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The design and synthesis of a non-centric diamond-like network based NH_4^+ ion†

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Two novel acentric hydrogen bonded two-dimensional sheet and three-dimensional 2-fold interpenetrating diamond-like networks have been designed and prepared based on a tetrahedral ammonium node and the O,O′-bifunctional linker molecules dipyridine dioxide (dpdo) and *trans*-bis(4-pyridyl)ethylene dioxide (bpedo).

Considerable effort has been focused on the supramolecular assembly of organic or organo-inorganic hybrid materials through covalent,[1] hydrogen bonding[2] or other intermolecular interactions.[3] Second order nonlinear optical materials require the absence of a symmetry center in the bulk solid.[4] Their rational preparation is a formidable challenge to synthetic chemists due to the fact that most compounds crystallize in centrosymmetric space groups.[5] Apparently, the topological structures of the resulting compounds are mostly dependent on the geometry of the nodes (connection centers) and the flexibility of the rods (supporting ligands). Several approaches toward the achievement of acentric crystal packing with promising NLO properties have appeared in recent years: for example, employing unsymmetrical bridging ligands to build up acentric metal–ligand coordination polymers;[6] modifying the symmetry of molecular pillars to create polar hydrogen bonded host frameworks;[7] tailoring head-to-tail alignment of dipolar guests confined in organic host channels.[8] Our strategy of rational design and synthesis is to use ammonium instead of metal ions. The ammonium ion, inherently possessing a non-centrosymmetric tetrahedral geometry, as a connection center, has potential applications in constructing acentric networks, especially for diamondoid nets,[9] which are predisposed to pack in an acentric space group. We present herein two non-centric multi-dimensional networks $NH_4(dpdo)_2PF_6{\cdot}0.5H_2O$ **1** and $NH_4(bpedo)_2PF_6{\cdot}3H_2O$ **2** based on ammonium and O,O′-bifunctional 4-pyridyl derivatives: dipyridine dioxide (dpdo) and *trans*-bis(4-pyridyl)ethylene dioxide (bpedo), which were chosen in consideration of their following salient features:[10] a) their strong ability to form hydrogen bonds that play an important role in the assembly of supramolecular compounds; b) their flexible angular connection modes.

Compounds **1** and **2** were prepared by mixing NH_4PF_6 and dpdo or bpedo in methanol solution under stirring and heating. Single-crystal X-ray diffraction analysis revealed that compound **1** is a hydrogen bonded two-dimensional sheet.‡ Each NH_4^+ ion lies on a two-fold axis and forms quadruple hydrogen bonds with four dpdo molecules [N3···O2 = 2.850(1) Å, N3–H1···O2 = 156.8(11)°; N3···O1a = 2.815(1) Å, N3–H2···O1a = 165.8(9)°; a $x - 0.5$, $-y + 0.5$, $z - 0.5$]. Meanwhile, each dpdo linker bridges adjacent NH_4^+ ions through hydrogen bonding, leading to a puckered layer with an $NH_4^+{\cdots}NH_4^+$ separation of 12.72 Å in the *a*–*b* plane as illustrated in Fig. 1a. These 2D sheets form a 3D network through π–π interactions [center-to-center and interplanar distances being 3.649 and 3.439 Å, respectively] between dpdo molecules belonging to different layers, giving large channels parallel to the [001] direction, in which disordered PF_6^- anions and water molecules are anchored through weak C–H···X (X = F, O) hydrogen bonds (Fig. 1b).

When substituting dpdo with the longer spacer bpedo, a three-dimensional interpenetrating hydrogen bonded network **2** was obtained (Fig. 2a). Each NH_4^+ ion lies on a two-fold axis and forms four hydrogen bonds with bpedo [N3···O1 = 2.657 Å, N3–H1···O3b = 166.75°; N3···O2 = 2.639 Å, N3–H2···O3 = 165.70°]. It gives a three-dimensional diamond-like net with $NH_4^+{\cdots}NH_4^+$ separation of 14.13 Å as shown in Fig. 2b, rather than a 2D sheet as observed in **1**. Due to the appearance of large voids, the structure has a tendency to interpenetration giving rise to a two-fold interpenetrating network, which has been strengthened by π–π interactions [center-to-center and interplanar distances being 3.760 and 3.386 Å, respectively] between bpedo molecules from different frameworks. In spite of its interpenetration, a large channel parallel to the [001] direction is left, in which disordered PF_6^- anions and water molecules are accommodated through weak C–H···X (X = F, O) hydrogen bonds (Fig. 3).

