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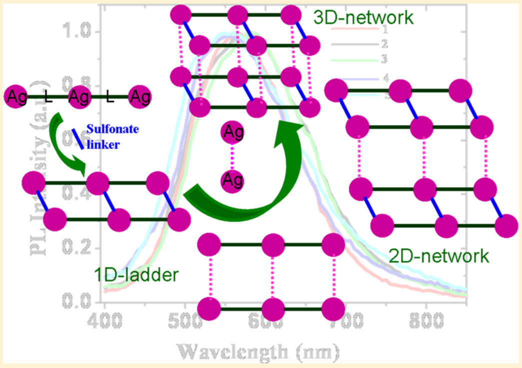
Design, Synthesis, and Photoluminescence Properties of One-, Two-, and Three-Dimensional Coordination Polymers: Anion-Assisted Argentophillic Interactions as Building Blocks

Kaustuv Banerjee, Sandipan Roy, and Kumar Biradha*

Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India

Supporting Information

ABSTRACT: Five new Ag(I) complexes of the formulae $\{[Ag_2(\mathbf{L_1})_2(NDS)]3H_2O\}_n$ (**1**), $\{[Ag_2(\mathbf{L_2})_2(NDS)]\cdot 2H_2O\}_n$ (**2**), $\{[Ag_3(\mathbf{L_2})_2(IQS)_2]\cdot(NO_3)\cdot 4H_2O\cdot 2MeOH\}_n$ (**3**), $\{[Ag_2(L_3)_2(NDS)]\cdot 4H_2O\}_n$ (**4**), and $\{[Ag_2(L_3)_2(IQS)]\cdot(NO_3)\cdot H_2O\}_n$ (**5**) ($\mathbf{L_1}$ = 2,5-bis-pyridine-3-ylmethylene-cyclopentanone, $\mathbf{L_2}$ = 2,5-bis-pyridine-3-ylmethylene-cyclohexanone, $\mathbf{L_3}$ = 2,5-bis-pyridine-4-ylmethylene-cyclopentanone, NDS = naphthalene disulfonate, and IQS = isoquinoline-5-sulfonate) have been synthesized and characterized by elemental analysis, IR, powder X-ray diffraction, and single-crystal X-ray diffraction. Complexes **1**−**3** were found to have sulfonate supported Ag···Ag interaction, and the sulfonate ions act as linkers to form higher dimensional networks (ladder, two- and three-dimensional networks). The complexes **4** and **5**, which contain 4-pyridyl substitution, do not form such Ag···Ag interactions, indicating a clear tendency of 3-pyridyl derivatives to promote such interactions over 4-pyridyl derivatives. This observation was also evidenced by the analysis of Ag(I) complexes in Cambridge Structural Database. Further, complexes **1**−**5** were found to exhibit solid-state photoluminescence in the green region at room temperature.



INTRODUCTION

The design, synthesis, and exploration of the properties of coordination polymers (CPs) have gained momentum given their fascinating network topologies and various functional properties such as luminescence, magnetic, and semiconductivity, gas sorption and separation, and molecular recognition.[1−6] For the construction of CPs, the ligands containing pyridyl and/or carboxylate functionalities are of major interest given their propensity for coordination with various metal atoms. In contrast, CPs formed via sulfonate linkers are very limited owing to the weak coordination abilities of sulfonates with several transition metal salts. However, they coordinate better with alkali ions, larger alkaline earth ions, and Ag(I) ions, as these ions do not have any preferable coordination number or geometries.[7] The Ag(I) ions are known to form argentophilic, Ag(I)···Ag(I), interactions with/without the help of anion templation. Such metallophilic interactions are known to be formed by heavy coinage transition metals containing nd^{10} configuration with a stability order of Au···Au > Ag···Ag > Cu···Cu.[8] We and others have recently shown that argentophilic interactions act as good templates for promoting solid state [2 + 2] reactions. These interactions were found to be often templated by anions such as acetates, nitrates, and to some extent by sulfonates. Such closed shell argentophilic interactions were also been utilized for the exploration of semiconducting and luminescent properties.[9] Notably, the contribution of short Ag···Ag interactions were found to play an important role in determining the solid state structures as well as the luminescence properties.[10]

The CPs of Ag(I) or hydrogen bonded complexes with $\mathbf{L_1}$−$\mathbf{L_3}$ and related derivatives have been extensively explored by us for their photochemical reactivity and guest inclusion abilities (Scheme 1).[11] From the studies of the CPs of Ag(I), it was

Scheme 1. Bis-Pyridyl Cyclic Ketones and Sulfonate Ligands Used in This Work

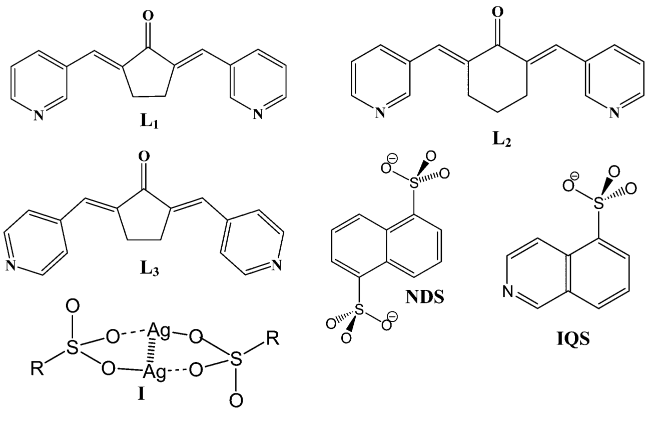


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Table 1. Crystallographic Parameters for the Crystal Structures of 1−5

