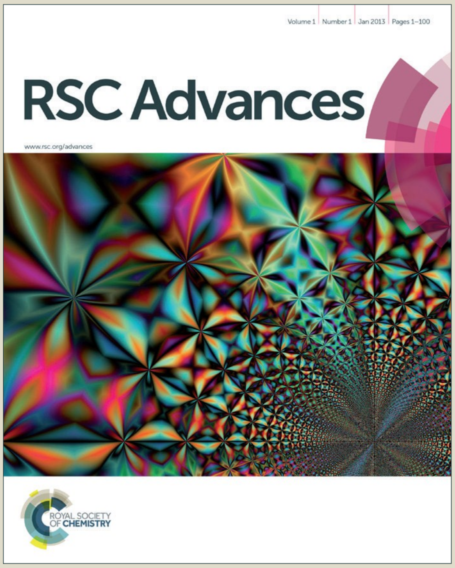
RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Hydrous salts of 1-aminoethylidenediphosphonic acid and piperazidine: temperature induced reversible structural transformation in humid environment

Di Tian,[a] Lang Li,[a] Liang-jie Yuan,*[a] Shuo-ping Chen,*[b]

Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

DOI: 10.1039/b000000x

Abstract: A series of hydrous salts construed by 1-aminoethylidenediphosphonic acid ($AEDPH_4$) and piperazidine (pip) were synthesized and structural characterized, namely $(AEDPH_3)\cdot(pipH_2)_{0.5}\cdot 0.5H_2O$ (**1**), $(AEDPH_3)\cdot(pipH_2)_{0.5}\cdot 2H_2O$ (**2**), and $(AEDPH_3)\cdot(pipH_2)_{0.5}\cdot 3H_2O$ (**3**). Compounds **1**-**3** all contain porous $[(AEDPH_3)\cdot(pipH_2)_{0.5}]_n$ supramolecular hosts with the same components, but illustrate different host structures, which allow different numbers of water molecules to lie in. Moreover, a reversible structural transformation circle is observed among the single crystals of the three hydrous salts, that is, compounds **1**-**3** can transformation to each other by changing the temperature in humid environment.

Introduction

In recent decades, structural transformation phenomena in crystalline states through the guest molecular exchange processes has become an attractive research area in crystallography and material science[1-2]. In various crystalline structures which can display structural transformation with guest molecular exchange[3], metal-organic frameworks (MOFs)[4] and metal-organic coordination complexes[5] are dominant. It is because that these compounds are constructed by relatively strong metal-ligand coordination bonds, and their crystal lattice host can be maintained stable before and after guest molecular exchange.

On the other hand, organic salts constructed by small organic acid and base molecules are also of current concerns, for they can afford novel supramolecular structures[6] and organic functional materials[7]. However, due to relative weak intermolecular force (such as hydrogen bond, π-π stacking interaction, and etc.) in organic salts, it is a great challenge to achieve a structural transformation in crystalline states with guest molecular exchange in organic salts. Excepted for a few examples[1,8], the supramolecular organic frameworks constructed by organic salts can be collapsed in the guest molecule exchange process. Thus, in the order to observe structural transformation phenomena in crystalline organic salts, it is necessary to choose suitable organic acid and base molecules to construct the organic host, and it is reported that some carboxylic acids[7], sulfonic acids[1] and aza-heterocyclic bases[9] can be the precursors.

The organophosphonic acid is a kind of supramolecular building block but receive much less attention compared with carboxylic acids and sulfonic acids, for its organic salts display relatively low solubility and difficulty for single crystal growth. However, organophosphonic acids may be a good precursors for designing organic functional materials with structural transformation properties in humid environment, for several reasons: (1) First, the organophosphonic acids can generate considerably strong hydrogen bonding which effectively construct stable supramolecular host; (2) Second, compared with carboxylic acids and sulfonic acids, organophosphonic acids may have more hydrogen bond donors and acceptors, which can display various hydrogen-bonded motifs and structural aggregates. Thus, it can be expected that, organophosphonic acids may form a series of "supramolecular host isomers" with suitable organic base, and such "supramolecular host isomers" may transform to each other in specially conditions; (3) Third, the organophosphonic acids contain several hydrophilic groups, thus its supramolecular networks may be sensitive to water molecule and contribute to a structural transformation in humid environment. In our previous investigation[10], an example of structural transformation in organic salts have been observed which constructed by 1-aminoethylidenediphosphonic acid ($AEDPH_4$) and ethylenediamine (en): the α-$(AEDPH_2)\cdot(enH_2)\cdot H_2O$ transform to its isomer single crystal, namely, *β*-$(AEDPH_2)\cdot(enH_2)\cdot H_2O$ in water. In the structural transformation process, the supramolecular aggregates of $AEDPH_2^{2-}$ anions change from 1D zigzag supramolecular chain to 1D linear double chain, which induce the water molecule aggregates to form D3 water cluster to R4 water cluster.

It is observed that, the monovalent anions of $AEDPH_4$, i.e. $AEDPH_3^-$, are usually self-assemble to form stable two-dimensional (2D) supramolecular layers. As shown in Fig.1, the $AEDPH_3^-$ is a flexible anion, and contains five proton donors and seven proton acceptors. Thus, the $AEDPH_3^-$ anions can display various assemble models when forming 2D supramolecular layers, in which one $AEDPH_3^-$ anion can connect other N (the number N maybe 3[11], 4[12], 5[13] or 6[14]) AEDPH$_3^-$ anions. In this case, the packing density of (AEDPH$_3^-$)$_n$ 2D supramolecular layers can be dynamic variable controlled. Furthermore, by combination with suitable organic base cations, the (AEDPH$_3^-$)$_n$ 2D supramolecular layers may induce and construct various three-dimensional (3D) porous supramolecular networks as host, which can be a benefit for the guest molecule exchange.

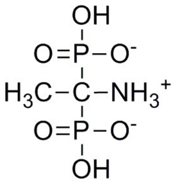


Fig. 1 Structure of AEDPH$_3^-$ anion.

Because of the hydrophilic properties of AEDPH$_3^-$, such kind of supramolecular host is also hydrophilic and can hold certain water molecules as guests. For example, the organic salt (AEDPH$_3$)·(pipH$_2$)$_{0.5}$·3H$_2$O[15] (pip = piperazidine), contain a typical porous [(AEDPH$_3$)·(pipH$_2$)$_{0.5}$]$_n$ supramolecular host constructed by 2D (AEDPH$_3^-$)$_n$ supramolecular layers and pipH$_2^{2+}$ as bridges, while the interspaces in the water molecules of the host are linked together to form a (H$_2$O)$_6$ cluster. The single crystal of this hydrous salt, is synthesized at a relatively low temperature (≦33 □), and it is expected that, by changing the temperature in humid environment, the structures of its 2D (AEDPH$_3^-$)$_n$ supramolecular layers can be changed, which can result different “supramolecular host isomers” of [(AEDPH$_3$)·(pipH$_2$)$_{0.5}$]$_n$, therefore, a structural transformation may be achieved.

