Halogen Bonds in Two Silver(I) Mixed-ligand Supramolecular Frameworks: Synthesis, Structure and Photoluminescence

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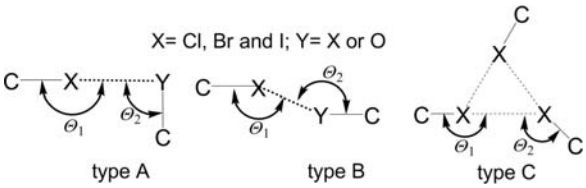
Two silver(I) tetrachlorophthalates incorporating aminopyrimidyl ligands, namely $[Ag_4(apym)_4(tcpta)_2]_n$ (**1**) and $[Ag_2(dmapym)(tcpta)]_n$ (**2**), (apym = 2-aminopyrimidine, dmapym = 2-amino-4,6-dimethylpyrimidine, H_2tcpta = tetrachlorophthalic acid), were synthesized and characterized by elemental analysis, IR spectroscopy and single-crystal X-ray diffraction. Both **1** and **2** form sheets which are assembled into 3D supramolecular frameworks *via* halogen bonds, hydrogen bonds and $\pi\cdots\pi$ interactions. Even adding two more methyl groups to the pyrimidyl ring does not change the dimensions of **1** and **2**, but it influences the arrangement of the *N*- and *O*-donors in the solid state which in turn results in different types of halogen bonds. The photoluminescence properties of **1** and **2** were investigated in the solid state at room temperature.

Key words: Silver(I), 2-Aminopyrimidine, Tetrachlorophthalic Acid, Halogen Bonds, Photoluminescence

Introduction

The non-covalent interaction (C–X$\cdots$Y–C) between a polarizable halogen atom (X) and an atom (Y) possessing a lone pair of electrons including oxygen and nitrogen, called halogen bonding, has been intensively investigated as a powerful tool in molecular recognition, chiral discrimination, supramolecular polymer formation, porous material design, chemical separation and biological systems [1 – 9]. Recently a renaissance of research on this interaction proved its effectiveness in self-assembly processes as a new paradigm in supramolecular chemistry [10 – 17]. The geometrical preference of halogen$\cdots$halogen interactions (C–X$\cdots$Y–C, X = Cl, Br and I; Y = X or O) has been identified as belonging to three different types (type A, type B and type C; Scheme 1) based on the geometrical C–X$\cdots$Y–C angles Θ_1 and Θ_2 [18 – 21]. Although tetrachlorophthalic acid is a versatile halogen bond donor due to the multi-orientation of the four peripheral chlorine atoms, these chlorine atoms also have an electron-withdrawing effect resulting in weak coordination ability of the carboxylate groups to transition metals. So its coordination and supramolecular chemistry received less attention [22 – 25]. During our recent studies, in order to search for a new class of non-covalent interactions in Ag(I)/aminopyrimidine/arylcarboxylate systems [26 – 33], we introduced auxiliary tetrachlorophthalate ligands as halogen bond donors into the above system and obtained two mixed-ligand silver(I) supramolecular frameworks involving halogen bonds, namely $[Ag_4(apym)_4(tcpta)_2]_n$ (**1**) and $[Ag_2(dmapym)(tcpta)]_n$ (**2**), (apym = 2-aminopyrimidine, dmapym = 2-amino-4,6-dimethylpyrimidine, H_2tcpta = tetrachlorophthalic acid).



Scheme 1. Geometrical preferences of halogen bonds type A: $\Theta_1 \approx 180°$, $\Theta_2 \approx 90°$; type B: $\Theta_1 \approx \Theta_2 \approx 180°$; type C: trigonal synthon. $\Theta_1 \approx 180°$, $\Theta_2 \approx 120°$.