compound	1	2	3	4	5
formula	$C_{44}H_{34}Ag_2N_4O_{11}S_2$	$C_{23}H_{19}AgN_2O_5S$	$C_{56}H_{46}Ag_3N_6O_{14}S_2$	$C_{23}H_{19}AgN_2O_5S$	$C_{34}H_{28}Ag_2N_6O_9S$
MW	1074.63	543.34	1490.84	1098.68	1032.51
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)
system	monoclinic	triclinic	triclinic	triclinic	triclinic
space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	24.0884(16)	7.5490(15)	7.4241(7)	8.496(3)	11.0439(10)
b (Å)	10.7929(8)	11.126(2)	14.8914(14)	11.529(4)	13.4634(11)
c (Å)	16.1990(11)	13.287(3)	14.959(2)	12.340(4)	16.3020(14)
α (deg)	90.00	103.367(6)	114.498(4)	102.401(10)	66.454(2)
β (deg)	90.677(2)	105.626(6)	99.310(4)	101.842(9)	73.330(2)
γ (deg)	90.00	93.767(6)	100.904(3)	106.290(9)	67.759(2)
vol (Å^3)	4211.2(5)	1035.8(4)	1423.3(3)	1086.7(6)	2030.3(3)
Z	4	1	1	1	2
D_{calc} (mg/m^3)	1.6950	1.7420	1.6506	1.7420	1.6299
R_1 ($I > 2\sigma(I)$)	0.0387	0.0390	0.0672	0.0787	0.0454
wR_2 (on F^2, all data)	0.1139	0.0585	0.1249	0.1593	0.0696

evident that the solid state [2 + 2] reactivity and the geometry of the products obtained depend on the presence of anions. These one-dimensional CPs of nitrate, perchlorate, and triflate salts of Ag(I) indicated that Ag···Ag interactions template such reactions to give double or single [2 + 2] reactions with variable product geometries. In particular, the triflate structure was found to have Ag···Ag interactions that are templated by triflate ions (**I**, Scheme 1). These studies inspired us to link such one-dimensional CPs with linkers containing sulfonates two produce two-dimensional (2D) networks with alignment of double bonds of $\mathbf{L_1}$, $\mathbf{L_2}$, and $\mathbf{L_3}$ for topochemical reactions. Such structures create an opportunity to produce crystalline coordination polymers of organic polymers, a new class of materials, which were explored by us and others very recently. Two sulfonate containing molecules were selected as linkers, namely, isoquinoline-5-sulfonic acid (IQSA) and naphthalene disulfonic acid (NDSA). To date, only four complexes of Ag(I) with naphthalene disulfonate (NDS) and pyridine containing ligands have been reported; among these only two have Ag···Ag interactions[12a,b] supported by sulfonates,[12] whereas no Ag(I) complex containing isoquinoline-5-sulfonate (IQS) has been reported to date.

In this paper, we describe our studies on the synthesis, crystal structures, and interesting photoluminscent properties of five new Ag(I) CPs of $\mathbf{L_1}$, $\mathbf{L_2}$, and $\mathbf{L_3}$ with NDS and IQS as linkers. In some of these CPs, as anticipated the Ag···Ag interactions were indeed templated by sulfonates, which are further linked to form 2D networks. More importantly, the CPs with short Ag···Ag contacts display significant differences in photoluminescence properties with respect to the CPs without such argentophillic interactions.

■ RESULTS AND DISCUSSION

The ligands $\mathbf{L_1}$, $\mathbf{L_2}$, and $\mathbf{L_3}$ were synthesized by following previously reported procedures by us.[13] The complexation reactions were carried out by mixing the DMF and MeOH solution of ligand with an aqueous solution of corresponding sodium salt of sulfonic acid. The addition of MeOH solution of $AgNO_3$ to the above mixture resulted in the precipitates which were dissolved by the addition of concentrated aq. NH_3 solution, and the resultant clear solution was kept undisturbed for crystallization. By following this procedure, single crystals suitable for single crystal X-ray diffraction analyses were obtained for CPs of **1**−**5**. In the case of NDS as a linker, single crystals were obtained for all three ligands, whereas in the case of IQS, single crystals were obtained only with $\mathbf{L_2}$ and $\mathbf{L_3}$. The crystal structure analysis reveals that four of the five complexes (**2**−**5**) exhibit triclinic, $P\bar{1}$ space group, and one complex exhibits monoclinic, $C2/c$ space group. The crystal structures of complexes **1**−**3** were found to have Ag···Ag interactions templated by sulfonate ions, while **4** and **5** does not exhibit such interactions. The overall network geometries were found to be different in all the structures, although they have similarities in terms of coordination geometry around Ag(I) and ligand coordination to Ag(I). For example, all the complexes contain one-dimensional -ML- chains via coordination of ligand to Ag(I) ions in near linear geometry. The pertinent crystallographic information for all the complexes **1**−**5** is given in Table 1.

