

基于大环醚和三价卤化铋阴离子的超分子杂化 化合物:合成、结构及性质

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摘要: 基于大环自组装和多卤阴离子合成了有机-无机杂化超分子化合物, $[(1,4\text{-PMNH}_3) \cdot (18\text{-crown-6})] \cdot [(H_3O) \cdot (18\text{-crown-6})]_2 \cdot [(H_2O) \cdot (18\text{-crown-6})] \cdot (18\text{-crown-6}) \cdot (Bi_2Cl_9)$ (**1**)。化合物属正交晶系, $Pca2_1$ 空间群, $a=2.483\ 0(3)\text{ nm}$, $b=1.161\ 8(3)\text{ nm}$, $c=3.316\ 1(2)\text{ nm}$, $V=9.566(2)\text{ nm}^3$ 。并通过其红外光谱、粉末衍射、热重分析和单晶结构分析对化合物进行了充分表征。在转子定子型的超分子化合物 **1** 中,大环超分子阳离子和 $(Bi_2Cl_9)^{3-}$ 阴离子交错堆积形成包合物结构。并在室温下对其固体荧光性质进行测试表征。通过 DSC 对其热稳定性进行了详细分析。

关键词: 晶体结构; 荧光; 五环自组装; 超分子

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Synthesis, Structure and Properties of a Supramolecular Hybrid Compound Based on Macrocyclic Assemblies

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Abstract: The first pentacyclic supramolecular hybrid compound based on macrocyclic assemblies and multichloro-metal anion, $[(1,4\text{-PMNH}_3) \cdot (18\text{-crown-6})] \cdot [(H_3O) \cdot (18\text{-crown-6})]_2 \cdot [(H_2O) \cdot (18\text{-crown-6})] \cdot (18\text{-crown-6}) \cdot (Bi_2Cl_9)$ (**1**), has been synthesized and characterized by single crystal X-ray diffraction, XRPD, elemental analysis, UV, DSC, TGA, IR and 1H NMR ($1,4\text{-PMNH}_3^+=1,4\text{-phenylenedimethanaminium}$). Compound crystallizes in the orthorhombic system, space group $Pca2_1$, with $a=2.483\ 0(3)\text{ nm}$, $b=1.161\ 8(3)\text{ nm}$, $c=3.316\ 1(2)\text{ nm}$ and $V=9.566(2)\text{ nm}^3$. There are five 18-crown-6 macrocyclic molecules with different structural parameters to build the pentacyclic structure. And the macrocyclic assemblies $[(1,4\text{-PMNH}_3) \cdot (18\text{-crown-6})]^+$, $[(H_3O) \cdot (18\text{-crown-6})]^+$ and $[(H_2O) \cdot (18\text{-crown-6})]$ were formed by the guest molecules ($1,4\text{-PMNH}_3^+$, H_3O^+ and H_2O) inserting into the crown-ether macrocycle through strong $N(O)_{\text{donor}}-H \cdots O_{\text{acceptor}}$ H-bonding interactions. The $(Bi_2Cl_9)^{3-}$ cluster was composed of three $\mu_2\text{-Cl}$ donors and six terminal Cl atoms. The macrocyclic assemblies and anion clusters were alternately stacked together to build the H-bonding supramolecular multi-component compound. CCDC: 917407.

Keywords: crystal structure; fluorescence; pentacyclic assembly; supramolecular

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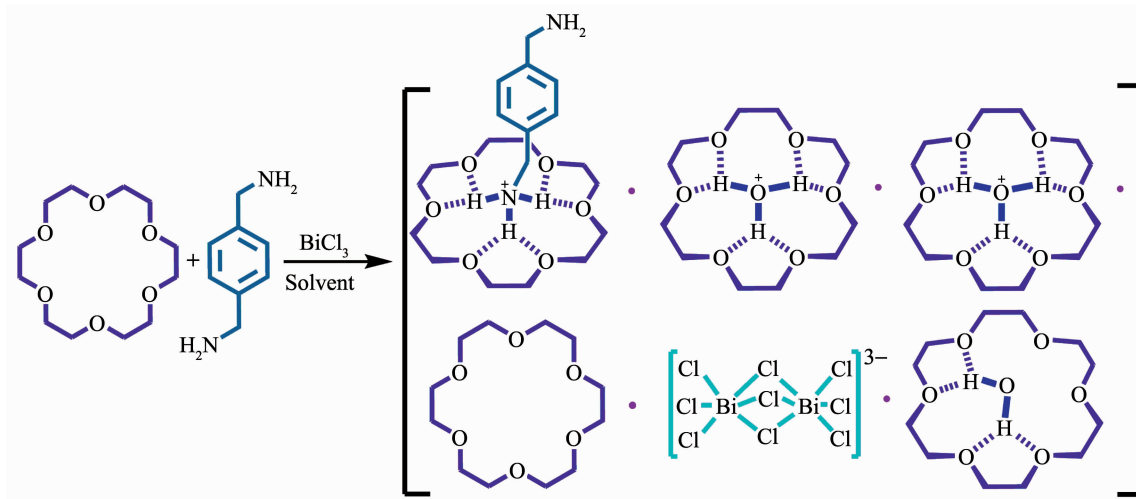
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0 Introduction

