Syntheses, crystal structures and photoluminescent properties of two novel Ag(i) coordination polymers with benzoguanamine and pyrazine-carboxylate ligands: From 1D helix to 1D → 2D interdigitation†

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Two novel coordination polymers (CPs) \([\text{Ag(bga)(pzc)}] \cdot 0.5\text{H}_2\text{O}]_n\) (1) and \([\text{Ag}_2(\text{bga})_2(\text{pzdc})(\text{H}_2\text{O})]_n\) (2) (bga = benzoguanamine, Hpzc = pyrazine-2-carboxylic acid, Hpzdc = pyrazine-2,3-dicarboxylic acid), have been prepared and characterized. Single-crystal X-ray structural analysis reveals that complex 1 is a novel 1D single-strand helical chain constructed from \(\mu_2-N^\prime\)-bga and \(\mu_1-(\eta_2-N,O)\)-pzc ligands. Complementary N–H···N hydrogen bonds link the alternate left- and right-handed helical chains to form the final racemic 2D supramolecular sheet. Complex 2 is a 1D U-shaped chain with \(\mu_1-N\)-bga and \(\mu_2-(\eta_2-N,O), N^\prime, (\eta_2-O^\prime,O^\prime')\)-pzdc ligands. Each U-shaped single chain containing \([\text{Ag}_2(\text{bga})_2(\text{pzdc})(\text{H}_2\text{O})]_n\) subunits is staggered along the \(c\) axis producing large interstices between adjacent bga ligands which accommodates two identical chains from both sides by interdigitation of the dangling bga ligands, producing a 1D → 2D interdigitated supramolecular sheet through complementary N–H···N hydrogen bonds. The structural dissimilarity between 1 and 2 is caused by the different auxiliary pyrazine-carboxylate ligands and different coordination modes of bga ligand. The complementary N–H···N hydrogen bonds play prominent roles in the formation of the final racemic 2D supramolecular sheet of 1 and 1D → 2D interdigitated sheet of 2. In addition, the thermal stabilities and emissive behaviors of them were also investigated.

1. Introduction

The continuing interest in the crystal engineering of coordination polymers (CPs) not only originates from their potential applications in catalysis, storage, conduction, non-linear optics (NLO), luminescence, ferroelectricity and magnetism, but also from their fascinating architectures and topologies. Compared to the simple coordination networks, a large number of appealing interpenetrated networks have been crystallographically characterized and well discussed in two comprehensive reviews by Batten. Nevertheless, despite substantial advances in the above fields, other types of entanglements including 1D infinite multiple helices, 2D warp-and-woof sheets, interdigitated structures, and polymeric analogues of catenanes and rotaxanes as well as Borromean links, are relatively sparse. Therefore, the rational exploration of novel entangled CPs still remains a long-term challenge, and in-depth research is necessary to enrich and develop this field.

On the other hand, Ag(i)-containing coordination complexes have attracted considerable attention due to the unpredictable coordination preferences of the metal center and the formation of significant Ag···Ag interaction, or so-called argentophilic, which largely contributes to the formation of fascinating silver aggregations and associates with photoluminescent properties. As excellent hydrogen donors and acceptors, aminotriazines and their derivatives have been widely used for the formation of supramolecular structures using complementary N–H···N hydrogen bonds. Benzoguanamine (bga) is a bulky aryl-substituent aminotriazine which can coordinate up to five metal centers and may exhibit miscellaneous metal binding patterns such as the endocyclic nitrogen atom or the exocyclic nitrogen atom of the amino group, occasionally in equilibrium, and simultaneously both positions, either in a chelating or bridging fashion, as evidenced by our and other group’s work. Moreover, the presence of the amino groups of bga could form complementary N–H···N hydrogen bond with the endocyclic nitrogen atom. The rigid aromatic phenyl ring on bga has the potential to generate π···π stacking, C–H···π and Ag···π interactions, which have great significance in the crystal packing and influence the architecture of the resulting crystal structure. Furthermore, the free rotation of the phenyl ring along the C–C
single bond can result in different steric effects influencing the coordination modes of the triazinyl ring. It is also noteworthy that the electron-deficient heteroaromatic triazine is a good candidate as a \( \pi \)-acidic system to form anion-\( \pi \) interactions\(^{16} \) based on experimental and extensive theoretical studies, when endocyclic nitrogen atoms coordinate with metal centers. The heterocycle aromatic carboxylates are also widely utilized as excellent ligands for building CPs due to their diverse coordination modes.\(^{17} \) In spite of the enthralling structures and properties that have been reported for Ag(i) CPs,\(^{18} \) the Ag(i)-bga CPs,\(^{19} \) especially Ag(i)-bga incorporating an auxiliary ligand system, are largely unexplored yet. Up to now, numerous mixed-ligand coordination networks\(^{20} \) have been successfully obtained, which indicates that the introduction of auxiliary ligands into a metal/N-donor system often realizes the structural modulation and affords unexpected networks.

