Mixed Linker Strategy for the Construction of a Fluorescent 2D Network Based on [Ag$_2$(COO)$_2$] as Secondary Building Unit

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The ultrasound-assisted reaction of AgNO$_3$, 2-amino-4,6-dimethylpyrimidine (dmapym) and 2,6-naphthalenedicarboxylic acid (H$_2$npd) gave rise to a new 2D network of the formula [Ag$_2$(dmapym)$_2$(npd)]$_n$ (**1**). The atoms Ag1 and Ag2 in the complex show seesaw and distorted tetrahedral coordination geometries, respectively. The dmapym ligand acts as a bidentate bridge to bind paired Ag(I) ions into a chain. The chains are further connected by npd linkers to form the resultant 2D network reinforced by N–H···O hydrogen bonds between dmapym and npd. Weak C–H···π interactions are also found in the crystal structure. Complex **1** exhibits photoluminescence in the solid state at room temperature with an emission maximum at 418 nm upon excitation at 330 nm.

Key words: Silver(I), 2-Amino-4,6-dimethylpyrimidine, 2,6-Naphthalenedicarboxylic Acid, Photoluminescence

Introduction

The directed assembly of small molecular building blocks into discrete supramolecules or extended networks is an ongoing challenge in the field of crystal engineering [1 – 3]. The synthesis of coordination polymers involving metal-ligand interactions has received much attention recently, and this field continues to expand [4 – 9]. Employing coordinative bonds coupled with other interactions such as hydrogen bonds, π···π stacking, C–H···π, lone-pair···π, anion···π and cation···π interactions is of current interest [10 – 13]. Despite the remarkable achievements to design and obtain crystalline products, there is still unpredictability of the assembly process [14 – 17].

The Ag(I) ion with its d^{10} closed-shell electron configuration shows diverse coordination geometries including linear, trigonal-planar, tetrahedral, trigonal-bipyramidal, and octahedral geometry [18, 19]. Aminopyrimidine and its derivatives are neutral ligands widely used as connectors in the construction of metal-containing compounds. Their metal binding patterns include the ring nitrogen atoms and the exocyclic amino groups in either a chelating or bridging fashion [20 – 22]. The amino group also has the ability to form very stable hydrogen-bonded arrays [23, 24].

Carboxylic ligands are widely used as spacers to diversify chemical structures, owing to their variable coordination modes [25, 26].

Based on the above considerations and our previous work [27], in this paper, we report the synthesis, crystal structure, and photoluminescence properties of a novel Ag-aminopyrimidine/dicarboxylate mixed-ligand coordination polymer, namely, [Ag$_2$(dmapym)$_2$(npd)]$_n$ (**1**) (dmapym = 2-amino-4,6-dimethylpyrimidine, H$_2$npd = 2,6-naphthalenedicarboxylic acid) (Fig. 1), which shows a 2D network based on a secondary building unit [Ag$_2$(COO)$_2$]. Compared to the closely related 1D fish-bone-shaped complex [Ag$_2$(mapym)$_2$(npd)·2H$_2$O]$_n$ (mapym = 2-amino-4-methylpyrimidine) [28], the change of dimensionality upon the simple addition of just one methyl group to the aromatic system in **1** indicates that substituent effects, such as steric and possibly also electronic factors, may have an important influence on the structures of the resulting coordination polymers.

Experimental Section

All reagents and solvents employed were commercially available and used without further purification. Elemental analyses (C, N and H) were determined with a Vario EL III
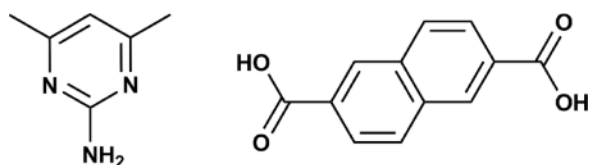
Fig. 1. The organic ligands used in the construction of complex **1**.

analyzer. Photoluminescence spectra were measured on a Hitachi F-7000 fluorescence spectrophotometer and IR spectra on a Nicolet 330 FTIR spectrometer in the range of $4000 - 400 \, \text{cm}^{-1}$.