Experimental Section

All reagents and solvents employed were commercially available and used as received without further purification. Infrared spectra were recorded on a Nicolet AVATAT FT-

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

Complexes	**1**	**2**
Formula	$Ag_4C_{32}H_{20}Cl_8N_{12}O_8$	$Ag_2C_{14}H_9Cl_4N_3O_4$
M_r	1415.68	640.78
Crystal system	monoclinic	triclinic
Space group	$C2/c$	$P\bar{1}$
a, Å	13.4957(3)	7.4859(15)
b, Å	24.8634(6)	8.8975(18)
c, Å	25.4326(7)	14.239(3)
α, deg	90	91.10(3)
β, deg	97.085(2)	100.41(3)
γ, deg	90	101.95(3)
Z	8	2
V, Å^3	8468.7(4)	911.0(3)
D_{calcd}, g cm^{-3}	2.22	2.34
μ, mm^{-1}	2.4	2.8
$F(000)$, e	5472	616
Unique reflns	8339	3478
Obsd reflns [$I \geq 2\sigma(I)$]	6398	2973
Ref. parameters	577	246
R_1 / wR_2 [$I \geq 2\sigma(I)$][a, b]	0.0252 / 0.0556	0.0363 / 0.0967
R_1 / wR_2 (all data)	0.0402 / 0.0582	0.0421 / 0.1030
GOF[c]	0.963	1.0089
Largest diff, peak / hole, e Å^{-3}	0.95 / −0.65	1.26 / −0.93

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; [c] $\mathrm{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

IR360 spectrometer from KBr pellets in the frequency range 4000 – 400 cm^{-1}. The elemental analyses (C, H, N contents) were determined on a CE instrument EA 1110 analyzer. Photoluminescence measurements were performed on a Hitachi F-4500 fluorescence spectrophotometer with solid powder on a 1 cm quartz round plate.

*Synthesis of complex [Ag$_4$(apym)$_4$(tcpta)$_2$]$_n$ (**1**)*

A mixture of Ag_2O (116 mg, 0.5 mmol), 4,4′-bipy ·2H_2O (194 mg, 1 mmol) and H_2bdc (166 mg, 1 mmol) was stirred in CH_3OH-H_2O mixed solvent (8 mL, v/v: 3/1). Then an 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 the dark at r. t. for several days to give colorless crystals of **1** (yield, 51 %). These were washed with small volumes of cold CH_3OH and diethyl ether. – Elem. anal. for $Ag_4C_{32}H_{20}Cl_8N_{12}O_8$ (1415.68): calcd. C 44.00, H 3.69, N 7.33 found C 43.95, H 3.64, N 7.38. – Selected IR (KBr): ν (cm^{-1}) = 3431 (s), 3046 (w), 2925 (w), 2855 (w), 1606 (s), 1559 (s), 1483 (w), 1428 (w), 1381 (s), 1220 (m), 1071 (w), 804 (w), 735 (w), 619 (w), 501 (w).

*Synthesis of complex [Ag$_2$(dmapym)(tcpta)]$_n$ (**2**)*

The synthesis of **2** was similar to that of **1**, but with dmapym (123 mg, 1 mmol) instead of apym. Colorless crystals of **2** (372 mg) were obtained in 58 % yield based on Ag_2O. – Elem. anal. for $Ag_2C_{14}H_9Cl_4N_3O_4$ (640.78): calcd. C 26.24, H 1.42, N 6.56; found C 26.30, H 1.47, N 6.62. – Selected IR (KBr): ν (cm^{-1}) = 3335 (s), 3155 (m), 1609 (s), 1591 (s), 1472 (w), 1426 (m), 1387 (w), 1344 (s), 652 (m), 615 (m).