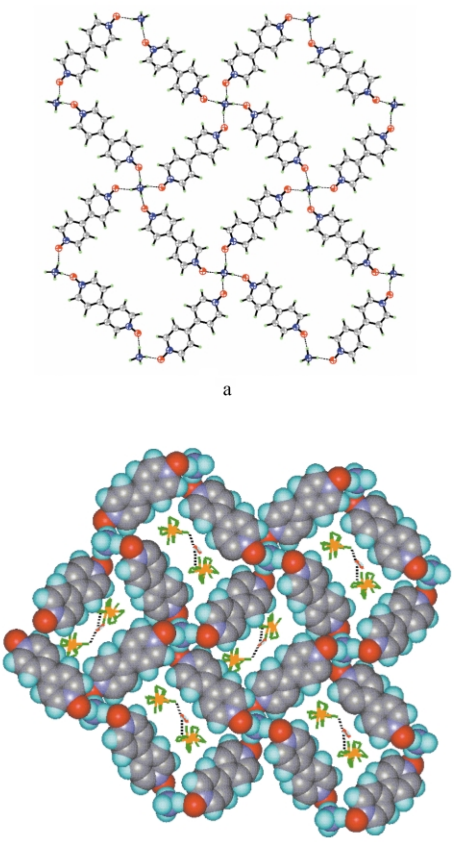
a
b

Fig. 1 a) Two-dimensional sheet of **1** formed through hydrogen bonding between NH_4^+ and dpdo in the (110) plane. b) Space filling diagram of **1**, showing the disordered PF_6^- anions and water molecules in channels.

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† Electronic supplementary information (ESI) available: experimental data. See http://www.rsc.org/suppdata/cc/b3/b306253h/

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The different topological architectures of **1** and **2** would be related to the different span and flexibility of the corresponding linker molecules. The longer and more flexible bpedo has a higher tendency to generate interpenetrating frameworks than dpdo.[11] Notwithstanding the interpenetrating nature of **2**, its free pore volume is significantly larger than that of **1** as reflected by more solvent inclusion, indicating that the longer spacer is conducive to the formation of solids with large cavities. More importantly and interestingly, both compounds indeed crystallize in non-centric space groups as expected, and **2** exhibits the desired diamond net. It is clear that the tetrahedral NH_4^+ center plays a significant role in determining the non-centric structure of resulting compounds. This conclusion is confirmed by the fact that a similar 2D layer with a centrosymmetric structure is generated when the tetrahedral NH_4^+ is replaced by a Ag^+ ion.[12] The use of angular hydrogen bond acceptor dpdo and bpedo linker molecules is also crucial, allowing multi-directional access to hydrogen bond donors. The torsion angles of N···O–O···N (NH_4^+–O,O–spacers–NH_4^+) are 110.5° and 89.1° in **1** and **2**, respectively, seriously deviating from linearity. It generates the acentric H···O–O···H subunit though the linker molecules are centrosymmetric, therefore producing the polarity of networks **1** and **2**. A preliminary second harmonic generation measurement on compounds **1** and **2** with a home-made optical setup confirmed their acentricity and gave a second order coefficient (β) approximately equivalent to that of KDP (potassium dihydrogen phosphate) (1.3 and 0.8 times of KDP for **1** and **2**, respectively). The current work provided a practical and efficient approach to the design and synthesis of a non-centric framework. The generality is demonstrated by the fact that replacement of PF_6^- by other counterions such as ClO_4^-, NO_3^-, BF_4^-, NCS^-, and halides also gave acentric supramolecular networks.[13]