Synthesis of [Ag$_2$(dmapym)$_2$(npd)]$_n$ (**1**)

A mixture of AgNO$_3$ (167 mg, 1 mmol), H$_2$npd (216 mg, 1 mmol) and dmapym (123 mg, 1 mmol) was stirred in the mixed solvent CH$_3$OH-H$_2$O (v/v, 1 : 1; 10 mL). 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 46 %). The product was washed with a small volume of cold CH$_3$OH and diethyl ether. – Anal. for Ag$_2$C$_{24}$H$_{20}$N$_6$O$_4$: calcd. C 42.88, H 3.00, N 12.50; found C 42.79, H 2.88, N 12.59 %. – IR (KBr): $\nu(\text{cm}^{-1}) = 3393(\text{m})$, 3317(m), 3137(m), 1653(s), 1591(s), 1567(s), 1400(m), 1360(m), 1235(m), 1028 (m), 787(m), 744(m), 564(w), 540(w).

X-Ray structure determination

Single crystals of complex **1** with appropriate dimensions were chosen under an optical microscope and quickly coated with high-vacuum grease (Dow Corning Corporation) before being mounted on a glass fiber for data collection. Data were collected on a Bruker Apex II CCD diffractometer with a graphite-monochromatized MoK_α radiation source ($\lambda = 0.71073 \, \text{Å}$). The data were measured using ω scans of $0.5°$ per frame for 10 s until a complete hemisphere was collected. Cell parameters were retrieved using the SMART software and refined with SAINT on all observed reflections [29]. Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS [29]. The structure was solved by Direct Methods using SHELXS-97 [30] and refined by full-matrix least-squares procedures on F^2 with SHELXL-97 [31]. Atoms were located from iterative examination of difference Fourier maps following least-squares refinements of the earlier models. Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2 – 1.5

Table 1. Crystal data and numbers pertinent to data collection and structure refinement of **1**.

Empirical formula	C$_{24}$H$_{24}$Ag$_2$N$_6$O$_4$
Formula weight	676.23
Temperature, K	173(2)
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	10.658(3)
b, Å	11.040(3)
c, Å	12.475(4)
α, deg	114.960(5)
β, deg	109.552(5)
γ, deg	91.748(5)
Volume, Å^3	1228.5(6)
Z	2
ρ_{calcd}, g cm^{-3}	1.83
$\mu(\text{Mo}K_\alpha)$, mm^{-1}	1.6
$F(000)$, e	672.0
Reflections collected / unique / R_{int}	6246 / 4243 / 0.0258
Data / restraints / parameters	4243 / 0 / 329
$[I > 2\sigma(I)]$	0.0375 / 0.0843
Final R_1 / wR_2 (all data)	0.0507 / 0.0882
Goodness-of-fit on F^2	0.980
Largest diff. peak / hole , e Å^{-3}	0.97 / –0.39

Table 2. Selected bond lengths (Å) and angles (deg) for **1**[a].

Ag1–N5^i	2.253(3)	Ag2–N3^{ii}	2.323(4)
Ag1–N1	2.259(3)	Ag2–O4	2.368(3)
Ag1–O1	2.562(3)	Ag2–O1	2.369(3)
Ag1–O3	2.596(3)	Ag2–N6	2.388(4)
Ag1···Ag2	3.4377(8)		
N5^i–Ag1–N1	149.09(13)	N3^{ii}–Ag2–O4	102.85(11)
N5^i–Ag1–O1	91.00(11)	N3^{ii}–Ag2–O1	116.29(12)
N1–Ag1–O1	119.13(11)	O4–Ag2–O1	124.31(11)
N5^i–Ag1–O3	101.67(12)	N3^{ii}–Ag2–N6	116.37(12)
N1–Ag1–O3	85.85(11)	O4–Ag2–N6	99.86(12)
O1–Ag1–O3	90.52(10)	O1–Ag2–N6	96.53(11)

[a] Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $-x+1, -y+1, -z+1$.

times U_{eq} of the attached C or N atoms. The crystal structure was examined using the Addsym subroutine of PLATON [32] to exclude higher symmetry. Pertinent crystallographic data collection and refinement parameters are given in Table 1. Selected bond lengths and angles are collected in Table 2.