The intermolecular weak interactions can play an important role for the design and synthesis of host-guest supramolecular compounds. And the selective recognition of guest molecules can easily be achieved if the host and guest molecules were combined together through the mentioned intermolecular weak forces, such as H-bonding, charge-transfer and van der Waals forces. That is, the host and guest should be provided with some special configurations and suitable groups^[1-9]. In this way, the host and guest molecules can be combined together to build the designed self-assembly structures through each distinctive building modes. Therefore, these supramolecular self-assembly compounds will be the potential functional materials applied in the fields of molecular recognition, molecular adsorption, mediated ion transport, ion exchange, self-assembly engineering, luminescence and anion-activated catalysis^[4-12]. Among such compounds, the most typical examples are the crown ether-based inclusion compounds. As we all know, the crown ether host shows a particularly high selectivity to the alkali metal ion guests (such as K^+ or Na^+) through metal-O bonding interactions. Similarly, the crown ether also possess a high selectivity to some nonmetallic ion guests (NH_4^+ , $R-NH_3^+$ and OH_3^+), and this macrocyclic host include the guests by automatically adjusting the sizes and shapes of the

macrocyclic cavity through H-bonding weak interactions^[13-19]. Thus, a large number of novel supramolecular structures based on 18-crown-6 macrocyclic host have been synthesized^[10-20], in which the intermolecular weak interactions played an important role, and the macrocyclic host with six $-O-CH_2-CH_2-$ repeating units showed excellent natural flexibility in the self-assembly process. Furthermore, the cation guests and balance anions can also affect the stoichiometry and molecular conformation of the host-guest inclusion complexes. In most cases, the $R-NH_3^+$ type of cations will be embedded in one side of the flexible 18-crown-6 macrocycle with 1:1 stoichiometry via three (or six) strong $R-N-H \cdots O_{18-crown-6}$ H-bonding interactions^[10-17]. In addition, the large multi-charged anions (multichloro-metal ion or heteropolyanion) can result in the formation of multi-component composites by the spatial stacking interactions. According to the above-mentioned synthesis strategies and characteristics, the benzyl diamine, $Bi_2Cl_9^{3-}$ and 18-crown-6 were selected to build the supramolecular compound **1**, $[(1,4-PMNH_3) \cdot (18-crown-6)] \cdot [(H_3O) \cdot (18-crown-6)]_2 \cdot [(H_2O) \cdot (18-crown-6)] \cdot (18-crown-6) \cdot (Bi_2Cl_9)$ (in which the 1,4- $PMNH_3=1,4$ -phenylenedimethanaminium) (Scheme 1). And the macrocyclic assemblies $[(1,4-PMNH_3) \cdot (18-crown-6)]^+$, $[(H_3O) \cdot (18-crown-6)]^+$ and $[(H_2O) \cdot (18-crown-6)]$ were formed by the guest molecules (1,4- $PMNH_3^+$, or H_3O^+ and H_2O) inserting into crown-ether macrocycle through strong $N(O)_{donor}-H \cdots O_{acceptor}$ H-



Scheme 1 Synthesis process and H-bonding modes of compound **1**

bonding interactions. There are five 18-crown-6 macrocyclic molecules with different structural parameters to build the first supramolecular multi-component compound with pentacyclic structure.

