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# Protonated *N*-oxide-4,4'-bipyridine: from luminescent Bi<sup>III</sup> complexes to hybrids based on H-bonded dimers or H-bonded open 2D square supramolecular networks†

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The *N*-oxide-4,4'-bipyridine (bp4mo) ligand has been rarely used in coordination or supramolecular chemistry. Depending on experimental conditions in the bp4mo/BiX<sub>3</sub> (X = Cl, Br) system, several compounds, in which the degree of protonation of bp4mo ( $\tau = \text{H}/\text{bp4mo}$ ) varies, have been stabilized. In acidic conditions, either a complete *N*-protonation and a partial *O*-protonation ( $\tau = 1.5$ ) or a complete *N*-protonation ( $\tau = 1.0$ ) can occur, leading to either a hybrid salt based on H-bonded dimers [H(Hbp4mo)<sub>2</sub>]<sup>3+</sup>, or to O(Hbp4mo)-Bi photoluminescent complexes. In neutral conditions, a partial *N*-protonation ( $\tau = 0.5$ ) occurs in [H(bp4mo)<sub>2</sub>][BiCl<sub>4</sub>]. Although the *N*-oxide parts are free to bind Bi<sup>3+</sup> cations, the organic entities prefer self-organizing through H-bonding (NH⋯N and CH⋯O) to give an impressive 2D supramolecular square network which accommodates the 1D BiCl<sub>4</sub><sup>-</sup> polymeric anion.

## Introduction

Compounds based on the *N*-oxide-4,4'-bipyridine (bp4mo) ligand are very scarce. Loeb and colleagues first published the crystal structures of four metal complexes with the metal ions bound to the N atoms of the pyridine parts of bp4mo.<sup>1</sup> More recently, we have stabilized the strongly photoluminescent 2D coordination polymer of [Pb(bp4mo)Cl<sub>2</sub>] in which, for the first time, the bp4mo ligand acts as a bridge between two metal centers, here two Pb<sup>2+</sup>.<sup>2</sup> The bridging ligand of bp4mo which combines a pyridyl ring on one side and a pyridyl *N*-oxide part on the other side, can be considered as a hybrid molecule of 4,4'-bipyridine and *N,N'*-dioxide-4,4'-bipyridine (bp4do). On one hand, the pyridyl group is both an intermediate base according to the HSAB theory<sup>3</sup> with abilities to link a large number of cations, and a weak Brønsted base ( $\text{p}K_{\text{a}} \cong 5$ ). On the other hand, the pyridyl *N*-oxide group may be considered as a rather hard base; this is highlighted in the chemistry of the well known bp4do ligand which has yielded a great number of complexes or CPs with cations whose acidity varies from intermediate (Cu<sup>2+</sup>, Pb<sup>2+</sup>, ...),<sup>4</sup> to strong (Ln<sup>3+</sup> cations).<sup>5</sup> As regards to its behaviour towards H<sup>+</sup>, however,

the pyridyl *N*-oxide group is a very weak Brønsted base ( $\text{p}K_{\text{a}}$  of 0.73 for the protonated derivative). And, for instance, only a few structures based on protonated bp4do molecules, Hbp4do<sup>6,7</sup> or H<sub>2</sub>bp4do<sup>2+,7</sup> are known, although they are good candidates for the building of H-bonded supramolecular polar chain based materials.

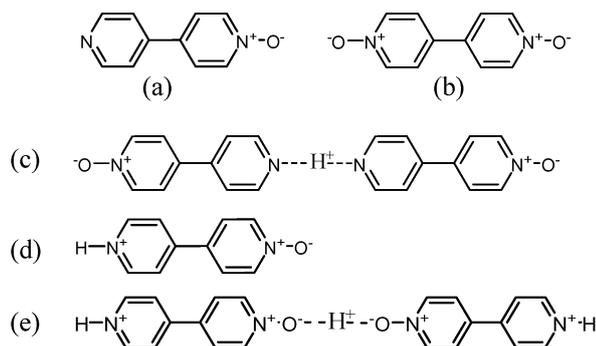
In the PbCl<sub>2</sub>/bp4mo system, depending on experimental conditions, two compounds have been obtained: in neutral conditions, as already mentioned, the strongly luminescent material [Pb(bp4mo)Cl<sub>2</sub>], and, in acidic conditions (HNO<sub>3</sub>), the coordination polymer of [Pb(Hbp4mo)<sub>2</sub>Cl<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>.<sup>2</sup> Their crystal structures are very close to each other, a "PbCl<sub>2</sub>" unit of "[Pb<sub>2</sub>(bp4mo)<sub>2</sub>Cl<sub>4</sub>]" being substituted by two HNO<sub>3</sub> molecules in [Pb(Hbp4mo)<sub>2</sub>Cl<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>. In the latter, the pyridyl part is then protonated while the pyridine-*N*-oxide part always binds Pb<sup>2+</sup> cations. However, in contrast with the optical properties of [Pb(bp4mo)Cl<sub>2</sub>], the Hbp4mo<sup>+</sup>-based material does not show any luminescence. Hbp4mo<sup>+</sup> can also be considered as a *N-R-N'*-oxide-4,4'-bipyridinium entity where R = H, and it is interesting to note that a similar ligand, the *N*-methyl-*N'*-oxide-4,4'-bipyridinium cation (MVO<sup>+</sup>, R = CH<sub>3</sub>), has afforded luminescent bismuth(III) complexes in the solid state.<sup>8</sup>