CCDC 742810 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Synthesis and IR spectra

The growth of single crystals of **1** was carried out in darkness to avoid photodecomposition. The reactions

of Ag(I) with carboxylates in aqueous solution often result in the formation of microcrystalline or amorphous insoluble silver salts, presumably due to the fast coordination of the carboxylates to Ag(I) ions to form polymers [33]. Hence, properly lowering the reaction speed, such as by using ammoniacal conditions to form [Ag(NH$_3$)$_n$]$^+$ species favors the formation of crystalline products [34, 35]. The ultrasonic method has found an important niche in the preparation of inorganic materials [36, 37]. The high local temperatures and pressures, combined with extraordinarily rapid cooling, provide a unique means for driving chemical reactions under extreme conditions. Compared to the conventional heating method, the ultrasound treatment could promote the dissolution of the precipitations, thus shorten the reaction time and enhance the yield. In this system, the ultrasound technique also realizes the rapid (10 min) and efficient preparation of the title compound.

Powder X-ray diffraction (PXRD) has been used to check the phase purity of the bulk samples in the solid state. The measured PXRD patterns matched the simulated patterns generated from the results of single-crystal diffraction data (Fig. S1; Supporting Information; see the note at the end of the paper for availability), indicative of an almost pure product. The IR spectrum (Fig. S2; Supporting Information) of complex **1** shows the characteristic absorption bands to be attributed to the asymmetric (ν_{as} at *ca.* 1600 cm^{-1}) and symmetric (ν_s at *ca.* 1385 cm^{-1}) stretching vibrations of the carboxyl groups. The absence of a band in the region 1690 – 1730 cm^{-1} indicates complete deprotonation of the carboxylic groups [38], which is consistent with the result of the X-ray diffraction analysis.

Crystal structure of [Ag$_2$(dmapym)$_2$(npd)]$_n$ (*1*)

Single-crystal X-ray diffraction analysis has revealed that complex **1** crystallizes in space group *P*1̄ with an asymmetric unit containing two crystallographically independent Ag(I) ions, two dmapym ligands and two halves of an npd ligand related by an inversion center. The structure of complex **1** is shown in Fig. 2. Each Ag(I) ion is four-coordinated by two nitrogen atoms from two different dmapym ligands and two carboxylate oxygen atoms from two different npd ligands. The Ag–O distances range from 2.368(3) to 2.596(3) Å, and the Ag–N distances range from 2.253(3) to 2.388(4) Å. The geometry of the four-
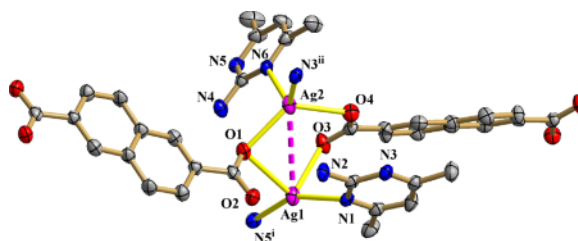

Fig. 2 (color online). The structure of **1** showing the coordination environment around the Ag(I) centers. Displacement ellipsoids are drawn at the 50 % probability level (symmetry codes: (i) $-x+1$, $-y+1$, $-z$; (ii) $-x+1$, $-y+1$, $-z+1$).

coordinated N$_2$AgO$_2$ unit can be described according to the calculated values of the τ_4 parameter introduced by Houser [39], which are 0.65 and 0.85 for Ag1 and Ag2, respectively (for an ideal tetrahedron $\tau_4 = 1$). Thus, the coordination geometries of Ag1 and Ag2 could be described as seesaw and distorted tetrahedron, respectively. The Ag1–O2 bond length is 2.698(2) Å, which falls in the secondary bonding range (the sum of the van derWaals radii of Ag and O is 3.24 Å), indicating weak Ag···O interactions. Two carboxylate groups with (κ^1)-(κ^1)-μ_2 and (κ^2)-(κ^0)-μ_2 coordination mode clamp binuclear silver(I) units to form a [Ag$_2$(COO)$_2$] secondary building unit (SBU). The Ag···Ag separation distance (3.4377(8) Å) is slightly shorter than the van der Waals contact distance for Ag···Ag (3.44 Å) [40], which is indicative of an intramolecular interaction between the two Ag(I) ions and affords supporting evidence to the significance of argentophilicity [41].