$\{[Ag_2(\mathbf{L_1})_2(NDS)]\cdot 3H_2O\}_n$, **1**
$\{[Ag_2(\mathbf{L_2})_2(NDS)]\cdot 2H_2O\}_n$, **2**
$\{[Ag_3(\mathbf{L_2})_2(IQS)_2]\cdot(NO_3)\cdot 4H_2O\cdot 2MeOH\}_n$, **3**
$\{[Ag_2(\mathbf{L_3})_2(NDS)]\cdot 4H_2O\}_n$, **4**
$\{[Ag_2(\mathbf{L_3})_2(IQS)]\cdot(NO_3)\cdot H_2O\}_n$, **5**

Ag···Ag Interactions As Building Blocks for 1D → 2D and 2D → 3D CPs. The complex **1** crystallized in the $C2/c$ space group, and the asymmetric unit is constituted by one unit each of Ag(I) and $\mathbf{L_1}$, half of NDS and $1^1/_2$ units of noncoordinated water molecules. The Ag(I) exhibits distorted T-shape geometry with the coordination of two $\mathbf{L_1}$ units and one anion. With respect to the coordination of the ligand, it forms 1D zigzag -ML- chains (N−Ag−N: 142.32(12)°) which are further interconnected to three-dimensional network via NDS and Ag···Ag (3.1086(7) Å) interactions. The ligands and anions separate the Ag(I) ions by 15.629 and 11.687 Å, respectively. The interconnection of -ML- chains by NDS leads to 2D layers containing herringbone geometry with (6,3) topology (Figure 1a,b)[14] in which each cyclic unit is generated by $Ag_6(\mathbf{L_1})_4(NDS)_2$. Two of these networks interpenetrate in parallel mode which are further interconnected with such neighbors to form a three-dimensional network via Ag···Ag interactions (Figure 1c). Only one of the O atoms of the sulfonate ion was found to bridge via argentophillic interaction, one of the Ag(I) bonds strongly (Ag−O: 2.363(3) Å), while with the other form weak interactions (3.872(3) Å). Interestingly, within the 3D network the naphthyl unit is

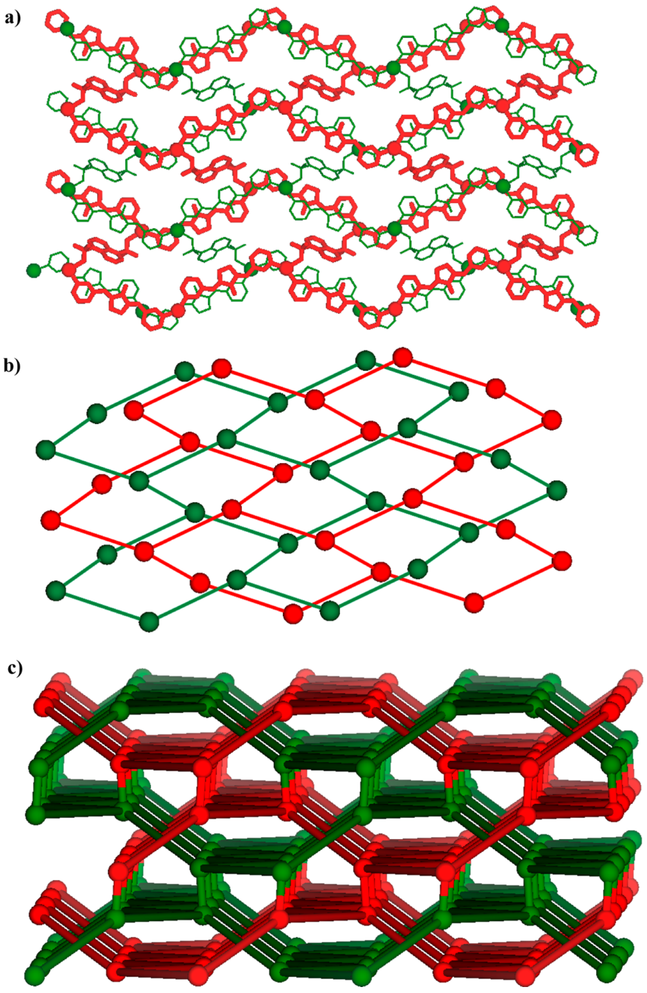

Figure 1. Illustrations for the crystal structure of **1**: (a) Doubly interpenetrated herringbone layers with (6,3) topology generated via connecting 1D (-ML-) chains via NDS; depiction of (b) 2D layers and (c) 3D-network, via Ag⋯Ag interactions, by reducing ligands to node connections and metals to nodes. The boxed part in (c) is nothing but the side view of the doubly interpenetrated layers.

sandwiched by aliphatic CH_2 groups of $\mathbf{L_1}$, and the pyridyl groups interact with each other via $\pi\cdots\pi$ interactions and with Ag(I) ions via Ag⋯π interactions. Further, the water molecules form a hydrogen bonded trimer with an O⋯O⋯O angle of 120.2(4)° and O⋯O distance of 2.945(7) Å, the terminal water molecules further bonded to sulfonates (O⋯O 2.850(6) Å) and C═O of $\mathbf{L_1}$ (O⋯O 2.943(6) Å).