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

Complex 1			
Ag1–N6	2.202(2)	Ag2–O5	2.456(2)
Ag1–N3	2.209(3)	Ag2–O7	2.5644(19)
Ag1–O3	2.442(2)	Ag3–N11	2.244(2)
Ag1–O1	2.575(2)	Ag3–N9	2.272(2)
Ag2–N5	2.204(2)	Ag4–N12	2.220(2)
Ag2–N8	2.205(2)	Ag4–N2^{i}	2.261(3)
Ag4–O6^{ii}	2.596(2)	O8–Ag4^{iii}	2.537(2)
N2–Ag4^{iv}	2.261(3)		
N6–Ag1–N3	150.86(9)	N12–Ag4–N2^{i}	142.85(9)
N6–Ag1–O3	102.00(8)	N12–Ag4–O8^{ii}	122.56(8)
N3–Ag1–O3	99.97(8)	N2^{i}–Ag4–O8^{ii}	94.58(8)
N6–Ag1–O1	108.75(8)	N12–Ag4–O6^{ii}	97.90(8)
N3–Ag1–O1	91.67(8)	N2^{i}–Ag4–O6^{ii}	85.96(8)
O3–Ag1–O1	85.83(6)	O8^{ii}–Ag4–O6^{ii}	84.21(6)
N5–Ag2–N8	150.76(9)	N5–Ag2–O7	105.78(8)
N5–Ag2–O5	102.08(8)	N8–Ag2–O7	92.12(7)
N8–Ag2–O5	102.41(8)	O5–Ag2–O7	84.79(6)
N11–Ag3–N9	142.44(9)		
Symmetry codes: [i] $x, y-1, z$; [ii] $x+1/2, y-1/2, z$; [iii] $x-1/2, y+1/2, z$; [iv] $x, y+1, z$.			
Complex 2			
Ag1–O3^{i}	2.170(3)	Ag2–O2	2.236(3)
Ag1–N1	2.188(3)	Ag2–N3^{ii}	2.302(3)
Ag1–O1	2.504(3)	Ag2–O4^{iii}	2.323(3)
N3–Ag2^{iv}	2.302(3)	Ag2–N2^{i}	2.760(4)
O3^{i}–Ag1–N1	163.11(11)	O2–Ag2–O4^{iii}	120.12(12)
O3^{i}–Ag1–O1	82.90(12)	N3^{ii}–Ag2–O4^{iii}	104.78(11)
N1–Ag1–O1	112.85(12)	O2–Ag2–N2^{i}	112.31(12)
O4^{iii}–Ag2–N2^{i}	75.26(10)	N3^{ii}–Ag2–N2^{i}	96.44(11)
O2–Ag2–N3^{ii}	130.97(12)		
Symmetry codes: [i] $-x+1, -y+2, -z$; [ii] $x+1, y+1, z$; [iii] $-x+2, -y+2, -z$; [iv] $x-1, y-1, z$.			

X-Ray structure determination

Intensity data of complexes **1** and **2** were collected on an Oxford Gemini S Ultra system (MoK_α radiation). Absorption corrections were applied by using multi-scan techniques (CRYSALIS). The structures were solved by Direct Methods using SHELXS-97 [34]. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods on F^2 (SHELXL-97 [35]). The hydrogen atoms attached to carbon and nitrogen were placed in calculated positions with U_{iso}(H) = 1.2 U_{eq} (C, N) in the riding model approximation. The crystallographic details of **1** and **2** are summarized in Table 1. Selected bond lengths and angles are collected in Table 2. The hydrogen bond parameters are listed in Table 3.

Table 3. Hydrogen bond geometries for **1** and **2**.

D–H···A	D–H	H···A	D···A	D–H···A
Complex 1				
N1–H1A···O1	0.88	2.46	3.043(3)	124
N1–H1B···O8^{v}	0.88	2.24	3.084(3)	162
N4–H4B···O3	0.88	1.97	2.850(3)	176
N4–H4C···O5	0.88	1.98	2.853(3)	174
N7–H7C···O7	0.88	2.53	3.069(3)	120
N7–H7B···O2^{vi}	0.88	2.21	3.064(3)	162
N10–H10B···O6^{ii}	0.88	2.01	2.879(3)	167
N10–H10C···O4^{ii}	0.88	1.98	2.838(3)	166
Symmetry codes: ^{ii} $x+1/2, y-1/2, z$; ^{v} $-x+3/2, y+1/2, -z+1/2$; ^{vi} $-x+3/2, y-1/2, -z+1/2$.				
Complex 2				
N2–H2A···O3	0.86	2.45	3.019(5)	124
N2–H2C···O4^{v}	0.86	2.17	3.013(4)	167
Symmetry code: ^{v} $-x+1, -y+1, -z$.				

