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Protonated *N,N′*-Dioxide-4,4′-bipyridine, an Interesting Synthon for the Building of Polar H-Bonded Networks?

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S *Supporting Information*

ABSTRACT: A slow liquid—gas diffusion method in strong acid conditions has allowed stabilizing for the first time in the solid state the diprotonated form of the 4,4′-bipyridine-*N,N′*-dioxide (bp4do), H_2bp4do^{2+} as two polymophs of the chloride salt $(H_2bp4do)Cl_2$, while in the presence of a metallic salt $M^{(III)}Br_3$ (M = Bi, Sb), the monoprotonated form $Hbp4do^+$ is mainly stabilized as $(Hbp4do)_2[Sb_2Br_8]$ and $(H_2bp4do)(Hbp4do)_4[Bi_4Br_{18}]\cdot 2H_2O$. The dehydration of this last phase leads to $(H_2bp4do)(Hbp4do)_4[Bi_4Br_{18}]$. In the structures of $(H_2bp4do)Cl_2$ salts, the hydroxyl H atoms point toward the chloride anions leading to close $(O)H\cdots Cl$ contacts in the range 1.831—1.839 Å. A one-dimensional network of H-bonded $Hbp4do^+$ cations is found in the structure of $(Hbp4do)_2[Sb_2Br_8]$, whereas H-bonded supramolecular cations of five entities are found in the structures of bromobismuthate salts. In all the halometallate structures, X-ray analyses (293 K and 120 K data) did not allow us to locate the acid H atoms of protonated bp4do molecules certainly due to a disorder phenomenon but also revealing an asymmetrical H-bonding situation. The bromobismuthate hybrids are nonlinear optical active with a powder second harmonic generation efficiency being half that of urea.
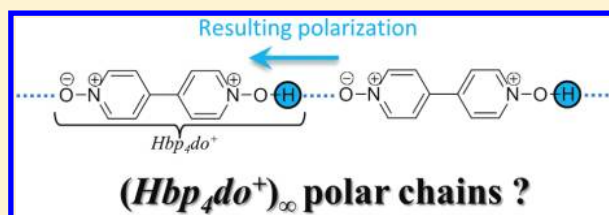
As is well-known, the 4,4′-bipyridine-*N,N′*-dioxide (named here bp4do), which can be considered as a neutral viologen type molecule, has been extensively used as a synthon in the construction of coordination polymer compounds.[1,2] Particularly, the ability of the $(N^+)-O^-$ group to bind lanthanide ions has led to the stabilization of many hybrid frameworks incorporating such metal centers.[2] The use of this molecule under its protonated forms, either $Hbp4do^+$ or H_2bp4do^{2+}, is much more scarce in material science. One reason certainly comes from the very weak dibase behavior of bp4do. The pK_a's of the corresponding diacid H_2bp4do^{2+} are not reported in the literature but can be considered to be close to the pK_a of the protonated pyridine-N-oxide entity (0.73 ± 0.15). And in fact, to the best of our knowledge, no crystal structure incorporating H_2bp4do^{2+} has been reported until now, while only two structures based on the monoprotonated entity $Hbp4do^+$ have been recently described.[3] We think that (many) other compounds based on these monocations can be stabilized, and above all, that such protonated entities can be good candidates for the building of H-bonded supramolecular polar chain based materials. In fact, an asymmetrical H-bonding situation, which is necessary for the achievement of polar chains such as ...HO-(R)-O⁻....HO-(R)-O⁻... (R = bipyridinium core), has been described in the structure of $(Hbp4do)_2AuCl_4$[3a] as well as in pyridine-N-oxide derivative structures in which the pyridine-N-oxide molecules and their protonated form built H-bonded dimers.[4] The materials based on H-bonded supramolecular polar chains can

