of the coordination polymers. The photoluminescent properties of **1–5** were also investigated.

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### 1. Introduction

The crystal engineering of coordination polymers (CPs) has drawn great interest within inorganic chemistry in recent years which is mainly due to their intriguing structural diversities and potential applications in the area of catalysis, ion exchange, intercalation chemistry, photochemistry and porous materials [1–6]. In particular, the chemistry of the silver(I) ion is extremely striking, because its coordination numbers can range from 2 to 6 and it usually exhibits closed-shell  $Ag \cdots Ag$  interactions [7–11]. These characteristics make it an appealing candidate for the production of interesting structural motifs [12–14] which are also widely influenced by several other factors such as the counter-anions, solvent systems, the metal-to-ligand ratio and the nature of the ligands [15–17]. However, the systematic studies, such as influences of the substituents, solvents and reactants ratios on the structures of CPs, are limited. The amino-containing heterocyclic ligands contain three potential binding sites with the capability of bridging at most three metal ions, while the amino group can interact with guest molecules or counter-anions through hydrogen bonds. As an ongoing research on the influence of carboxylates on the assembly of Ag-N-heterocyclic ligand CPs [18–21], we selected 2-aminopyrimidine, 4,6-methyl substituted 2-aminopyrimidine and

2-aminopyrazine as major ligands and pyromellitic acid as auxiliary ligand to react with  $Ag_2O$  and obtained five CPs:  $[Ag_4(apym)_2(pma)\cdot(H_2O)_2]_n$  (**1**),  $\{[Ag_4(dmapym)_4(pma)\cdot(H_2O)_2]\cdot(H_2O)_6\}_n$  (**2**),  $[Ag_2(apyz)_2(H_2pma)\cdot(H_2O)_4]_n$  (**3**),  $\{[Ag_4(apyz)_2(pma)\cdot(H_2O)_2]\cdot(H_2O)_2\}_n$  (**4**) and  $[Ag_4(NH_3)_8(pma)\cdot(H_2O)_6]_n$  (**5**) (Scheme 1).

### 2. Experimental

#### 2.1. Chemicals and methods

All reagents and solvents were obtained commercially and used without further purification. IR spectra were measured on a Nicolet 740 FTIR spectrometer at the range of 4000–400  $cm^{-1}$ . Elemental analyses (C, H, N contents) were carried out on a CE instruments EA 1110 elemental analyzer. Photoluminescent properties were measured on a Hitachi F-4500 fluorescence spectrophotometer with solid powder on a 1 cm quartz round plate.

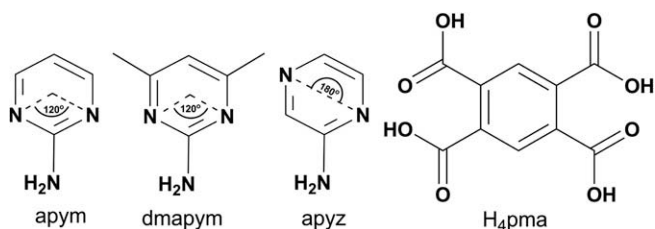
#### 2.2. Syntheses of complexes 1–5

##### 2.2.1. $[Ag_4(apym)_2(pma)\cdot(H_2O)_2]_n$ (**1**)

A mixture of  $Ag_2O$  (116 mg, 0.5 mmol), *apym* (48 mg, 0.5 mmol) and *H<sub>4</sub>pma* (127 mg, 0.5 mmol) was added to  $C_2H_5OH-H_2O$  mixed solvent (6 ml, v/v: 1/2) in conical flask under ultrasonic treatment (160 W, 40 KHz) for 30 min at room temperature. Then aqueous  $NH_3$  solution (0.5 ml, 25%) was dropped into the mixture to give

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Scheme 1. Schematic representation of the ligands.

a clear colourless solution. The resultant solution was allowed slowly to evaporate in darkness at room temperature for several weeks to give colourless block crystals of **1**. The crystals were washed by deionized water and dried in air. Yield: Ca. 45% based on Ag. Elemental analysis: *Anal. Calc.* for  $\text{Ag}_4\text{C}_{18}\text{H}_{16}\text{N}_6\text{O}_{10}$ : C, 23.81; H, 1.78; N, 9.26. Found: C, 23.86; H, 1.72; N, 9.30%. Selected IR peaks (KBr,  $\text{cm}^{-1}$ ): 3411(s), 3306(s), 1630(m), 1481(m), 1421(m), 1376(s), 1146(m), 870(w), 520(w).

#### 2.2.2. $\{[\text{Ag}_4(\text{dmapym})_4(\text{pma})\cdot(\text{H}_2\text{O})_2]\cdot(\text{H}_2\text{O})_6\}_n$ (**2**)

The synthesis of **2** was similar to that of **1**, but with dmapym (66 mg, 0.5 mmol) in place of apym. Colorless crystals of **2** were washed by deionized water and dried in air. Yield: Ca. 58% based on Ag. Elemental analysis: *Anal. Calc.* for  $\text{Ag}_4\text{C}_{34}\text{H}_{54}\text{N}_{12}\text{O}_{16}$ : C, 30.98; H, 4.13; N, 12.75. Found: C, 31.02; H, 4.04; N, 12.81%. Selected IR peaks (KBr,  $\text{cm}^{-1}$ ): 3430(s), 2972(w), 2925(w), 1631(s), 1600(s), 1576(s), 1466(m), 1387(w), 1056(m).

#### 2.2.3. $[\text{Ag}_2(\text{apyz})_2(\text{H}_2\text{pma})\cdot(\text{H}_2\text{O})_4]_n$ (**3**)

The synthesis of **3** was similar to that of **1**, but with apyz (48 mg, 0.5 mmol) in place of apym. Yellow crystals of **3** were washed by deionized water and dried in air. Yield: Ca. 62% based on Ag. Elemental analysis: *Anal. Calc.* for  $\text{Ag}_2\text{C}_{18}\text{H}_{22}\text{N}_6\text{O}_{12}$ : C, 29.61; H, 3.04; N, 11.51. Found: C, 29.58; H, 2.98; N, 11.59%. Selected IR peaks (KBr,  $\text{cm}^{-1}$ ): 3438(s), 1561(vs), 1490(s), 1426(s), 1371(s), 1142(m), 819(m).