Based on the above-mentioned points and as an extension of our previous work,\(^{21} \) herein we focus on the self-assembly of silver(I) and bga combining heterocycle aromatic carboxylates as auxiliary ligands and obtained two novel CPs, namely, \([\text{Ag(bga)}(\text{pzdc})]_{n} \cdot 0.5\text{H}_{2}\text{O}]_{n} \) (1) and \([\text{Ag}_{2}\text{(bga)}_{2}(\text{pzdc})(\text{H}_{2}\text{O})]_{n} \) (2) (bga = benzoguanamine, Hpzc = pyrazine-2-carboxylic acid, H\(_{3}\)pzdc = pyrazine-2,3-dicarboxylic acid), which show a 1D helical chain and a 1D \( \rightarrow \) 2D interdigitated supramolecular sheet, respectively (Scheme 1).

2. Experimental

2.1. Materials and methods

All chemicals and solvents used in the syntheses were of analytical grade and used without further purification. IR spectra were measured on a Nicolet 330 FTIR Spectrometer at the range of 4000–400 cm\(^{-1} \). Elemental analyses were carried out on a CE instruments EA 1110 elemental analyzer. X-ray powder diffractions were measured on a Panalytical X-Pert pro diffractometer with Cu-K\( \alpha \) radiation. Thermogravimetric analyses were performed on a NETZSCH TG 209 F1 Iris\(^{\circledR} \) Thermogravimetric Analyser from 30 to 800 °C at a heating rate 10 °C min\(^{-1} \) under a N\(_{2}\) atmosphere (20 mL min\(^{-1} \)).

2.2. Syntheses

2.2.1. Synthesis of \([\text{Ag(bga)}(\text{pzdc})]_{n} \cdot 0.5\text{H}_{2}\text{O}]_{n} \) (1). Reaction of Ag\(_{2}\)O (46 mg, 0.2 mmol), Hpzc (25 mg, 0.2 mmol) and bga (37 mg, 0.2 mmol) in water–ethanol–methanol–DMF (9 mL, v/v/v/v: 2/4/2/1) in the presence of ammonia (0.8 mL) under ultrasonic treatment (160 W, 40 kHz, 50 °C). The resultant solution was allowed to evaporate slowly in darkness at room temperature for several days to afford the product as colorless crystals of 1. Yield: ca. 48% based on Ag. Elemental analysis: anal. calc. for Ag\(_{2}\)C\(_{2}\)H\(_{2}\)N\(_{14}\)O\(_{5}\): C 39.36, H 3.07, N 22.95%. Found: C 39.37, H 3.52, N 21.69%. Selected IR peaks (cm\(^{-1} \)) = 3424 (s), 3313 (m), 1941 (s), 1825 (w), 1710 (w), 1622 (s), 1536 (m), 1421 (m), 1394 (m), 1020 (w), 825 (w), 814 (w), 781 (w), 689 (w).