With the aim of learning the hydrous salts of AEDPH$_4$ and pip, as well as their structural transformations in humid environment, a series of hydrous salts contained porous [(AEDPH$_3$)·(pipH$_2$)$_{0.5}$]$_n$ supramolecular host, namely (AEDPH$_3$)·(pipH$_2$)$_{0.5}$·0.5H$_2$O (**1**), (AEDPH$_3$)·(pipH$_2$)$_{0.5}$·2H$_2$O (**2**), and (AEDPH$_3$)·(pipH$_2$)$_{0.5}$·3H$_2$O (**3**), were designed and synthesized as single crystals by the reaction of AEDPH$_4$ and pip with the same mole ratio but at different crystalline temperature. The three compounds all contain [(AEDPH$_3$)·(pipH$_2$)$_{0.5}$]$_n$ supramolecular hosts with the same components, but the structures of their [(AEDPH$_3$)·(pipH$_2$)$_{0.5}$]$_n$ supramolecular hosts are different, which can be recognized as three “supramolecular host isomers”. The three supramolecular host isomers are all porous but have different pore sizes and shapes, which can contain different numbers of water molecules. Moreover, by changing the temperature in humid environment, the three supramolecular host isomers can transform to each other, and a structural transformation can be observed among the single crystals of the three hydrous salts. Herein we report the synthesis, crystal structures and structural transformations of compounds **1**-**3**.

Experimental Section

Materials and measurement

The 1-aminoethylidenediphosphonic acid (AEDPH$_4$) were prepared following the U. S. Patent 4239695. The piperazine (pip) was purchased from Sinopharm Chemical Reagent Co., Ltd. The elemental analysis data (C, H, N) were obtained with a PerkinElmer 240B elemental analyzer. IR spectra were recorded as KBr pellets at a range of 400–4000 cm^{-1} on a Nicolet 5700 FT-IR spectrometer with a spectral resolution of 4.00 cm^{-1}. Thermogravimetric analysis (TGA) was performed with a NETZSCH STA 449C at a heating rate of 10 K min^{-1} in air. The powder X-ray diffraction (PXRD) patterns were obtained with a Bruker D8 advanced diffractometer with Cu Ka radiation (λ = 1.54056 Å) at 40 kV and 40 mA and a scan speed of 4° min^{-1} (2θ).

Synthesis of (AEDPH$_3$)·(pipH$_2$)$_{0.5}$·0.5H$_2$O (1)

A mixture of 0.3075 g AEDPH$_4$ (1.5mmol), 0.1459 g piperazine (0.75 mmol) and 6 ml distilled water was sealed in a 25 ml sealing reagent bottle, and then heated at 80℃ for 7 days. Colourless block single crystals were obtained. Then the sealing reagent bottle was taken out and the crystals were filtrated immediately, and then dried in air. Yield: 71 % (based on AEDPH$_4$). Elemental analysis: found, %: C 18.92, H 5.942, N 10.98. Calculated for C$_8$H$_{30}$N$_4$O$_{13}$P$_4$: C18.67, H 5.834, N 10.89.

Synthesis of (AEDPH$_3$)·(pipH$_2$)$_{0.5}$·2H$_2$O (2)

A mixture of 0.3075g AEDPH$_4$ (1.5 mmol), 0.1459g piperazine (0.75 mmol) and 12 ml distilled water was sealed in a 25 ml sealing reagent bottle, and then heated at 80℃until all the reactants were completely dissolved. After that, the sealing reagent bottle was moved to another oven at 40 ℃ right now, and heated at 40 ℃ for 5 days. Colourless needle-like single crystals were obtained. Then the sealing reagent bottle was taken out and the crystals were filtrated immediately, and then dried in air. Yield: 74 % (based on AEDPH$_4$). Elemental analysis: found, %: C 17.19, H 6.510, N 9.976. Calculated for C$_4$H$_{18}$N$_2$O$_8$P$_2$: C 18.045, H 6.015, N 10.52.

Synthesis of (AEDPH$_3$)·(pipH$_2$)$_{0.5}$·3H$_2$O (3)

In our previous investigation[15], single crystals of compound **3** was obtained by vaporizing clear solution of 0.4100g AEDPH$_4$ (2 mmol), 0.0860 g anhydrous pip (1 mmol) and 20 mL distilled water at 33 ℃ for 5 d. However, in this paper , single crystals of **3** were obtained by this method: A mixture of 0.3075g AEDPH$_4$ (1.5mmol), 0.1459g piperazine (0.75 mmol) and 12 ml distilled water was sealed in a 25 ml sealing reagent bottle, and then heated at 80℃until all the reactants were completely dissolved. After that, the sealing reagent bottle was moved to another oven at 40 ℃right now, and heated at 40 ℃for 2 days. The the sealing reagent bottle was taken out, and placed at room temperature for 1 day. Colourless block single crystals were obtained. Then the sealing reagent bottle was taken out and the crystals were filtrated immediately, and then dried in air. Yield: 59 % (based on AEDPH$_4$). Elemental analysis: found, C 15.95, H 6.610, N 9.260. Calculated for C$_4$H$_{20}$N$_2$O$_9$P$_2$: C 15.90, H 6.67, N 9.27.

X-Ray crystallographic analysis

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

Crystallographic measurements were obtained on a Bruker SMART CCD area-detector diffractometer. All structures were performed using graphite monochromated Mo-Kα radiation (λ=0.71073Å). The structures were analyzed by direct method using the SHELXS-97 program. Non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on F^2 using SHELXL-97. All oxygen hydrogen atoms were obtained from difference Fourier maps, and the other hydrogen atoms were geometrically fixed. Several DFIX commands were applied on hydrogen atoms in compounds **1-3**. Drawings were produced using Mercury 1.4.1 software. Crystallographic data and structural refinement parameters are listed in Tab. 1. Hydrogen bond distances and angles are listed in the ESI, Table S6-8.†