In this work, we report the results of our investigations in the bp4mo/BiX<sub>3</sub> (X = Cl, Br) system. In neutral conditions, a partial protonation of the N atoms of bp4mo occurs in [H(bp4mo)<sub>2</sub>][BiCl<sub>4</sub>] (1). Although the *N*-oxide parts are free to bind Bi<sup>3+</sup> cations, the organic entities prefer self-organizing through H-bonding (NH⋯N and CH⋯O) to give a very nice 2D supramolecular square network which includes the

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† Electronic supplementary information (ESI) available: Tables of crystal data, X-ray crystallographic files in CIF format and XRPD patterns for 1–5; UV-vis spectra of 2–4; TGA of 5. CCDC 952307–952311. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ce41579a



**Scheme 1** bp4mo (a) and bp4do (b) molecules, and the bp4mo protonated forms  $[\text{H}(\text{bp4mo})_2]^+$  ( $\tau = 0.5$ ) (c),  $[\text{Hbp4mo}]^+$  ( $\tau = 1.0$ ) (d) and  $[\text{H}(\text{Hbp4mo})_2]^{3+}$  ( $\tau = 1.5$ ) (e), found in **1**, **2–4**, and **5**, respectively.

1D  $\text{BiCl}_4^-$  polymeric anion. In moderate acidic conditions, the complete *N*-protonation of bp4mo occurs, leading to dimeric complexes, *ap*- $[(\text{Hbp4mo})_2\text{Bi}_2\text{Cl}_8]$  (**2**) and *eq*- $[(\text{Hbp4mo})_2\text{Bi}_2\text{Br}_8]$  (**3**), or to a 1D coordination polymer,  $[(\text{Hbp4mo})\text{BiBr}_4]$  (**4**) which display photoluminescence properties, the quantum yield of **2** being 11%. Finally, in stronger acidic conditions, a tricationic entity,  $[\text{H}(\text{Hbp4mo})_2]^{3+}$ , resulting from two H-bonded  $\text{Hbp4mo}^+$  cations (partial *O*-protonation of  $\text{Hbp4mo}^+$ ) counterbalances a isolated  $\text{BiCl}_6^{3-}$  anion in  $[\text{H}(\text{Hbp4mo})_2][\text{BiCl}_6]\cdot\text{DMSO}$  (**5**). The bp4mo and bp4do molecules, as well as the bp4mo protonated forms found in **1** ( $\tau = 0.5$ ), **2–4** ( $\tau = 1.0$ ) and **5** ( $\tau = 1.5$ ) are illustrated in Scheme 1.

## Experimental

### Synthesis

The hydrated *N*-oxide-4,4'-bipyridine (bp4mo-2H<sub>2</sub>O) has been synthesized according to the literature.<sup>9</sup> Compounds **1** and **5** were obtained with a slow liquid–gas diffusion method from bp4mo-2H<sub>2</sub>O and BiCl<sub>3</sub>, and hydrochloric acid in the case of **5**. The starting materials were dissolved in the minimum of DMSO in a pill box (**1**: bp4mo-2H<sub>2</sub>O (31.4 mg, 0.151 mmol), BiCl<sub>3</sub> (47.5 mg, 0.150 mmol); **2**: bp4mo-2H<sub>2</sub>O (26.5 mg, 0.127 mmol), BiCl<sub>3</sub> (42.0 mg, 0.128 mmol), HCl (20 drops, 8.18 mol)). The pill box was then covered with a holed aluminum paper and inserted in a jar filled with ethanol. The jar was then covered with a lid and sealed with parafilm. A few days later, crystals appeared. They were filtered, washed with ethanol and dried in an oven at 50 °C (**1**: 38.9 mg (82% yield); **2**: 36.7 mg (91% yield)). Compounds **2–4** were prepared by a solvothermal method using a Teflon-lined PARR autoclave (internal volume 25 mL). To 0.127 mmol of BiCl<sub>3</sub> (40.2 mg), 0.127 mmol of bp4mo-2H<sub>2</sub>O (26.5 mg) and 0.327 mmol of HCl (1 drop) (**2**) or to 0.127 mmol of BiBr<sub>3</sub> (57.0 mg), 0.127 mmol of bp4mo-2H<sub>2</sub>O (26.5 mg) and H<sub>2</sub>O (10 drops) (**3**) or to 0.127 mmol of BiBr<sub>3</sub> (57.0 mg), 0.127 mmol of bp4mo-2H<sub>2</sub>O (26.5 mg) and 0.198 mmol of HBr (1 drop) (**4**) were added 10 mL of methanol. The autoclave was heated in a programmable oven with the following parameters: **2**: 6 h of heating from 25 to 75 °C, 10 h remaining at 75 °C, and then 4 h of cooling down to 25 °C. Crystals with pale yellow color were collected by filtration and

washed with methanol (yield 95% on the basis of BiCl<sub>3</sub>); **3**: 18 h of heating from 25 to 65 °C, 26 h remaining at 65 °C, and then 12 h of cooling down to 25 °C. Large yellow block type crystals were collected by filtration and washed with methanol (yield 88% on the basis of BiBr<sub>3</sub>); **4**: 8 h of heating from 25 to 75 °C, 12 h remaining at 75 °C, and then 6 h of cooling down to 25 °C. Yellow crystals were collected by filtration and washed with methanol (yield 80% on the basis of BiBr<sub>3</sub>).