In **1**, the [Ag$_2$(COO)$_2$] SBUs are linked by he bidentate dmapym molecules to form cation chains (Fig. 3a) in which two dmapym ligands are arranged oppositely. Two adjacent chains are bridged by (κ^1)-(κ^1)-μ_2 and (κ^2)-(κ^0)-μ_2 carboxylate groups of npd anions into a 2D network (Fig. 3b), which is reinforced by N–H···O hydrogen bonds between amino groups of dmapym and carboxylate groups of npd ligands with N···O distances ranging from 2.819(5) to 2.888(5) Å

Table 3. Hydrogen bond parameters (Å, deg) for complex **1**[a].

D–H···A	D–H	H···A	D···A	D–H···A
N1–H1B···O4[ii]	0.88	2.01	2.888(5)	179
N1–H1A···O2	0.88	1.95	2.819(5)	168
N4–H4A···O3[i]	0.88	1.98	2.859(5)	173
N4–H4B···O1	0.88	1.98	2.826(5)	160

[a] Symmetry codes: (i) $-x+1$, $-y+1$, $-z$; (ii) $-x+1$, $-y+1$, $-z+1$.
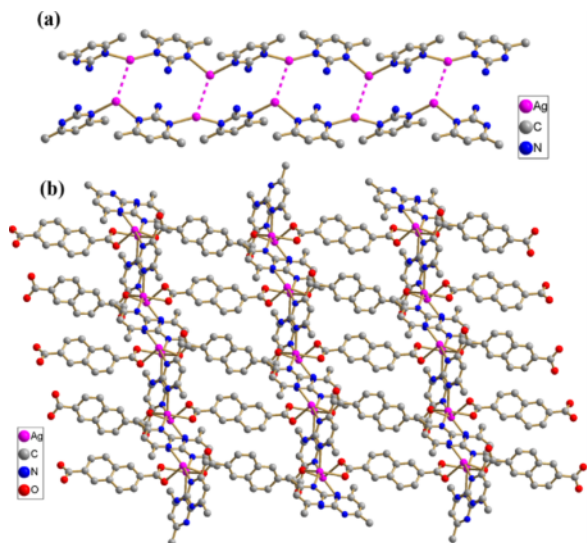
Fig. 3 (color online). (a) Ball-and-stick view of the chain; (b) schematic representation of the 2D network.

Fig. 4 (color online). Solid-state excitation spectra of complex **1** and the free ligands at room temperature.

(Table 3). Adjacent 2D nets are packed together by C–H···π interactions (C9–H9···Cg1 = 3.575(6) Å, Fig. S3, Supporting Information), but no π···π interactions are found.

Photoluminescence properties

The solid-state photoluminescence data for both free ligands and for complex **1** at room temperature are shown in Fig. 4. Complex **1** exhibits photoluminescence in the solid state, with an emission maximum at 418 nm, upon excitation at 330 nm. To understand the nature of the emission band, we analyzed the photoluminescence properties of the corresponding free ligands and found that dmapym and H$_2$npd emit photoluminescence at 342 and 458 nm, respectively, which can be tentatively assigned to the $\pi* \rightarrow \pi$ or $\pi* \rightarrow n$
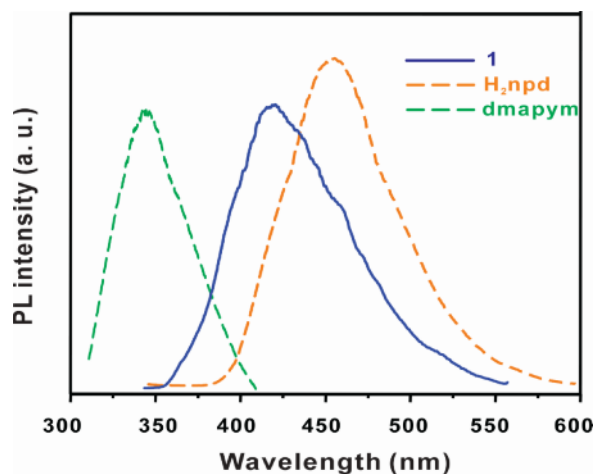
transition [42]. The observed emission of complex **1** is assigned to npd^{2-} intraligand π-$\pi*$ transitions because a similar emission is observed for the free H$_2$npd ligand and complex **1**, the shift being caused by the silver coordination.

Supporting information

Figures of the experimental and calculated PXRD patterns, IR spectrum and the C–H···π interactions in **1** are given as Supporting Information available online (DOI: 10.5560/ZNB.2013-3013).

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