Tab. 1 Crystallographic data and structure refinement parameters for compounds

Identification code	**1**	**2**	**3**
Empirical formula	$C_8H_{30}N_4O_{13}P_4$	$C_4H_{18}N_2O_8P_2$	$C_4H_{20}N_2O_9P_2$
Formula weight	514.24	284.14	302.16
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	*C2/c*	*P-1*	*C2/c*
a / Å	22.6149(19)	5.7389(14)	19.629(8)
b / Å	6.6814(6)	9.985(2)	6.963(3)
c /Å	13.5696(12)	11.457(3)	20.786(11)
α (deg.)	90	115.505(4)	90
β (deg.)	100.5980(10)	94.461(4)	117.990(5)
γ (deg.)	90	92.251(4)	90
V/ Å^3	2015.4(3)	588.8(2)	2508.8(19)
Z	4	2	8
μ/mm^{-1}	0.447	0.400	0.386
F (000)	1080	300	1280
D_{cacld}/mg·cm^{-3}	1.695	1.603	1.600
Goodness-of-fit on F^2	1.100	1.065	1.118
Final *R* indices [I>2σ (I)]	R1 = 0.0257 wR2 = 0.0732	R1 = 0.0328 wR2 = 0.0821	R_1 = 0. 0.0274 wR_2 = 0.0765
R indices (all data)	*R1 = 0.0280* *wR2 = 0.0745*	R1 = 0.0371 wR2 = 0.0841	R_1 = 0.0298 wR_2 = 0.0784
(Δρ)max,(Δρ)min (e/Å^3)	0.384, -0.324	0.378, -0.349	0.390, -0.286

$R_1 = [\Sigma(|F_0| - |F_c|) /\Sigma|F_0|$;

$wR_2 = [\Sigma[w(|F_0|^2 - |F_c|^2)^2] /\Sigma[w(|F_0|^2)^2]^{1/2}$, $w = 1 / [\sigma^2|F_0|^2 + (xp)^2 + yp]$; where $p = [|F_0|^2 + 2|F_c|^2] /3$.

Structural transformation among compounds 1-3

Transformation from 1 to 2: 0.1 g single crystals of **1** and 0.1 g distilled water were sealed in a 5 ml sealing reagent bottle, and then placed in an oven at 40 ℃ for 5 days. Through the naked eyes, most crystals did not dissolve and remained crystalline state. After the transformation, the resulted crystals were filtrated immediately, and then dried in air. PXRD analysis shows that the resulted crystals are compound **2**.

Transformation from 2 to 1: 0.1 g single crystals of **2** and 0.1 g distilled water were sealed in a 5 ml sealing reagent bottle, and then placed in an oven at 100 ℃ for 1 day. Through the naked eyes, most crystals did not dissolve and remained crystalline state. After the transformation, the resulted crystals were filtrated immediately, and then dried in air. PXRD analysis shows that the resulted crystals are compound **1**.

Transformation from 1 to 3: 0.1 g single crystals of **1** and 0.1 g distilled water were sealed in a 5 ml sealing reagent bottle, and then placed in an oven at 33 ℃ for 3 days. Through the naked eyes, most crystals did not dissolve and remained crystalline state. After the transformation, the resulted crystals were filtrated immediately, and then dried in air. PXRD analysis shows that the resulted crystals are compound **3**.

Transformation from 3 to 1: 0.1 g single crystals of **3** and 0.1 g distilled water were sealed in a 5 ml sealing reagent bottle, and then placed in an oven at 100 ℃ for 1 day. Through the naked eyes, most crystals did not dissolve and remained crystalline state. After the transformation, the resulted crystals were filtrated immediately, and then dried in air. PXRD analysis shows that the resulted crystals are compound **1**.

Transformation from 2 to 3: 0.1 g single crystals of **2** and 0.1 g distilled water were sealed in a 5 ml sealing reagent bottle, and then placed in an oven at 33 ℃ for 3 days. Through the naked eyes, most crystals did not dissolve and remained crystalline state. After the transformation, the resulted crystals were filtrated immediately, and then dried in air. PXRD analysis shows that the resulted crystals are compound **3**.

Transformation from 3 to 2: 0.1 g single crystals of **3** and 0.1 g distilled water were sealed in a 5 ml sealing reagent bottle, and then placed in an oven at 100 ℃ for 1 day, After that, the sealing reagent bottle was moved to another oven at 40 ℃, and then heated at 40 ℃ for 5 day. In the eventual transformation process, the solid in the sealing reagent bottle remain single crystals. The resulted crystals were filtrated immediately, PXRD analysis shows that the resulted crystals are compound **2**.

Crystal structure

Structure of $(AEDPH_3)\cdot(pipH_2)_{0.5}\cdot 0.5H_2O$ (1)

There is one $AEDPH_3^-$ anion, half a $pipH_2^{2+}$ cation and half a water molecule in the asymmetric unit of compound **1**. As shown in Fig. 2a, the $AEDPH_3^-$ anions in **1** firstly form a 1D zigzag supramolecular chain along *b* axis by strong hydrogen bonds among adjacent phosphonate groups and amino groups, including O5–H5···O1#2 (2.5234(15) Å), O2–H2···O6#3 (2.5359(14) Å), N1–H1B···O1#6 (2.7956(15) Å), and N1–H1C···O2#3 (3.0281(15) Å). Then hydrogen bond N1–H1A···O6#7 (2.7543(15) Å) joins neighboring 1D supramolecular chains together, forming a 2D $(AEDPH_3^-)_n$ supramolecular layer along *bc* plane. In this layer, each $AEDPH_3^-$ anion can connect five adjacent $AEDPH_3^-$ anions with hydrogen bonds, which indicates that $AEDPH_3^-$ anions adopt a close packing model in these layers (see Fig. 2b).

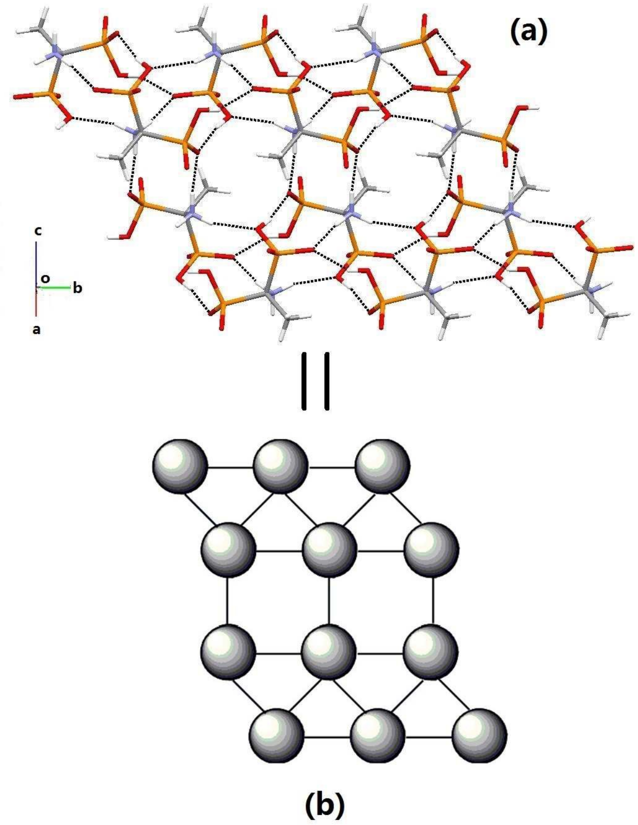


Fig. 2 (a) 2D $(AEDPH_3^-)_n$ supramolecular layer of **1**. Dashed lines represent hydrogen bonds; (b) Schematic illustration showing models of the 2D $(AEDPH_3^-)_n$ supramolecular layer of **1.** Small balls represent $AEDPH_3^-$ anions, and black lines represent hydrogen bonding interactions.

