# Self-assembly of *N*,*N*′,*N*″-tris(4-pyridyl)trimesic amide and *N*,*N*′,*N*″-tris(3-pyridyl)trimesic amide with $Ag^{I}$ or $Cd^{II}$ ions†

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We report herein an interesting family of tripyridyltriamides (**L1** ≡ *N*,*N*′,*N*″-tris(3-pyridyl)trimesic amide, **L2** ≡ *N*,*N*′,*N*″-tris(4-pyridyl)trimesic amide) used as tridentate bridging ligands to carry out crystal-engineering studies. The reaction of $AgPF_6$ with **L1** leads to a 2-D coordination polymer, $[Ag(\mathbf{L1})PF_6]_n$ (**1**). The 48-membered macrocycles constructed from three-coordinate $Ag^{I}$ ions as connectors and three tripyridyltriamide moieties propagate into 2-D extended structures. Indeed, the $Ag^{I}\cdots\pi$ interaction (the distance of the $Ag^{I}\cdots$centroid of benzene is 3.209 Å) increases the supramolecular complexity, and leads to inter-sheet dimerization. The reaction of $CdCl_2$ with **L2** forms a 3-D coordination network, $[Cd(\mathbf{L2})_2Cl_2]_n$ (**2**). The open channels with a diameter of *ca.* 7.5 Å containing the tripyridyltriamide moieties propagate into 3-D extended structures. This is an interesting example of 3-D coordination networks containing tripyridyltriamides as functional moieties inside the channels. However, the channels are filled with disordered water molecules and chloride anions, where the latter are appended through hydrogen-bonding interactions with the amide moieties inside the channels. In addition, **1** displays a high-energy emission with a maximum at *ca.* 450 nm, whereas **2** shows a low-energy emission with a maximum at *ca.* 532 nm. The former with a *ca.* 450 nm emission is assigned to an intraligand transition, and the latter with a *ca.* 532 nm emission is tentatively ascribed to a metal-to-ligand charge-transfer transition.

## Introduction

The widespread use of the coordinative-bond approach in the construction of supramolecular coordination compounds by self-assembly is well established and has been attracting much attention.[1] So far, a wide range of one-, two- and three-dimensional infinite solid-state coordination architectures[2] as well as discrete molecular structures have been isolated and structurally characterized.[1] Moreover, applications including chemical sieving, sensing and catalysis based on supramolecular coordination compounds have been also conducted, and some have really shown exciting and valuable progress.[3] Organic amides have been proved to be very useful in self-assembly through hydrogen bonding, and the assembled products have relevance to biological systems. With reference to the intricate work reported by Ghadiri and coworkers,[4] cyclic oligoamides can be used as building units to give interesting nanotubes or zeolite-like frameworks through inter-ring or inter-tube NH···O=C hydrogen bonding, representing potentially a new and important class of functional materials. However, the related study based on metal-containing cyclic amides is still in its infancy. Puddephatt and coworkers pioneered to report an intriguing work based on this novel idea toward construction of a metal-containing ($Pt^{II}$ ions) molecular triangle taking advantage of dipyridylamides (*N*-pyridin-4-ylisonicotinamide) as a bridging ligand and of $Pt^{II}$ ions as a connector in the assembly process.[5] The complex cation appears to be a rare example of a cyclic coordination compound that forms a dimeric architecture similar to that formed by cyclic peptides, and it suggests that the biomimetic approach to organization of the coordination networks has considerable promise.