### X-ray diffraction characterization

X-ray powder diffraction measurements were carried out on a D8 Bruker diffractometer using Cu-K $\alpha_{1,2}$  radiation, equipped with a linear Vantec super speed detector. The X-ray powder diffraction (XRPD) patterns of all samples **1–5** showed that all the observed reflections can be indexed in the unit cell parameters obtained from single crystal X-ray diffraction experiments (ESI†). X-ray diffraction data of selected single crystals were collected on a Bruker-Nonius KAPPA-CDD diffractometer equipped with graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). A summary of crystallographic data and refinement results for **1–5** is listed in Table 1. Structures were solved and refined using the Shelxl97 package. Positions and agitation parameters were refined by full-matrix least-squares routines against  $F^2$ . All hydrogen atoms were treated with a riding model. In **5**, the non-bonded DMSO molecule is disordered, leading to allocate a site occupation factor of 0.5 for the sulfur atom and to locate the riding hydrogen atoms of the methyl groups over two positions. In **1**, the H atom between two N(2) atoms, as indicated by the short distance between them ( $d_{\text{N}(2)\cdots\text{N}(2)} = 2.724(1)$  Å), could not be located. It was then localized at 0.86 Å from N(2) in half site occupation factor, thus appearing disordered over two positions. Finally, refinements of positions and anisotropic displacement parameters of all non-H atoms lead to  $R_1 = 0.034$  (**1**);  $R_1 = 0.045$  (**2**);  $R_1 = 0.037$  (**3**);  $R_1 = 0.052$  (**4**);  $R_1 = 0.035$  (**5**). A more complete summary of crystallographic data for **1–5** are given as ESI† CCDC 952307 (**1**), 952308 (**2**), 952309 (**3**), 952310 (**4**) and 952311 (**5**) contain the supplementary crystallographic data for this paper.

### Photoluminescence measurements

Photoluminescence quantum yield measurements for the solid state materials were carried out using a home-made integrating sphere according to the procedure already described.<sup>10</sup>

## Results

### Partial *N*-protonation of bp4mo

In the bp4mo/BiCl<sub>3</sub> system, the synthesis in neutral conditions was carried out with the aim to stabilize a coordination polymer type compound in which both N and O atoms of bp4mo molecules would bind the Bi<sup>3+</sup> cations, as it has been found starting from Pb<sup>2+</sup>. Unfortunately, any such compound has been stabilized, but an unexpected compound with a very interesting structural layout has been

Table 1 Crystallographic data for 1–5

	1	2	3	4	5
Formula	C <sub>20</sub> H <sub>17</sub> BiCl <sub>4</sub> N <sub>4</sub> O <sub>2</sub>	C <sub>20</sub> H <sub>18</sub> Bi <sub>2</sub> Cl <sub>8</sub> N <sub>4</sub> O <sub>2</sub>	C <sub>20</sub> H <sub>18</sub> Bi <sub>2</sub> Br <sub>8</sub> N <sub>4</sub> O <sub>2</sub>	C <sub>10</sub> H <sub>9</sub> BiBr <sub>4</sub> N <sub>2</sub> O	C <sub>22</sub> H <sub>25</sub> BiCl <sub>6</sub> N <sub>4</sub> O <sub>3</sub> S
<i>M<sub>r</sub></i>	696.16	1047.94	1403.62	701.81	847.23
System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/a</i>	<i>C2/c</i>
<i>a</i> /Å	23.695(1)	18.8244(8)	10.1031(6)	8.4049(8)	19.2567(8)
<i>b</i> /Å	26.662(1)	9.7773(2)	12.8928(5)	21.201(2)	13.3429(5)
<i>c</i> /Å	7.2913(5)	16.5190(7)	12.574(1)	9.3965(6)	12.3084(7)
<i>α</i> /°	90	90	90	90	90
<i>β</i> /°	95.95(1)	94.87(1)	104.08(1)	107.24(1)	107.43(1)
<i>γ</i> /°	90	90	90	90	90
<i>V</i> /Å <sup>3</sup>	4581.5(4)	3028.9(2)	1588.7(2)	1599.2(2)	3017.2(2)
<i>Z</i>	8	4	2	4	4
<i>T</i> /K	293	293	293	293	293
<i>μ</i> (MoKα) mm <sup>-1</sup>	8.19	12.34	21.15	21.00	6.47
Measured reflns	67 247	22 424	22 302	30 390	20 645
Unique reflns ( <i>R</i> (int))	7990 (0.080)	5215 (0.065)	4610 (0.065)	5525 (0.110)	4384 (0.084)
Refined parameters	285	167	167	167	175
GO <i>F</i> ( <i>F</i> <sup>2</sup> )	1.02	1.03	1.04	1.00	0.97
<i>R</i> <sub>1</sub> ( <i>F</i> ) ( <i>I</i> > 2σ( <i>I</i> ))	0.034	0.045	0.037	0.052	0.035
w <i>R</i> <sub>2</sub> ( <i>F</i> <sup>2</sup> ) all data	0.055	0.063	0.058	0.125	0.061

crystallized: [H(bp4mo)<sub>2</sub>][BiCl<sub>4</sub>] (1). A partial *N*-protonation of molecules has occurred certainly due to the presence of a small amount of water in the initial solution. The structure reveals the presence of [H(bp4mo)<sub>2</sub>]<sup>+</sup> entities in which one H<sup>+</sup> ion is shared by two molecules. This situation is well known, for instance in 4,4'-bipyridine-based compounds.<sup>11</sup> The main structural feature of (1) is that the O atoms of the [H(bp4mo)<sub>2</sub>]<sup>+</sup> entity which were still free to bind Bi<sup>3+</sup> – it has been shown in the past that the pyridine *N*-oxide ligand has capabilities to link Bi<sup>3+</sup> cations<sup>8,12</sup> – are finally engaged through H-bonding with other organic entities, thus leading to a 2D supramolecular layered network. Thus, the crystal structure of (1) can be described as built from the packing of these 2D supramolecular layers, slightly shifted one from each other along the (*a* + 2*c*) direction, which accommodate the polymeric anion of BiCl<sub>4</sub><sup>-</sup> (Fig. 1). Such polymeric anion consisting of edge sharing [BiCl<sub>6</sub>] octahedra is well known in the chemistry of halobismuthate salts.<sup>13,14</sup>