1 Experimental

1.1 Material and instrument

All the reagents and solvents employed were commercially available and used as supplied without further purification. Elemental analyses for carbon, hydrogen and nitrogen were performed on a Vario EL III elemental analyzer. The infrared spectra ($4\,000\sim 500\text{ cm}^{-1}$) were recorded by using KBr pellet on a SHIMADZU IRprestige-21 FTIR-8400S spectrometer. UV/Vis spectrum was measured at room temperature using SHIMADZU UV-2450 UV-Vis spectrophotometer. The X-ray powder diffraction (XRD) data were collected with a Siemens D5005 diffractometer with Cu $K\alpha$ radiation ($\lambda=0.154\,18\text{ nm}$). Luminescence spectra were recorded on an F-4600 fluorescence spectrophotometer at room temperature using the solid sample.

1.2 Preparation of complex 1

Compound **1** was synthesized by employing mild solvothermal method in the presence of organic 1,4-phenylenedimethanamine (1,4-MPNH₂), BiCl₃, 18-crown-6 and dilute HCl. BiCl₃ (4 mmol, 1.26 g) was added into an 20 mL H₂O/DMF/MeOH/HCl mixture solvent (volume ratio 5:2:5:1) under constant stirring. To this solution, 0.22 g (2 mmol) of 1,4-MPNH₂ was slowly added. Finally, 1.58 g (6 mmol) of 18-crown-6 and additional 1 mL of HCl (36%) were added into the mixture, and the mixture was stirred for 1 h to obtain a homogeneous gel. The final mixture with the molar composition of BiCl₃/18-crown-6/1,4-MPNH₂ (2:3:1) was transferred into a 25 mL Teflon-lined acid digestion bomb and heated at 100 °C for 2 d under autogenously pressure. Then the reaction was slowly cooled to room temperature at a rate of 5 °C · h⁻¹. Colorless block monophasic crystals suitable for X-ray diffraction were obtained in 47% yield (based on BiCl₃). This compound is only slightly soluble in water. ¹H NMR (300 MHz, D₂O, TMS, 298 K): δ (ppm): 7.72 (d, 2 H, aromatic-H), 7.51 (d, 2H,

aromatic-H), 3.24~3.28 (s, 4H, methylene-H) and 3.45~3.50 (d, 120H, methylene-H of 18-crown-6). Elemental analysis for **1**, C₆₈H₁₄₁Bi₂Cl₉N₂O₃₃ (2251.84): Anal. Calcd.(%): C 36.25, H 6.26, N 1.24; Found(%): C 35.88, H 6.13, N 1.17. IR spectrum (cm⁻¹, KBr): 3 505(s), 3 481(s), 3 402(m), 3 393(s), 3 354(s), 3 328 (m), 3 277(m), 3 103(w), 2 918(s), 2 871(s), 2 381(w), 1 583 (m), 1 543 (w), 1 479 (m), 1 421 (s), 1 361 (w), 1 288(s), 1 221(m), 1 210(m), 1 129(s), 1 051(w), 933 (m), 871(w), 824(w), 778(m), 730(w), 704(m), 648(w), 569 (w), 538 (w), 502 (w). In addition, the analogous tertiary amine and secondary amine molecules (1,4-PM-NHMe, 1,4-PM-NMe₂, 1,4-PM-NHEt and 1,4-PM-NEt₂, that is, the H atoms of 1,4-PM-NH₂ were substituted by methyl or ethyl) were additionally added into the reaction solutions, respectively. These corresponding ammonium cations were not involved in the crystallization, and did not affect the yield and purity of compound **1**.

1.3 Crystal structure determination

A single crystal of the title complex with approximate dimensions 0.30 mm×0.20 mm×0.20 mm was selected for data collection at 93(2) K, using a Rigaku SCXmini diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.071\,073\text{ nm}$). The structure parameters were obtained by CrystalClear^[21] with the θ range for data collection from 2.29° to 27.41°. Of the 57 938 reflections collected, there were 20 246 unique reflections ($R_{\text{int}}=0.131\,8$). The absorption correction was carried out by multi-scan method. The structure was solved by direct methods with SHELXS-97 and refined by full matrix least squares on F^2 with SHELXL-97^[22-23]. All non-H atoms were refined anisotropically. The H atoms attached on N and O were located on Fourier map and refined with $U_{\text{iso}}(\text{H})=1.5U_{\text{eq}}$. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}$. The Flack parameter is 0.00(3). Detailed data collection and refinement of the compound **1** are summarized in Table 1, and the selected bond distances and angles are listed in Table 2.