These $(AEDPH_3^-)_n$ layers are then bridged by $pipH_2^{2+}$ cations and extended to a $[(AEDPH_3)\cdot(pipH_2)_{0.5}]_n$ supramolecular host (host **1**) by hydrogen bonds N2–H2B···O3#4 (2.7266(16) Å) and N2–H2A···O4#5 (2.6963(17) Å). The host **1** is porous with extended 1D channels along *b* axis with small aperture of ca. 4×2 Å (See Fig. 3a) . The effective free volume of host **1** is calculated by PLATON analysis being 2.5% percent of void, which only allow half of a water molecule per unit to lay in. The water molecule (O7) connect with the host **1** with a pair of hydrogen bonds O7–H7···O3#7 (2.8300(14) Å), that is, this water molecule only sever as proton donor in hydrogen bonding, and the distance of the nearest two water molecules is 6.681 Å (See Fig. 3b).

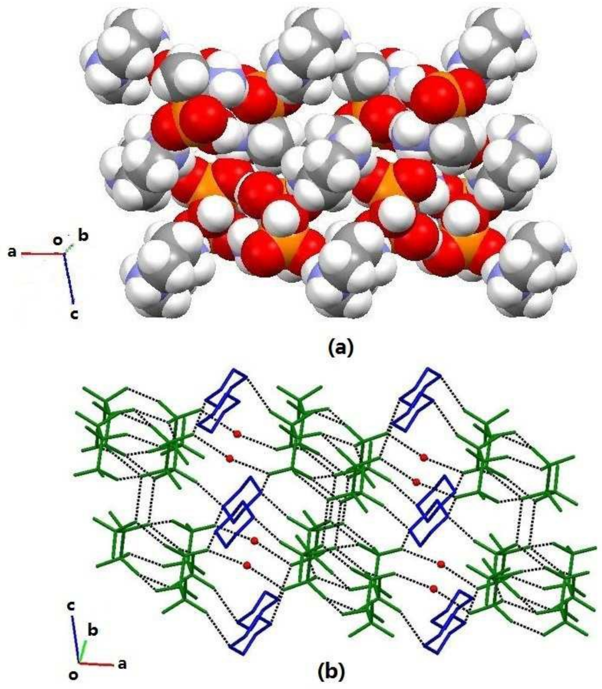


Fig. 3 (a) The host **1** showed in space fill model; (b) 3D supramolecular structure of **1**. Green: $AEDPH_3^-$ anions; Blue: $pipH_2^{2+}$ cation; The water molecules are shown in ball and stick model; Dashed lines represent hydrogen bonds; The hydrogen atoms are omitted for clarity.

Structure of $(AEDPH_3)\cdot(pipH_2)_{0.5}\cdot2H_2O$ (2)

There is one $AEDPH_3^-$ anion, half a $pipH_2^{2+}$ cation and two water molecules in the asymmetric unit of compound **2**. As shown in Fig. 4a, the $AEDPH_3^-$ anions adopt a herringbone packing model. Along *a* axis, the adjacent $AEDPH_3^-$ anions connect each other with hydrogen bonds N3–H1A···O2#4 (2.8075(19) Å) and N3–H1C···O4#4 (2.8021(18) Å), forming a 1D linear supramolecular chain. On the other hand, two pairs of hydrogen bonds (O6–H6···O4#2 = 2.5614(18) Å, O1–H7···O2#3 = 2.5794(19) Å) join $AEDPH_3^-$ anions along *b* axis, extending the 1D linear supramolecular chains to a 2D herringbone $(AEDPH_3^-)_n$ supramolecular layers. Different from that in **1**, each $AEDPH_3^-$ anions in **2** can connect four adjacent $AEDPH_3^-$ anions with hydrogen bonds, which indicates that the $AEDPH_3^-$ anions adopt a looser packing model than that in **1** (See Fig. 4b).

These $(AEDPH_3^-)_n$ layers are then bridged by $pipH_2^{2+}$ cations and extended to a $[(AEDPH_3)\cdot(pipH_2)_{0.5}]_n$ supramolecular host (host **2**) by hydrogen bond N1–H2D···O5 (2.750(2) Å), The host **2** is a porous host with extended 1D channels along *a* axis, whose aperture is of ca. 5×4 Å, which is larger than that of host **1** (See Fig. 5a) . The effective free volume of the host **2** is calculated by PLATON analysis being 2.7% percent of void. Thus, there are two water molecules per unit to lay in the host. Different from that of **1**, the two water molecules (O7 and O8) can not only serve as proton donors, but also serve as proton acceptors. They can connect with the host **2** with various of hydrogen bonds, such as N3–H1B···O8#4 (2.738(2) Å), N1–H2E···O7#5 (2.680(2) Å), O7–H3···O5#6 (2.739(2) Å), O7–H4···O3 (2.671(2) Å), O8–H5···O3 (2.830(2) Å), and O8–H2···O5#6 (2.927(2) Å), and the distance of the nearest two water molecules is 3.563 Å (See Fig. 5b)