potentially exhibit ferroelectric properties if they crystallize in a polar space group. In the field of ferroelectric materials, the hydrogen-bonded organic systems are very promising.[5] They are compounds for which the reversal of polarization arises from a collective transfer or displacement of protons. The great advantage of such ferroelectric, in comparison with ferroelectrics based on molecular reorientation (dipole reorientation), is that the moving of protons in the hydrogen bond minimizes steric difficulties for the reversal of polarization. The prototype molecules are molecules having at least two basic sites as N-(R)-N or ^-O_2C-(R′)-CO_2^-, which can lead typically to single component H-bonded chains H^+N-(R)-N---H^+N-(R)-N or HO_2C-(R′)-CO_2^----HO_2C-(R′)-CO_2^-. The specified materials can be of organic type, but also inorganic or organic—inorganic as exemplified by the potassium dihydrogenophosphate (KDP) and triglycine sulfate (TGS) compounds, respectively.[5a] During the past decade, we paid considerable attention to organic—inorganic hybrid compounds due to the opportunity to combine useful properties of both components as well as the possibility to tune the physical properties thanks to the great diversity of structures of the organic moieties, especially playing on weak hydrogen or halogen bonding at the organic—inorganic interface.[6] Recently, we described methylviologen halobismuthate salts (methylviologen =
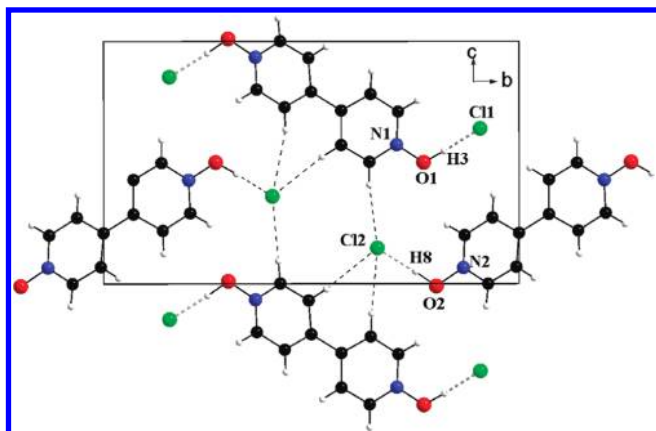
Figure 1. Part of the structure of $(H_2bp4do)Cl_2$ (**4**) showing H-bonding between chloride anions and H_2bp4do^{2+} dications.

4,4′-bipyridine-$N,N′$-dimethyl) exhibiting ferroelectric properties, the polarization of materials mainly originating from the stereoactivity of the ns^2 electron lone pair of Bi^{3+} ions.[7] Using the N-oxide viologen type molecule bp4do, our first goal was to synthesize hybrid materials based on H-bonded networks of Hbp4do$^+$ entities. We report in this communication the results of our investigations of the MBr$_3$/bp4do/HBr system (M = Bi, Sb). We show that a one-dimensional (1D) network of H-bonded Hbp4do$^+$ cations is found in the structure of $(Hbp4do)_2[Sb_2Br_8]$ (**1**), while H-bonded oligomers of five entities are found in the structures of $(H_2bp4do)(Hbp4do)_4[Bi_4Br_{18}]\cdot 2H_2O$ (**2**) and corresponding dehydrated phase (**3**). In all the three structures, X-ray analyses did not allow us to locate the acid H atoms of protonated bp4do molecules. As a consequence, the polarity of the H-bonded networks remains questionable. This point will be discussed in the light of the analysis of crystal structures and second-order nonlinear optical (NLO) measurements. We also report the crystal structures of two polymorphs of $(H_2bp4do)Cl_2$ (**4**, **5**) incorporating for the first time in the solid state the H_2bp4do^{2+} dication.

All compounds **1**−**5** were obtained by using a slow liquid−gas diffusion method in strong acid conditions (HBr: (**1**), (**2**), HCl: (**4**), (**5**)) (Supporting Information). The two polymorphic chloride salts (**4**) and (**5**) based on the H_2bp4do^{2+} dications have been obtained separately, depending on the solvent used. In the presence of a metallic salt as the starting material, it is worth noting that the monocationic form Hbp4do$^+$ is preferentially stabilized in the solid state, in $(Hbp4do)_2[Sb_2Br_8]$ (**1**) and in $(H_2bp4do)(Hbp4do)_4[Bi_4Br_{18}]\cdot 2H_2O$ (**2**).