#### 2.2.4. $\{[\text{Ag}_4(\text{apyz})_2(\text{pma})\cdot(\text{H}_2\text{O})_2]\cdot(\text{H}_2\text{O})_2\}_n$ (**4**)

The synthesis of **4** was similar to that of **3**, but with  $\text{Ag}_2\text{O}$  (232 mg, 1 mmol), apyz (48 mg, 0.5 mmol) and  $\text{H}_4\text{pma}$  (127 mg, 0.5 mmol). Yellow crystals of **4** were washed by deionized water and dried in air. Yield: Ca. 71% based on Ag. Elemental analysis: *Anal. Calc.* for  $\text{Ag}_4\text{C}_{18}\text{H}_{20}\text{N}_6\text{O}_{12}$ : C, 22.91; H, 2.14; N, 8.90. Found: C, 22.87; H, 2.20; N, 8.82%. Selected IR peaks (KBr,  $\text{cm}^{-1}$ ): 3420(s), 3309(s), 1645(m), 1480(m), 1420(m), 1374(s), 1130(m), 865(w), 512(w).

#### 2.2.5. $[\text{Ag}_4(\text{NH}_3)_8(\text{pma})\cdot(\text{H}_2\text{O})_6]_n$ (**5**)

The synthesis of **5** was similar to that of **1–3**, but with  $\text{C}_2\text{H}_5\text{OH–NH}_3$  (25%) mixed solvent (6 ml, v/v: 2/1). The formation of **5** is not affected by changes of the N-heterocyclic ligands. Colorless crystals of **5** were washed by deionized water and dried in air. Yield: Ca. 53% based on Ag. Elemental analysis: *Anal. Calc.* for  $\text{Ag}_4\text{C}_{10}\text{H}_{37}\text{N}_8\text{O}_{13}$ : C, 13.21; H, 4.10; N, 12.33. Found: C, 13.25; H, 4.06; N, 12.38%. Selected IR peaks (KBr,  $\text{cm}^{-1}$ ): 3420(s), 1627(s), 1565(vs), 1443(s), 1372(vs), 1210(m), 1106(w), 774(w), 734(m), 520(w).

### 2.3. X-ray crystallography

Data collection for **1–5** were performed on an Oxford, Gemini S Ultra CCD diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ), Absorption correction and data reduction were carried out by using the program CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.32.5. The structures were solved by di-

rect methods, and non-hydrogen atoms were refined anisotropically by least-squares on  $F^2$  using the SHELXS [22] and SHELXL program [23]. For all complexes, all H atoms were refined using a riding model, with C–H = 0.93 (aromatic) or 0.96  $\text{Å}$  ( $\text{CH}_3$ ), and the N–H = 0.86 ( $\text{NH}_2$ ) or 0.91  $\text{Å}$  ( $\text{NH}_3$ ). The positions of the water H atoms were refined with the O–H distances restrained to 0.85  $\text{Å}$ . The H atoms of all complexes were refined with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{O}, \text{C} \text{ or } \text{N})$ . The crystallographic details of **1–5** are summarized in Table 1. Selected bond lengths and angles of **1–5** are listed in Table 2 and selected hydrogen-bonding parameters of **1–5** are shown in Table S1.

## 3. Result and discussion

### 3.1. Structure descriptions

#### 3.1.1. Crystal structure of $[\text{Ag}_4(\text{apym})_2(\text{pma})\cdot(\text{H}_2\text{O})_2]_n$ (**1**)

Single-crystal X-ray diffraction analysis reveals that **1** possesses 3D framework and there are four Ag(I) ions, two apym ligands, one  $\text{pma}^{4-}$  and two solvent  $\text{H}_2\text{O}$  molecules in an asymmetric unit (Fig. 1a). The  $\text{pma}^{4-}$  lies on an inversion center. Ag1 and Ag2 are in the tetrahedral coordination environments, connected by three O atoms from three different pma anions and one N atom from apym. The bond angles around Ag1 and Ag2 open up to 158.8(1) and 136.9(1) $^\circ$ , respectively. The distortion of the tetrahedron can be indicated by the calculated value of the  $\tau_4$  parameter introduced by Houser and co-workers [24] to describe the geometry of a four-coordinate metal system., which is 0.69 and 0.76 for Ag1 and Ag2 respectively (for perfect tetrahedral geometry,  $\tau_4 = 1$ ). Ag3 and Ag4 are in the T-shaped and linear coordination geometries, respectively. Both Ag–O and Ag–N bonds distances are in the normal ranges [25]. The Ag1, Ag2 and Ag3 arrange in a trigonal geometry to form a Ag-based secondary building unit (SBU). The Ag $\cdots$ Ag distances in the SBU range from 2.890(1) to 3.342(1)  $\text{Å}$  which are shorter than twice the van der Waals radii of Ag(I) (3.44  $\text{Å}$ ) [26] and indicate ligand-supported Ag $\cdots$ Ag interactions [27]. The SBUs are linked by  $\mu_8-(\kappa^1\text{O}1, \kappa^1\text{O}2, \kappa^2\text{O}3, \kappa^1\text{O}1^v, \kappa^1\text{O}2^v, \kappa^2\text{O}3^v)-$  and  $\mu_{10}-(\kappa^1\text{O}5, \kappa^2\text{O}6, \kappa^1\text{O}7, \kappa^1\text{O}8, \kappa^1\text{O}5^vi, \kappa^2\text{O}6^vi, \kappa^1\text{O}7^vi, \kappa^1\text{O}8^vi)-\text{pma}^{4-}$  [28–31] to form a 2D sheet (Fig. 1b) which is further extended by  $\mu_2$ -apym to form a 3D framework (Fig. 1c).