Recently, Stang and coworkers have utilized **L2** to construct a $Pd^{II}$ coordination cage with the $(Pd_3\mathbf{L2}_2)^{6+}$ moiety, characterized by NMR and ESI-mass spectra.[6] Lah and coworkers have also reported a novel single-crystal structure of the truncated octahedral $[Pd_6\mathbf{L1}_8]^{12+}$ cages.[7] Thus, **L1** and **L2** show potential as tridentate bridging ligands for the construction of molecular cages. We have previously reported work on the metal-containing ($Zn^{II}$ or $Au^{I}$ ions) cyclic amides or molecular rectangles based on a dipyridylamide (*N*,*N*′-bis-4-methylpyridyl oxalamide).[8] Very recently, a new tetradentate ligand 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrakis(pyridin-4-ylamide) has been also utilized for a crystal-engineering study by us.[9] Different from the cage formation for the above references,[6,7] we report herein the solid-state structures and luminescence properties of $Ag^{I}$ and $Cd^{II}$ coordination polymers based on an interesting family of tridentate ligands, *N*,*N*′,*N*″-tris(3-pyridyl)trimesic amide (**L1**) or *N*,*N*′,*N*″-tris (4-pyridyl)trimesic amide (**L2**), with three pyridylamides as functional appendages.

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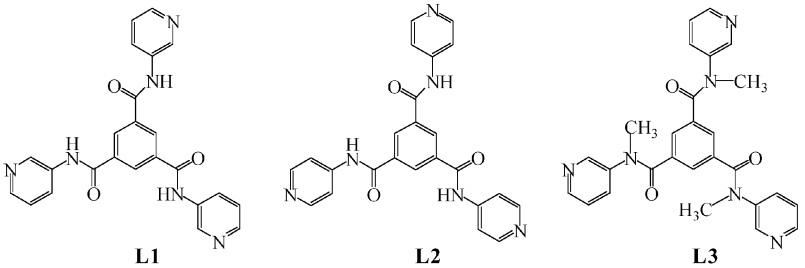
† The HTML version of this article has been enhanced with colour images.



L1 L2 L3



## Experimental

### General information

All solvents for syntheses (analytical grade) were used without further purification, and metal salts [$AgPF_6$, $CdCl_2$] were commercially available. **L1** and **L2** were prepared following literature methods.[10] Steady-state emission spectra were recorded on a SPEX Fluorolog-2 spectrophotometer.

### Synthesis of $[Ag(L1)PF_6]_n$ (1)

The reaction of **L1** (44 mg, 0.1 mmol) dissolved in MeOH with $AgPF_6$ (25 mg, 0.1 mmol) at room temperature for 30 min gave a white precipitate. Recrystallization of the crude product by diffusion of diethyl ether into a DMF solution afforded colorless crystals with a *ca.* 75% yield. FTIR (KBr): $\nu_{NH}$ 3278 and $\nu_{C=O}$ 1675 $cm^{-1}$. Anal. Calc. (%) for $C_{24}H_{18}AgF_6N_6O_3P$: C, 41.70; H, 2.62; N, 12.16. Found (%): C, 41.93; H, 2.49; N, 12.31.

### Synthesis of $[Cd(L2)_2Cl_2]_n$ (2)

$CdCl_2$ (5.5 mg, 0.03 mmol) dissolved in 2 ml $CH_3CN$ was carefully layered onto a 3 ml DMF solution of **L2** (26 mg, 0.06 mmol). Colorless crystals were obtained in two days with a *ca.* 65% yield. FT-IR (KBr): $\nu_{NH}$ 3257 and $\nu_{C=O}$ 1686 $cm^{-1}$. Anal. Calc. (%) for $C_{48}H_{36}CdCl_2N_{12}O_6$: C, 54.38; H, 3.42; N, 15.85. Found (%): C, 54.67; H, 3.22; N, 16.08.