The structure of the two polymorphs of $(H_2bp4do)Cl_2$[8] are built from the stacking of the same kind of corrugated layers. The main difference comes from the shift of two consecutive layers leading to a monoclinic (**4**) or to an orthorhombic (**5**) symmetry (see Supporting Information). Such a layer results from the H-bonding of both anionic and cationic entities as shown in Figure 1 for **4**. In both **4** and **5**, the hydrogen atoms of hydroxyl groups have been located from the Fourier difference map, resulting in an O−H bond distance of 1.03(1) Å (O1−H3 and O2−H8 (**4**)) and 1.00(1) Å (**5**), and in a N−O−H bond angle of 106.3° (N1−O1−H3), 108.7° (N2−O2−H8) in (**4**) and 101.2° (N1−O1−H1) in (**5**). As expected, the N−O bond distances, d(N1−O1) = 1.370(2) Å, d(N2−O2) = 1.380(2) Å (**4**), d(N1−O1) = 1.373(2) Å (**5**), are much greater than those

observed for free bp4do (average 1.32 Å) and also slightly longer than those of coordinated bp4do.[1,2] In the layer, hydroxyl H atoms point toward the chloride anions (O−H−Cl bond angle close to 180°) leading to close (O)H···Cl contacts of 1.831 Å (H8−Cl2) and 1.839 Å (H3−Cl1) in (**4**). The chlorides complete their surroundings with three other H atoms belonging to pyridil rings (d(H···Cl) in the 2.580−2.757 Å range) (Figure 1).

The structure of $(Hbp4do)_2[Sb_2Br_8]$[8] (**1**) can be described as 1D inorganic chains running along a, separated from each other by walls of molecules (Figure 2a). The inorganic chains are built from units of two edge-sharing octahedra which are linked together along the chain axis through apical bromides (Figure 2b). It is easy to notice the alternation of short and long Sb−Br distances along the chain axis (d = 2.535(1) Å and d = 3.518(1) Å), which reveals the $5s^2$ lone pair stereoactivity of Sb$^{(III)}$ centers.[9] When viewed along the chain axis, each bioctahedra unit appears to be encapsulated in windows formed by four Hbp4do$^+$ entities. Obviously, these windows can be more easily seen thanks to a space filling representation of the organic network (Figure 2c). The short O1···O2 distance of 2.439(4) Å unambiguously reveals the presence of one H atom between two molecules, leading to zigzag H-bonded chains of Hbp4do$^+$ cations running along c, the presence of two Hbp4do$^+$ per unit cell being in accordance with one Sb$_2$Br$_8^{2-}$ entity. In the literature, two types of H-bonding are described for such a short (N^+)-O$^-$ ... $^-$O-(N^+) distance,[4,10,11] particularly in pyridine-N-oxide derivative structures: a symmetrical situation[10] (nevertheless, we notice that the corresponding H atoms are often fixed on symmetry centers) and an asymmetrical situation with a short O−H and longer O···H distances.[4] In the case of the structure of (**1**), solving the structure in $P2_1/c$, Pc, or $P2_1$, using RT or 120 K (Supporting Information) X-ray data, the acid H atoms could not be located, while in contrast, H atoms of pyridyl rings could be easily seen in the Fourier difference map. This feature probably reveals an asymmetrical H-bonded situation,[12] the disorder of such H atoms over (at least) two positions precluding their location from the X-ray study. Moreover, this situation corresponds to the one described in the structure of $(Hbp4do)_2AuCl_4$:[3a] in fact, zigzag H-bonded chains of Hbp4do$^+$ cations are found in this structure (data collection at 113 K) with a O···O distance of 2.433(5) Å and with refined H atom located at 1.00(4) Å from one oxygen atom. This results in strong OH···$^-$O hydrogen bonds, which are considered as negative charge assisted hydrogen bonds according to Gilli and co-workers,[13] and in polar chains HO-(R)-O$^-$....HO-(R)-O$^-$... (R = bipyridinium core). In the hypothesis of asymmetrical H-bonding, the silent H atom in (**1**) could result from a dynamical or statistical disorder at room temperature, and certainly from a statistical disorder at 120 K if considering that polar chains are well-defined in the structure of $(Hbp4do)_2AuCl_4$ at 113 K, whereas the $P2_1/c$ space group symmetry (chosen space group) is compatible with the presence of polar chains in **1**; however, the statistical disorder can result both from the symmetry center which connects two consecutive chains along b and from the network translation of the a vector. We can add that the two N−O bond distances in **1** are nearly equal, d(N1−O1) = 1.350(4) Å and d(N2−O2) = 1.340(4) Å, the average bond being intermediate between N−O bonds in free bp4do (≅1.32 Å) and N−OH bonds in H_2bp4do^{2+} of **4** and **5** (≅1.38 Å).