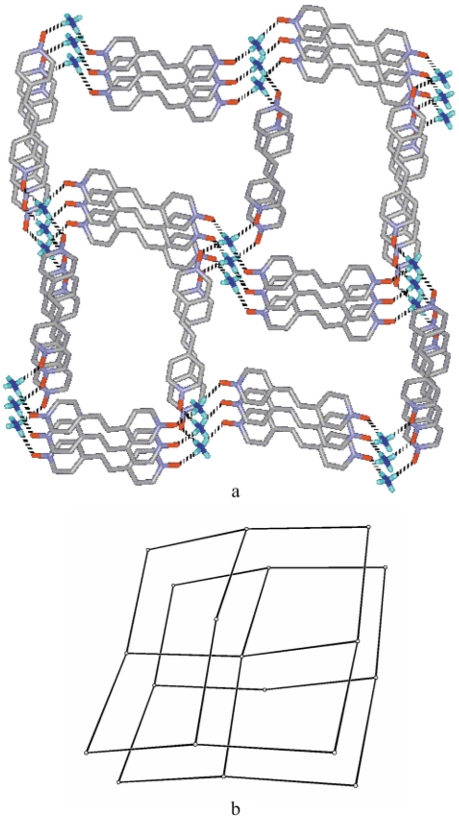

Fig. 2 a) Three-dimensional diamond-like network in **2**. b) A schematic representation of a single diamond net.

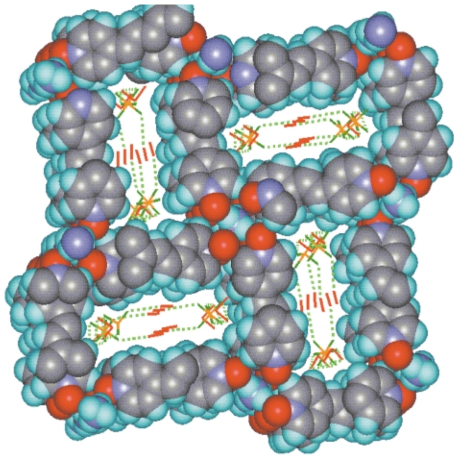

Fig. 3 Space filling diagram of two-fold interpenetrating network of **2**, showing the disordered PF_6^- anions and water molecules in channels.

In conclusion, two novel 2D and 3D acentric hydrogen bonded supramolecular networks with predictable architectures have been constructed, combining a tetrahedral ammonium center and O,O-bifunctional spacers. This offers a viable pathway to design and prepare polar supramolecular networks, which may have important optic applications.

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Notes and references

‡ *Crystal data*: Compound **1**, $C_{20}H_{21}F_6N_5O_{4.5}P$, M = 548.39, tetragonal, $P\bar{4}n2$, $a = b$ = 17.9935(13), c = 7.2554(7) Å, U = 2349.1(3) Å^3, Z = 4, D_c = 1.551 Mg m^{-3}, μ = 0.205 mm^{-1}, F(000) = 1124, GoF = 1.052. A total of 18737 reflections were collected and 2998 are unique (R_{int} = 0.040). R_1 and wR_2 are 0.0649 and 0.1816, respectively, for 248 parameters and 2627 reflections [$I > 2\sigma(I)$]. Compound **2**, $C_{24}H_{30}F_6N_5O_7P$, M = 645.50, tetragonal, $I\bar{4}2d$, $a = b$ = 28.0095(18), c = 7.4018(9) Å, U = 5807.0(9) Å^3, Z = 8, D_c = 1.477 Mg m^{-3}, μ = 0.184 mm^{-1}, F(000) = 2672, GoF = 1.060. A total of 20508 reflections were collected and 2544 are unique (R_{int} = 0.0773). R_1 and wR_2 are 0.0884 and 0.2326, respectively, for 227 parameters and 2083 reflections [$I > 2\sigma(I)$]. CCDC 200424–200425. See http://www.rsc.org/suppdata/cc/b3/b306253h/ for crystallographic data in .cif or other electronic format.

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12 Compound $Ag(dpdo)_2PF_6{\cdot}H_2O$ crystallizes in a centrosymmetric space group with unit cell parameters $a = b$ = 17.493(3), c = 3.702(1) Å, α = 90, β = 90, γ = 90°. It shows a similar layered structure to **1**. The structural refinement is in progress and it will be reported elsewhere.

13 B. Q. Ma, H. L. Sun and S. Gao, unpublished results.