### X-Ray crystallography

Suitable single crystals of $\mathbf{1}\cdot 3DMF$ and $\mathbf{2}\cdot 2H_2O$ were mounted on a glass capillary and data collection was carried out on a Bruker SMART CCD diffractometer with Mo-K$\alpha$ radiation (0.710 73) at 150(1) K for $\mathbf{1}\cdot 3DMF$ and at 295(2) K for $\mathbf{2}\cdot 2H_2O$, respectively. A preliminary orientation matrix and unit cell parameters were determined from three runs of 15 frames each, each frame corresponding to a 0.3° scan in 20 s, followed by spot integration and least-square refinement. Data were measured using an $\omega$ scan of 0.3° per frame for 20 s until a complete hemisphere had been collected. Cell parameters were retrieved using SMART[11] software and refined with SAINT[12] on all observed reflections. Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS.[13] The structure was solved by direct methods with the SHELXS-97[14] program and refined by full-matrix least-squares methods on $F^2$ with SHELXL-97.[15] All non-hydrogen atomic positions were located in difference Fourier maps and refined anisotropically, except solvated water and $Cl^-$ anions in $\mathbf{2}\cdot 2H_2O$. Hydrogen atoms were constrained to the ideal geometry using an appropriate riding model. Detailed data collection and refinement of the four complexes are summarized in Table 1, and selected bond distances and angles in the structures are summarized in Table 2.

CCDC reference numbers 604029 and 604030.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b604446h

## Results and discussion

The presence of $C_3$-symmetry tends to induce void space in crystals, which Nature may compensate for by producing concatenated or interpenetrated structures or by incorporation of appropriate guest molecules. Recently published single-crystal structures of **L1** and **L2** demonstrate the occurrence of N–H···N supramolecular synthons that lead to the formation of 2-D porous networks with hydrophobic channels, which are suggested to be good candidates as hydrogelators.[16] It seems that in the particular molecules of **L1** and **L2** an acceptable compromise is found between void space, concatenation of

**Table 1** Crystallographic data for $\mathbf{1}\cdot 3DMF$ and $\mathbf{2}\cdot 2H_2O$

| | $\mathbf{1}\cdot 3DMF$ | $\mathbf{2}\cdot 2H_2O$ |
|---|---|---|
| Empirical formula | $C_{33}H_{39}AgF_6N_9O_6P$ | $C_{48}H_{40}CdCl_2N_{12}O_8$ |
| $M_r$ | 910.57 | 1096.22 |
| Crystal system | Rhombohedral | Cubic |
| Space group (no.) | $R\bar{3}c$ | $Ia\bar{3}$ |
| $a$/Å | 14.7469(7) | 24.7843(4) |
| $b$/Å | 14.7469(7) | 24.7843(4) |
| $c$/Å | 59.386(3) | 24.7843(4) |
| $\alpha$/° | 90 | 90 |
| $\beta$/° | 90 | 90 |
| $\gamma$/° | 120 | 90 |
| $V$/Å$^3$, $Z$ | 11 184.5(9), 12 | 15 224.0(4), 8 |
| $F(000)$/e | 5568 | 4464 |
| $\mu$(Mo-K$\alpha$)/mm$^{-1}$ | 0.671 | 0.400 |
| $T$/K | 150(1) | 295(2) |
| Reflections collected | 35101 | 24102 |
| Indep. reflections ($F_o \geq 2\sigma(F_o)$) ($R_{int}$) | 2857 (0.088) | 2925 (0.077) |
| Refined parameters | 172 | 106 |
| Goodness-of-fit on $F^2$ | 0.970 | 1.090 |
| $R$,[a] $R_w$[b] ($I \geq 2\sigma(I)$) | 0.041, 0.075 | 0.086, 0.276 |
| $R^a$, $R_w{}^b$ (all data) | 0.069, 0.084 | 0.125, 0.311 |
| $\Delta\rho_{fin}$ (max., min.)/e Å$^{-3}$ | 0.571, −0.733 | 1.221, −0.511 |