The IR spectrum of (**1**), which is very similar to the one of $(Hbp4do)_2AuCl_4$,[3a] shows an intense and broad absorption in the 1600−500 cm^{-1} region (Figure 3). This absorption is
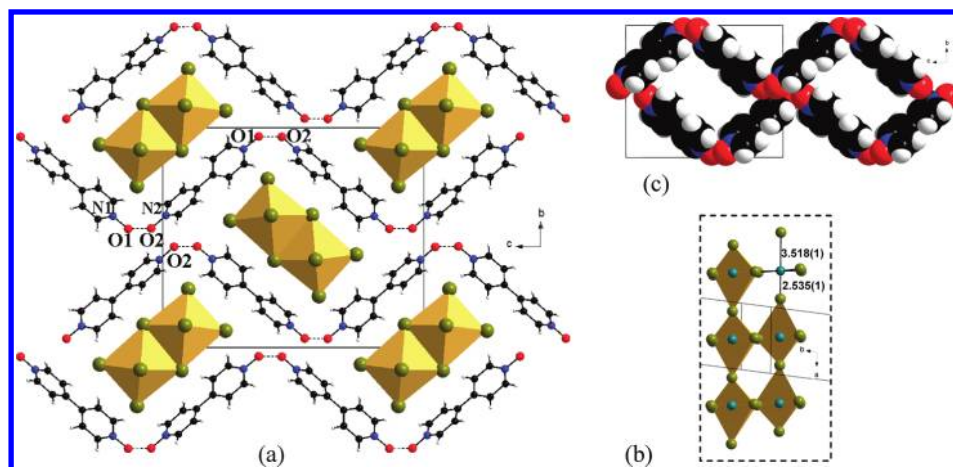
Figure 2. (a) View along a of the structure of $(Hbp4do)_2[Sb_2Br_8]$ (**1**) showing the inorganic units embedded by the 1D H-bonded chains of H_2bp4do^{2+} entities (H atoms between O1 and O2 (short contacts shown by bold dashed lines) have not been located). (b) View of the 1D inorganic network along c. (c) Space-filling representation of the H-bonded organic network in (**1**) viewed along a.
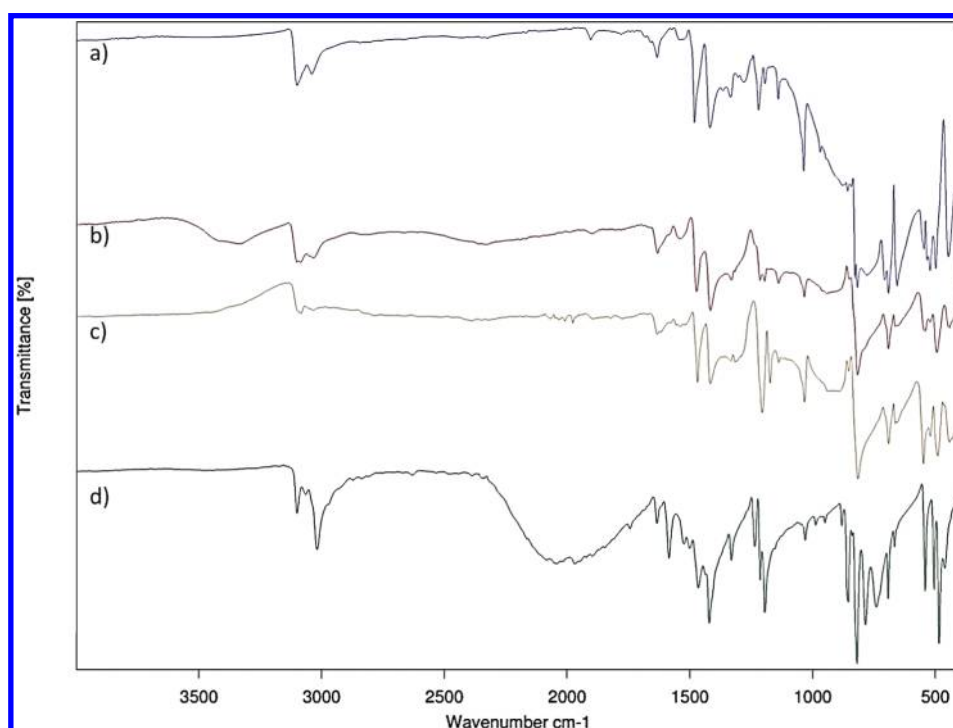