2.2.2. \([\text{Ag}_{2}\text{(bga)}_{2}(\text{pzdc})(\text{H}_{2}\text{O})]_{n} \) (2). The synthesis of 2 was similar to that of 1, but used H\(_{2}\)pzdc (34 mg, 0.2 mmol) instead of Hpzc. Yellow crystals of 2 were obtained in 43% yield based on Ag. Elemental analysis: anal. calc. for Ag\(_{2}\)C\(_{2}\)H\(_{2}\)N\(_{12}\)O\(_{5}\): C 37.23, H 3.07, N 22.95%. Found: C 37.28, H 3.52, N 21.69%. Selected IR peaks (cm\(^{-1} \)) = 3415 (s), 3295 (s), 3164 (s), 1618 (s), 1544 (s), 1404 (m), 1341 (w), 1108 (w), 825 (w), 814 (w), 781 (w), 688 (w), 627 (w).

2.3. X-ray crystallography

Single crystals of the complexes 1 and 2 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 for 1 were collected on a Rigaku R-AXIS RAPID Image Plate single-crystal diffractometer with graphite-monochromated Mo-K\( \alpha \) radiation source (\( \lambda = 0.71073 \) A) operating at 50 kV and 90 mA in \( \omega \) scan mode. A total of 44 \( \times \) 5.00° oscillation images was collected, each being exposed for 100 s. The cell refinement and data reduction for 1 were accomplished with the PROCESSAUTO processing program.\(^{22} \) Absorption correction was applied by correction of symmetry-equivalent reflections using the ABSCOR program.\(^{23} \) Data for 2 were collected on a Bruker-AXS CCD single-crystal diffractometer with graphite-monochromated Mo-K\( \alpha \) radiation source (\( \lambda = 0.71073 \) A). A preliminary orientation matrix and unit cell parameters were determined from 3 runs of 20 frames each, each frame corresponds to a 0.3° scan in 5 s, followed by spot integration and least-squares refinement. For 2, data were measured using \( \omega \) scans of 0.3° per frame for 10 s until a complete hemisphere had been collected. Cell parameters were retrieved using SMART software and refined with SAINT on all observed reflections.\(^{24} \) Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS.\(^{24} \) In all cases, the highest possible space group was chosen. All structures were solved by direct methods using SHELXS-97\(^{25} \) and refined on \( F^2 \) by full-matrix least-squares procedures with SHELXL-97.\(^{26}\) Atoms were located from iterative examination of difference \( F \)-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 times \( U_{eq} \) of the attached C or N atoms. The hydrogen atoms attached to the oxygen atom of water were refined with O–
Goodness–of–fit on indices (all data)

geometry of Ag(I) is not necessarily predictable when the coordination number is well defined, the coordination hindrance of the phenyl ring (Fig. S1†, ESI). As we know, even /C23 and 1.07 two perpendicular distances between the plane and Ag1 of 0.93 of the triazinyl ring and displace out the triazinyl plane giving A pair of symmetry-related Ag1 ions are located in the two sides resulting in a distorted tetrahedral geometry (Ag1–N5 = 2.284 (2), Ag1–N1 = 2.357(2), Ag1–N4 = 2.491(2) and Ag1–O2 = 2.425(2) Å). The distortion of the tetrahedron can be indicated by the calculated value of the t4 parameter introduced by Houser28 to describe the geometry of a four-coordinated metal system, which is 0.65 for Ag1 (for perfect tetrahedral geometry, t4 = 1). The Ag–N and Ag–O bond lengths fall in the normal ranges and are comparable to the related complexes.19 It can be clearly seen that the phenyl and triazinyl rings of the bga are not located in the same plane and the corresponding interplanar angle is 39.9°. A pair of symmetry-related Ag1 ions are located in the two sides of the triazinyl ring and displace out the triazinyl plane giving two perpendicular distances between the plane and Ag1 of 0.93 and 1.07 Å, respectively, which may be caused by the steric hindrance of the phenyl ring (Fig. S1†, ESI). As we know, even when the coordination number is well defined, the coordination geometry of Ag(i) is not necessarily predictable29 because the Ag (i) ion is expected to have a coordination geometry dominated by steric factors. The shortest Ag⋯Ag separation is 6.26 Å which is twice as long as the van der Waals radii for Ag (3.44 Å), precluding any argentophilic interaction in 1.10a