CCDC: 917407.

Table 1 Crystal data and structure refinement for compound **1**

Empirical formula	C ₆₈ H ₁₄₁ N ₂ O ₃₃ Bi ₂ Cl ₉₃	θ range for data collection / (°)	2.29~27.41
Formula weight	2 251.842 3	Limiting indices	$-32 \leq h \leq 32, -14 \leq k \leq 15, -42 \leq l \leq 34$
Crystalsystem	Orthorhombic	Reflections collected	57 983
Space group	<i>Pca</i> 2 ₁	Independent reflections (<i>R</i> _{int})	20 246 (0.131 8)
<i>a</i> / nm	2.483 0(3)	Completeness to $\theta=25.98^\circ$ / %	99.18
<i>b</i> / nm	1.161 8(3)	Absorption correction	Semi-empirical from equivalents
<i>c</i> / nm	3.316 1(2)	Refinement method	Full-matrix least-squares on <i>F</i> ²
Volume / nm ³	9.566(2)	Data / restraints / parameters	20 246 / 849 / 1 016
<i>Z</i>	4	Goodness-of-fit on <i>F</i> ²	1.017
<i>D_c</i> / (g·cm ⁻³)	1.563	Final <i>R</i> indices (<i>I</i> >2σ(<i>I</i>))	<i>R</i> ₁ =0.078 0, <i>wR</i> ₂ =0.178 6
<i>F</i> (000)	4 854	<i>R</i> indices (all data)	<i>R</i> ₁ =0.120 8, <i>wR</i> ₂ =0.224 9

Table 2 Selected bond-length (nm) and bond-angle (°) of compound **1**

Bi(1)-Cl(1)	0.255 4(4)	Bi(1)-Cl(2)	0.260 4(3)	Bi(1)-Cl(3)	0.261 9(3)
Bi(1)-Cl(4)	0.291 5(3)	Bi(1)-Cl(5)	0.292 2(3)	Bi(1)-Cl(6)	0.305 6(3)
Cl(1)-Bi(1)-Cl(2)	94.37(11)	Cl(1)-Bi(1)-Cl(3)	91.50(11)	Cl(2)-Bi(1)-Cl(3)	92.23(11)
Cl(1)-Bi(1)-Cl(4)	89.89(10)	Cl(2)-Bi(1)-Cl(4)	172.17(10)	Cl(3)-Bi(1)-Cl(4)	94.23(10)
Cl(1)-Bi(1)-Cl(5)	92.91(10)	Cl(2)-Bi(1)-Cl(5)	92.53(10)	Cl(3)-Bi(1)-Cl(5)	173.25(10)
Cl(4)-Bi(1)-Cl(5)	80.67(9)	Cl(1)-Bi(1)-Cl(6)	165.89(10)	Cl(2)-Bi(1)-Cl(6)	96.10(10)
Cl(3)-Bi(1)-Cl(6)	97.50(10)	Cl(4)-Bi(1)-Cl(6)	78.67(9)	Cl(5)-Bi(1)-Cl(6)	77.23(9)

2 Results and discussion

2.1 Synthesis

For the synthesis of compound **1**, the reaction conditions and the proportion of raw materials are very important. The pure compound **1** with highest yield can be obtained by controlling the mole ratio of 1,4-MPNH₃⁺ and 18-crown-6 to be 1:3 under mild solvothermal conditions. Otherwise, a large amount of white powder will be precipitated with the increase in the proportion of 1,4-MPNH₃⁺ ions, which was identified as the [(1,4-PMNH₃)·(18-crown-6)]₃·(Bi₂Cl₉) compound by elemental analysis and TG. On the contrary, the yield will be reduced as the decrease in the proportion of 1,4-MPNH₃⁺. In addition, the analogous tertiary amine and secondary amine molecules (1,4-PM-NHMe, 1,4-PM-NMe₂, 1,4-PM-NHEt and 1,4-PM-NEt₂, that is, the H atoms of 1,4-PM-NH₂ were substituted by methyl or ethyl) were additionally added into the reaction solutions, respectively. However, these corresponding ammonium cations were not involved in the crystallization, and did not affect the

yield and purity of compound **1**. Moreover, only the [(OH₃)·(18-crown-6)]₃·(Bi₂Cl₉) compound can be obtained when the 1,4-MPNH₃⁺ cation was absent, regardless of whether the other ammonium cations are present in this solution (even with a very high concentration). This experiment provides evidence that the flexible 18-crown-6 ether shows high selectivity to 1,4-MPNH₃⁺ and OH₃⁺ cations, and the 1,4-MPNH₃⁺ guest possess a priority to be selectively identified.