Figure 3. Solid state IR spectra of $(Hbp4do)_2[Sb_2Br_8]$ (**1**) (a), $(H_2bp4do)(Hbp4do)_4[Bi_4Br_{18}]\cdot2H_2O$ (**2**) (b) and corresponding dehydrated phase (**3**) (c), and $(H_2bp4do)Cl_2$ (**4**) (d).

characteristic of a short OH$\cdots$O bond, in contrast with a specific OH stretching band at higher energy (3200−3600 cm^{-1}) in the case of free HO group. For instance, the addition of concentrated HCl in a solution of bp4do results in the growth of two broad bands at 3500 cm^{-1} and 2350 cm^{-1}.[3a] It is also worth noting that no band in the 3200−3600 region is observed in the solid state IR spectrum of (**4**) (Figure 3) and (**5**), in good accordance with strong and directional interactions between Cl$^-$ and H_2bp4do^{2+} entities. With regard to the broad band at 2050 cm^{-1} (Figure 3), it can be compared to the 2350 cm^{-1} band observed in solution for H_2bp4do^{2+} (shift probably due to a solid state effect).

The structure of the dehydrated phase (H_2bp4do)-$(Hbp4do)_4[Bi_4Br_{18}]^8$ (**3**) belongs to the same family of compounds as **1**. In fact, according to the dimensional reduction concept,[14] **3** can be conceptually obtained by the reaction of the mother phase $(Hbp4do)_2[Bi_2Br_8]_\infty$ (hypothetical isotype of **1**), that we can write $(Hbp4do)_4[Bi_4Br_{16}]$, with $(H_2bp4do)Br_2$ according to the following reaction: $(Hbp4do)_4[Bi_4Br_{16}]$ + $(H_2bp4do)Br_2$ = $(H_2bp4do)(Hbp4do)_4[Bi_4Br_{18}]$ (**3**). Thus, the Bi_4Br_{18} clusters running along the b axis (Figure 4) can be considered as resulting from the cut of 1D inorganic chains $[Bi_2Br_8]_\infty$ every two bioctahedra units and the addition of two bromides. As in (**1**), the acid H atoms of bp4do could not be

located from the room temperature (RT) and 120 K X-ray data, neither in $P\bar{1}$ nor in the corresponding $P1$ acentric space group. Nevertheless, short O···O distances (d(O1···O2) = 2.460(9) Å, d(O3···O4) = 2.439(10) Å (RT data, $P\bar{1}$; Figure 5a) indicate that protonated bp4do are connected to each other through H bonding forming a 0D network of five entities (Figures 4 and 5a). To counterbalance the charge of −6 of one inorganic cluster, six H$^+$ are expected on the five bp4do entities leading to [(H$_2$bp4do)(Hbp4do)$_4$]$^{6+}$ supramolecular cations. This also
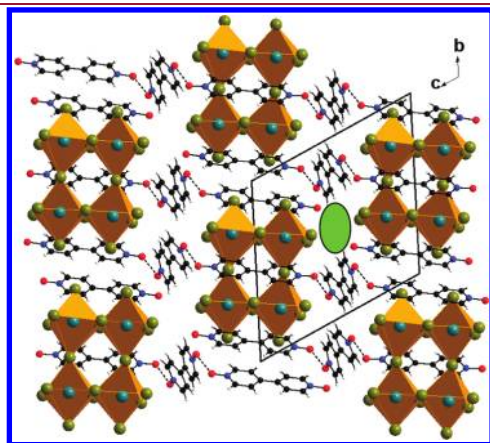
Figure 4. View along a of the structure of (H$_2$bp4do)(Hbp4do)$_4$-[Bi$_4$Br$_{18}$] (**3**) showing the Bi$_4$Br$_{18}$ inorganic units and the H-bonded organic networks. The H atoms of H$_2$bp4do^{2+} and Hbp4do$^+$ entities have not been located. Dashed lines are drawn for short O···O contacts. The green oval shows free space in which water molecules are located in the corresponding hydrated phase (**2**).