CCDC 762003 and 7620047 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Synthesis and IR spectra

The syntheses of complexes **1** and **2** were carried out in the dark to avoid photodecomposition. The formation of the products is not significantly affected by changes of the molar 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 structural characteristics as determined by X-ray diffraction on single crystals (*vide infra*). The IR spectra exhibit strong absorptions centered at ~ 3400 and $\sim 3300\ \mathrm{cm}^{-1}$ corresponding to asymmetric and symmetric N-H stretching bands of amino groups. Strong characteristic bands of carboxylate groups are observed in the range from ~ 1610 to $\sim 1590\ \mathrm{cm}^{-1}$ for the asymmetric vibrations and from ~ 1420 to $\sim 1350\ \mathrm{cm}^{-1}$ for the symmetric vibrations. The absence of the characteristic bands at around $\sim 1700\ \mathrm{cm}^{-1}$ attributed to the carboxylate groups indicates complete deprotonation of all carboxylate groups.

*Structure descriptions of **1** and **2***

*Crystal structure of $[Ag_4(apym)_4(tcpta)_2]_n$ (**1**)*

Complex **1** crystallizes in the monoclinic space group $C2/c$. Fig. 1a shows the coordination environments of the Ag(I) ions. The structure features a sheet

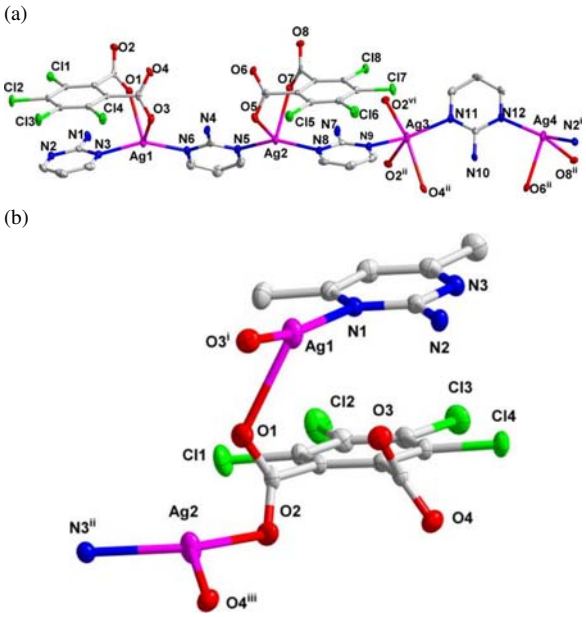


Fig. 1 (color online). Molecular structures of **1** and **2** in the crystal: (a) the coordination environment of the Ag(I) ions in **1** Symmetry codes: ^{i} $x, y-1, z$; ^{ii} $x+1/2, y-1/2, z$; ^{vi} $-x+3/2, y-1/2, -z+1/2$; (b) the coordination environment of the Ag(I) ions in **2**. Symmetry codes: ^{i} $-x+1, -y+2, -z$; ^{ii} $x+1, y+1, z$; ^{iii} $-x+2, -y+2, -z$.

containing infinite Ag-apym chains and bridging tcpta ligands. The Ag1, Ag2 and Ag4 ions are located in distorted tetrahedral geometries and coordinated by one tcpta and two apym ligands. The distortion of the tetrahedra can be indicated by the calculated value of the τ_4 parameter introduced by Houser [36] to describe the geometry of a four-coordinate metal system, which is 0.72, 0.73 and 0.67 for Ag1, Ag2 and Ag4, respectively (for perfect tetrahedral geometry, τ_4 = 1). The Ag3 ion, coordinated by two N atoms from two different apym ligands and three O atoms from two different tcpta, is located in a square-pyramidal environment. The distortion of a square pyramid can be indicated by the τ_5 parameter [37], which is 0.14 for Ag3 (for ideal square-pyramidal geometry, τ_5 = 0). The Ag–O and Ag–N bond lengths are in the range of 2.442(2)–2.596(2) and 2.202(2)–2.272(2) Å, respectively, both of which match well those observed in similar complexes [38–52].