Further analyzing the crystal packing of the molecules, we found the existence of the closest contacts between Ag and the phenyl ring of bga which is associated with the C10 and C14 atoms (Fig. S2†). To the best of my knowledge, many Ag(i)-PAH (polycyclic aromatic hydrocarbon) complexes have been reported and show that arenes usually function as neutral π donors to exhibit the πe coordination mode.30 In 1, the closest Ag⋯C (Ag1⋯C10) contact is 3.017(3) Å which falls within the normal ranges reported for the related complexes.31 In spite of the fact that the second closest Ag⋯C contact (Ag1⋯C14 = 3.151(3) Å) is slightly longer compared to those found for Ag(i)-PAH complexes, it is still shorter than the sum of the van der Waals radii of the Ag(i) ion and carbon atom (3.42 Å).32 In accordance with the previously documented Ag(i)-PAH complexes, Ag(i) preferred to ligate at the shortest C⋯C bond due to the high

### Table 1 Crystal data for 1 and 2

<table>
<thead>
<tr>
<th>Complex</th>
<th>1</th>
<th>2</th>
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<tr>
<td>Formula</td>
<td>Ag_{2}C_{3}H_{15}N_{14}O_{5}</td>
<td>Ag_{2}C_{2}H_{12}N_{11}O_{5}</td>
</tr>
<tr>
<td>M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystal system</td>
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<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
<td>C2/c</td>
</tr>
<tr>
<td>a/A</td>
<td>23.8597(8)</td>
<td>49.174(8)</td>
</tr>
<tr>
<td>b/A</td>
<td>7.2670(2)</td>
<td>8.9007(15)</td>
</tr>
<tr>
<td>c/A</td>
<td>19.5048(10)</td>
<td>12.382(2)</td>
</tr>
<tr>
<td>β (°)</td>
<td>117.7130(10)</td>
<td>92.613(3)</td>
</tr>
<tr>
<td>V/A³</td>
<td>2993.96(18)</td>
<td>5288.4(15)</td>
</tr>
<tr>
<td>Z</td>
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<td>F(000)</td>
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</tr>
<tr>
<td>µ/mm⁻¹</td>
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<td>1.544</td>
</tr>
<tr>
<td>Ref. collected/unique</td>
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<td>12148/5110</td>
</tr>
<tr>
<td>Rint</td>
<td>0.0300</td>
<td>0.0367</td>
</tr>
<tr>
<td>Final R indices [I &gt; 2σ(I)]</td>
<td>R1 = 0.0223 wR2 = 0.0615</td>
<td>R1 = 0.0666 wR2 = 0.1718</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0253 wR2 = 0.0790</td>
<td>R1 = 0.0684 wR2 = 0.1732</td>
</tr>
<tr>
<td>Goodness–of–fit on F²</td>
<td>1.195</td>
<td>1.087</td>
</tr>
</tbody>
</table>