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

**Table 2** Selected bond distances (Å) and angles (°) for **1** · 3DMF · and **2** · $2H_2O$

| **1** · 3DMF | | | |
|---|---|---|---|
| Ag(1)–N(1) | 2.253(2) | O(1)–C(6) | 1.224(3) |
| N(1)–C(5) | 1.342(3) | N(1)–C(1) | 1.343(3) |
| N(2)–C(6) | 1.361(3) | N(2)–C(4) | 1.412(3) |
| N(1)–Ag(1)–N(1A) | 119.984(3) | C(5)–N(1)–C(1) | 118.5(2) |
| C(5)–N(1)–Ag(1) | 114.38(18) | C(1)–N(1)–Ag(1) | 126.98(18) |
| **2** | | | |
| Cd(1)–N(1) | 2.381(4) | O(1)–C(3) | 1.222(7) |
| N(1)–C(4) | 1.330(7) | N(1)–C(8) | 1.341(7) |
| N(2)–C(3) | 1.346(8) | N(2)–C(6) | 1.387(7) |
| N(1A)–Cd(1)–N(1) | 91.22(15) | N(1)–Cd(1)–N(1B) | 88.78(15) |
| N(1)–Cd(1)–N(1C) | 180 | | |

molecules and inclusion of guests. Surprisingly, unlike some tridentate ligands (*e.g.* 1,3,5-triazine,[17,18] 1,3,5-tricyanobenzene,[17] 1,3,5-tris(ethynylbenzonitrile)benzene,[19–21] or tris(4-pyridyl)triazine[22]), the pyridylamide based ligands **L1** and **L2** studied here represent rare examples to carry out crystal-engineering studies. A methanolic solution of equimolar $AgPF_6$ and **L1** was stirred to give a white precipitate of **1**. Recrystallization of the crude product by diffusion of diethyl ether into a DMF solution afforded colorless crystals of **1** · 3DMF in 75% yield. An acetonitrile solution of $CdCl_2$ was carefully layered onto a DMF solution of **L2**, whereupon colorless crystals of **2** · $2H_2O$ were obtained in 65% yield within a couple of days. The compounds are all air stable and photoluminescent in the solid state.

## Description of crystal structures

Compounds **1** and **2** have been isolated and their molecular structures determined by the X-ray diffraction study with their respective space groups being $R\bar{3}c$ and $Ia\bar{3}$, and confirmed the formation of 2-D and 3-D coordination polymers in the solid state, respectively. In Fig. 1(a), each $Ag^I$ center with threefold symmetry is coordinated by three nitrogen atoms from three **L1** in a trigonal-planar geometry, where the $C_3$ axis passes through the center of phenyl rings of **L1**, and such a connection mode in combination with tridentate bridging **L1** makes **1** a 2-D coordination network as shown in Fig. 1(b). Each $Ag^I$ center also shows weak interactions with three F atoms (3.110 Å) on one side of the trigonal plane and the benzyl moiety (the