In **1**, the Ag(I) ions are linked by bidentate apym ligands to form zigzag chains. The adjacent chains are connected by the μ_2-tcpta ligands into 2D sheets (Fig. 2a) where the apym and tcpta ligands alternate along the *a* axis and are stacked through $\pi\cdots\pi$ inter-

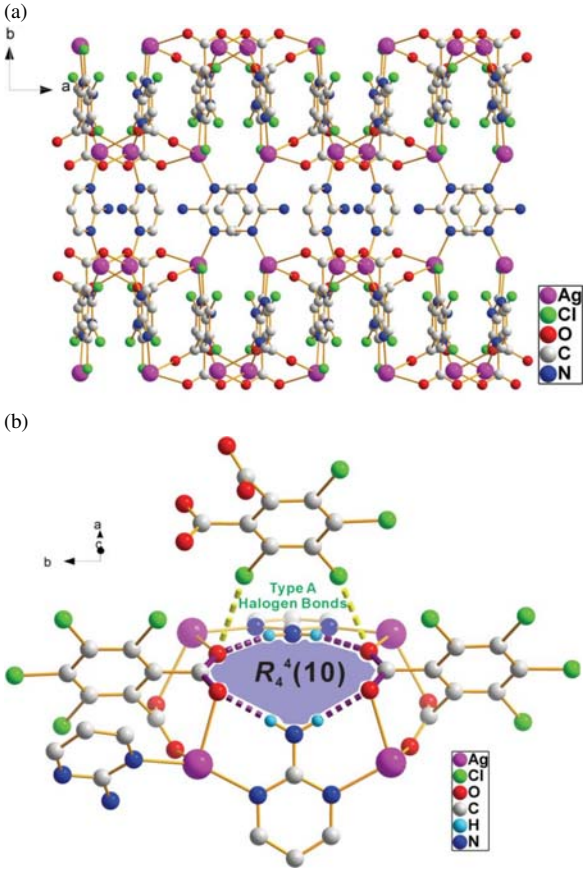


Fig. 2 (color online). (a) The sheet structure of **1**; (b) the type A Cl···O halogen bonds (yellow dashed lines) and the $R_4{}^4(10)$ hydrogen bonding motif.

actions with centroid···centroid distances in the range 3.3788(16)–3.6008(15) Å. Intra-sheet N–H···O hydrogen bonds involving amino groups of apym and carboxylate groups of tcpta form an $R_4{}^4(10)$ motif when using the graph-set notation [53] (Fig. 2b). The $\pi\cdots\pi$ interactions and the intra-sheet hydrogen bonds reinforce the sheet.

The most striking feature in **1** are the remarkable Cl···O halogen bonds (Fig. 2b) observed between the Lewis acid donors Cl_{tcpta} (Cl3 and Cl4) and the Lewis base acceptors O_{tcpta} (O4 and O6). The distances Cl4···O4 and Cl3···O6 are 3.115(2) and 3.038(2) Å respectively, which are shorter than the sum of van der Waals radii for oxygen and chlorine (3.27 Å) [54]. The angles Θ_1 (∠C–Cl···O) and Θ_2 (∠Cl···O–C) are ranging from 158.67(11) to 160.55(11)° and from 97.76(16) to 100.53(16)°, respectively. The geometrical characteristics of the Cl···O interactions show that they belong to type A halogen bonds according to a model that assigns a positive polarization to the polar region of the Cl atom and a negative polarization to its equatorial region [55–57]. The halogen bonds are associated with nonclassical C_{apym}–H···O hydrogen bonds linking adjacent sheets into a 3D supramolecular framework. In **1**, halogen and hydrogen bonds show an interesting geometrical relationship where halogen bonds (Cl4···O4 and Cl3···O6) seem to be perpendicular to and energetically independent of classical hydrogen bonds (N10···O4 and N10···O6), proving that they can be considered to be orthogonal molecular interactions as first introduced by Ho [58]. The orthogonal geometry of hydrogen and halogen bonds may originate from a combination of electrostatic and steric effects. Although this preferential geometrical relationship is common in protein-ligand complexes, such as polypeptides and polynucleotides [59], it still attracts less attention in coordination polymers.