means that each terminal O5 atom bears one H$^+$, the four others being located between O1 and O2, and between O3 and O4 (Figure 5a). The corresponding N−O bond distances ($P\bar{1}$ space group) are as follows: d(N1−O1) = 1.345(10) Å, d(N2−O2) = 1.340(11) Å, d(N3−O3) = 1.360(11) Å, d(N4−O4) = 1.326(11) Å, d(N5−O5) = 1.368(12) Å. We notice that the longer distance N5−O5 is in good accordance with the expected terminal N−OH group. In the case of a symmetrical H-bonding situation for the four shared H atoms, or in the case of a symmetrical situation for the supramolecular cation with the presence of the diprotonated H$_2$bp4do^{2+} entity at the center of it, the H atoms should have been certainly located from X-ray data. The fact that these H atoms remain silent even at 120 K certainly reveals a disorder phenomenon as in the case of **1**. An interesting feature is that grounded crystals of **3** exhibit a second harmonic generation (SHG) activity (Supporting Information). The SHG signal is quite weak, corresponding to half the signal intensity of urea, but this property unambiguously shows that the material is acentric. This is in favor of an acentric nature of the whole organic network in **3** since the inorganic clusters are clearly related by a symmetry center according to the X-ray study. So we have to look at a higher supramolecular level, and in fact, we notice that the supramolecular cations of five protonated bp4do, which have been described above, interact with each other through weak O···O contacts along the c (d(O2···O3) = 3.318(13) Å) and a axes (d(O3···O5) = 3.382(13) Å) (Figure 5a), as highlighted by the space-filling representation of the Figure 5b. A coupling of the supramolecular cations may be possible, giving rise to a two-dimensional (2D) supramolecular network, at least.

The hydrated phase (H$_2$bp4do)(Hbp4do)$_4$[Bi$_4$Br$_{18}$]·2H$_2$O (**2**) also exhibits a SHG activity half that of urea, and its crystal
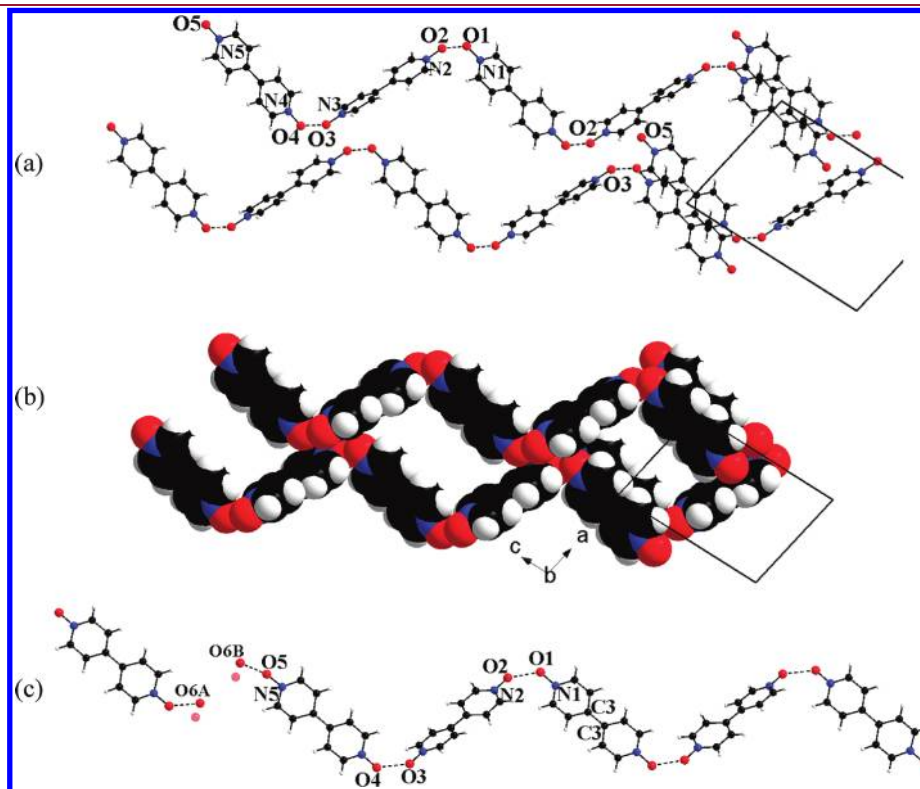
Figure 5. Ball-and-stick and space-filling partial representation of consecutive supramolecular cations of five protonated bp4do in (H$_2$bp4do)-(Hbp4do)$_4$[Bi$_4$Br$_{18}$] (**3**) (a), (b), and in (H$_2$bp4do)(Hbp4do)$_4$[Bi$_4$Br$_{18}$]·2H$_2$O (**2**) (c). O6A and O6B atoms of water molecules in (**2**) are disordered. The H atoms of water molecules and H$_2$bp4do^{2+} and Hbp4do$^+$ entities have not been located. Dashed lines show short O···O contacts.