a R1 = Σ||Fobs| − |Fcal||/Σ|Fobs|, wR2 = [Σw(Fobs² − Fcalc²)]/Σw(Fobs²)]²/2.
The fascinating feature of complex 1 is that the 1D helical chains run through the solid state structure (Fig. 1b). The $\mu_2$-N,N'-bga links the Ag(i) to form a 1D single-stranded helix along the 2$_1$ screw axis. The formation of a helical chain in 1 may be attributed to a favorable combination of the skewed conformer of bga and the suitable geometry around the N–Ag–N bond. The helical pitch, defined by the distance between equivalent atoms generated by one full rotation of the crystallographic 2$_1$ screw axis, is 7.27 Å, which is equal to the b-axis length. The $\mu_1$-(N$_{12}$-N, O)-pzdc ligands bound to the Ag(i) ions point away from the helical chain and do not contribute to the extension of the 1D helical chain to any higher dimensionalities. Within the 1D helical chain, the N–H···O hydrogen bonds (N7–H7C···O2$^\ast$ = 2.898(3) Å, Fig. S3†), Ag···C interaction and face-to-face $\pi$···$\pi$ stacking (Cg1···Cg2$^\ast$ = 3.5720(17) Å and Cg1···Cg2$^\ast$ = 3.7080(17) Å, Cg1 and Cg2 are centroids of rings N3/C6/N4/C8/N5/C7 and C9–C14, respectively, Fig. S4†) coexist and cooperatively contribute to the stability of the resulting 1D helical chain. The alternate left- and right-handed helical chains interact with each other through complementary N–H···N hydrogen bonds (centrosymmetric $R_2^2$(8) motif) with the N6···N3$^\ast$ distance of 3.046(3) Å, leading to the formation of racemic 2D supramolecular sheet (Fig. 1c). The adjacent sheets interdigitated with each other to form a 3D framework through $\pi$···$\pi$ stacking between pyrazinyl rings with the Cg···Cg distance of 3.5359(17) Å and a slippage of 1.44 Å (Fig. S5†). Uncordinated water molecules function as guests and hydrogen bonds between them and pzc are formed (Table S1†). (Symmetry codes: (ii) $-x + 3/2$, $-y + 1/2$, $-z + 3/2$; (v) $-x + 3/2$, $y + 1/2$, $-z + 3/2$; (vi) $-x + 3/2$, $y - 1/2$, $-z + 3/2$.)

Fig. 1 (a) The coordination environment of the Ag(i) ion and the linkage modes of ligands in 1 with 50% thermal ellipsoid probability. Hydrogen atoms and solvents are omitted for clarity. (b) Perspective views of the 1D helical structures of 1. (c) The 2D supramolecular sheet constructed from complementary N–H···N hydrogen bonded alternate left- and right-handed helices along the b axis. (Symmetry code: (i) $-x + 3/2$, $y - 1/2$, $-z + 3/2$).

3.2. Structure description of [Ag$_2$(bga)$_2$(pzdc)(H$_2$O)$_2$]$_n$ (2)

X-ray crystallography of a crystal of 2 revealed that it crystallizes into the same space group as that of 1. The asymmetric unit of 2 consists of two crystallographically independent Ag(i) ions, two bga ligands, one pzdc and one coordinated water molecule. As shown in Fig. 2a, the Ag1 is coordinated by two N atoms (one N$_{bga}$ and one N$_{pzdc}$) and two O atoms from the same pzdc. The

Fig. 2 (a) The coordination environment of the Ag(i) ions and the linkage modes of ligands in 2 with 50% thermal ellipsoid probability. Hydrogen atoms are omitted for clarity. (b) Perspective views of the 1D single chain of 2 with large interstices (Symmetry code: (i) $x$, $-y + 2$, $z + 1/2$).
Ag2 is also coordinated by two N atoms and two O atoms, but two O atoms are from pdzc and water molecule, respectively. The average Ag–N and Ag–O bond lengths are 2.224(7) and 2.548(6) Å, respectively. Both Ag1 and Ag2 adopt distorted tetrahedral coordination geometries with the bond angles spanning from 66.88(18) to 159.5(2) and 70.8(2) to 156.7(3)°, respectively. The τd parameter is 0.69 for Ag1 and 0.47 for Ag2, respectively. In 2, the phenyl and triazinyl rings of two bga ligands are approximately coplanar with two small interplanar angles of 8.7° and 12.1°, respectively. Differently, two Ag(i) ions in 2 coordinate to bga with a nearly coplanar conformation. The small interplanar angles between the phenyl and triazinyl rings of bga and coplanar coordination fashion can be attributed to the small steric effect of unidentate bga ligand in 2. The short Ag···C contacts are also observed. (Ag1–C21 vi = 3.100(10) and Ag1–C20vi = 3.347(9) Å). (Symmetry codes: (vi) x, y – 1, z).