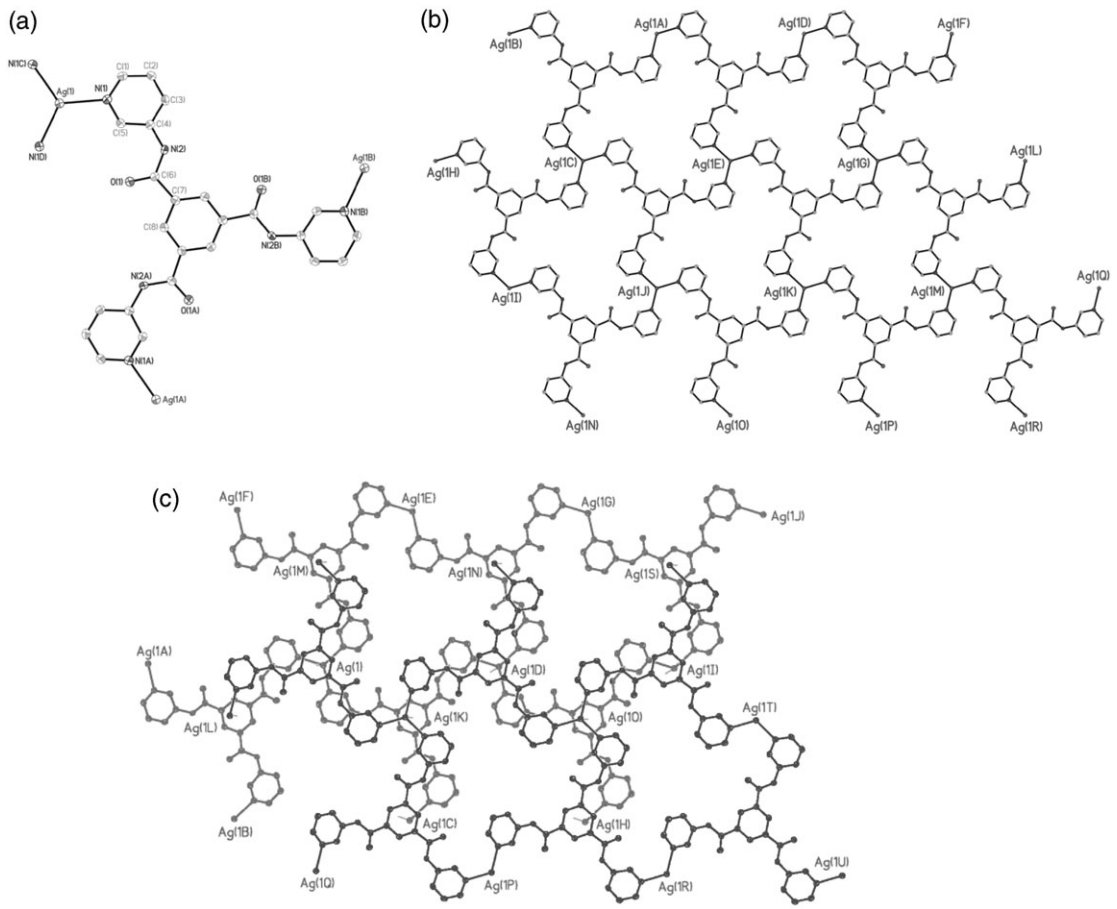



**Fig. 1** (a) Molecular structure of complex **1**. The ORTEP diagram shows 50% probability ellipsoids, (b) its two-dimensional extended framework with solvates omitted for clarity (viewing through the *c* axis) in the solid state, and (c) the inter-sheet dimeric structure based on the $Ag^I \cdots \pi$ interaction of 3.209 Å. For Ag(1A), Ag(1B) and another 2/3 **L1** (moieties A and B) have the symmetry elements: $(x - y, -x, +z)$, $(-y, x - y, +z)$. For the next layer, the symmetry element is $(-x + y + 1/3, y + 2/3, z + 1/6)$.

distance of the $Ag^{I}\cdots$centroid of benzene is 3.209 Å, where the sum of the van der Waals radii is 3.42 Å) on the other side. Indeed, the $Ag^{I}\cdots\pi$ interaction in not uncommon in some $Ag^{+}$ complexes,[17,18,23] but this does increase the supramolecular complexity by inducing the formation of the inter-sheet dimerization as shown in Fig. 1(c), in spite of the absence of the $Ag^{I}\cdots Ag^{I}$ interaction, a common phenomenon in $d^{10}$-metal systems.[24] The $PF_6^-$ anions also with three-fold symmetry and DMF solvates are filled into the interstices between the dimerized sheets. Significantly, the 48-membered macrocycles constructed from three-coordinate $Ag^{I}$ ions as connectors and three pyridylamide moieties propagate into the 2-D extended structures, and the structure is reminiscent of the novel structural framework based on the $Ag^{I}$ complex of 1,3,5-tris(3-ethynylbenzonitrile)benzene reported by Lee and coworkers,[17] where it shows an interesting zeolite-like behavior of a coordination network. Hydrogen-bonding interactions between the amide moiety of **L1** and DMF [N(2)–H(2A)$\cdots$O(2): N(2)$\cdots$O(2) 2.856 Å, N(2)–H(2A)$\cdots$O(2), 160.1°] are observed in the solid state.