2.2 Spectral properties

The structure of compound **1** was identified by satisfactory elemental analysis, IR and XRPD^[24-26]. The IR spectra shown a series of characteristic peaks of aromatic ring at 1 583, 1 479, 1 210, 778 and 704 cm⁻¹, and the sharp peak at 3 103 cm⁻¹ corresponds to the aromatic C-H vibration of 1,4-MPNH₃⁺^[24-26]. The strong broad band around 3 300~3 400 cm⁻¹ suggests that the -NH₂ group and H₂O molecules were protonated to form the intermolecular N-H···O or O-H···O H-bonds. Moreover, the double sharp peaks at 3 505 and 3 481 cm⁻¹ showed the presence of unprotonated -NH₂ group. And the double sharp peaks at

2 918 and 2 871 cm^{-1} are corresponds to the $\nu_{\text{as}}(\text{C-H})$ and $\nu_{\text{s}}(\text{C-H})$ of methylene, respectively. The characteristic peaks of crown ether are presented at 1 421, 1 361, 1 288, 1 221 and 1 129 cm^{-1} , which are attributed to the specific -O-C-C- structural unit. The corresponding UV/Vis spectra of the compound **1** and 1,4-PMNH₂ were measured in the solid state at room temperature and exhibit an absorption bands at the range of 200~400 nm. The above spectral analyses are in agreement with the determined single-crystal structure.

X-ray powder diffraction (XRPD) analysis: The agreement between the experimental and simulated XRPD patterns indicated the phase purity of **1** (Fig.1). The difference in reflection intensities between the simulated and experimental patterns was mainly due to the different powder size during collection of the experimental XRPD data.

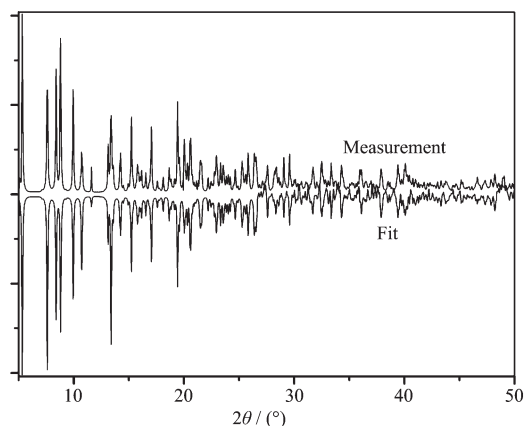
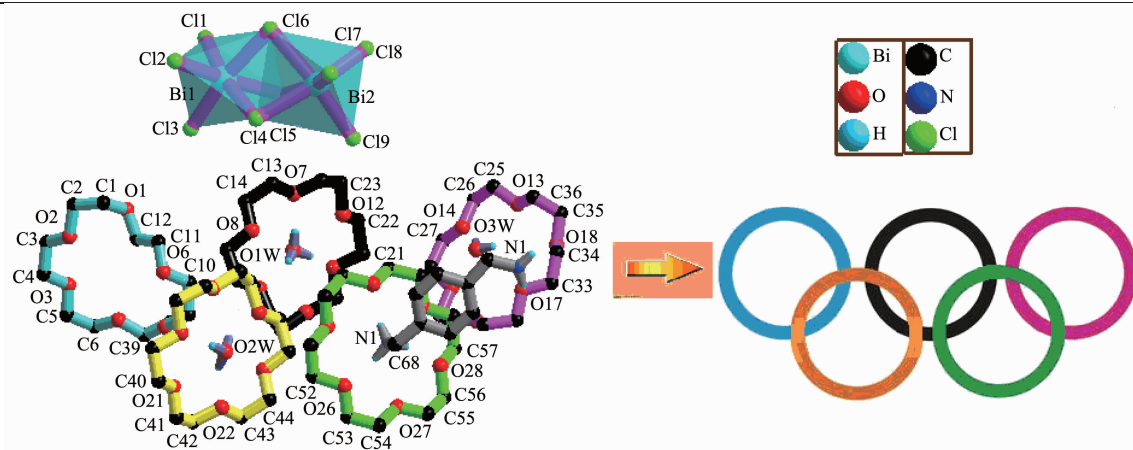