The μ1-N-bga and μ2-(η2-N,O), N', (η2-O',O'')-pzdc ligands complete a [Ag3(bga)2(pzdc)(H2O)] subunit which is linked by a η2-O',O'' carboxyl group to form a U-shaped 1D chain (Fig. 2b). In the 1D chain, the [Ag3(bga)2(pzdc)(H2O)] subunits are staggered along the c axis producing large interstices between adjacent bga ligands with an approximately width of 10 Å. The large significant interstices within a single chain could be effectively occupied by adjacent identical chains through mutual interdigitation, which belongs to one of three distinctly different strategies, namely, interdigitation, interpenetration and intercalation of guests, to circumvent the void in the crystal packing.

The most striking structural feature of 2 is that each single 1D chain is chemically independent but physically interdigitated with the same independent chains in two inverse directions, whose unique entangled mode can be described stepwise.

Firstly, each U-shaped single chain has a depth and width of 11 and 16 Å (Fig. 3a), respectively, and simultaneously interdigitates with its two neighbours located left and right through complementary N–H···N hydrogen bonds (N9–H9C···N6m = 3.034(10) and N10–H10C···N7m = 3.033(10) Å), as a result, a 1D → 2D interdigitated sheet along the bc plane is formed (Fig. 3b). Secondly, the 2D sheet interdigitates with its opposite one to form a 2D double sheet (thickness, ca. 25 Å) through another complementary N–H···N hydrogen bond (N4–H4A···N2h = 3.086(10) Å) along the a axis (Fig. 3c and Fig. S6†). Therefore, complex 2 represents a new example of interdigitation, that is a progression from a 1D single chain, to a 2D single supramolecular sheet, to finally a 2D double supramolecular sheet. In 2, complementary hydrogen bonds play a significant direction role in the resulting 1D → 2D interdigitated sheet which has not been documented before. To the best of our knowledge, in natural systems, complementary hydrogen bonding between base pairs plays an important role in the construction of the double helix of DNA, but the artificial complementary hydrogen bonding system, especially complementary hydrogen bonding directed entangled structure, is still lacking. (Symmetry codes: (ii) x, y + 1, z; (iii) x, y + 3, z + 1/2; (iv) x, y + 3, z – 1/2)

3.3. Structural comparison of 1 and 2

As is shown in the descriptions above, two novel silver(I) CPs 1 and 2 with benzoguanamine and different heterocycle aromatic dicarboxylates were successfully synthesized and characterized. Based on the X-ray analysis results, both 1 and 2 are shown to be 1D infinite chains with different structural motifs ranging from a 1D helical chain to 1D U-shaped chain which not only indicates that the introduction of different auxiliary heterocycle aromatic dicarboxylates into the silver/bga system, but also that the different coordination modes of benzoguanamine play important roles in determining the final structures of 1 and 2 (Scheme 2).

For 1, the bidentate μ2-η1-N, η′-bga obliquely extend the Ag(i) into a 1D helical chain and μ1-(η2-N,O)-pzc functions as a chelating ligand dangling on the 1D helical chain which does not contribute to any extension of the 1D chain. For 2, bga changes to a unidentate ligand, while pdzc has one more carboxyl groups than pzc ligand and is a chelating/bridging ligand with a coordination mode of μ1-(η2-2N,O), N', (η2-O',O''). Two bridging N sites link the Ag(i) ions to form [Ag4(bga)2(pzdc) (H2O)] subunits which are extended to a 1D U-shaped chain by chelating O atoms of the pdzc ligand. It is also noteworthy that remarkable complementary N–H···N hydrogen bonds play a crucial role in the formation of the 2D racemic supramolecular sheet in 1 and the 1D → 2D interdigitated supramolecular sheet.

![Fig. 3](image-url)  
(a) Perspective view of a 1D single chain along the c axis. (b) 2D single sheet formed by interdigitation of a 1D chain. (c) 2D double sheet formed by interdigitation of a 2D single sheet.

![Scheme 2](image-url)  
Coordinations modes of bga and heterocycle aromatic dicarboxylates.
in 2. In other words, the different auxiliary heterocycle aromatic dicarboxylates as well as bga with different coordination modes significantly contributed to the different structures of 1 and 2.