*Crystal structure of $[Ag_2(dmapym)(tcpta)]_n$ (**2**)*

Single-crystal X-ray diffraction analysis has revealed that **2** crystallizes in the triclinic space group $P\bar{1}$. Fig. 1b shows the coordination environment of the Ag(I) ions in **2**, which are three-coordinated by two O atoms and one N atom in a Y-shaped geometry. The bond lengths Ag–N and Ag–O are within the expected ranges reported for Ag(I) complexes. Complex **2** also exhibits a 2D sheet structure consisting of Ag-tcpta 1D chains. The μ_2-dmapym ligands connect adjacent chains producing a sheet as shown in Fig. 3a. The arrangement of dmapym and tcpta is alternating along the *c* axis incorporating weak $\pi\cdots\pi$ interactions (centroid···centroid = 3.644(3) Å).

As Cl···Cl interactions are weak and basically electrostatic in nature, they were subject to less concern compared to the strong I···I interactions with some degree of covalent character [60–62]. In **2**, there are Cl···Cl halogen bonds between the adjacent sheets involving pairs of Cl2 and Cl3. The distance Cl2···$Cl3^{vii}$ (3.456(2) Å) is 0.04 Å shorter than the sum of two van der Waals radii of Cl (3.50 Å). The angles Θ_1 and Θ_2 are 156.67(17) and 135.54(17)°, respectively. The halogen bonds can be tentatively assigned to type B being of the van der Waals type, such that the shortest among these are repulsive in nature. Not only inter-sheet Cl···Cl complementary halogen bonds, but also intra-sheet four-center (trifurcated) Cl···O halo-

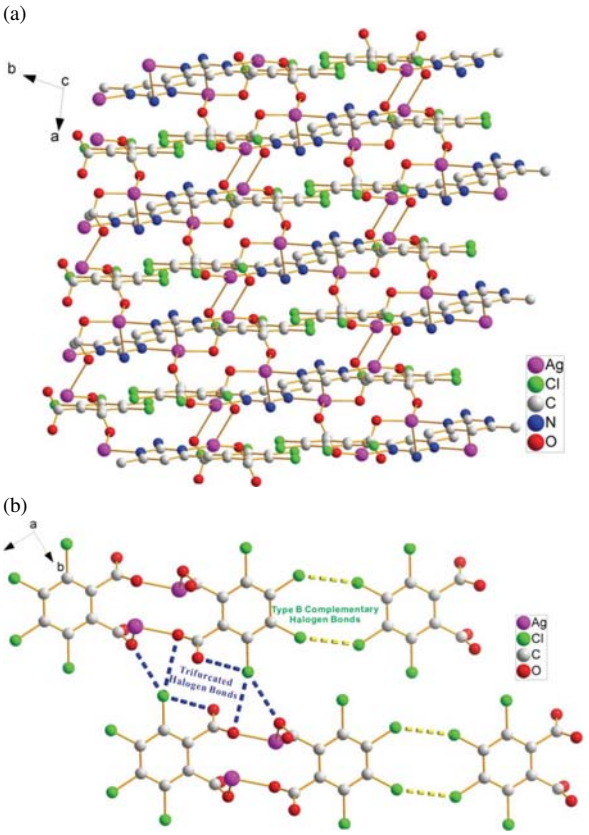


Fig. 3 (color online). (a) The sheet structure of **2**; (b) the type B Cl···Cl halogen bonds (yellow dashed lines) and the trifurcated Cl···O halogen bonds (blue dashed lines).