Fig.1 Experiment and simulated XRPD curves for compound **1**

2.3 Description of crystal structure

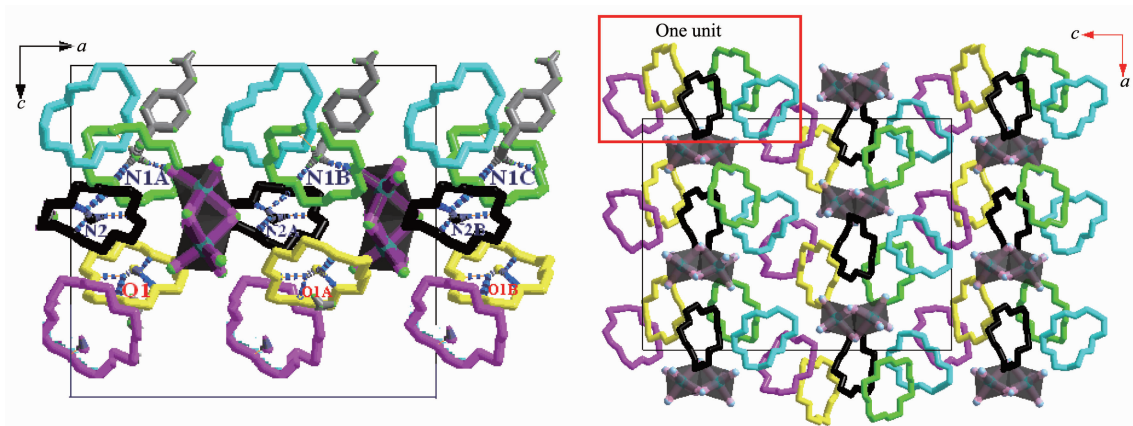
Single-crystal X-ray analysis reveals that complex **1** crystallized in the orthorhombic space group $Pca2_1$. The asymmetric unit were composed of five 18-crown-6 molecules with different shapes, one 1,4-PMNH₃⁺ cations, two OH₃⁺ cations, two Bi(III) cations, one water molecule, three μ_2 -bridged Cl⁻ and six terminal Cl⁻ anions (Fig.2). Two water molecules and one of the -NH₂ groups (1,4-PMNH₂ molecule contains two terminal -NH₂ groups, 1,4-PMNH₃⁺=H₂N-CH₂-Ar-CH₂-NH₃⁺) were protonated to form the tridentate H-bonding donors (-NH₃⁺ and OH₃⁺). Then the tridentate 1,4-

PMNH₃⁺ H-bonding donor involved in the formation of macrocycle-based [(1,4-PMNH₃)·(18-crown-6)]⁺ assembly with 18-crown-6 acceptor, via strong N-H···O hydrogen-bonding interactions. The -NH₃⁺ side of H₂N-CH₂-Ar-CH₂-NH₃⁺ guest was connected to the crown-ether host through three short linear N-H···O H-bonds and three longer acute interactions. Similarly, the OH₃⁺ and H₂O connected with the crown-ether molecules through strong O_{water}-H···O_{18-crown-6} hydrogen bonds to result in the formation of [(OH₃)·(18-crown-6)]⁺ and [(H₂O)·(18-crown-6)] assemblies. The distances between the H-bonding donor atoms (N or O_{water}) and the acceptor atoms (O_{18-crown-6}) in the macrocyclic assemblies are very short as shown below, indicating strong intermolecular hydrogen-bonding attractions (the N1···O_{18-crown-6} distances are 0.284 7(2), 0.286 0(2), 0.297 3(2), 0.299 4(2), 0.287 9(2) and 0.291 3(2) nm; O1W···O_{18-crown-6} distances are 0.259 7 (2), 0.268 7(2), 0.265 4(2), 0.285 2(2), 0.281 9(2) and 0.292 2(2) nm; O2W···O_{18-crown-6} distances are 0.268 9(2), 0.296 4(2), 0.265 5(2), 0.288 9(2), 0.271 6(2) and 0.285 5(2) nm; and 0.286 0(2) and 0.295 9(2) nm for O3W···O_{18-crown-6} respectively). All the hydrogen-bond geometry in the above mentioned assemblies are similar to those in related compounds containing 18-crown-6 and alkylammonium salts^[15-20]. In addition, the tridentate H-bonding donor -NH₃⁺ and OH₃⁺ are almost perpendicular to each crown-ether mean plane along the gyro-axis of the assemblies, and the N1, O1W, O2W and O3W atoms are out of each plane with 0.071 3(3), 0.026 1(3), 0.048 6(3) and 0.174 5(5) nm, respectively. The shape and structural parameters of the five 18-crown-6 macrocyclic molecules are different, but all the macrocycles are based on the same conformation of approximate C_{3v} symmetry, with all O-CH₂-CH₂-O torsion angles being gauche and alternating in sign, similarly, all CH₂-O-CH₂-CH₂ torsion angles being trans. And the O_{crown ether} atoms are nearly coplanar, that is, three O atoms are located slightly above the mean plane of O_{crown ether}, and the other three O atoms below the plane, with average deviations of the O atoms from the O_{crown ether} planes of 0.365, 0.479, 0.452, 0.521 and 0.689 for the five 18-crown-6 macrocycles, respectively.