The representation of the inorganic part as metal polyhedra is very common and, in 1, allows defining polymeric chains which extend along the *c* axis across the supramolecular layered networks (Fig. 1b). However, it is also easy to notice that all Bi<sup>3+</sup> and Cl<sup>-</sup> ions lie in layers (Fig. 1b). One layer is represented in Fig. 2. It clearly appears that the square defined by the 4 Cl atoms of one [BiCl<sub>4</sub>] entity fit well in the windows defined by the supramolecular network of partially protonated bp4mo entities. Numerous of Cl<sup>-</sup>⋯H(C) interactions (not represented on Fig. 2) in the range of 2.80 Å–2.90 Å are found between each Cl and H atom of the pyridine cycles (the sum of van der Waals radii of Cl and H is 2.90 Å). In the asymmetrical unit, one independent molecule (including O1 and N2 atoms) and two half molecules (one including the O2 and N3 atoms, the other the O3 and N5 atoms) are defined. As a consequence, there are two types of [H(bp4mo)<sub>2</sub>]<sup>+</sup> dimers. The first one is defined by two molecules related to each other by a 2-fold axis. The short N(2)⋯N(2) distance of 2.724(1) Å

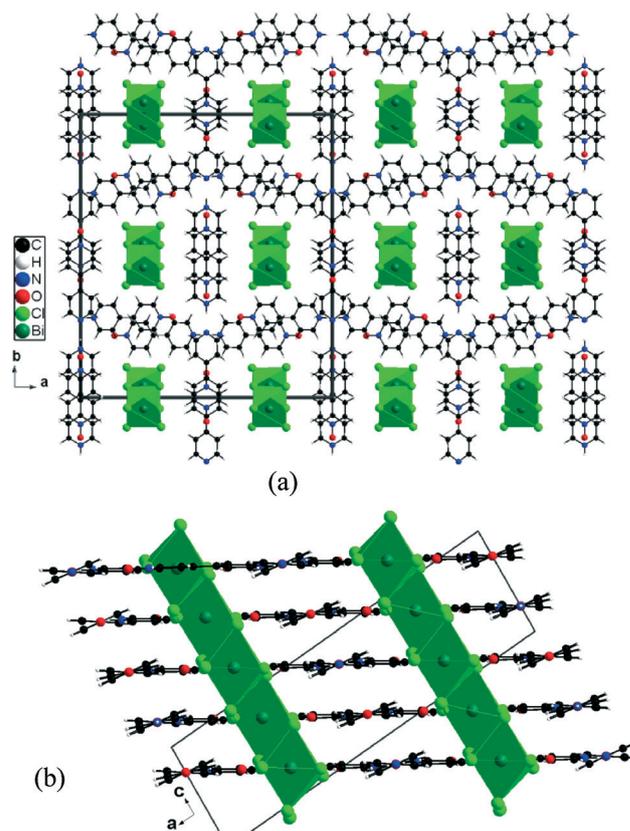
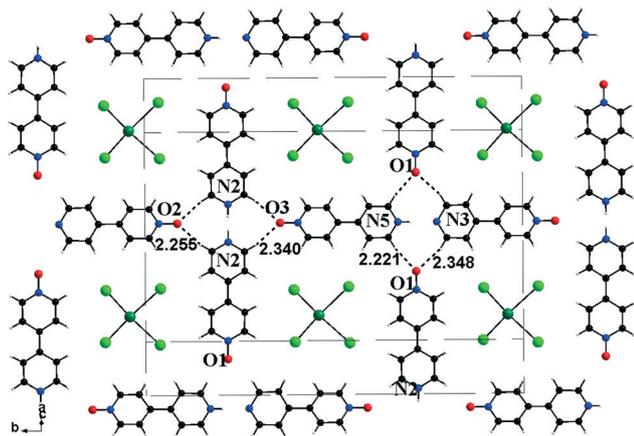


Fig. 1 Crystal structure of [H(bp4mo)<sub>2</sub>]BiCl<sub>4</sub> (1) viewed along the *c* axis (a) and along the *b* axis (b) showing the polymeric BiCl<sub>4</sub><sup>-</sup> anions extending across the 2D supramolecular networks of organic entities.