In addition to the coordination bond, hydrogen bonds and  $\pi\cdots\pi$  interactions also coexist in **1**. The D–A (donor–acceptor) distances fall in the range of 2.713(5)–3.048(5)  $\text{Å}$  (Table S1). The amino group (N1 and N4), water (O1 W and O2 W) and acceptor O atoms (O4 and O2) of carboxylic group form two kinds of hydrogen bonding motifs:  $R_2^2(10)$  and  $R_3^3(12)$  [32]. The two motifs share the same acceptor O atom (O4). The  $R_4^3(10)$  hydrogen bonds motif is also observed between  $R_2^2(10)$  and  $R_3^3(12)$  motifs in which two solvent water molecules (O1 W and O2 W) and O4 atom act as donors and acceptor, respectively. The shortest contact distance between the centroids of neighbouring pyrimidyl and phenyl rings is 3.730(3)  $\text{Å}$  which is suggestive of the weak  $\pi\cdots\pi$  interaction (Fig. S1). C–H $\cdots\pi$  interaction (C2–H2A $\cdots$ Cg1 $^{viii}$  = 3.343(5)  $\text{Å}$ ; Cg1 is the centroid of C14/C15/C16/C14 $^{vi}$ /C15 $^{vi}$ /C16 $^{vi}$  ring, Fig. S2) combines the hydrogen bonds and  $\pi\cdots\pi$  stacking interactions to consolidate the resulting structure. (symmetry codes: (v)  $-x+2, -y+1, -z+1$ ; (vi)  $1-x, -y, -z$ ; (viii)  $x, 1+y, z$ ).

#### 3.1.2. Crystal structure of $\{[\text{Ag}_4(\text{dmapym})_4(\text{pma})\cdot(\text{H}_2\text{O})_2]\cdot(\text{H}_2\text{O})_6\}_n$ (**2**)

In the structure of **2**, there are two Ag(I) ions, two dmapym ligands, one half  $\text{pma}^{4-}$ , one coordinated  $\text{H}_2\text{O}$  and three solvent  $\text{H}_2\text{O}$  molecules in an asymmetric unit (Fig. 2a). The  $\text{pma}^{4-}$  lies on an inversion center. The Ag1 adopts a Y-shaped coordination geometry, coordinated by two O atoms from two pma anions and one N atom from dmapym. Ag2 is coordinated by two O atoms

**Table 1**  
Crystal data for 1–5.

Compound	1	2	3	4	5
Formula	Ag <sub>4</sub> C <sub>18</sub> H <sub>16</sub> N <sub>6</sub> O <sub>10</sub>	Ag <sub>4</sub> C <sub>34</sub> H <sub>54</sub> N <sub>12</sub> O <sub>16</sub>	Ag <sub>2</sub> C <sub>18</sub> H <sub>22</sub> N <sub>6</sub> O <sub>12</sub>	Ag <sub>4</sub> C <sub>18</sub> H <sub>20</sub> N <sub>6</sub> O <sub>12</sub>	Ag <sub>4</sub> C <sub>10</sub> H <sub>37</sub> N <sub>8</sub> O <sub>13</sub>
Formula weight	907.83	1318.38	730.16	943.88	908.96
Crystal size (mm)	0.23 × 0.12 × 0.08	0.20 × 0.15 × 0.15	0.18 × 0.15 × 0.10	0.22 × 0.18 × 0.16	0.30 × 0.20 × 0.20
Crystal System	triclinic	triclinic	triclinic	triclinic	monoclinic
Space group	<i>P</i> 1̄	<i>P</i> 1̄	<i>P</i> 1̄	<i>P</i> 1̄	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	6.8551(14)	10.196(2)	6.729(3)	6.9807(14)	19.048(7)
<i>b</i> (Å)	10.298(2)	10.627(2)	7.1850(17)	9.1849(18)	7.178(3)
<i>c</i> (Å)	16.242(3)	13.624(3)	12.871(8)	11.711(2)	18.409(7)
$\alpha$ (°)	89.25(3)	71.10(3)	95.01(3)	98.31(3)	90
$\beta$ (°)	78.22(3)	84.47(3)	94.88(5)	99.86(3)	96.351(9)
$\gamma$ (°)	80.89(3)	61.52(3)	103.12(3)	101.91(3)	90
<i>V</i> (Å <sup>3</sup> )	1108.1(4)	1224.6(4)	600.2(5)	711.2(2)	2501.5(16)
<i>T</i> (K)	298(2) K	298(2)	298(2)	298(2)	173(2)
<i>Z</i> , <i>D</i> <sub>calcd</sub> (g/cm <sup>3</sup> )	2, 2.721	2, 1.788	2, 2.020	2, 2.204	4, 2.414
<i>F</i> (0 0 0)	868	658	362	454	1780
$\mu$ (mm <sup>-1</sup> )	3.556	1.651	1.708	2.780	3.159
Reflection collected/unique	9467/4342	9802/4638	4787/2500	5341/2488	5844/2400
<i>R</i> <sub>int</sub>	0.0325	0.0766	0.1609	0.0457	0.0414
Parameters	343	302	172	183	163
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0339, <i>wR</i> <sub>2</sub> = 0.0823	<i>R</i> <sub>1</sub> = 0.0472, <i>wR</i> <sub>2</sub> = 0.1044	<i>R</i> <sub>1</sub> = 0.0869, <i>wR</i> <sub>2</sub> = 0.2248	<i>R</i> <sub>1</sub> = 0.0897, <i>wR</i> <sub>2</sub> = 0.2307	<i>R</i> <sub>1</sub> = 0.0552, <i>wR</i> <sub>2</sub> = 0.1536
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0387, <i>wR</i> <sub>2</sub> = 0.0853	<i>R</i> <sub>1</sub> = 0.0672, <i>wR</i> <sub>2</sub> = 0.1196	<i>R</i> <sub>1</sub> = 0.1519, <i>wR</i> <sub>2</sub> = 0.3249	<i>R</i> <sub>1</sub> = 0.1006, <i>wR</i> <sub>2</sub> = 0.2369	<i>R</i> <sub>1</sub> = 0.0649, <i>wR</i> <sub>2</sub> = 0.1610
Goodness-of-fit (GOF) on <i>F</i> <sup>2</sup>	1.035	0.989	1.084	1.127	1.155
Maximum/minimum $\Delta\rho$ (e Å <sup>-3</sup> )	2.838/−1.568	0.849/−0.764	3.173/−1.760	2.469/−1.443	1.189/−1.101
Completeness (%)	99.8	96.4	95.4	99.4	97.4

$$R_1 = \sum \|F_o\| - F_c / \sum \|F_o\|, wR_2 = [\sum w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^{1/2}.$$