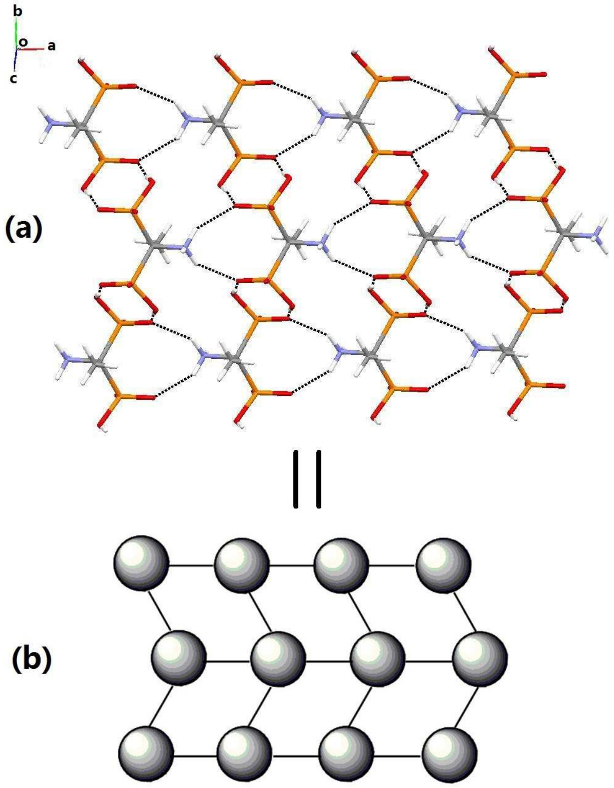


Fig. 4 (a) 2D $(AEDPH_3^-)_n$ supramolecular layer of **2**. Dashed lines represent hydrogen bonds; (b) Schematic illustration showing models of the 2D $(AEDPH_3^-)_n$ supramolecular layer of **.** Small balls represent $AEDPH_3^-$ anions, and black lines represent hydrogen bonding interactions.

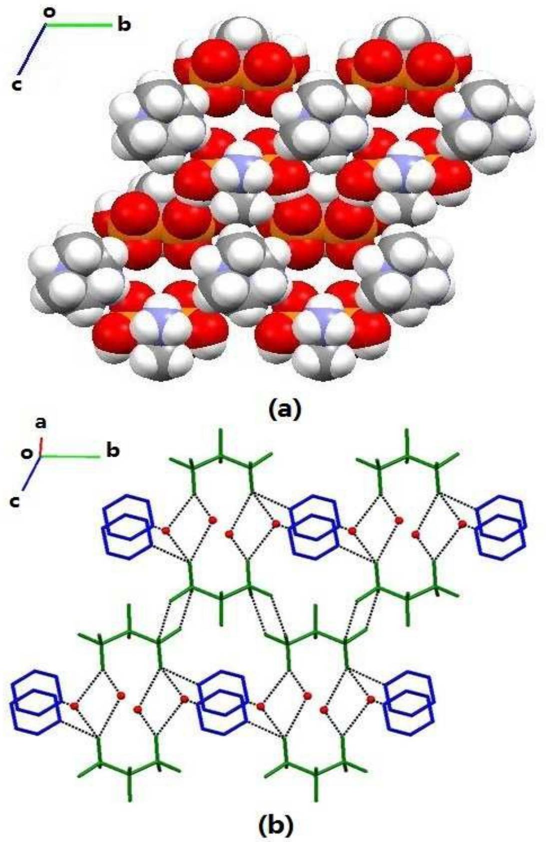


Fig. 5 (a) The host **2** showed in space fill model; (b) 3D supramolecular structure of **2**. Green: $AEDPH_3^-$ anions; Blue: $pipH_2^{2+}$ cation; The water molecules are shown in ball and stick model; Dashed lines represent hydrogen bonds. The hydrogen atoms are omitted for clarity.

Structure of $(AEDPH_3)\cdot(pipH_2)_{0.5}\cdot3H_2O$ (3)

The asymmetric unit of compound **3** contains one $AEDPH_3^-$ anion, half a $pipH_2^{2+}$ cation and three water molecules. Different from that in compounds **1** and **2**, the $AEDPH_3^-$ anions in compound **3** form a hexagonal supramocular layers: Firstly, the $AEDPH_3^-$ anions form a 1D zigzag supramolecular chain along *b* axis by strong hydrogen bonds N1−H1B···O2#9 (2.789(2) Å), O1−H1···O4#2 (2.539(2) Å), and N1−H1C···O1#2 (2.951(2) Å), then extend to a 2D hexagonal $(AEDPH_3^-)_n$ supramolecular layers along *ab* plane with a pair of hydrogen bonds O5–O5−H5···O6#3 (2.514(2) Å) with a $R_2^2(8)$ motif. In compound **3,** each $AEDPH_3^-$ anion only can connect three adjacent $AEDPH_3^-$ anions with hydrogen bonds, which indicates that the $AEDPH_3^-$ anions adopt a looser packing model than that in **1** and **2**. In addition, the hexagonal $(AEDPH_3^-)_n$ layers in **3** is porous with holes of ca. 4×3 Å (See Fig. 6).

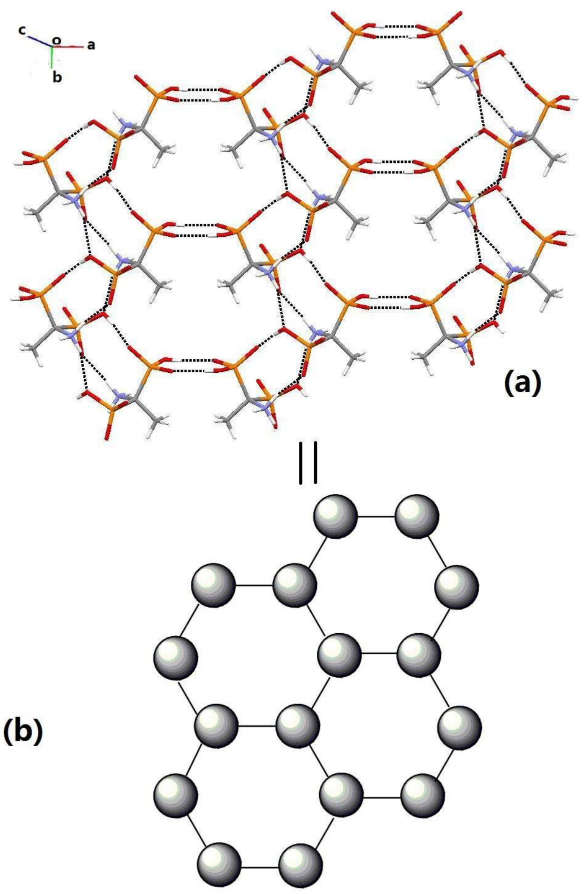
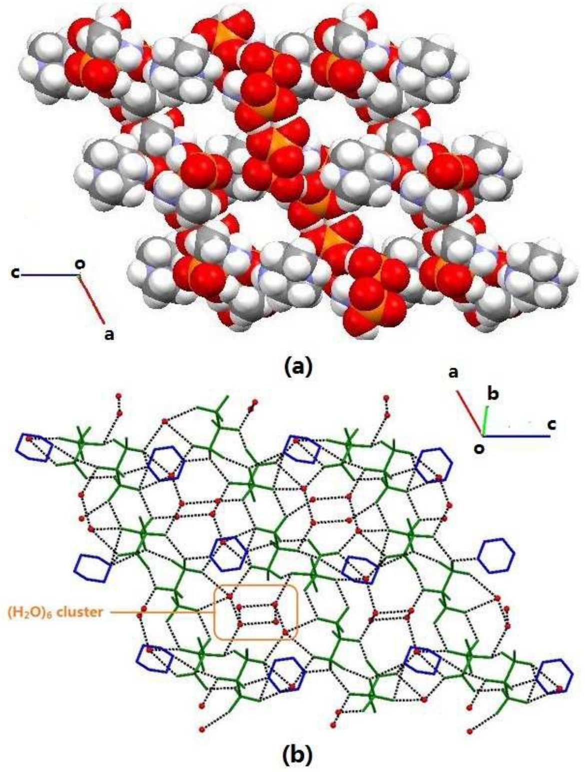