structure is like the one of the dehydrated phase, except for the presence of water molecules in the free space of the structure of **3** (Figure 4). Solving the structure in $P\bar{1}$ or $P1$ using RT or 120 K X-ray data does not allow locating H atoms of both water molecules and N−O groups. Finally, the structure was solved in $P\bar{1}$,[8,15] the two independent water molecules with half occupation rate being disordered over two positions. The resulting situation appears in Figure 5c showing a local asymmetrical situation (because the two O atoms cannot be O6A). The water molecules strongly interact with N−OH groups of protonated bp4do entities as highlighted by short O5···O(water) distances (d(N5−O5(H)···O6A) = 2.55(3) Å, d(N5−O5-(H)···O6A) = 2.41(13) Å). The distance between O6A and O6B of two neighboring water molecules is 3.79(5) Å.

In conclusion, we have presented here rare examples of materials incorporating protonated 4,4′-bipyridine-*N*,*N*′-dioxide. The diprotonated H_2bp4do^{2+} cation is stabilized for the first time in the solid state in the two polymorphic chloride salts (H_2bp4do)Cl$_2$ (**4**, **5**). In the MBr$_3$/bp4do/HBr system (M = Bi, Sb), (Hbp4do)$_2$[Sb$_2$Br$_8$] (**1**), (H_2bp4do)(Hbp4do)$_4$[Bi$_4$Br$_{18}$]·2H$_2$O (**2**) and the corresponding dehydrated phase (**3**) are obtained. A 1D network of H-bonded Hbp4do$^+$ cations is found in the structure of **1**, while supramolecular cations of five H-bonded protonated bp4do entities are found in the structures of **2** and **3**. In all three structures **1**−**3**, the H atoms which are comprised of two oxygen atoms of neighboring bp4do molecules are X-ray silent (down to 120 K). This feature is in favor of an asymmetrical H-bonding, thus leading in (**1**) to polar 1D supramolecular networks. The SHG activity of **2** and **3**, which shows the acentric nature of structures, strengthens the hypothesis of an asymmetrical H-bonding situation leading to an acentric organization for the whole organic network. These first results show that the protonated 4,4′-bipyridine-*N*,*N*′-dioxide synthon has a strong ability to build H-bonded networks of polar nature. This opens a route to achieve polar materials based on Hbp4do$^+$ by selecting a suitable anionic component, for instance, using chiral anions.

■ ASSOCIATED CONTENT

⑤ Supporting Information. Details of synthesis procedures and SHG measurements. Complete crystal data (RT for **1**−**5**, and 120 K for **1**−**3**). X-ray powder diffraction pattern of **1**, **2**, **4**, and **5**. DSC and TGA analysis of **2** and **4**. UV−vis spectra of **1** and **2**. IR spectrum of **5**. This information is available free of charge via the Internet at http://pubs.acs.org/.