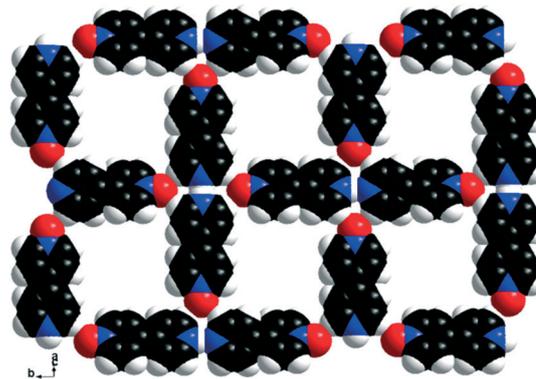
clearly indicates the presence of one H<sup>+</sup> in between the two nitrogen centers – and this is expected to counterbalance the negative charge of the inorganic chain. Two situations can be found, either a symmetrical one (N⋯H⋯N), or an asymmetrical one (N–H⋯N). The X-ray analysis did not allow us to see



**Fig. 2** The 2D square H-bonded supramolecular networks of partially protonated bp4mo molecules in **1**, which accommodates one  $\text{Bi}^{3+}$  and 4  $\text{Cl}^-$  ions in windows. Selected H-bonds, drawn as dashed lines, as well as their bond distance are indicated. Due to the 2-fold axis along  $b$ , the H atom born by the N(2) atom is disordered over two positions.

any H atom of the first category, which is certainly in favour of the asymmetrical situation. In fact, due to the 2-fold axis, the H atom localized at 0.86 Å from N(2) appears disordered over two positions (half occupation rate – Fig. 2). In the second  $[\text{H}(\text{bp4mo})_2]^+$  dimer involving two molecules located on the 2-fold axis, it is worth noting that the X-ray analysis allowed us to locate one H atom near N(5) (finally fixed at 0.86 Å) resulting in an asymmetrical N(5)–H $\cdots$ N(3) situation (Fig. 2). The two types of dimers are perpendicular to each other in such a way that all O atoms are engaged in hydrogen interactions with pyridyl H atoms bearing by carbon atoms  $\alpha$  to nitrogen centers (Fig. 2). The interaction distances are in the range of 2.221(1)–2.348(1) Å which are much shorter than the sum of van der Waals radii of H and O atoms ( $1.2 + 1.4 = 2.6$  Å), and the values of (N–O $\cdots$ H) angles ( $132.5(3)$ – $137.4(3)^\circ$ ) are in good accordance with the geometry of interactions commonly observed in structures of pyridyl- $N$ -oxide based compounds. The concerted effect of the two types of H-bonds, N–H $\cdots$ N and O $\cdots$ H–C, involving four adjacent molecules finally leads to a H-bond graph set of two adjacent  $\text{R}_3^2(8)$  rings according to the Etter's notation.<sup>15</sup> As a consequence, a nice 2D open square supramolecular network is formed (Fig. 2 and 3).

H-bonding is an interesting tool in the field of organic ferroelectrics, particularly when an asymmetrical situation such as a B–H $\cdots$ B interaction – B being a basic site – is present.<sup>16</sup> For instance in the case of B–R–B type ligands, such as 4,4'-bipyridine or  $N,N'$ -dioxide-4,4'-bipyridine, this can lead to  $[\text{B–R–B–H}\cdots\text{B–R–B–H}\cdots]_n$  polar chains, and further can lead to polar structures. The peculiar situation of bp4mo molecules which have two very different N and O basic sites is not in favour of the building of polar chains. However, in **1**, we remember that the H atom between N(5) and N(3) has been found to be bound to N(5), which means that the chains are polar along the  $b$  direction. It is somewhat surprising to observe a preferential basic site for the H atom due to the

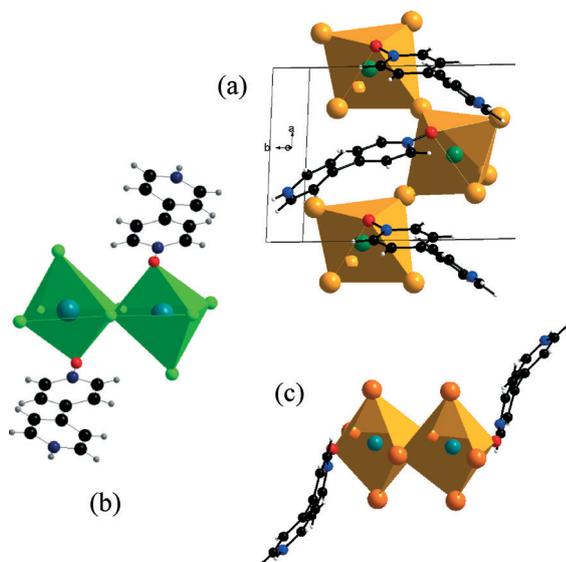


**Fig. 3** Space filling representation of the 2D square H-bonded supramolecular network of partially protonated bp4mo molecules in **1**.

distance between two such  $[\text{H}(\text{bp4mo})_2]^+$  dimers along  $b$  or along the  $(a + 2c)$  direction. But we notice that the localization of the H atom is in good accordance with the strength of the O $\cdots$ H(C) interaction: the (O $\cdots$ H) distance is short as the H is activated,  $d = 2.221(4)$  Å when H belongs to the pyridinium ring and  $d = 2.348(4)$  Å when H belongs to the pyridyl ring (Fig. 2). For the chain extending along the  $(a + 2c)$  direction, the 2-fold axis perpendicular to it precludes a polar nature of chains. Attempts to work in the  $Cc$  space group have lead to refinements of the whole structure of bad quality. Anyway, this 2D supramolecular network could be of interest in the field of polar materials. The growth of crystals of **1** as well as the synthesis of other compounds based on such a network will be carried out in the near future.