Displacement ellipsoids at 30% probability level; Different color represents different 18-crown-6 assemblies

Fig.2 Viewing of the asymmetric unit and showing the coordination environment in complex **1**



Different color represents different 18-crown-6 assemblies; Hydrogen atoms which not be included in H-bonds are excluded for clarity

Fig.3 Self-assembly packing of the 18-crown-6 assemblies and $(\text{Bi}_2\text{Cl}_9)^{3-}$ anion units viewed along the b axis (a) and the simplified diagram by omitted the guests (3b)

For the $\text{Bi}_2\text{Cl}_9^{3-}$ anion, it was presented as counter-ions to the supramolecular guest-host cation assemblies, in which, the irregular octahedral Bi(III) centers adopt a six-coordinate geometry composing of three μ_2 -chelated chloride atoms and three terminal chloride atoms. And the μ_2 -chelated Cl atoms (Cl4, Cl5 and Cl6) bridged the metal ions into a binuclear Bi_2Cl_3 unit, with the Bi-Cl bond distances in the range of 0.305 6(5)~0.289 1(3) nm, and Bi-Cl-Bi bond angles in the range of 85.66(3)°~83.31(2)°. In addition to the three mono-valent assemblies (one $[(-\text{NH}_3) \cdot (18\text{-crown-6})]^+$ and two $[(\text{OH}_3) \cdot (18\text{-crown-6})]^+$), where there are two zero-valent assemblies (one $[(\text{H}_2\text{O}) \cdot (18\text{-crown-6})]$ and one 18-crown-6) within the asymmetric unit, they were alternately stacked together through the interactions of the $\text{Bi}_2\text{Cl}_9^{3-}$ anions. This combined

mode may be due to the presence of the trivalent $\text{Bi}_2\text{Cl}_9^{3-}$ anion, which is relatively larger than the other common anions. This is very similar to the known $[\text{Ni}(\text{dmit})_2]^-$ and $[\text{PMo}_{12}\text{O}_{40}]^{4-}$ anions^[18-19]. So the $\text{Bi}_2\text{Cl}_9^{3-}$ can be embedded into large and structurally diverse macrocyclic assemblies to result in the pentacyclic supramolecular structure (as shown in Fig.3).

2.4 Fluorescent properties

The fluorescent properties of the complex **1** and 1,4-MPNH₂ were investigated at room temperature in the solid state. The intense broad emission band at 391 nm was observed for compound **1** upon excitation at $\lambda=315$ nm, as illustrated in Fig.4. Moreover, the free 1,4-MPNH₂ presents a weak photoluminescence emission at 380 nm under the same experimental conditions. The emission of complex **1** is red-shifted

about 11 nm compared to that of free ligand 1,4-MPNH₂. Obviously, the emissions derived from the conjugated systems of the aromatic amine molecules. After coordination, one of the -NH₂ groups of 1,4-MPNH₂ molecule was protonated, and the arm-like -NH₃⁺ group was firmly bound in the crown ether cavity through six strong N-H···O H-bonding interactions, then the parent aromatic ring was fixed and showed a better plane conjugacy. Therefore, the rigidity and the conjugated effect of this aromatic system has been promoted during the molecular packing, which plays the main role to the luminescence intensity and red-shift effect. Thus, the compound **1** and the 1,4-MPNH₂ have shown different luminescence properties.