In **2**, the asymmetric unit is constituted by one each of $\mathbf{L_2}$, Ag(I) and uncoordinated water and NDS with half occupancy. The Ag(I) ion exhibits distorted T-shape geometry with N−Ag−N of 162.32(12)° and N−Ag−O of 85.89(12)° and 110.21(12)°. The zigzag -ML- 1D chains are interconnected to the ladder network by NDS (Figure 2a), unlike in **1** that forms herringbone layer. Such ladders are interconnected to form corrugated 2D layers via Ag⋯Ag (3.0759(9) Å) interactions (Figure 2b) which are found to be bridged by sulfonate ion (Figure 2c), one of O atom coordinates to Ag(I) strongly (Ag−O 2.655(3) Å) as the other forms weak interaction (Ag⋯O 3.065(3) Å). The water molecules lie in between the 2D layers and form −C-H⋯Ow (C⋯O, C−H⋯O: 3.310(5) Å, 150.37°) with Sp_2 C−H of $\mathbf{L_2}$ and Ow-H⋯O (O⋯O: 2.804(5) Å) with

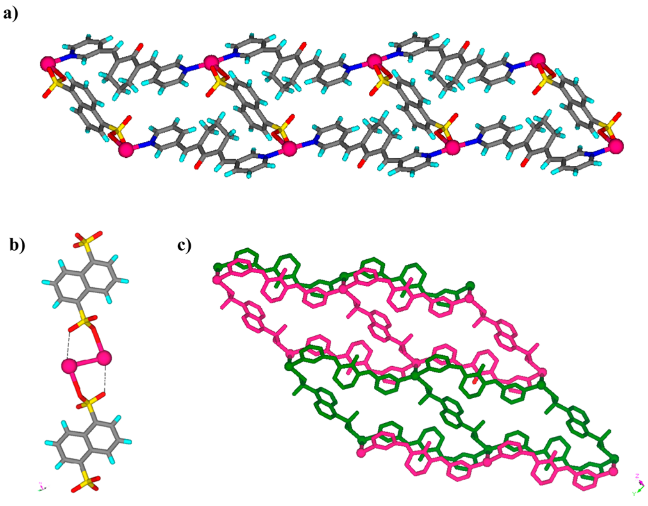

Figure 2. Illustrations for the crystal structure of **2**: (a) ladderlike network generated via linking 1D zigzag -ML- chains by NDS, (b) argentophilic interaction templated by sulfonates of NDS, (c) 2D layers generated by the interconnection of ladders via Ag⋯Ag interactions.

sulfonate ions for three-dimensional packing. Further, the layers also linked via other C−H⋯O hydrogen bonds between C═O, sulfonate and aromatic C−H groups.

In a similar fashion, the ligands $\mathbf{L_1}$ and $\mathbf{L_2}$ are reacted with Ag(I) by considering IQS as an anionic linker in the place of NDS. However, single crystals suitable for X-ray diffraction studies were obtained only in the case of $\mathbf{L_2}$ in the form of complex **3**. In this structure, the asymmetric unit was found to be constituted by two Ag(I) ions one with full occupancy and the other with half occupancy, one each of $\mathbf{L_2}$, IQS, and MeOH and two water molecules. Interestingly, two of the IQS moieties are inter connected by Ag(I) ion (Ag1, sits on inversion center and exhibits linear coordination geometry) to form a disulfonate like linker. The second Ag(I) ion (Ag2), similar to complexes **1** and **2**, exhibits a distorted T-shape geometry and coordinates to two L_2 units and O atom of IQS (N−Ag−N: 163.0(3)° and N−Ag−O: 107.7(3)° and 88.9(19)°). Similar to complex **2**, linking of 1D chains of -ML- by $Ag(IQS)_2$ leads to formation of a ladderlike structure (Figure 3a) with Ag⋯Ag separation of 17.3 Å between the chains, which is much higher than that of complex **2** (13 Å). These ladders are further interconnected to 2D layer via Ag⋯Ag (3.135(1) Å) interactions that are supported by sulfonate ions (Ag−O: 2.571(6) Å; Ag⋯O: 3.390(6) Å) (Figure 3b). The layers are highly corrugated and pack via Ag⋯π-naphthyl (Ag⋯C: 3.287(8) Å) and other weak interactions (Figure 3c). Two of the water molecules form dimer (O⋯O: 2.810(3)), which are further hydrogen bonded to the sulfonate O atom (O⋯O: 2.781(16)).

NDS and NO_3 Ions As Linkers of -ML- Chains To Form 1D → 2D and 1D → Ladder CPs. The reaction of $\mathbf{L_3}$, which contains 4-pyridyl substitution, and Ag(I) with both the sulfonate linkers NDS and IQS resulted in the single crystals of complexes **4** and **5** respectively. Unlike the complexes of **1**−**3**, **4** and **5** do not exhibit Ag⋯Ag interactions. The asymmetric unit of complex **4** contains one unit of $\mathbf{L_3}$, half unit of NDS, two half units of Ag(I) ion, and two water molecules. Both the Ag(I) ions coordinate to two units of $\mathbf{L_3}$ (N−Ag−N: 180°) to generate a wavy 1D chain. In addition, the 1D chains are interconnected through the bridging of one of the Ag(I) ion by