### Complete $N$ -protonation of bp4mo

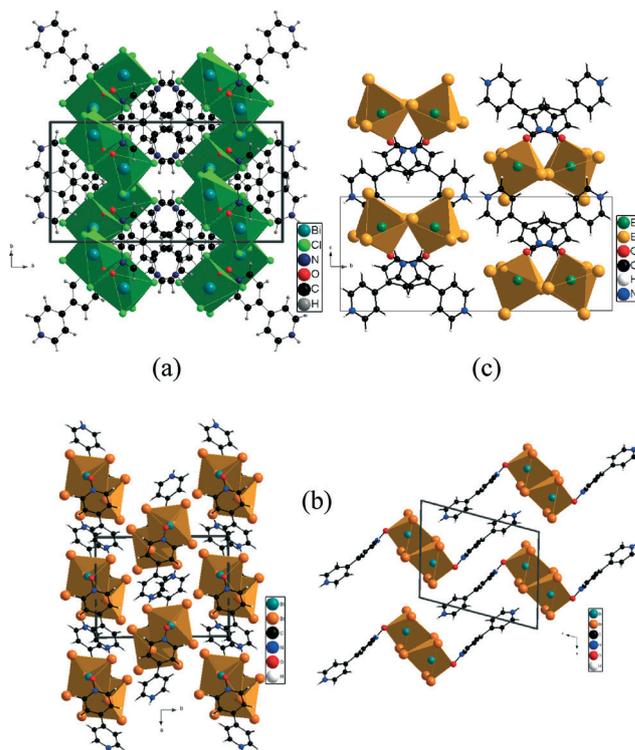
In moderate acidic conditions, an expected  $N$ -protonation leads to the formation of the pyridinium-based cation  $\text{Hbp4mo}^+$ . The  $N$ -oxide part remains free, and binds the bismuth cations. Three compounds are obtained:  $ap$ - $[(\text{Hbp4mo})_2\text{Bi}_2\text{Cl}_8]$  (**2**) when  $X = \text{Cl}$ , and, depending on experimental conditions,  $eq$ - $[(\text{Hbp4mo})_2\text{Bi}_2\text{Br}_8]$  (**3**) and  $[(\text{Hbp4mo})\text{BiBr}_4]$  (**4**) when  $X = \text{Br}$ . These hybrids, which are all based on 1  $\text{Hbp4mo}^+$ , 1  $\text{Bi}^{3+}$  and 4  $X^-$  ( $X = \text{Cl}, \text{Br}$ ) are isomers. This illustrates the structural diversity generally observed in the chemistry of halometalate chemistry.<sup>13,17</sup> **2** and **3** are positional isomers. They are both centrosymmetric complexes which consist of two edge-sharing  $\text{BiX}_5\text{O}$  polyhedra, each bismuth cation being linked to one  $\text{Hbp4mo}^+$ . However, while the O atoms are apical atoms in **2**, they are equatorial atoms in **3** (the equatorial planes are defined by the bridged bromides and the bismuth cations) (Fig. 4). In contrast, **4** is a one-dimensional coordination polymer which consists of chains of *cis*-connected  $\text{BiBr}_5\text{O}$  polyhedra. The O atoms are apical atoms, and it is worth noting that all  $\text{Hbp4mo}^+$  are linked to  $\text{Bi}^{3+}$  on the same side of the chains (Fig. 4). The N–O $\cdots$ Bi bond angles are close to  $120^\circ$  in **2**–**4** ( $118.4^\circ$  (**2**),  $121.7^\circ$  (**3**),  $126.2^\circ$  (**4**)) in accordance with the  $\text{sp}^2$  geometry of O atoms as well as values reported in pyridine- $N$ -oxide based materials.<sup>4,5,8</sup>



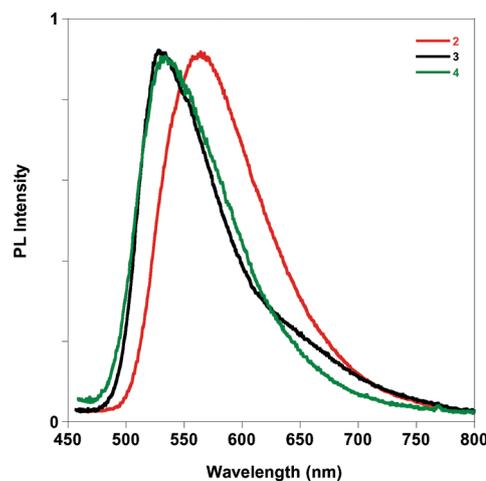
**Fig. 4** One system (1 Hbp4mo<sup>+</sup>, 1 Bi<sup>3+</sup>, 4 X<sup>-</sup> (X = Cl, Br)), three isomers: the one-dimensional coordination polymer [(Hbp4mo)BiBr<sub>4</sub>] (**4**) (a) and the two positional isomers, *ap*-[(Hbp4mo)<sub>2</sub>Bi<sub>2</sub>Cl<sub>8</sub>] (**2**) (b) and *eq*-[(Hbp4mo)<sub>2</sub>Bi<sub>2</sub>Br<sub>8</sub>] (**3**) (c).

The structural organization of the [(Hbp4mo)<sub>2</sub>Bi<sub>2</sub>X<sub>8</sub>] complexes in the structures of **2** and **3** are very different. When viewed along *c*, a segregation of the inorganic parts and the organic moieties appears in **2**, whereas **3** can be considered as a layered compound with layers in the (*a,c*) plane consisting of interpenetrated complexes (Fig. 5). In **4**, the acentric chains running along the *a* axis are related by a symmetry center, leading to a head-to-tail arrangement (Fig. 5). Pyridinium-based materials, particularly of the viologen type, are known to potentially exhibit photochromic properties upon UV irradiation, the color change being due to the presence of radicals which result from the electron transfer from a donor (D) (mainly, chlorides<sup>18</sup> (not observed for other halides), carboxylates,<sup>19</sup> or organic molecules<sup>20</sup>) to the pyridinium moiety. Recently, we have highlighted several key structural parameters for the observation of this phenomenon, among them the geometry of the N<sup>+</sup>⋯D interaction.<sup>21</sup> Any of the compounds **1**–**5**, particularly the chloride-based materials, is photochromic when irradiated by a UV lamp (360 nm). This can be correlated to the structural features. For instance in **2**, a quite short N<sup>+</sup>⋯Cl contact is observed (*d* ≈ 3.47 Å), nevertheless with an angle between the (N⋯Cl) line at the pyridinium ring far from the expected angle of 90° (≈ 120°).