It is noted that in the case of 1,3,5-benzene tricarboxamide with three *N*-methylaniline groups (**L3**), all three anilide substituents were found to be orientated to the same side of the central benzene, denoted the "methyl amide effect".[25] The ligand's structure showed that the three carbon atoms *meta* to the amide groups are close to the central $C_3$-axis. Substitution with nitrogen atoms in these positions would clearly aid to adopt a tripodal form for the ligands. Thus, this orientation of the ligands could be rigidly fixed to lead to the formation of tetrahedral or octahedral complexes. Due to the "methyl amide effect", the N-methylated 1,3,5-benzene tricarboxamide can only form a mononuclear complex with $Ag^{I}$ ions, where the $C_3$ ligand acts as a tridentate chelate ligand. Different from the convergent coordination mode for N-methylated 1,3,5-benzene tricarboxamide, the reaction of **L1** and $Ag^{I}$ ions form the 2-D network, since **L1** adopts a tridentate bridging and divergent coordination mode.

The molecular structure and its extended structural framework of **2** are shown in Fig. 2. Unlike the 2-D sheet structure for **1**, **2** forms an interesting 3-D coordination network with octahedral $Cd^{II}$ ions coordinating to six nitrogen atoms from six tripyridyltriamides **L2** as shown in Fig. 2(b). Significantly, these open channels with a diameter of *ca.* 7.5 Å containing the tripyridyltriamide moieties propagating into the 3-D extended structures make this 3-D coordination framework potentially a functional material. Indeed, this represents an interesting example of 3-D molecular materials containing the tripyridyltriamides as functional moieties inside the channels.[26] In addition, there are disordered water molecules and $Cl^-$ anions existing in the channels, where the latter are appended in the channels through hydrogen-bonding interactions with the amide moieties [N(2)–H(2A)$\cdots$Cl(1): N(2)$\cdots$Cl(1) 2.920 Å, N(2)–H(2A)$\cdots$Cl(1) 162.1°].[27] However, although **2** has a high *R*-value due to the crystal quality, there is no doubt that the structural framework of **2** can be still corroborated by the X-ray diffraction study. The thermal stability has also been examined by TGA analysis and is shown in Fig. 3. The weight loss is around 3.87% upon heating the sample to 110 °C, which is consistent with the calculated weight loss of 3.29%