gen bonds involving Cl4, O1^{viii}, O3^{v} and O4 are observed with Cl···O distances of 3.171(4), 3.206(3) and 3.172(3) Å. Cl4···O1^{viii} and Cl4···O3^{v} belong to type B halogen bonds (Θ_2 = 154.0(3) and 164.34(16)°, respectively), and Cl4···O4 belongs to type A halogen bonds with an angle Θ_2 of 79.67(16)° (Fig. 3b). Complex **2** forms a 3D supramolecular framework propagated *via* pairs of Cl···Cl complementary halogen bonds. (Symmetry codes: (vii) $1-x, 1-y, 1-z$; (viii) $x, -1+y, z$).

Photoluminescence properties

The solid-state photoluminescence data for the free ligands and complex **1** at r. t. are shown in Fig. 4. Complex **1** exhibits photoluminescence in the solid state, with an emission maximum at 456 nm upon excitation at 330 nm at r. t. To understand the nature of the emission bands, we analyzed the photoluminescence properties of the corresponding free ligands and found

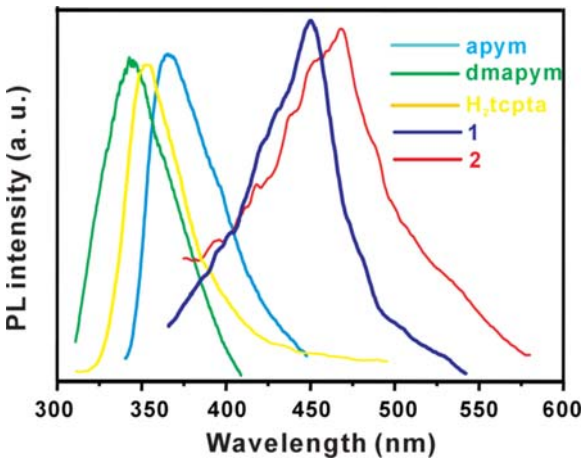


Fig. 4 (color online). Solid-state emission spectra for **1** and **2**, as well as for the free ligands at room temperature.

that free bipy and H_2bdc ligands emit photoluminescence at 436 and 383 nm, respectively [27]. Therefore, the emission band of **1** is probably due to $\pi* \rightarrow n$ or $\pi* \rightarrow \pi$ transitions. The combination of d^{10} metal centers and organic ligands in coordination polymers provides an efficient route to a new type of photoluminescent materials because of their structure- and metal-dependent emission. The photoluminescence properties of **1** and **2** as well as of the free ligands were examined in the solid state at r. t. As shown in Fig. 4, the apym, dmapym and H_2tcpta ligands display photoluminescence emission at 359, 342 and 352 nm, respectively, under 300 nm radiation which is probably due to $\pi* \rightarrow n$ (*O*-donor) or $\pi* \rightarrow \pi$ (*N*-donor) transitions [63–65]. When excited at 330 nm, **1** and **2** have similar emission bands (λ_1 = 463 and λ_2 = 471 nm) which may be tentatively assigned to intra-ligand transitions of coordinated *N*-donor ligands [66].

Conclusion

In summary, we have described a strategy for designing and constructing supramolecular frameworks through directional halogen bonds (type A, type B and trifurcated halogen bonds) in combination with hydrogen bonds and $\pi\cdots\pi$ interactions. The additional substituents on the pyrimidyl ring in **2** are responsible for an arrangement of *N*- and *O*-donors in the solid state with different types of halogen bonds as compared to **1**. The relationship of halogen bonds and hydrogen bonds in crystal structures has also been discussed. The photoluminescence properties of **1** and **2** were investigated in the solid state.

Acknowledgement

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