The compounds **2**–**4**, in which bismuth cations are linked to Hbp4mo<sup>+</sup> through the O atom have photoluminescence properties (Fig. 6), while the others (**1** and **5**) do not show photoluminescence. The complexes **2**–**4** can be compared to the recently reported bismuth complexes based on the *N*-methyl-*N'*-oxide-4,4'-bipyridinium ligand (MVO<sup>+</sup>), [BiX<sub>6</sub>(MVO)(DMSO)] (X = Cl, Br), in which a Bi–O bond is also present.<sup>8</sup> In fact, we can consider Hbp4mo<sup>+</sup> as resulting from the substitution of the methyl group of MVO<sup>+</sup> by the H atom. The MVO-based complexes both show photoluminescence properties, and it is worth noting that the shape, the emission



**Fig. 5** Crystal structures of *ap*-[(Hbp4mo)<sub>2</sub>Bi<sub>2</sub>Cl<sub>8</sub>] (**2**) (a), *eq*-[(Hbp4mo)<sub>2</sub>Bi<sub>2</sub>Br<sub>8</sub>] (**3**) (b), general view (left) and view of one layer in the (*a,c*) plane (right), and [(Hbp4mo)BiBr<sub>4</sub>] (**4**) (c).



**Fig. 6** Room temperature solid state photoluminescence ( $\lambda_{exc} = 380$  nm) spectra of **2** (red line), **3** (black line) and **4** (green line).

wavelength ( $\lambda = 560$  nm) and (roughly) the intensity of luminescence of these two isostructural compounds (QY of 10% and 5% for the Br and Cl compounds, respectively) are similar, indicating no great influence of the nature of the halide. Here, if the shape of the emission spectra is roughly the same, a slight shift of the emission band ( $\lambda = 530$  nm for **3** and **4**,  $\lambda = 560$  nm for **2**) is observed (Fig. 6, normalized spectra) and, above all, a great difference concerns the intensity of photoluminescence which is weak for **3** and **4**, and quite high

for **2** with a quantum yield of 11%. As known in solid state photoluminescence, the crystal packing may have a great influence on quantum yields. The analysis of all weak interactions in the crystal structures of **2–4** is somewhat difficult. We will only focus on some structural features.

Fig. 7 gives details of structures of **2–4** showing the relative disposition of two close molecular entities. Two features can be noted: the long axes of two consecutive molecules are perpendicular to each other in **2** and **4**, while they are parallel in **3**, and quite short O...C interactions are found in **3** ( $d \cong 3.20$  Å) and **4** ( $d \cong 3.07$  Å) between one O atom and one C atom belonging to the C–C central bond (both O and C atoms approximately coincide on the projections of Fig. 7b and c). The shortest contact in **2** is of 3.55 Å between two carbon atoms. Additionally, it is worth noting that the dihedral angle between the two rings of one Hbp4mo<sup>+</sup> is 19.5° in **2**, 33.3° in **3** and 43.4° in **4**. So, it appears that the highest QY is observed for compound **2** in which the organic cation is the least distorted, and makes a minimum number of interactions with neighbouring organic entities. As in the [BiX<sub>4</sub>(MVO)(dmsO)] complexes where a Bi–O(ligand) bond occurs, the photoluminescence in **2–4** may mainly originate from a LMCT process.<sup>8</sup>

#### Complete N-protonation and partial O-protonation of bp4mo

Finally, in stronger acidic conditions, a complete N-protonation and a partial O-protonation ( $\tau = 1.5$ ) occurs, leading to the formation of the unprecedented tricationic entity, [H(Hbp4mo)<sub>2</sub>]<sup>3+</sup>. It results from two H-bonded Hbp4mo<sup>+</sup> cations as shown in Fig. 8a with the shared H atom located on a symmetry center between two O atoms ( $d(\text{O} \cdots \text{O}) = 2.426(4)$  Å,  $d(\text{H} \cdots \text{O}) = 1.213(3)$  Å). As in **2–4**, the N–O...A (A = electron acceptor, A = H in **5**) bond angle is close to 120° in **5** (111.2°) in accordance with the sp<sup>2</sup> geometry of the O atom. In the structure, the tricationic entities counterbalance isolated BiCl<sub>6</sub><sup>3–</sup> anions. Along the *a* axis, two consecutive organic entities are oriented at 90° to each other in such a way that an overlap of two pyridyl rings (of