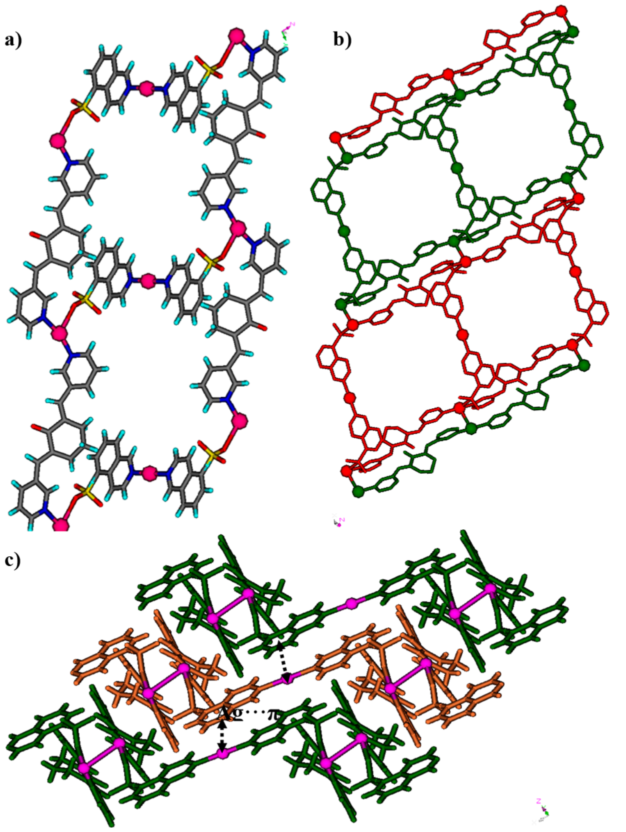

Figure 3. Illustrations for the crystal structure of **3**: (a) ladderlike structures generated via linking 1D (-ML-) chains by Ag(IQS)$_2$, (b) extended 2D layer generated via argentophilic interaction, (c) Ag···π interaction between adjacent 2D layers.

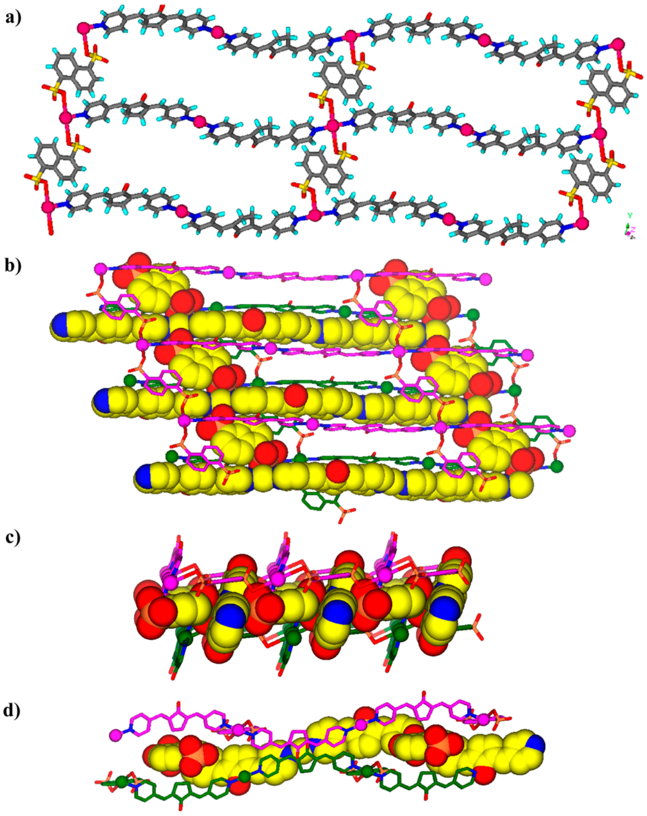

Figure 4. Illustrations for the crystal structure of **4**: (a) (4,4) layer of rectangular grids generated via linking 1D (-ML-) wavy chains by NDS, note that the sulfonates are very weakly coordinated (Ag···O: 2.954 Å); depiction of packing of the layers (shown with different colors): (b) top view (*ab* plane); side views; (c) along the *a*-axis, (d) along the *b*-axis. Notice the interdigitation of the layers.

NDS (Ag···O: 2.883(7) Å) to form a (4,4)-layer containing rectangular grids (Figure 4a), while the second Ag(I) weakly bonds to two H_2O molecules (Ag···OH_2: 2.992(8) Å). In effect, both silver ions exhibit a square planar coordination geometry. The corrugated layers pack on each other along the *c*-axis with shortest interlayer separation 4.15 Å due to the interdigitation (Figure 4b,c). Notably, among other weak interactions Ag···O═C (3.897 Å) interactions found to contribute for packing of the layers.[15] The water molecules also form a hydrogen-bonded dimer (O···O: 2.829(13) Å), which further linked NDS ions via O−H···O hydrogen bonds (O···O: 2.743(10) and 2.823(11) Å).

In the case of **5**, the asymmetric unit contains two each of Ag(I) and $\mathbf{L_3}$ and one each of IQS, NO_3^- ion, and one noncoordinated water molecule. Both the Ag(I) ions coordinate to two $\mathbf{L_3}$ units to form wavy -ML- chains which are interconnected further by μ_2 bridging of nitrate ion (Ag···O: 2.918 and 3.123 Å) such that there is a formation of twisted double chain (Figure 5a).[16] Interestingly, the IQS unit does not involve in the bridging; however it was found to bind weakly to one of the Ag(I) atom (Ag···O: 2.897 Å). The interdigitation of these twisted 1D chains via plethora of weak interactions generates the 3D packing (Figure 5b,c).