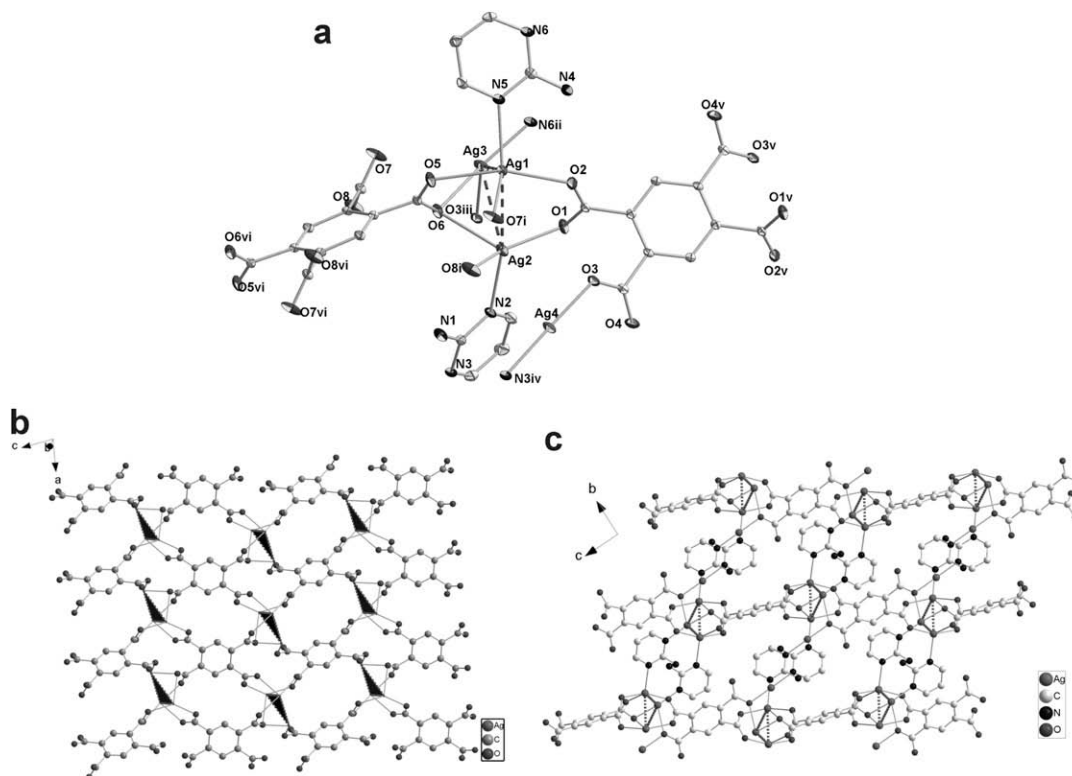
**Table 2**  
Selected bond lengths (Å) and angles (°) for compound 1–5.

<b>Complex 1</b>					
Ag1–O2	2.316(3)	Ag2–N2	2.348(4)	Ag4–N3 <sup>iv</sup>	2.164(4)
Ag1–N5	2.328(4)	Ag2–O6	2.652(4)	Ag3–O6	2.193(3)
Ag1–O5	2.373(3)	Ag2–Ag3	3.342(1)	Ag3–O3 <sup>iii</sup>	2.633(4)
Ag1–O7 <sup>i</sup>	2.454(3)			Ag4–O3	2.140(3)
Ag1–Ag2	2.890(1)	Ag3–N6 <sup>ii</sup>	2.162(4)	Ag2–O1	2.236(3)
Ag1–Ag3	3.103(1)	Ag2–O8 <sup>i</sup>	2.292(4)		
O2–Ag1–N5	103.8(1)	N6 <sup>ii</sup> –Ag3–O3 <sup>iii</sup>	113.8(1)	N2–Ag2–O6	96.6(1)
O2–Ag1–O5	158.8(1)	O6–Ag3–O3 <sup>iii</sup>	78.3(1)	O3–Ag4–N3 <sup>iv</sup>	178.4(1)
N5–Ag1–O5	95.3(1)	N6 <sup>ii</sup> –Ag3–O6	163.9(1)	N5–Ag1–O7 <sup>i</sup>	122.9(1)
O2–Ag1–O7 <sup>i</sup>	93.2(2)	O5–Ag1–O7 <sup>i</sup>	83.9(1)	O8 <sup>i</sup> –Ag2–O6	95.9(1)
O1–Ag2–O8 <sup>i</sup>	136.9(1)	O1–Ag2–O6	115.9(1)		
<b>Complex 2</b>					
Ag1–N3	2.267(4)	Ag1–Ag2	3.103(1)	Ag2–N6	2.196(4)
Ag1–O3 <sup>i</sup>	2.280(3)	Ag2–O1 W	2.183(5)	Ag1–O2	2.338(4)
N3–Ag1–O3 <sup>i</sup>	136.4(2)	N3–Ag1–O2	114.7(2)	O3 <sup>i</sup> –Ag1–O2	101.6(2)
O1 W–Ag2–N6	172.5(2)				
<b>Complex 3</b>					
Ag1–N2	2.22(1)	Ag1–O1	2.50(1)	N2–Ag1–N3 <sup>i</sup>	168.1(5)
Ag1–N3 <sup>i</sup>	2.22(1)	Ag1–Ag1 <sup>ii</sup>	3.368(3)	N3 <sup>i</sup> –Ag1–O1	94.8(4)
<b>Complex 4</b>					
Ag1–N3	2.24(1)	Ag1–Ag2	3.205(2)	Ag2–N2 <sup>ii</sup>	2.15(1)
Ag1–O1	2.28(1)	Ag2–O2 W	2.10(1)	Ag1–O3 <sup>i</sup>	2.32(1)
N3–Ag1–O1	135.5(4)	O1–Ag1–O3 <sup>i</sup>	107.4(4)	O2 W–Ag2–N2 <sup>ii</sup>	174.3(6)
N3–Ag1–O3 <sup>i</sup>	115.9(4)				
<b>Complex 5</b>					
Ag1–N1	2.097(7)	Ag1–Ag1 <sup>i</sup>	3.027(1)	Ag2–N3	2.071(6)
Ag1–N2	2.110(6)	Ag1–Ag2	3.115(1)	Ag2–N4	2.080(6)
N1–Ag1–N2	174.6(3)	N3–Ag2–N4	178.7(2)		