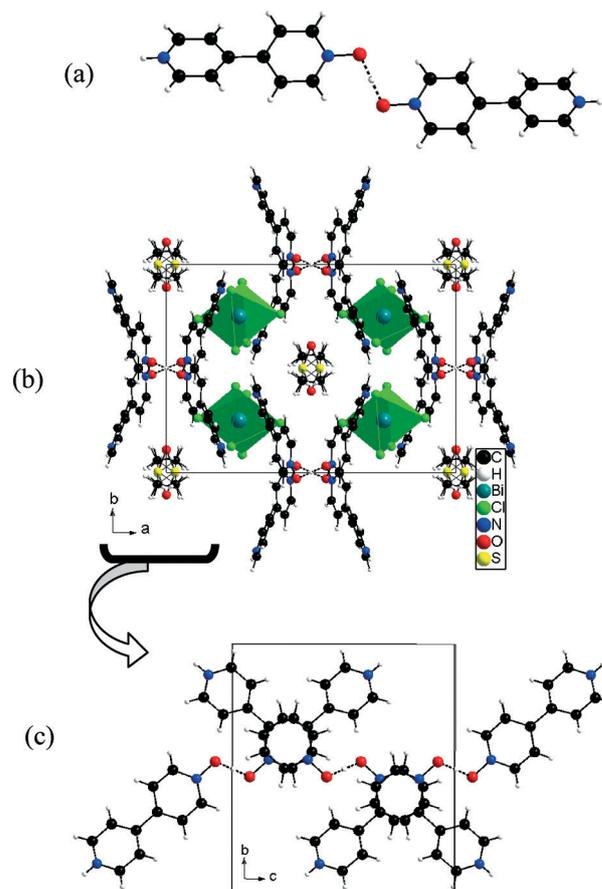


Fig. 8 Crystal structure of [H(Hbp4mo)<sub>2</sub>][BiCl<sub>6</sub>]·DMSO (**5**): the [H(Hbp4mo)<sub>2</sub>]<sup>3+</sup> entity (a), general layout viewed along the *c* axis (b), and part of the structure showing three [H(Hbp4mo)<sub>2</sub>]<sup>3+</sup> entities (c).

pyridine-*N*-oxide parts) occurs (Fig. 8c, distance between the centers of rings of  $\cong 3.60$  Å). These organic networks (running along the *c* axis) alternate along the *b* axis, enclosing disordered DMSO molecules (Fig. 8b).

## Conclusions

Using the *N*-oxide-4,4'-bipyridine (bp4mo) ligand with BiX<sub>3</sub> (X = Cl, Br), five new compounds have been stabilized. A protonation of bp4mo entities occurs whatever the experimental, acidic or neutral, conditions, while the degree of protonation  $\tau$  ( $\tau = \text{H}/\text{bp4mo}$ ) varies depending on the initial quantity of HX acid. In strong acidic conditions, a complete N-protonation and a partial O-protonation ( $\tau = 1.5$ ) leads to the formation of [H(Hbp4mo)<sub>2</sub>]<sup>3+</sup> entities which counterbalance isolated BiCl<sub>6</sub><sup>3–</sup> anions in the structure of [H(Hbp4mo)<sub>2</sub>][BiCl<sub>6</sub>]·DMSO (**5**). In moderate acidic conditions, a complete N-protonation ( $\tau = 1.0$ ) is observed, leading to O(Hbp4mo)–Bi complexes, that are *ap*-[(Hbp4mo)<sub>2</sub>Bi<sub>2</sub>Cl<sub>8</sub>] (**2**), *eq*-[(Hbp4mo)<sub>2</sub>Bi<sub>2</sub>Br<sub>8</sub>] (**3**) and [(Hbp4mo)BiBr<sub>4</sub>] (**4**). In contrast with salts **1** and **5**, complexes **2–4** display photoluminescence properties with quantum yields up to 11% (**2**), clearly showing that this is related to the presence of O–Bi bonds. In neutral conditions, certainly

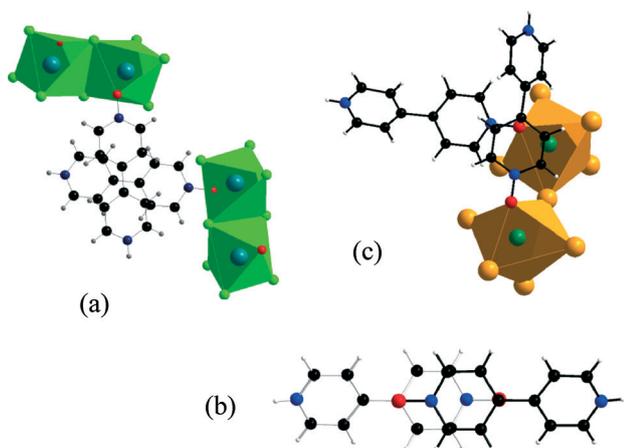


Fig. 7 Relative disposition of two close molecular entities in the structures of *ap*-[(Hbp4mo)<sub>2</sub>Bi<sub>2</sub>Cl<sub>8</sub>] (**2**) (a), *eq*-[(Hbp4mo)<sub>2</sub>Bi<sub>2</sub>Br<sub>8</sub>] (**3**) (b), and [(Hbp4mo)BiBr<sub>4</sub>] (**4**) (c).

due to the presence of a small amount of water in the initial solution, a partial *N*-protonation ( $\tau = 0.5$ ) occurs leading to  $[\text{H}(\text{bp4mo})_2][\text{BiCl}_4]$  (**1**). Although the *N*-oxide parts are free to bind  $\text{Bi}^{3+}$  cations, the organic entities prefer self-organizing through H-bonding ( $\text{NH}\cdots\text{N}$  and  $\text{CH}\cdots\text{O}$ ) to give an impressive 2D supramolecular square network which accommodates the 1D  $\text{BiCl}_4^-$  polymeric anion. Such a 2D supramolecular network could be of interest in the field of molecular ferroelectrics.

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