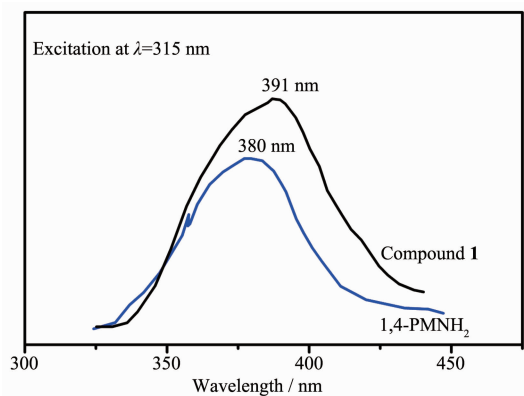


Fig.4 Fluorescent emission spectra of compound **1** and free 1,4-MPNH₂

2.5 Thermal analysis

The thermal behaviors of the title compound have been discussed in detail through the thermogravimetric (TG) and differential scanning calorimetry (DSC) measurements from 20 to 700 °C. As shown in Fig.5, there are four thermal anomaly peaks in the corresponding DSC curve. The first endothermic stage occurs with the peak temperature at 181 °C, which proves that three water molecules were lost. And the next endothermic peak with large thermal anomaly value was observed at 263 °C indicating the escape of four free 18-crown-6 molecules. The third endothermic peak indicates the escape of [(1,4-PMNH₃)·(18-crown-6)] assembly in the range of 298 to 312 °C. The last exothermic stage, with very broad range of nearly 150 °C, corresponds to the decomposition of inorganic

parts. For compound **1**, [(1,4-PMNH₃)·(18-crown-6)]·[(H₃O)·(18-crown-6)]₂·[(H₂O)·(18-crown-6)]·(18-crown-6)·(Bi₂Cl₉), the multi-component characteristic makes the weight loss becoming a little more complicated. Corresponding to the DSC, there are also four weight-loss peaks in the TG diagram in the temperature range of room temperature to 700 °C. The structure remains undecomposed up to 182 °C where the first weight loss start with the weight loss of about 2.53%, which indicates the escape of three water molecules (Calcd. 2.49%). The second step of weight loss was observed in the range of 260 to 273 °C, amounting to about 46.77% weight loss and corresponding to the escape of four crown ether molecules (Calcd. 46.91%). The remaining [(1,4-PMNH₃)·(18-crown-6)] assemblies part has been lost until a high temperature of 301 °C with the weight loss of 17.69% (Calcd. 17.81%). Then, the last weight loss appeared, which indicate the decomposition of the remaining inorganic parts. This is the special feature for multi-component hybrid supramolecular compound.

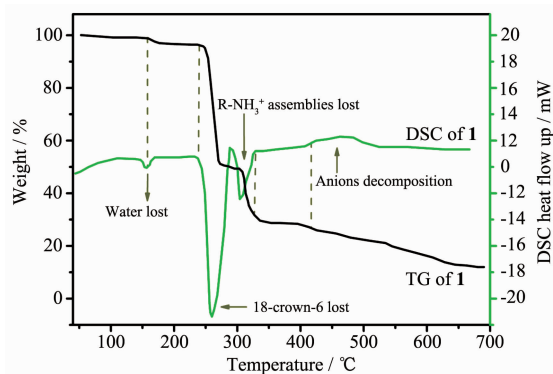


Fig.5 DSC and TGA curves for compound **1**

3 Conclusions

In summary, the novel supramolecular compound has been synthesized successfully by effectively controlling the reaction conditions, in which the different shapes were adopted for the five 18-crown-6 macrocyclic molecules. The ether-based cation assemblies and trivalent anion clusters were introduced into the multi-component crystal material by performing the supramolecular self-assembly method. And this experiment provides valid evidence that the flexible 18-crown-6 ether shows distinct

selectivity to different guests, and the R-NH_3^+ guest possess a priority to be selectively identified. This supramolecular synthesis strategies allow us to modulate the structural assemblies effectively, thus many macrocyclic supramolecular compounds with useful properties will be obtained.

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