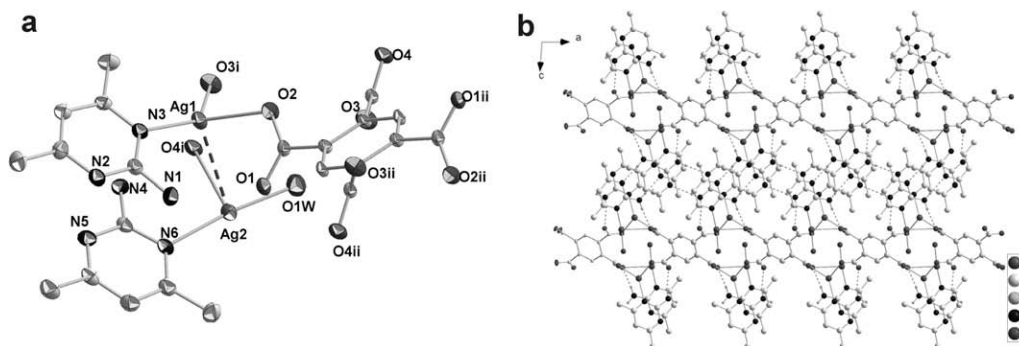
Symmetry codes for **1**: (i)  $x+1, y, z$ ; (ii)  $-x+1, -y, -z+1$ ; (iii)  $x-1, y, z$ ; (iv)  $-x+2, -y+1, -z$ ; **2**: (i)  $-x-1, -y+1, -z$ ; (ii)  $-x, -y+1, -z$ ; **3**: (i)  $x, y+1, z$ ; (ii)  $-x, -y, -z+1$ ; **4**: (i)  $2-x, -y, 1-z$ ; (ii)  $1-x, -y, -z$ ; **5**: (i)  $-x+1, y, -z+3/2$ ; (ii)  $-x+1/2, -y+3/2, -z+1$ .

from pma and solvent H<sub>2</sub>O, respectively, and one N atom from dmapym to form a T-shaped coordination geometry. The maximum angles around Ag1 and Ag2 are 136.4(2) and 172.5(2)°, respectively (Table 2). The Ag1...Ag2 distance is 3.1031(11) Å, indicating the presence of argentophilic interaction. The pma<sup>4-</sup>

adopts  $\mu_6-(\kappa^1O2, \kappa^1O3, \kappa^1O4, \kappa^1O2^{ii}, \kappa^1O3^{ii}, \kappa^1O4^{ii})$ -mode [33,34] to link Ag(1) ions to form 1D chains. The dmapym ligands, which are nearly perpendicular to the 1D chain, coordinate to Ag(1) ions with monodentate mode. The N–H...O, N–H...N and O–H...O hydrogen bonds further extend the 1D chains to form a 2D



**Fig. 1.** (a) The coordination geometries of Ag(I) in **1** with the thermal ellipsoids at 30% probability level. Solvent H<sub>2</sub>O molecules and hydrogen atoms are omitted for clarity. (b) View of the 2D sheet structure containing Ag<sub>3</sub> SBU (blue trigon) in **1**. (c) View of the 3D framework of **1**. (Symmetry codes: (i)  $x + 1, y, z$ ; (ii)  $-x + 1, -y, -z + 1$ ; (iii)  $x - 1, y, z$ ; (iv)  $-x + 2, -y + 1, -z$ ; (v)  $-x + 2, -y + 1, -z + 1$ ; (vi)  $-x + 1, -y, -z$ .)



**Fig. 2.** (a) The coordination geometries in **2** with the thermal ellipsoids at 30% probability level. Solvent H<sub>2</sub>O molecules and hydrogen atoms are omitted for clarity. (b) View of the 2D supramolecular sheet structure formed by 1D Ag-pma chains in **2**. Hydrogen bonds are indicated with dashed line. Hydrogen atoms and solvent water molecules are omitted for clarity. (Symmetry codes: (i)  $-x - 1, -y + 1, -z$ ; (ii)  $-x, -y + 1, -z$ .)

supramolecular sheet structure (Fig. 2b, Table S1). The neighbouring sheets stacked into 3D supramolecular framework through inter-sheet O<sub>water</sub>–H···O hydrogen bonds.