3.4. FT-IR spectra, X-ray powder diffraction analyses and thermogravimetric analyses

The IR spectra (Fig. S7†) display absorption bands around 3410, 3300 and 3180 cm⁻¹, respectively, attributable to the ν(O–H) vibration of the water molecule and ν(N–H) vibration of the amino group in both 1 and 2. Both complexes exhibit characteristic asymmetric (νas) and symmetric (νs) absorptions of the carboxylate groups. The difference between νas and νs (Δ = νas−νs) has been widely used to discriminate between the unidentate, chelating (bidentate) and bridging coordination mode of the carboxyl group. Generally, the unidentate carboxylate exhibits a much larger Δ value than the chelating one, and the value for the bridging mode is intermediate. In 1 and 2, the νas(COO) and νs(COO) vibrations appear as strong bands at about 1620 and 1410 cm⁻¹, respectively. The large Δ value (νas−νs = 210 cm⁻¹) is consistent with the unidentate coordination mode of the carboxyl group, as revealed by structural analysis.

Powder X-ray diffraction (PXRD) has been used to check the phase purity of the bulky samples in the solid state (Fig. 4). For complexes 1 and 2, the peak positions of simulated and experimental patterns are in good agreement with each other, demonstrating the phase purity of the product. The dissimilarities in intensity may be due to the preferred orientation of the crystalline powder samples.

Thermogravimetric (TG) measurements were performed in a N₂ atmosphere on polycrystalline samples of complexes 1 and 2 and the TG curves are shown in Fig. 5. The TGA curve of 1 displays a weight loss of 2.37% (calcd: 2.11%) at 70–135 °C, corresponds to complete loss of lattice water molecules. The higher observed temperature than the boiling point of water is attributed to the presence of hydrogen bonds between the network and water molecules. Its framework is stable to 220 °C and then the framework begins to collapse. Complex 2 shows a first weight loss of 1.35% at 80–190 °C, corresponding to the loss of a coordinated water molecule (calcd: 2.06%). Then the framework decomposes in three steps, accompanying the loss of organic ligands bga and pzdc.

3.5. Photoluminescence properties

Photoluminescent CPs are of great current interest because of their various applications in chemical sensors, photochemistry and electroluminescent display. The room-temperature photoluminescence spectra of complexes 1 and 2 are shown in Fig. 6. The free ligand bga displays photoluminescence with emission maxima at 376 and 435 nm (λex = 280 nm, Fig. S8†). It can be presumed that the broad peak at 376 nm and the shoulder at 435 nm originate from the π* → π and π* → n transitions, respectively. Noting that both free H₂pzdc and H₂pzdc ligands display very weak photoluminescence in the solid state at ambient temperature, so the heterocycle aromatic dicarboxylates almost have no contribution to the emissions of as-synthesized 1 and 2. Complex 1 has a broad emission region ranging from 400 to 470 nm, and complex 2 has an emission peak at 422 nm. These emissions probably can be assigned to Ag(I)-perturbed intraligand (IL) π* → π transition of bga ligand because very similar emission is also observed for the bga ligand. The different band shapes in the photoluminescent emissions might be due to the different structural motifs. The enhancement of photoluminescence in 1 and 2 is probably due to the coordination of bga to Ag(i) enhancing the conformational rigidity of the ligand, thereby reducing the nonradiative decay of the intraligand π* → π excited state.

![Fig. 4 PXRD patterns for (a) as-synthesized 1, (b) simulated 1, (c) as-synthesized 2, (d) simulated 2.](Image)

![Fig. 5 The TG curves for complexes 1 and 2.](Image)
4. Conclusions

In conclusion, we prepared and characterized two novel mixed-ligand Ag(i) 1D chains, a 1D helical chain and a 1D U-shaped chain. The different structural motifs result from the various heterocyclic aromatic dicarboxylates and diverse coordination modes of bga. Interestingly, two complexes provide a way of understanding the complementary N–H···N hydrogen bonds in directing the formation of the racemic 2D supramolecular sheet of 1 and the 1D → 2D interdigitated sheet of 2. In addition, they display solid-state photoluminescences and moderate thermal stabilities.

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References