Fig. 6 (a) 2D $(AEDPH_3^-)_n$ supramolecular layer of **3**. Dashed lines represent hydrogen bonds; (b) Schematic illustration showing models of the 2D $(AEDPH_3^-)_n$ supramolecular layer of **3.** Small balls represent $AEDPH_3^-$ anions, and black lines represent hydrogen bonding interactions.

These $(AEDPH_3^-)_n$ layers are then bridged by $pipH_2^{2+}$ cations and extended to a $[(AEDPH_3)\cdot(pipH_2)_{0.5}]_n$ ·supramolecular host (host **3**) by a serious of hydrogen bonds (N2−H2D···O4#4 = 2.953(2) Å, N2−H2E···O6#4 = 3.037(2) Å, N2−H2E···O3#4 = 2.926(2) Å, N2−H2D···O2 = 2.781(2) Å). The host **3** is also porous with extended 1D channels along *b* axis, whose aperture is of ca. 10×9 Å, much larger than that of **1** and **2**. The effective free volume of $(AEDPH_3)\cdot(pipH_2)_{0.5}$ host in **3** is calculated by PLATON analysis being 26.9% percent of void. So this host can allow more water molecules per unit to lay in (See Fig. 7a). In this host, six water molecules (two O1W, two O2W and two O3W) in the interspaces of the 3D network are linked together to form a $(H_2O)_6$ cluster: firstly, four water molecules (two O1W and two O2W) self-assemble to create a cyclic water tetramer via hydrogen bonds O1W–H2W1···O2W (2.821(3) Å) and O2W–H2W2···O1W#6 (2.797(3) Å. Then two O3W are connected to the cyclic water tetramer by hydrogen bond O2W–H1W2···O3W#5 (2.757(3) Å), resulting in a water hexamer, which connects to the host via various hydrogen bonds and makes the 3D supramolecular network more stable.



(a)

(b)

Fig. 7 (a) The host **3** which show in space fill model; (b) 3D supramolecular structures of **3**. Green: AEDPH$_3^-$ anions; Blue: pipH$_2^{2+}$ cation; The water molecules are shown in ball and stick model; Dashed lines represent hydrogen bonds. The hydrogen atoms are omitted for clarity.

Temperature induced structural transformation in humid environment

Single crystals of compounds **1-3** all can be obtained by the reaction of AEDPH$_4$ and pip with a mole ratio of 2:1 in water, while the water temperature is the critical factor to affect the structure of the final product. On the other hand, there are three "supramolecular host isomers" forming in the AEDPH$_4$-pip-H$_2$O system. Thus, it is expected that the single crystals of compounds **1-3** can transform to each other by changing the temperature in humid environment. In order to observe this structural transformation, 0.1 g single crystals and 0.1g distilled water were sealed in a sealing reagent bottle, and then placed at a certain temperature. Because of a relative high solid-to-liquid ratio, most crystals of compounds **1-3** can remain crystalline solids in the transformation process. After a certain time, the resulted crystals were filtrated immediately, dried in air, grinded to powders and then characterized by powder X-ray diffraction (PXRD), the PXRD patterns of the original crystals of compounds **1-3** were also obtained as contrast (See Experimental Section).

Compounds **1-3** all can be stable in dry place at room temperature, and can not transform to each other. However, in humid environment, the three hydrous salts can only be stable at a certain temperature. As shown in Fig. 9 and Fig. 10, compound 3 is stable at low temperature (≦33℃) in humid environment. If single crystals of **1** or **2** placed at 33 □ or below with a small amount of water for 3 days, both the two compound can be easily transform to compound **3**.

By contraries, compound **1** prefer at hot water (≧80 □). In fact, compound **1** displays the best thermal stability among the three hydrous salts, which can stable up to 150 □ (See Fig. S5 in ESI). As shown in Fig. 8 and Fig. 9, crystals of **1** can be easily form by heating single crystals of compound **2** or **3** in humid environment at 100 ℃ for 1 day.

Compound **2** can be stable in warm water (about 40 □). However, compared with compounds **1** and **3**, the structural transformation toward compound **2** is much more difficult. Single crystals of **1** can basically transform to **2** after placing in 40□ water for 5 days (See Fig. 8). It seems that single crystals of **3** can not directly transform to **2**, compound **3** can remain itself even placed at 40□ water for 1 month. Whereas, the structural transform form **3** to **2** can be achieved with a two-step strategy: single crystals of **3** can be firstly placed in 100 □ water for 1 day (forming crystals of **1**), and then placed at 40 □ for 5 days, which finally form crystals of **2** (See Fig. 10). In sum, by placing in humid environment at different temperate, a complete transformation circle among compounds **1-3** can be achieved (See Fig. 10).

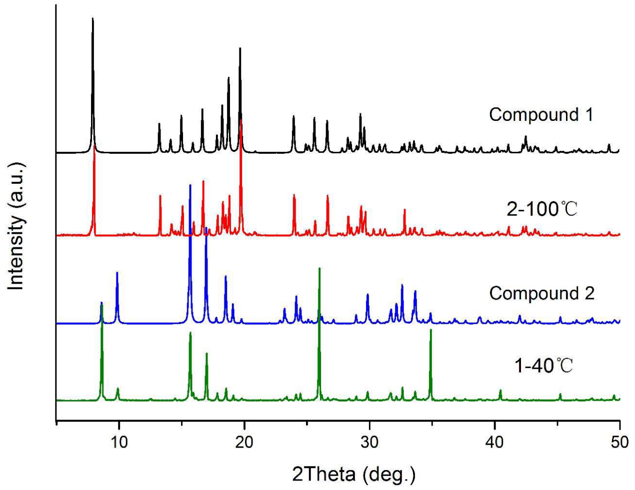


Fig. 8 PXRD patterns of the structural transformation between compounds **1** and **2**. Form top to bottom: PXRD pattern of the original crystals of **1**; PXRD pattern of the result crystals by placing compound **2** in 100 □ water for 1 day, PXRD pattern of the original crystals of **2**; PXRD pattern of the result crystals by placing compound **1** in 40 □ water for 5 days.