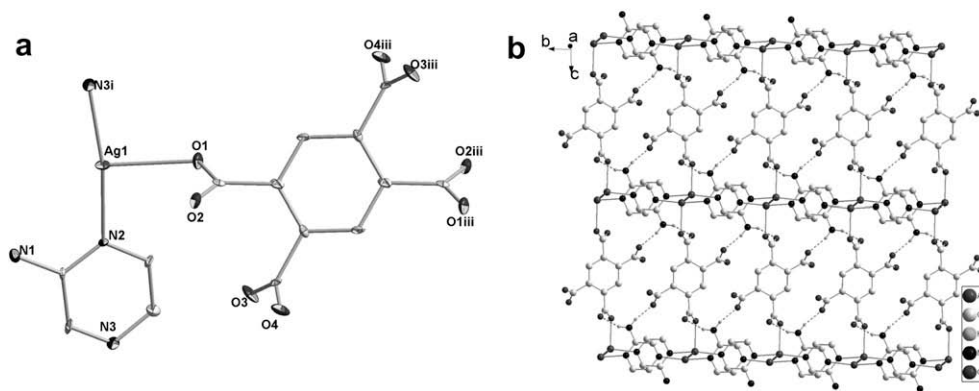
### 3.1.3. Crystal structure of [Ag<sub>2</sub>(apyz)<sub>2</sub>(H<sub>2</sub>pma)·(H<sub>2</sub>O)<sub>n</sub>] (3)

In the asymmetric unit of **3**, there are one Ag(I) ion, one apyz, one half H<sub>2</sub>pma<sup>2-</sup> and two solvent H<sub>2</sub>O molecules. The H<sub>2</sub>pma<sup>2-</sup> lies on an inversion center. The Ag(I) ion is in a T-shaped geometry, coordinated by two N atoms from two different apyz ligands and one O atom from H<sub>2</sub>pma<sup>2-</sup> (Fig. 3a). The average bond length of Ag–N is 2.22 Å (Table 2). The apyz acts as a bidentate N, N'-donor to link Ag(I) ions to form a 1D cationic chain along the *b* axis, within the polymeric chain the N–Ag–N angle is slightly bent at an angle of 168.1(5)°. The adjacent Ag-apyz chains are linked by μ<sub>2</sub>-H<sub>2</sub>pma<sup>2-</sup> to form a 1D ladder structure (Fig. 3b). The 1D ladders

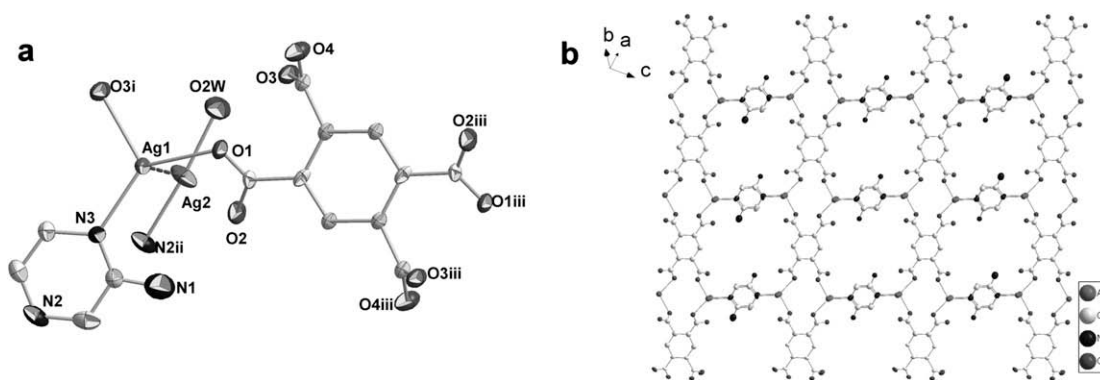
are further extended to form a 2D sheet structure by weak Ag···Ag interaction (3.368(3) Å), hydrogen bonds (Table S1) and inter-chain π···π interactions (Fig. S3) (Cg1···Cg1<sup>v</sup> = 3.60(1); Cg1···Cg1<sup>viii</sup> = 3.58(1) Å, Cg1 is the centroid of N2/C1/C2/N3/C3/C4 ring). (Symmetry codes: (v)  $-x, -y - 1, -z + 1$ ; (viii)  $1 - x, -y - 1, -z + 1$ .)

### 3.1.4. Crystal structure of {[Ag<sub>4</sub>(apyz)<sub>2</sub>(pma)·(H<sub>2</sub>O)<sub>2</sub>]·(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub> (4)

The structure of **4** is a 2D grid. There are two Ag(I) ions, one apyz, one half pma<sup>4-</sup>, one coordinated H<sub>2</sub>O molecule and one solvent H<sub>2</sub>O molecule in an asymmetric unit (Fig. 4a). The coordination environments of Ag1 and Ag2 can be described as Y-shaped and linear geometries, respectively. Y-shaped geometry is formed by two carboxyl O atoms from two different pma anions and one N atom from apyz. The sum of three angles around Ag1 is



**Fig. 3.** (a) The coordination geometry in **3** with the thermal ellipsoids at 30% probability level. Solvent H<sub>2</sub>O molecules and hydrogen atoms are omitted for clarity. (b) View of the 2D supramolecular sheet structure incorporating 1D ladder in **3**. (Symmetry code: (i)  $x, y + 1, z$ ; (iii)  $-x, -y, -z + 2$ .)



**Fig. 4.** (a) The coordination geometries in **4** with the thermal ellipsoids at 30% probability level. Solvent H<sub>2</sub>O molecules and hydrogen atoms are omitted for clarity. (b) View of the 2D grid structure in **4**. Hydrogen atoms are omitted for clarity. (Symmetry codes: (i)  $-x + 2, -y, -z + 1$ ; (ii)  $-x + 1, -y, -z$ ; (iii)  $-x + 3, -y + 1, -z + 1$ .)

358.8(4)° (Table 2). One O atom from coordinated H<sub>2</sub>O and one N atom from apyz form the linear geometry of Ag<sub>2</sub> with N–Ag–O angle being 174.3(6)°. The Ag(I) ions, apyz ligands and coordinated H<sub>2</sub>O molecule form a rectangular [Ag<sub>4</sub>(apyz)<sub>2</sub>O]<sup>4+</sup> SBU through the Ag<sub>2</sub>···Ag<sub>2</sub> interaction (3.205(2) Å) and  $\pi$ ··· $\pi$  interaction (Fig. S4) between adjacent pyrazinyl rings (Cg1···Cg1<sup>ii</sup> = 3.51(1) Å, Cg1 is the centroid of N2/C2/C1/N3/C4/C3 ring). The SBUs are further extended to form a 2D grid by  $\mu_4$ -pma<sup>4-</sup> [35] (Fig. 4b). The hydrogen bonds involving N–H···O and O–H···O contribute to the stability of the resulting 3D supramolecular framework (Table S1). (Symmetry code: (ii)  $-x + 1, -y, -z$ .)