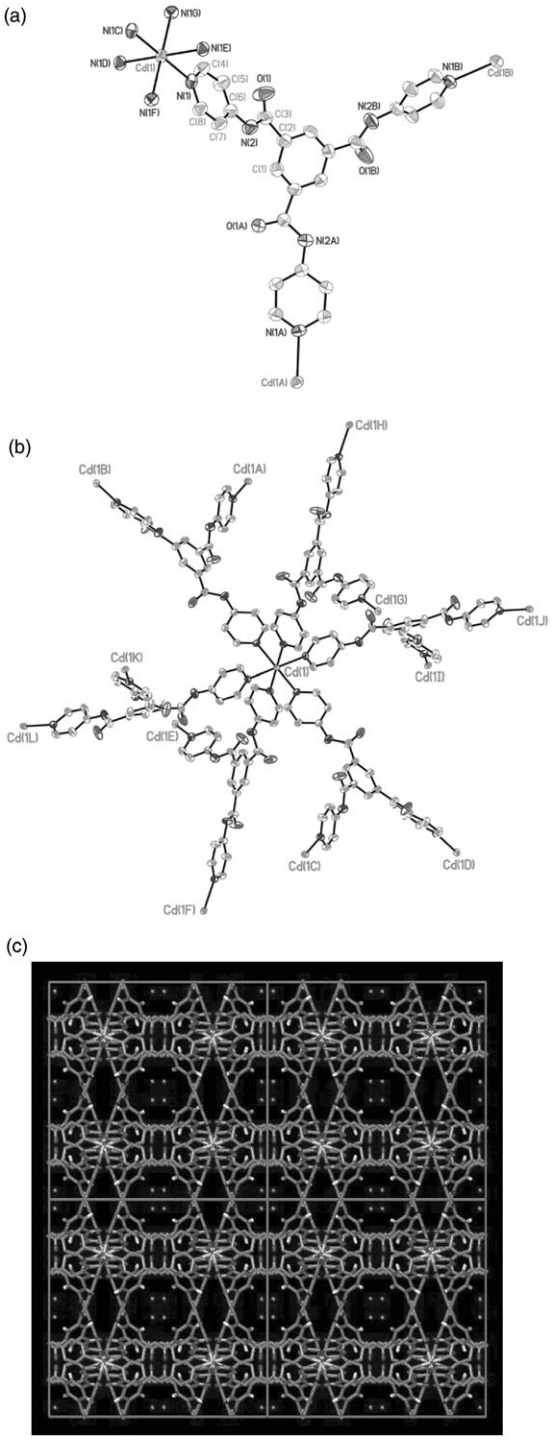



**Fig. 2** (a) Molecular structure of complex **2**. ORTEP diagram shows 50% probability ellipsoids, (b) the three-dimensional extended framework, and (c) the stick model showing the channel structures in the solid state with chloride anions and water molecules (omitted for clarity) in the channels. For Cd(1A), Cd(1B) and another 2/3 **L1** (moieties A and B) have the symmetry elements: ($z + 1/2$, $-x + 1/2$, $-y + 1$), ($-y + 1/2$, $-z + 1$, $x + 1/2$). For the Cd coordination geometry, C, D, E, F and G have the symmetry elements: ($-x + 1/2$, $-y + 1/2$, $-z + 1/2$), ($-z + 1$, $x + 1/2$, $-y + 1/2$), ($z - 1/2$, $-x$, $y$), ($y + 1/2$, $-z + 1/2$, $-x + 1$), ($+y$, $-z$, $x - 1/2$).

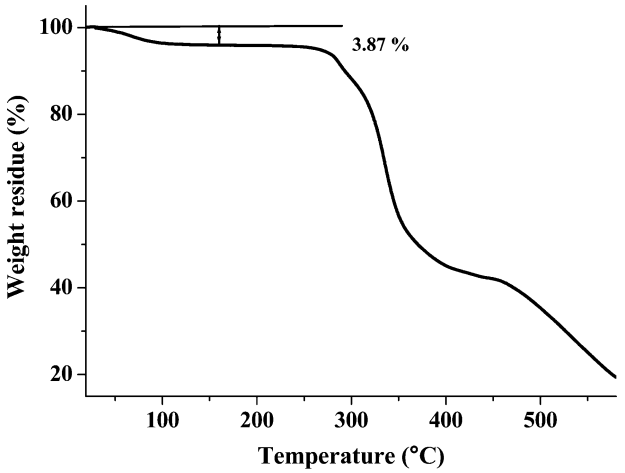



**Fig. 3** TGA analysis of **2**.

for two water molecules. After 260 °C, **2** starts to decompose and the weight loss greatly increases.

In this study, it is interesting to find that given the different metal ions ($Ag^{I}$ or $Cd^{II}$) reacting with 3-pyridyl- or 4-pyridyl-triamides, the structural motif dramatically changes and the supramolecular complexity increases upon a coordination geometry change for metal ions from trigonal planar (three-coordinate) $Ag^{I}$ to octahedral (six-coordinate) $Cd^{II}$ ions. Unlike the tetradentate ligand 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrakis(pyridin-4-yl)amide with a flexible cyclen moiety as a core,[7] the benzyl moieties of **L1** and **L2** represent a rigid core in contributing to construct robust structural frameworks such as **2**.