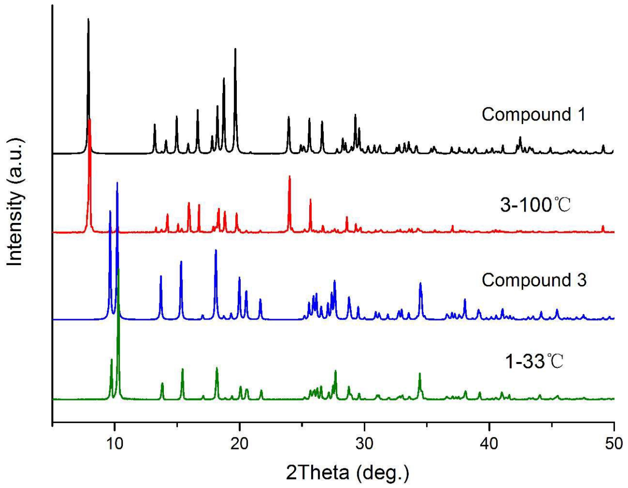


Fig. 9 PXRD patterns of the structural transformation between compounds **1** and **3**. Form top to bottom: PXRD pattern of the original crystals of **1**; PXRD pattern of the result crystals by placing compound **3** in 100 □ water for 1 day, PXRD pattern of the original crystals of **3**; PXRD pattern of the result crystals by placing compound **1** in 33 □ water for 3 days.

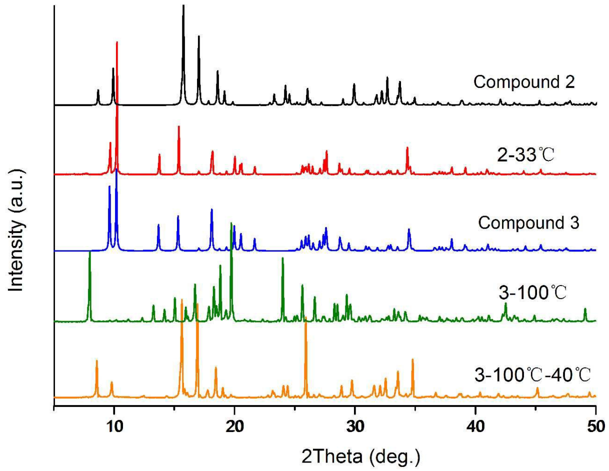


Fig. 10 PXRD patterns of the structural transformation between compounds **2** and **3**. From top to bottom: PXRD pattern of the original crystals of **2**; PXRD pattern of the result crystals by placing compound **2** in 33 □ water for 3 days, PXRD pattern of the original crystals of **3**; PXRD pattern of the result crystals by placing compound **3** in 100 □ water for 1 day; PXRD pattern of the result crystals by placing compound **3** in 100 □ water for 1 day, then in 40 □ water for 5 days.

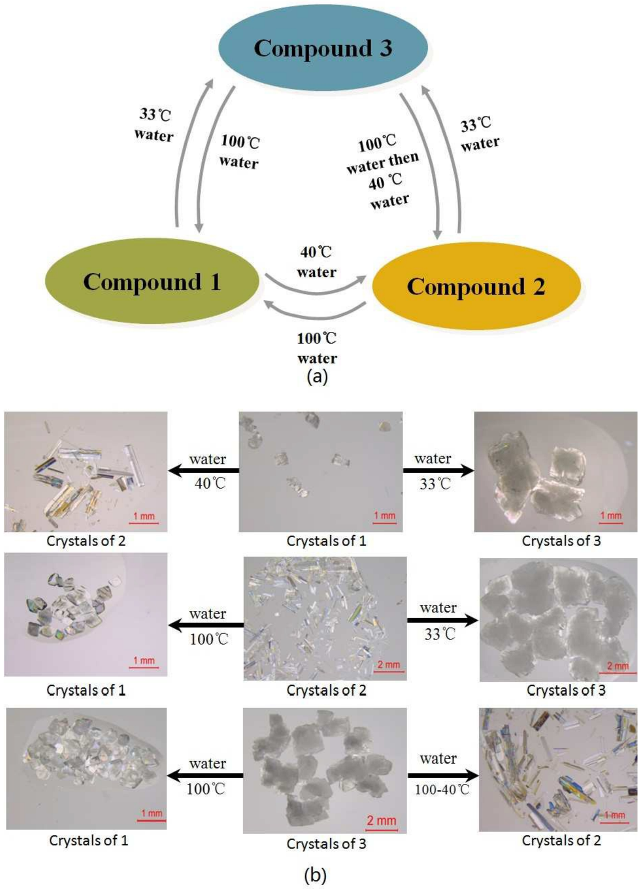


Fig. 11 (a) Schematic illustration showing the structural transformation circle among compounds 1-3; (b) The photos of structural transformation process of single crystals of compounds 1-3 in humid environment.

Conclusion

In this paper, we have designed and synthesized three hydrous salts in the AEDPH$_4$-pip-H$_2$O system, namely (AEDPH$_3$)·(pipH$_2$)$_{0.5}$·0.5H$_2$O (**1**), (AEDPH$_3$)·(pipH$_2$)$_{0.5}$·2H$_2$O (**2**), and (AEDPH$_3$)·(pipH$_2$)$_{0.5}$·3H$_2$O (**3**). Compounds **1-3** all has [(AEDPH$_3$)·(pipH$_2$)$_{0.5}$]$_n$ supramolecular hosts but display different host structure with different pore sizes and shapes, thus can contain different numbers of water molecules. Moreover, single crystals of the three compounds can display an interesting temperature induced structural transformations in humid environment. The result shows that, organophosphonic acids (such as AEDPH$_4$) have unique advantage in designing novel supramolecular structures with structural transformation properties, for their various hydrogen-bonded motifs and structural aggregates may form a series of "supramolecular host isomers" and finally result in structural transformation circle, moreover, the hydrophilic properties of organophosphonic acids is benefit for achieving structural transformation in humid environment.