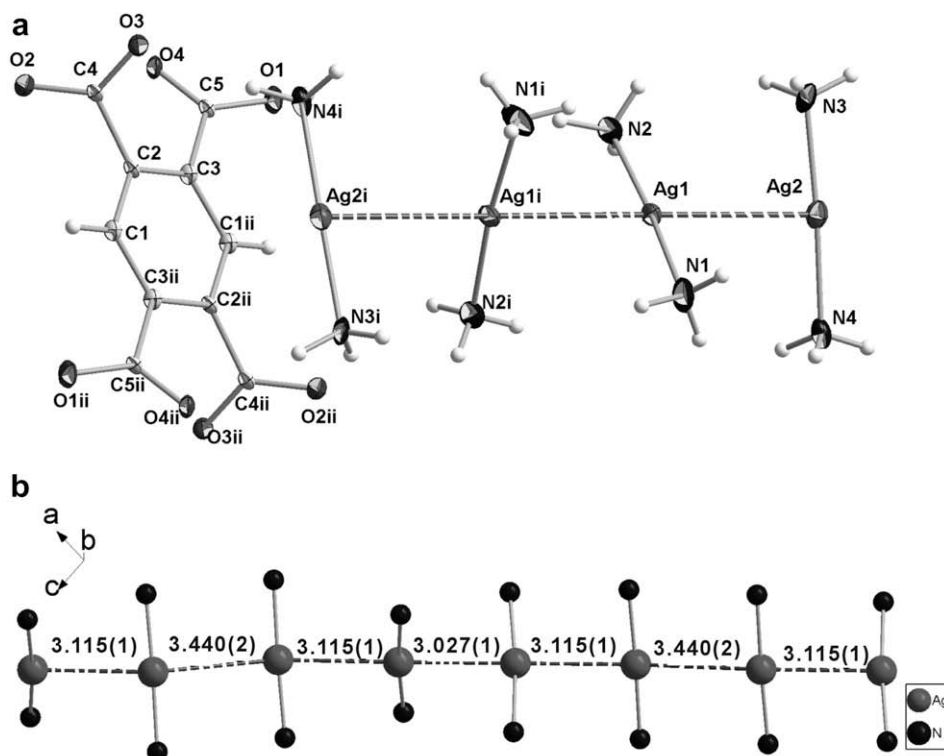
### 3.1.5. Crystal structure of [Ag<sub>4</sub>(NH<sub>3</sub>)<sub>8</sub>(pma)·(H<sub>2</sub>O)<sub>6</sub>]<sub>n</sub> (**5**)

Different from complexes **1–4**, the structure of **5** does not involve N-donor ligands and is comprised of 1D cationic {[Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>]<sub>n</sub> and anionic {[pma-H<sub>2</sub>O]<sup>4-</sup>]<sub>n</sub> supramolecular chains. The most significant structural feature is that the 1D unprecedented {[Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>]<sub>n</sub> chains are trapped in complicated supramolecular interactions. There are two Ag(I) ions, four coordinated NH<sub>3</sub> molecules, one half pma<sup>4-</sup> and three solvent H<sub>2</sub>O molecules in an asymmetric unit (Fig. 5a). All Ag(I) ions are linearly coordinated by two NH<sub>3</sub> molecules with average Ag–N length and N–Ag–N angle being 2.09 Å and 175°, respectively. Although few [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> monomers [36–38] and dimers [39] captured by hydrogen bonding in the supramolecular framework have been documented, the infinite {[Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>]<sub>n</sub> chains have not appeared until now. Within the {[Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>]<sub>n</sub> chains, there are three kinds of Ag<sub>2</sub>···Ag interactions with Ag1···Ag2, Ag1···Ag1<sup>i</sup> and Ag1···Ag2<sup>iii</sup> being 3.115(1), 3.027(1) and 3.440(2) Å, respectively. The torsion angles are 53(3) and 47(2)° for N1–Ag1···Ag2–N4 and N2–Ag1···Ag2–N3,

respectively. The cationic 1D {[Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>]<sub>n</sub> chains interact with 1D anionic {[pma-H<sub>2</sub>O]<sup>4-</sup>]<sub>n</sub> chains [40] through hydrogen bonds and weak Ag<sub>2</sub>··· $\pi$  interaction (Ag2<sup>i</sup>···Cg1 = 3.416 Å, Cg1 is the centroid of C1/C2/C3/C1<sup>ii</sup>/C2<sup>ii</sup>/C3<sup>ii</sup>/ ring). (Symmetry codes: (i)  $-x + 1, y, -z + 3/2$ ; (ii)  $-x + 1/2, -y + 3/2, -z + 1$ ; (iii)  $-x + 3/2, -y + 1/2, -z + 2$ .)