Photoluminescence of L_1, L_2 L_3, and Complexes 1−5. Luminescent CPs are of great interest due to their diverse applications in chemical sensors, electroluminescent displays, and photochemistry.[17] Therefore, the photoluminescence properties of the crystalline solids of **1**−**5** and the free ligands ($\mathbf{L_1}$, $\mathbf{L_2}$, $\mathbf{L_3}$) were investigated at room temperature using an excitation wavelength of 325 nm. All three ligands $\mathbf{L_1}$, $\mathbf{L_2}$, and $\mathbf{L_3}$ were found to exhibit almost the same broad bands between 560 and 585 nm (Figure 6a) with λ_{max} values of 579, 560, and 587 nm, respectively. Interestingly, as depicted in Figure 6b, solids of **1**−**5** also exhibit photoluminescence with emission maxima at 561, 571, 580, 548, and 554 nm, respectively. Compared to the λ_{max} values of their respective ligands, the complexes **1**, **4**, and **5** are blue-shifted, while those **2** and **3** exhibit a red shift. These results indicate that the emissions of all complexes mainly originate from ligand-based luminescence, corresponding shifts originate from ligand-to-metal charge transfer (LMCT) transition, and the presence of ligand supported short Ag···Ag and Ag···π interactions. We note here that recently a similar observation was made for cuprophillic interactions in the CPs of Cu(I) complexes.[18]

CSD Analysis on the Propensity of Ag···Ag Interactions for 3-Pyridyl and 4-Pyridyl-Containing Complexes. From the above observations, it is clear that 3-pyridyl containing ligands have a higher tendency to form Ag···Ag interactions that are supported by sulfonates. The Cambridge Structural Database (CSD)[19] analysis was carried out to examine this observation further. It reveals that in general the 4-pyridyl and 3-pyridyl containing Ag(I) complex have almost same propensity to form Ag···Ag interactions. In particular, 252 out of 1056 Ag(I) complexes (24%) containing 4-pyridyl were found to exhibit such interactions,[20] whereas in the case of 3-pyridyl, 140 out of 540 complexes (26%) were found to exhibit such interactions. When only organic sulfonate containing

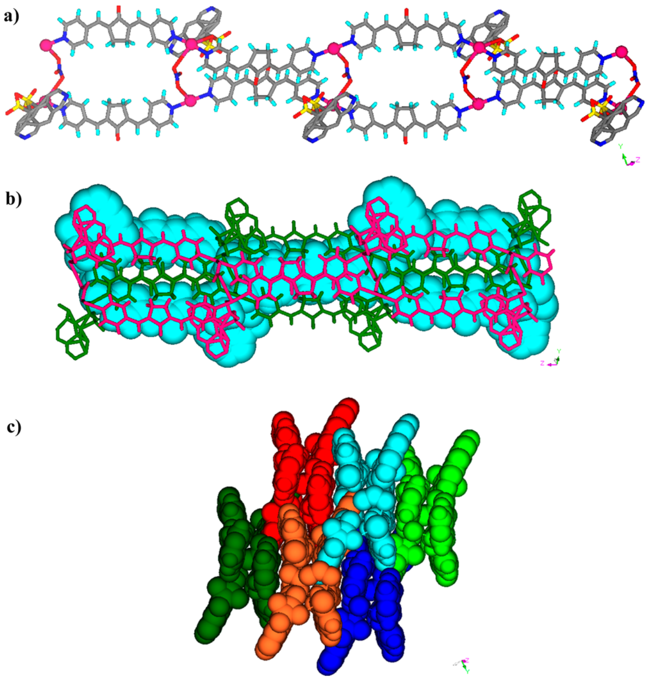

Figure 5. Illustrations for the crystal structure of **5**: (a) wavy (-ML-) chains interconnected via μ-2 bridging by NO_3^- ions, (b) interdigitation between three adjacent twisted double chains via Ag···O═C interaction, (c) side view of interdigitated twisted double chains.

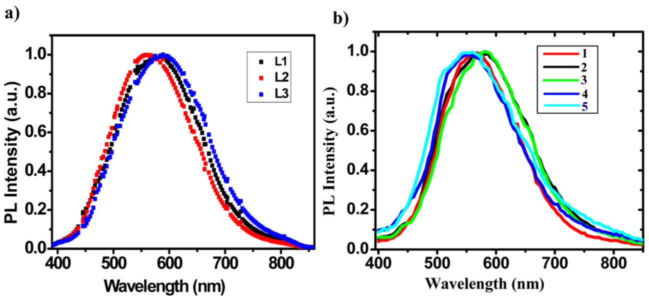

Figure 6. Solid-state photoluminescence (PL) spectra of (a) for ligands L_1−L_3 and (b) complexes **1**−**5**.

Ag(I) complexes were considered, it was found that the propensities for the formation of Ag···Ag interactions are 40% and 23% for complexes containing 3-pyridyl (32 out of 88) and 4-pyridyl (34 out of 150) respectively. These statistics clearly support our observations.

