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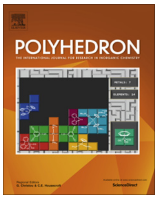

Tunable luminescent behaviors of Ag-containing metal coordination polymers with *N*-heterocyclic and sulfonate group

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ABSTRACT

Three new metal coordination polymers, namely, [Ag(**BPYE**)(**BS**)] (**1**), [Ag_2(**BPY**)$_2$(**BS**)(NO_3)(H_2O)$_2$]·H_2O (**2**), and [Ag_2(**BPY**)$_2$(**ABS**)(NO_3)]·H_2O (**3**) [**BS** = benzenesulfonate, **BPYE** = 1,2-bi(4-pyridyl)ethene, **BPY** = 4,4′-bipyridine, **ABS** = *p*-aminobenzenesulfonate], have been obtained under solvothermal conditions, which were structurally characterized by X-ray single-crystal diffraction, EA, PXRD, FT-IR, thermogravimetry analysis (TGA) and differential scanning calorimetric (DSC). These complexes show a one-dimensional (1D) polymeric structure, which will further be constructed a three-dimensional (3D) supramolecular framework via hydrogen bonding, $\pi\cdots\pi$ stacking interactions and C—H$\cdots\pi$ interactions. The shortest distances of $\pi\cdots\pi$ packing interactions of complexes **1**–**3** are 3.644, 3.558 and 3.780 Å, respectively. The luminescent properties of complexes **1**–**3** were investigated in the solid state at room temperature, where the maximal emission peaks can be observed at 418 (λ_{ex} = 350), 364 (λ_{ex} = 320) and 474 nm (λ_{ex} = 364 nm), respectively. Obviously, the emission maxima are proportional to the intermolecular $\pi\cdots\pi$ packing distances.

1. Introduction

The design and development of metal coordination polymers (MCPs) have attracted extensive attention in materials research areas owing to their intriguing architectures and their potential applications for luminescence [1], catalysis [2], sensing [3], gas storage/separation [4], nonlinear optics [5], drug delivery [6] as well as magnetic materials [7]. From the structural point of view, the organic ligands and central metals paly crucial factors in the coordination self-assembly process and final properties [8]. Consequently, rational selection of metal ions and suitable organic ligands is still a challenge for construct expected architectures with unique properties. In coordination polymers, the Ag, a d^{10} metal transition ion, has a tendency to reveal a highly flexible and irregular coordination number and geometry because of its intrinsic electronic configuration [9], which can form various types of fascinating coordination architectures. Meanwhile, silver(I) has high affinity for N and O donors and the existences of Ag$\cdots$Ag, Ag$\cdots\pi$, Ag$\cdots$S and Ag$\cdots$O weak interactions also make the complexes exhibit interesting structures and potential properties [10].

Additionally, —SO_3— group has three *O*-donors which can participate in coordinating the metal ion and act as the acceptor of hydrogen bonds. Thus, its coordination mode is diverse, flexible and modifiable. Besides, some silver(I) sulfonate compounds involving nitrogen-based secondary ligands have been reported [11]. The neutral *N*-containing secondary ligands give a variety of interesting structural motifs and $\pi\cdots\pi$ stacking interactions between aromatic rings. It has been demonstrated that the existence and change of the neutral secondary ligands in silver(I) sulfonates has a great effect on the structural motifs and properties of MCPs. Accordingly, the introduction of neutral *N*-containing secondary ligands is an important strategy for the construction of silver(I) sulfonate coordination polymers [12].

To investigate the effect of different sulfonic ligands and different *N*-heteroaromatic pyridine ligands on the crystal structures and properties of the final MCPs, herein, we would like to report the syntheses and characterization of three Ag(I) coordination polymers based on the sulfonate ligand and specific *N*-donor ligand: [Ag(**BPYE**)(**BS**)] (**1**), [Ag_2(**BPY**)$_2$(**BS**)(NO_3)(H_2O)$_2$]·H_2O (**2**), and [Ag_2(**BPY**)$_2$(**ABS**)(NO_3)]·H_2O (**3**) [**BS** = benzenesulfonate, **BPYE** = 1,2-bi(4-pyridyl) ethene, **BPY** = 4,4′-bipyridine, **ABS** = *p*-aminobenzenesulfonate], which have been obtained under solvothermal conditions. These MCPs have been characterized by X-ray single-crystal diffraction, PXRD, IR, thermogravimetry analysis (TGA) and differential scanning calorimetric (DSC). The

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photoluminescent behaviors of these complexes were tuned by the intermolecular stacking interactions.

2. Experimental

2.1. Materials and measurements

The reagents and solvents employed were commercially available and used as received without further purification. Elemental analyses were performed on an Elementar vario EL III microanalyser. Powder X-ray diffraction (**PXRD**) were recorded on a Bruker D8 Advance diffractometer at 40 kV, 40 mA with a Cu-target tube and a graphite monochromator; 2θ falls in the range of 5–60°. The experimental powered X-ray diffraction patterns are in agreement with the corresponding simulated ones except for the relative intensity variation because of the preferred orientations of the crystals. Therefore, the phase purity of the as-synthesized products is substantiated. FT-IR spectra were conducted on KBr pellets from 400 to 4000 cm^{-1} on a Bruker spectrometer. At room temperature, solid-state fluorescent studies were conducted on a HITACHI F-4600 system. TGA data were collected with a TA SDT Q600 analyzer in N_2 at a heating rate of 10 °C min^{-1} from 30 to 800 °C.