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(8) Data collections were carried out on a Bruker KappaCCD diffractometer, graphite-monochromated, MoKα radiation (λ = 0.71073 Å) at 293 K (**1**−**5**) and 120 K (**1**−**3**). The structures were solved by direct methods and refined by full-matrix least-squares routines against F^2 using the Shelxl97 package, and all non-H atoms were refined anisotropically. The hydrogen atoms of pyridil rings were treated with a riding model. Hydoxyl H atoms were located only in the structures of **4** and **5** and were refined isotropically. H atoms of water molecules in **2** have not been located. (Hbp4do)$_2$[Sb$_2$Br$_8$] (**1**) (C$_{20}$H$_{18}$Br$_8$N$_4$O$_4$Sb$_2$): M = 1261.20.1, monoclinic $P2_1/c$, a = 6.0397(9) Å, b = 15.037(1) Å, c = 18.109(2) Å, β = 99.52(1), V = 1622.0(3) Å^3, Z = 2, D_{calc} 2.578, T = 293 K, μ = 11.55 mm^{-1}, $2\theta_{max}$ = 64°, 33516 measured reflns, 5606 unique reflns (R(int) = 0.061), R(F) = 0.039 (3237 reflns, $I/\sigma(I) > 2$, 172 parameters), wR_2(F2) = 0.081 (all data). (H$_2$bp4do)(Hbp4do)$_4$[Bi$_4$Br$_{18}$]·2H$_2$O (**2**) (C$_{50}$H$_{50}$Bi$_4$Br$_{18}$N$_{10}$O$_{12}$): M = 3257.2, triclinic $P\bar{1}$, a = 9.522(1) Å, b = 15.1320(5) Å, c = 15.646(2) Å, α = 116.11(1)°, β = 99.34(1)°, γ = 91.89(1)°, V = 1983.5(3) Å^3, Z = 1, D_{calc} 2.718, T = 293 K, μ = 17.97 mm^{-1}, $2\theta_{max}$ = 64°, 77529 measured reflns, 13384 unique reflns (R(int) = 0.116), R(F) = 0.063 (6648 reflns, $I/\sigma(I) > 2$, 433 parameters), wR_2(F2) = 0.181 (all data). (H$_2$bp4do)(Hbp4do)$_4$[Bi$_4$Br$_{18}$] (**3**) (C$_{50}$H$_{46}$Bi$_4$Br$_{18}$N$_{10}$O$_{10}$): M = 3221.2, triclinic $P\bar{1}$, a = 9.522(1) Å, b = 15.0481(5) Å, c = 15.256(1) Å, α = 115.36(1)°, β = 98.47(1)°, γ = 92.45(1)°, V = 1946.2(2) Å^3, Z = 1, D_{calc} 2.743, T = 300 K, μ = 18.31 mm^{-1}, $2\theta_{max}$ = 64°, 68012 measured reflns, 13330 unique reflns (R(int) = 0.075), R(F) = 0.047 (7005 reflns, $I/\sigma(I) > 2$, 415 parameters), wR_2(F2) = 0.125 (all data). (H$_2$bp4do)Cl$_2$ (**4**) (C$_{10}$H$_{10}$Cl$_2$N$_2$O$_2$): M = 261.1, monoclinic $P2_1/a$, a = 7.0757(1) Å, b = 16.7851(2) Å, c = 9.8164(1) Å, β = 94.27(1)°, V = 1162.62(6) Å^3, Z = 4, D_{calc} 1.492, T = 293 K, μ = 0.54 mm^{-1}, $2\theta_{max}$ = 64°, 27268 measured reflns, 4013 unique reflns (R(int) = 0.056), R(F) = 0.037 (2732 reflns, $I/\sigma(I) > 2$, 154 parameters), wR_2(F2) = 0.096 (all data). (H$_2$bp4do)Cl$_2$ (**5**) (C$_{10}$H$_{10}$Cl$_2$N$_2$O$_2$): M = 261.1, orthorhombic $Pcab$, a = 7.3066(8) Å, b = 9.8027(5) Å, c = 16.057(1) Å, V = 1150.1 (2) Å^3, Z = 4, D_{calc} 1.508, T = 293 K, μ = 0.55 mm^{-1}, $2\theta_{max}$ = 64°, 12858 measured reflns, 1969 unique reflns (R(int) = 0.042), R(F) = 0.040 (1224 reflns, $I/\sigma(I) > 2$, 94 parameters), wR_2(F2) = 0.085 (all data).

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(12) We cannot completely eliminate the hypothesis of a symmetrical H-bonding situation with H atoms disordered over two positions on the midline of the O···O segment. Such location has been encountered in the structure of a protonated pyridine-N-oxide salt;[10a] nevertheless, the H atom was only free to move on the 2-fold axis which related the two linked molecules.

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(15) Interestingly, when solved in $P1$ (RT and 120 K data), the disorder of water molecules disappeared. Thus, two independent molecules which were not related to each other by a symmetry center were defined. This peculiar local acentric situation may be correlated to an acentric situation of the H-bonded supramolecular cations $[(H_2bp4do)(Hbp4do)_4]^{6+}$, and to the whole organic network, also. Nevertheless, refinements in $P1$ were not convergent, particularly with nonpositive agitation parameters of many light atoms, and we chose to solve the structure of **3** in $P\bar{1}$.

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