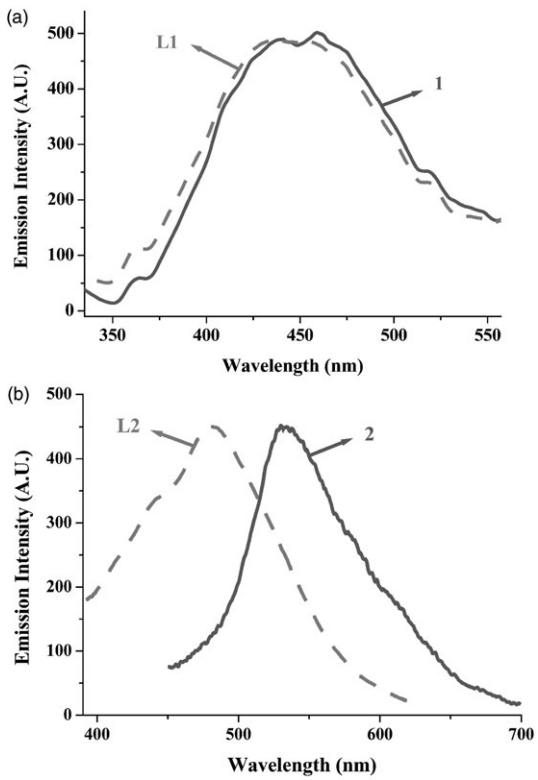



**Fig. 4** The solid-state emission spectra of (a) **L1** and **1** and (b) **L2** and **2** measured at room temperature with an excitation wavelength at 300–330 nm.

### Solid-state emission spectra

**L1**, **L2**, **1** and **2** are all luminescent in the solid state, and the solid-state emission spectra were measured with solid samples at room temperature. Upon photoexcitation at 300 nm, **L1** shows a broad emission with a maximum at *ca.* 450 nm, whereas **1** displays a similar emission also at *ca.* 450 nm. Given the close similarity between these emissions, it seems reasonable that the excited state responsible for the emission for **1** is ascribed to an intraligand transition (IL). More importantly, **2** shows a low-energy emission with a maximum at *ca.* 532 nm upon photoexcitation at 330 nm, whereas **L2** displays only a blue-shifted one at *ca.* 482 nm as shown in Fig. 4. Given a significant red shift from **L1** to **2**, the low-energy emission at *ca.* 532 nm is unlikely to originate purely from **L2** itself (IL). With reference to the literature and our earlier study,[28] this low-energy emission could be tentatively assigned as a metal-to-ligand charge-transfer (MLCT) transition. However, the IL transition mixing with MLCT can not be excluded.

## Conclusions

A interesting family of tripyridyltriamides (**L1** and **L2**) have been utilized as tridentate bridging ligands to carry out crystal-engineering studies. **1** forms a 2-D coordination polymer upon reaction of $AgPF_6$ with **L1**, and each $Ag^{I}$ center shows weak interactions with three F atoms on one side of the trigonal plane and the benzyl moiety on the other side. The $Ag^{I}\cdots\pi$ interaction increases the supramolecular complexity by inducing the formation of inter-sheet dimerization. The 48-membered macrocycles constructed from three $Ag^{I}$ ions and three tripyridyltriamide moieties propagate into 2-D extended structures. The reaction of $CdCl_2$ and **L2** leads to the formation of a 3-D coordination network in the solid state. These open channels with a diameter of *ca.* 7.5 Å containing the tripyridyltriamide moieties propagate into the 3-D extended structures. This is an interesting example of 3-D coordination networks containing the tripyridyltriamides as functional moieties inside the channels. Complex **1** displays a high-energy emission with a maximum at *ca.* 450 nm, whereas **2** shows a low-energy emission with a maximum at *ca.* 532 nm. When compared with those of **L1** and **L2**, the *ca.* 450 nm emission of **1** is assigned to an intraligand transition whereas that of **2** at *ca.* 532 nm is tentatively ascribed to a metal-to-ligand charge-transfer transition based on a significant red shift from **L2** to **2** and literature studies.[22] However, the IL transition mixing with MLCT can not be excluded.

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