### 3.2. Multifactor effects on the structures of coordination polymers

Structural transformation and diversification are evidently observed in the reaction system of Ag<sub>2</sub>O, N-heterocyclic ligands and H<sub>2</sub>mpa. In complexes **1** and **2**, apym and dmapym show the bidentate and monodentate coordination modes, respectively, which lead to the decrease of dimensions from **1** to **2** (3D → 1D). It seems reasonable to conclude that the substituent groups on the pyrimidyl rings—the steric hindrance of methyl groups prevents dmapym from coordinating to Ag(I) ions in another direction which results the absence of extension of 1D chain to 3D framework. When we compared **3** and **4**, as the ratios of Ag<sub>2</sub>O/apyz/H<sub>4</sub>pma vary from 1:1:1 to 2:1:1, the structure of **3** is a 1D ladder structure built from Ag–apyz double chains and pma<sup>4-</sup>, while the structure of **4** is a 2D grid. Adding more Ag<sub>2</sub>O results fully deprotonation of H<sub>4</sub>pma which affords more coordination sites to Ag(I) ions and gives **4** a 2D sheet structure. For investigating the isomeric effect on the structures, we fix the metal-to-ligand ratio in the synthesis of complexes **1** and **3**, apym and apyz have the same molecular formula but different orientation of N-coordination sites. The coordination sites in apym orient with the angle of 120° in complex **1**, whereas in complex **3** the apyz is linear dipodal orientation. The differences of structures between **1** and **3** confirm that ligand

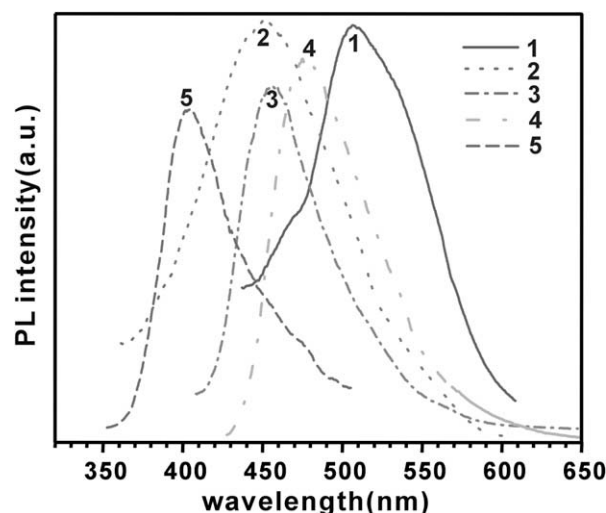


**Fig. 5.** (a) The coordination geometry in **5** with the thermal ellipsoids at 30% probability level. Solvent  $\text{H}_2\text{O}$  molecules are omitted for clarity. (b) 1D ligand-unsupported  $\{[\text{Ag}(\text{NH}_3)_2]^+\}_n$  chain incorporating different  $\text{Ag} \cdots \text{Ag}$  interactions. (Symmetry codes: (i)  $-x + 1, y, -z + 3/2$ ; (ii)  $-x + 1/2, -y + 3/2, -z + 1$ .)

isomers have a tuning effect upon the CPs assembly [41]. In final, the complex **5** was obtained in different solvent systems with that of **1–4**. Adding much more  $\text{NH}_3$  aqueous solution increases the concentration of  $[\text{Ag}(\text{NH}_3)_2]^+$  which easily aggregates to the chains through three kinds of  $\text{Ag} \cdots \text{Ag}$  interactions in the help of the stable effect of hydrogen bonds. The formation of **5** is not affected by change of the N-heterocyclic ligands, which indicates the  $\{[\text{Ag}(\text{NH}_3)_2]^+\}_n$  may be the precursor reacting with the other softer lewis bases concomitance of escape of  $\text{NH}_3$ . The above results show that substituents, ratio of reactants, ligand isomers and solvent systems have tuning effects upon the CPs assembly.

### 3.3. Photoluminescence properties

Recent interests in photoluminescent materials has mostly focus on polynuclear  $d^{10}$  metal complexes and mixed inorganic–organic hybrid Ag(I) coordination polymers [42–45] and the direct metal–metal interactions may be one of important factors contributing to the photoluminescent properties of  $d^{10}$  metal coordination compounds [46]. However, owing to the intense spin-orbital coupling of Ag(I), most of photoluminescent Ag(I) complexes exhibit weak photoluminescence at low temperature [47] and limited Ag(I) complexes exhibit photoluminescence at room temperature [48–52]. The photoluminescent properties of the free ligands apym, dmapym, apyz,  $\text{H}_4\text{pma}$  and **1–5** have been investigated in the solid state at room temperature (Fig. 6, Table 3). The free ligands apym, dmapym, apyz and  $\text{H}_4\text{pma}$  display photoluminescence with emission maxima at 359, 341, 394 and 337 nm, respectively, under 330 nm excitation. Intense emissions are observed at 505 nm for **1**, 451 nm for **2**, 457 nm for **3**, 478 nm for **4** and 404 nm for **5**, respectively. The photoluminescence of **1** and **2** at 505 and 451 nm should be assigned to be an admixture of ligand-to-metal-charge-transfer (LMCT) and metal-centered (d-s) transitions of the type  $4d^{10} \rightarrow 4d^9 5s^1$  and  $4d^{10} \rightarrow 4d^9 5p^1$  on the



**Fig. 6.** Photoluminescence of **1–5**.

**Table 3**  
Wavelengths  $\lambda$  (nm) of the emission maxima and excitation.

Complex	1	2	3	4	5
$\lambda_{\text{em}}$	505	451	457	478	404
$\lambda_{\text{ex}}$	320	310	380	330	320
Ligand	apym	dmapym	apyz	$\text{H}_4\text{pma}$	
$\lambda_{\text{em}}$	359	341	394	337	
$\lambda_{\text{ex}}$	330	330	330	330	

Ag(I) centres. For **3** and **4**, the photoluminescent emissions can be tentatively assigned to LMCT [53,54]. The emission peak of **5** is probably due to the  $\pi-\pi^*$  transitions of pma ligand.

## 4. Conclusions

In this work, we systematically synthesized and characterized five new Ag(I) coordination polymers based on three N-heterocyclic ligands apym, dmapym and apyz in combination with rigid tetracarboxylate ligand. The structural diversities of complexes **1–5** depending on the substituents, metal-to-ligand ratio, isomeric effects and solvents were discussed. Moreover, the photoluminescence properties of compounds **1–5** have been examined.

## Acknowledgements

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## Appendix A. Supplementary data

CCDC 745931, 745932, 745933, 745934 and 745935 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](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](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.poly.2010.02.032](https://doi.org/10.1016/j.poly.2010.02.032).

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