CONCLUSIONS

Five examples for a new series of Ag(I) CPs were synthesized and characterized using ligands such as L_1, L_2, and L_3 and aromatic sulfonate linkers such as NDS and IQS. In the case of **1**, **2**, and **3**, 1D wavy (-ML-) chains are linked via sulfonates to form 1D → 2D and 1D chains → 1D-ladderlike networks, which are further linked to 2D → 3D and ladder → 2D layers via Ag···Ag interactions. In all three complexes, the argentophillic interactions were found to be supported by sulfonate ions, whereas complexes **4** and **5** do not contain such Ag···Ag interactions, and only in **4** NDS weakly coordinates with Ag(I) to form a 2D-layer containing rectangular grids. In **5**, NO_3 ion bridges 1D chains to a ladderlike network. Further, our studies and CSD analysis reveal that the 3-pyridyl containing ligands have more of a tendency to form Ag···Ag interactions than the 4-pyridyl containing ligands in the presence of organic sulfonates. We note here that all the five complexes contain water molecules, and they were found to prefer to form hydrogen bonds over coordination to Ag(I). Moreover, all of these complexes exhibit solid-state photoluminescence in the green region at room temperature, which suggests that they may be good candidates for optical materials.

EXPERIMENTAL SECTION

FTIR spectra were recorded with a PerkinElmer instrument, Spectrum Rx, serial no. 73713. ^1H NMR (200 MHz) spectra were recorded on a BRUKER-AC 200 MHz spectrometer. Powder XRD data were recorded with a PHILIPS Holland PW-171 defractometer. The diffuse reflectance spectra (DRS) of the inclusion crystals were recorded with a Cary model 5000 UV−visible-NIR spectrophotometer. Elemental analyses were carried out with a PerkinElmer Series II 2400, and melting points were taken using a Fisher Scientific melting point apparatus cat. No. 12-144-1.

Synthesis of 2,6-Di(3-pyridylmethylidene)cyclohexanone L_1. A mixture of 3-pyridinecarbaldehyde (1.071 g, 0.01 mol) and cyclohexanone (0.0981 g, 0.005 mol) in 20 mL of water was stirred and cooled to 5 °C, 1 mL of 20% sodium hydroxide solution was added, and vigorous stirring was continued for 5 h at 25 °C. The solution was neutralized with diluted hydrochloric acid, and the yellow colored solid was collected by filtration. Recrystallization from ethanol gave 2.10 g (72.0%) yellow crystals. mp = 139 °C. IR (cm^{-1}): 1670 (C═C) 1610 (C═O), ^1H NMR ($CDCl_3$, δ, ppm): 1.83 (2H, m, 4 $-CH_2$), 2.92 (4H, m, 3- and 5-CH_2), 7.33 (2H, dd, 5′-Py), 7.74 (4H, m, 4′-H Py and −CH═), 8.55 (2H, d, and 6′-H Py), 8.70 (2H, s, 2′-H Py).

Synthesis of 2,6-Di(3-pyridylmethylidene)cyclopentanone L_2. L_2 was prepared using a similar procedure as described for L_1 except that cyclopentanone (0.0981 g, 0.005 mol) was used instead of cyclohexanone. mp = 216 °C.IR (cm^{-1}): 1670 (C═C) 1610 (C═O), ^1H NMR ($CDCl_3$, δ, ppm): 3.16 (4H, s, -CH_2), 7.33 (2H, dd,), 7.57 (2H, s, CH═), 7.87 (4H, d), 8.59 (2H, d,), 8.85 (2H, s br).

Synthesis of 2,6-di(4-Pyridylmethylidene)cyclopentanone L_3. L_3 was prepared in a similar procedure as described for L_1 except that cyclopentanone (0.0981 g, 0.005 mol) was taken instead of cyclohexanone and 4-pyridinecarbaldehyde (1.071 g, 0.01 mol) was taken instead of 3-pyridinecarbaldehyde. mp = 239 °C.IR (cm^{-1}): 1670 (C═C) 1630 (C═O), ^1H NMR ($CDCl_3$, δ, ppm): 3.16(4H, s, -CH_2), 7.42 (4H, d,), 7.49 (2H, s, CH═), 8.70 (4H, d).

Synthesis of Coordination Polymers of 1−5. *Preparation of **1**.* A 2 mL aqueous solution of Na_2NDSA (0.017 g, 0.05 mmol) was added to a hot 5 mL MeOH and DMF (1:1 v/v) solution of L_1 (0.013 g, 0.05 mmol). To this solution, the addition of 3 mL MeOH solution of $AgNO_3$ (0.0169 g, 0.1 mmol) resulted in a yellow-colored precipitate, which was dissolved by the gradual addition of conc. aqueous NH_3 solution. Deep yellow-colored crystals were obtained after 2 days and dried in the air to give 0.012 g of **1**. Yield: 64.23% based on L_1, Elemental analysis: (%) Calc. for $C_{44}H_{34}Ag_2N_4O_{11}S_2$: C, 49.20; H, 3.20; N, 5.20. Found C,48.69; H,3.15; N,5.02. IR (cm^{-1}): 3569.24(s), 3447.94(s), 1684.08(s), 1654.11(s), 1627.83(s), 1601.70(s), 1584.60(s), 1562.34(s), 1499.91(s), 1477.21(s), 1449.75(s), 1413.90(s), 1333.73(s), 1293.91(s), 1265.84(s), 1239.19(s), 1205.66(s), 1161.72(s), 1044.54(s), 988.83(s), 954.15(s), 785.93(s), 769.40(s), 690.29(m), 614.63(s), 572.64(s), 530.14(s), 467.77(m).