2.2. Synthesis of [Ag(BS)(BPYE)] (**1**)

A solution of $AgNO_3$ (0.0169 g, 0.10 mmol) in water (2 ml) was added to a stirred solution of benzenesulfonic acid (**BS**) (0.0158 g, 0.10 mmol), **BPYE** (0.0182 g, 0.10 mmol), and NaOH (0.004 g, 0.1 mmol) in a mixture of CH_3OH (2 ml) and H_2O (2 ml). The reaction solution was stirred for 30 min. Then, it was stood for 3 days under the dark environment under 40 °C. The colorless block crystals of **1** suitable for X-ray diffraction analysis were obtained (0.0226 g, yield: 50.56% based on $AgNO_3$). Elemental analysis calcd (%) for $C_{18}H_{15}AgN_2O_3S$ (447.25): C, 48.34; H, 3.38; N, 6.26; Found (%): C, 48.41; H, 3.37; N, 6.27. IR: 3434(w), 3045(vw), 1606(s), 1434(w), 1189(vs), 1117(m), 1026(w), 827(w), 610(m).

2.3. Synthesis of $[Ag_2(BS)(NO_3)(BPY)_2(H_2O)_2]\cdot H_2O$ (**2**)

The synthetic procedure of compound **2** is similar to that of **1** except that 4,4′-bipyridine (**BPY**) (0.0156 g, 0.10 mmol) took place of **BPYE**. The pale-yellow block crystals of **2** suitable for X-ray diffraction analysis were obtained (0.0272 g, yield: 33.96% based on $AgNO_3$). Elemental analysis calcd (%) for $C_{26}H_{27}Ag_2N_5O_9S$ (801.32): C, 38.97; H, 3.40; N, 8.74; Found (%): C, 38.89; H, 3.41; N, 8.73. IR: 3426(w), 3100(w), 1606(m), 1417(m), 1370(s), 1198 (vs), 1118(w), 809(w), 729(w), 610(m).

2.4. Synthesis of $[Ag_2(ABS)(NO_3)(BPY)_2]\cdot H_2O$ (**3**)

The synthetic procedure of compound **3** is similar to that of **2** except that *p*-aminophenylsulfonic acid (**ABS**) (0.0173 g, 0.10 mmol) replaced **BS** (0.0173 g, 0.10 mmol). The yellow block crystals of **3** suitable for X-ray diffraction analysis were obtained (0.0318 g, yield: 39.85% based on $AgNO_3$). Elemental analysis calcd (%) for $C_{26}H_{26}Ag_2N_6O_8S$ (798.33): C, 39.12; H, 3.28; N, 10.53; Found (%): C, 39.17; H, 3.27; N, 10.54. IR: 3470(w), 3389(w), 3199(w), 3090(w), 1598(vs), 1422(m), 1362(s), 1171(s), 1118(m), 1017(m), 809(m), 691(w), 565(m).

2.5. Single-crystal structure determination

Single-crystal structures of the complexes **1**–**3** were measured on Bruker Smart CCD diffractometer equipped with a graphite-monochromator and Mo Kα radiation (λ = 0.71073 Å). The lattice parameters were obtained by a least-squares refinement of the diffraction data. All the measured independent reflections were used in the structural analysis, and semi-empirical absorption corrections were applied using the SADBAS program [13]. The program SAINT was used for integration of the diffraction profiles [14]. The structure was solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL [15]. All non-hydrogen atoms were situated in successive difference Fourier synthe-

Table 1
Crystal data and structure refinement data for **1**–**3**.

Compound reference	**1**	**2**	**3**
Chemical formula	$C_{18}H_{15}AgN_2O_3S$	$C_{26}H_{27}Ag_2N_5O_9S$	$C_{26}H_{26}Ag_2N_6O_8S$
Formula Mass	447.25	801.32	798.33
Crystal system	Triclinic	Monoclinic	Triclinic
a (Å)	8.3392(3)	13.7371(2)	10.6825(2)
b (Å)	9.8679(4)	11.4134(2)	10.9956(2)
c (Å)	11.1619(4)	18.6278(3)	14.6541(2)
α (°)	64.369(2)	90	70.3490(10)
β (°)	88.671(2)	101.3912(9)	84.2230(10)
γ (°)	84.800(2)	90	63.2970(10)
V (Å)	824.59(6)	2863.07(8)	1445.54(4)
T (K)	296(2)	293(2)	293(2)
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
No. of formula units per unit cell (Z)	2	4	2
Radiation type	Mo Kα	Mo Kα	Mo Kα
Absorption coefficient (μ/mm^{-1})	1.369	1.503	1.487
No. of reflections measured	7419	23 829	23 472
No. of independent reflections	4045	6564	6688
R_{int}	0.0133	0.0397	0.0174
Final R_1 values ($I > 2\sigma(I)$)	0.0330	0.0380	0.0307
Final wR (F^2) values ($I > 2\sigma(I)$)	0.0942	0.0922	0.0864
Final R_1 values (all data)	0.0392	0.0636	0.0373
Final wR (F^2) values (all data)	0.0991	0.1092	0.0906
Goodness of fit (GOF) on F^2	1.015	1.011	1.027
CCDC number	1814927	1814928	701487

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.

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