Acknowledgment

This work was supported by grants of the National Nature Science Foundation of China (No. 21071112 and No. 21471119), Starting Research Foundation from the Guilin University of technology (No. 002401003378), Sharing Foundation of Ministry-province jointly-constructed cultivation base for state key laboratory of Processing for non-ferrous metal and featured materials (No. 13KF-9), University Scientific Research Project Foundation of the Guangxi Education Department (No. ZD2014060), as well as Sharing Foundation of Guangxi Key Laboratory in Universities of Clean Metallurgy and Comprehensive Utilization for Non-ferrous Metals Resources (No. 15-009).

Notes and references

[a] *College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, P. R. China. *Corresponding author. E-mail: ljyuan@whu.edu.cn. Tel: +86-27-6875-2800*

[b] *College of Materials Science and Engineering, Guilin University of technology, Guilin 541004, P. R. China. *Corresponding author. E-mail: chenshuoping_777@163.com. Tel: +86-773-5896290.*

† *Electronic Supplementary Information (ESI) available: Figure S-1-3: The ORTEP of compound 1-3 with thermal ellipsoids at the 30% probability level.; Figure S-4: IR spectra of compounds 1-3; Figure S-5: TG curves of compounds 1-3 in air; Table S-6-8: Hydrogen bonds of compound 1-3.*

[1] (a) D. Braga, F. Grepioni, L. Chelazzi, M. Campana, D. Confortini and G. C. Viscomi, CrystEngComm, 2012, **14**, 6404.; (b) D. E. Braun, R. M. Bhardwaj, J. B. Arlin, A. J. Florence, V. Kahlenberg, U. J. Griesser, D. A. Griesser, D. A. Tocher and S. L. Price, *Cryst. Growth Des.,* 2013, **13**, 4071−4083.

[2] (a) S. Bhattacharya, A. J. Bhattacharyya and S. Natarajan, *Inorg. Chem.*, 2015, **54**, 1254–1271; (b) C. Wang, L. J. Li, J. G. Bell, X. X. Lv, S. F. Tang, X. B. Zhao and K. M. Thomas, *Chem. Mater.*, 2015, **27**, 1502–1516; (c) X. J. Zhang, V. Vieru, X. W. Feng, J. L. Liu, Z. J. Zhang, B. Na, W. Shi, B. W. Wang, A. K. Powell, L. F. Chibotaru, S. Gao, P. Cheng and J. R. Long, *Angew.Chem. Int .Ed,*. 2015, **54**, 9861–9865.

[3] W. C. Xiao, C. H. Hu and M. D. Ward, *J. Am. Chem. Soc.*, 2014, **136**, 14200−14206.

[4] (a) F. J. Casado, M. R. Riesco, M. I. Redondo, D. C. Lazarte, S. L. Andres and J. A. Cheda, *Cryst. Growth Des.*, 2011, **11**, 1021–1032; (b) F. A. Paz and J. Klinowski, *CrystEngComm*, 2003, **5**, 238–244; (c) A. Bajpai, P. Chandrasekhar, S. Govardhan, R. Banerjee and J. N. Moorthy, *Chem. Eur. J.,* 2015, **21**, 2759–2765.

[5] (a)C. P. Li, J. Chen, W. Guo and M. Du, *Journal of Solid State Chemistry*, 2015, **223**, 95–103; (b) G. K. Kole, T. Kojima and J. J. Vittal, *Angew. Chem. Int. Ed.,* 2014, **53**, 2143 –2146; (c) X. X. Wu, Y. Y. Wang, P. Yang, Y. Y. Xu, J. Z. Huo, B. Ding, Y. Wang and X. G. Wang, *Cryst. Growth Des.*, 2014, **14**, 477−490.

[6] J. Kawada, T. Yui, K. Okuyama, K. Ogawaw and Biosci, *Bietechnol. Biochem.*, 2001, **65**, 2542-2547.

[7] Y. Yoshii, K. Sakai, N. Hoshino, T. Takeda, S. Noro, T. Nakamura and T. Akutagawa, *CrystEngComm,* 2015, **17**, 5962.

[8] J. P. Zhang, Y. Y. Lin, W. X. Zhang and X. M. Chen, *J. Am. Chem. Soc,*. 2005,**127**, 14162-14163.

[9] M. Juribasic, N. Bregovic, V. Stilinovic,V. Tomisic, M. Cindric, P. Sket, J. Plavec, M. Rubcic and K. Uzarevic, *Chem. Eur. J.,* 2014, **20**, 17333 – 17345.

[10] S. P. Chen, L. L. Pan, Y. X. Yuan, X. X, Shi and L. J. Yuan, *Cryst. Growth Des.*, 2009, **9**, 2668-2673.

[11] S. M. Wu, S. P. Chen, M. Li, J. F. Xiang, Y. Xiao and L. J. Yuan, *CrystEngComm*, 2007, **9**, 907–914.

[12] (a) S. M. Wu, S. P. Chen, M. Li, J. F. Xiang, Y. Xiao and L. J. Yuan, *CrystEngComm*, 2007, **9**, 907–914; (b) S. P. Chen, Y. X. Xuan, L. L. Pan, S. Q. Xu, H. Xia and L. J. Yuan, *Cryst. Growth Des.*, 2009, **9**, 874-879; (c) S. P. Chen, L. Hu, Y. Q. Zhang, P. Deng, C. Li, X. Chen and L. J. Yuan, *Chem. Commun*., 2012,**48**, 552–554.

[13] S. P. Chen, L. Hu, X. J. Hu, Y. X. Xuan, L. L. Pan and L. J. Yuan, *Cryst. Growth Des.*, 2009, **9**, 3835-3839.

[14] D. Tian, J. Xiong, X. C. Liang, J. Deng and L. J. Yuan, S. P. Chen, *CrystEngComm*, 2014, **16**, 2732-2737.

[15] S. P. Chen, Y. Q. Zhang, L. Hu, H. Z. He and L. J. Yuan, *CrystEngComm*, 2010, **12**, 3327–3336.

A series of hydrous salts construed by 1-aminoethylidenediphosphonic acid ($AEDPH_4$) and piperazidine (pip) were synthesized and structural characterized, namely $(AEDPH_3)\cdot(pipH_2)_{0.5}\cdot 0.5H_2O$ (1), $(AEDPH_3)\cdot(pipH_2)_{0.5}\cdot 2H_2O$ (2), and $(AEDPH_3)\cdot(pipH_2)_{0.5}\cdot 3H_2O$ (3). Compounds 1-3 all contain porous $[(AEDPH_3)\cdot(pipH_2)_{0.5}]_n$ supramolecular hosts with the same components, but illustrate different host structures, which allow different numbers of water molecules to lie in. Moreover, a reversible structural transformation circle is observed among the single crystals of the three hydrous salts, that is, compounds 1-3 can transformation to each other by changing the temperature in humid environment.