*Preparation of **2**.* The compound of **2** was prepared in a similar procedure as described for **1** except L_2 was taken in the place of only L_1. The dark yellow crystals were obtained and dried in the air to give 0.0098 g. Yield: 55.65% based on L_2, Elemental analysis: (%) Calc. for $C_{23}H_{19}AgN_2O_5S$: C, 50.80; H, 3.50; N, 5.20. Found C, 50.69; H,3.45; N,5.12. IR (cm^{-1}):. 3568.64(s), 3449.20(m), 1607.90(s), 1581.86(s), 1474.53(s), 1276.98(s), 1205.90(s), 1164.35(s), 1143.13(s), 1045.47(s), 1022.06(s), 785.96(s), 769.70(s), 709.15(s), 615.99(s), 540.31(s).

Preparation of ***3***. It was prepared in a similar procedure as described for **1** except instead of Na_2NDSA, isoquinoline-5-sulfonic acid (0.0105 g, 0.05 mmol) was taken. The pale yellow-colored crystals were obtained and dried in the air to give 0.011 g. Yield: 60.23% based on $\mathbf{L_1}$, Elemental analysis: (%) Calc. for $C_{56}H_{46}Ag_3N_6O_{14}S_2$: C, 47.50; H, 3.30; N, 5.90. Found C, 47.39; H, 3.05; N, 5.82. IR (cm^{-1}): 3568.73(s), 3448.59(m), 2943.00(s), 1611.67(s), 1592.52(s), 1578.06(s), 1413.70(s), 1324.32(s), 1276.23(s), 1205.79(s), 1171.38(s), 1146.12(s), 1044.20(s), 995.11(s), 971.95(s), 939.90(s), 816.82(s), 785.90(s), 769.45(s), 614.91(s), 573.00(m), 536.17(s).

Preparation of ***4***. The complex **4** was prepared in a similar procedure as described for **1** except instead of $\mathbf{L_1}$, $\mathbf{L_3}$ (0.013 g, 0.05 mmol) was taken. The deep yellow-colored crystals were obtained and dried in the air to give 0.0105 g. Yield: 62.12% based on $\mathbf{L_3}$, Elemental analysis: (%) Calc. for $C_{22}H_{17}AgN_2O_6S$: C, 48.50; H, 3.10; N, 5.10. Found C,48.39; H,3.02; N,5.01. IR (cm^{-1}): 3569.08(s), 3448.78(m), 1696.11(s), 1630.93(s), 1608.75(s), 1595.48(s), 1418.12(s), 1327.24(s), 1291.32(s), 1205.87(s), 1174.37(s), 1161.83(s), 1044.22(s), 999.48(s), 927.23(s), 813.08(s), 785.95(s), 769.29(s), 614.22(s), 572.49(s), 532.55(s), 523.23(m).

Preparation of ***5***. The compound of **5** was prepared in a similar procedure as described for **3** except $\mathbf{L_3}$ (0.013 g, 0.05 mmol) was used in place of only $\mathbf{L_1}$. Pale yellow-colored crystals were obtained and dried in the air to give 0.011 g. Yield: 63.75% based on $\mathbf{L_3}$, calc. for $C_{34}H_{28}Ag_2N_6O_9S$: C, 41.00; H, 2.80; N, 8.40. Found C, 40.29; H, 2.22; N, 7.51. IR (cm^{-1}): 3421.31(s), 2367.99(m), 2341.56(s), 1696.16(s), 1607.70(s), 1595.86(s), 1418.48(s), 1348.28(s), 1326.72(s), 1291.39(s), 1251.51(s), 1218.52(s), 1170.08(s), 1075.73(s), 1055.23(s), 999.59(s), 983.31(s), 927.49(s), 839.53(s), 813.98(s), 749.16(s), 708.84(s), 629.90(s), 574.56(s), 533.74(s), 523.23(s).

Crystal Structure Determination. All the single crystal data were collected on a Bruker-APEX-II CCD X-ray diffractometer that uses graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature (293 K) by the hemisphere method. The structures were solved by direct methods and refined by least-squares methods on F^2 using SHELX-97.[21] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were fixed at calculated positions and refined using a riding model. The H atoms attached to the O atom or N atoms are located wherever possible and refined using the riding model. The nitrate ion in **3** could not be located. In the case of **5**, IQS was found to be highly disordered, and NO_3 and H_2O were found to have high thermal motions. Therefore, they were removed in the final refinement and Platon squeeze option was used.[22]

ASSOCIATED CONTENT

Supporting Information

^{1}H NMR spectra for $\mathbf{L_1}$, $\mathbf{L_2}$, and $\mathbf{L_3}$, IR spectra of the complexes **1−5**, TGA thermograms for the complexes **1−5**, calculated and experimental PXRD patterns for the complexes **1−5**, DRS for the complexes **1−5**. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Fax: +91-3222-282252. Tel: +91-3222-283346. E-mail: kbiradha@chem.iitkgp.ernet.in.

Notes

The authors declare no competing financial interest.

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