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ORIGINAL PAPER

Supramolecular Architectures Constructed from Piperazine and Substituted Benzoic Acids

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Abstract Piperazine (pip) were reacted with benzoic acid (Hba) and different substituted benzoic acid, such as *o*-chlorobenzoic acid (Hocba), *m*-chlorobenzoic acid (Hmcba), *p*-chlorobenzoic acid (Hpcba), *o*-aminobenzoic acid (Hoaba), *p*-aminobenzoic acid (Hpaba), affording a series of compounds $[H_2pip][ba]_2$ (**1**), $[H_2pip][ocba]_2$ (**2**), $[H_2pip][mcba]_2$ (**3**), $[H_2pip][pcba]_2$ (**4**), $[H_2pip][oaba]_2$ (**5**), and $[H_2pip][paba]_2$ (**6**). Extensive N–H···O hydrogen bonds are found in **1**–**6**, featuring different hydrogen-bonding motifs. Compounds **1**–**4** have two-dimensional layers stabilized by strong N–H···O hydrogen bonds, while compounds **5** and **6** exhibit one-dimensional ribbons formed by N–H···O hydrogen bonds. Moreover, in compound **6**, the existence of water molecules extends the one-dimensional ribbons into a three-dimensional supramolecular structure via hydrogen bonds. CCDC: 672374, (**1**); 672375, (**2**); 672376, (**3**); 672377, (**4**); 672378, (**5**); 672379, (**6**).

Keywords Piperazine · Benzoic acid · Hydrogen bonds

Introduction

Organic crystals built from acid–base complexes have received considerable attention in the predictable assembly of supramolecular architectures [1–4]. One of the important ways is the utilization of self-assembly of small molecules through N–H···O and N–H···N hydrogen bonding interactions and other weak intermolecular interactions to construct one-, two- and three-dimensional networks [5–8]. As an excellent hydrogen bond donor, piperazine (pip) has been employed widely in constructing supramolecular architectures, mainly in combination with aliphatic chain carboxylic acids [9–14]. In contrast, only a few examples of crystals of aromatic acids with pip have been reported [14–24], including five examples of crystals of benzoic acids and pip have been reported so far [25–28]. Different from the benzoic acids complexes, the substituted benzoic acids with functional groups can construct different supramolecular architectures with pip. In our previous work, we have reported several molecular supromolecular networks constructed by pip with dicarboxylic acids [29]. Different from the dicarboxylic acids, benzoic acids and its substituents can construct different networks with pip. Herein, we report crystal structures of pip and with benzoic acid (Hba) and different substituted benzoic acid, such as *o*-chlorobenzoic acid (Hocba), *m*-chlorobenzoic acid (Hmcba), *p*-chlorobenzoic (Hpcba), *o*-aminobenzoic acid (Hoaba), *p*-aminobenzoic acid (Hpaba) (Chart 1), namely, $[H_2pip][ba]_2$ (**1**), $[H_2pip][ocba]_2$ (**2**), $[H_2pip][mcba]_2$ (**3**), $[H_2pip][pcba]_2$ (**4**), $[H_2pip][oaba]_2$ (**5**), and $[H_2pip][paba]_2$ (**6**).

Experimental Section

Materials and Physical Measurements

All reagents and solvents used were commercially available and used as received without further purification. The C, H and N microanalyses were carried out with an Elementar Vario EL elemental analyzer.

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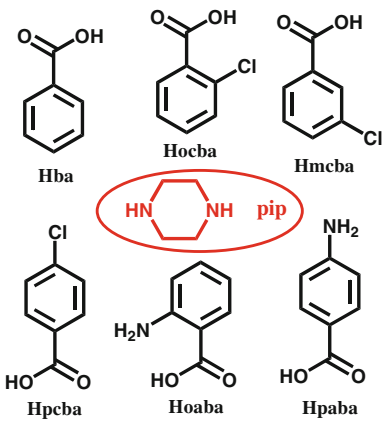

Chart 1 Structure of pip and substituted benzoic acids

Synthesis

(**1**): An ethanol solution (10 mL) of Hba (0.244 g, 2.0 mmol) was added to a stirred solution (5 mL) of pip (0.086 g, 1.0 mmol) and the reaction mixture was stirred for 5 min. The resulting colorless solution was allowed to stand in air at room temperature for 5 days yielding colorless crystals in ca. 60% yield (Found: C, 65.48; H, 6.67; N, 8.52%. Calc. for $C_{18}H_{22}N_2O_4$: C, 65.44; H, 6.71; N, 8.48%).

(**2**): An ethanol solution (10 mL) of Hocba (0.312 g, 2.0 mmol) was added to a stirred solution (5 mL) of pip (0.086 g, 1.0 mmol) and the reaction mixture was stirred for 5 min. The resulting colorless solution was allowed to stand in air at room temperature for 3 days yielding colorless crystals in ca. 60% yield (Found: C, 54.20; H, 5.09; N, 7.10%. Calc. for $C_{18}H_{20}N_2O_4Cl_2$: C, 54.15; H, 5.05; N, 7.02%)

(**3**): An ethanol solution (10 mL) of Hmcba (0.312 g, 2.0 mmol) was added to a stirred solution (5 mL) of pip (0.086 g, 1.0 mmol) and the reaction mixture was stirred for 5 min. The resulting colorless solution was allowed to stand in air at room temperature for 4 days yielding colorless crystals in ca. 64% yield (Found: C, 54.19; H, 5.01; N, 7.10%. Calc. for $C_{18}H_{20}N_2O_4Cl_2$: C, 54.15; H, 5.05; N, 7.02%).

(**4**): An ethanol solution (10 mL) of Hpcba (0.312 g, 2.0 mmol) was added to a stirred solution (5 mL) of pip (0.086 g, 1.0 mmol) and the reaction mixture was stirred for 5 min. The resulting colorless solution was allowed to stand in air at room temperature for 4 days, yielding colorless crystals in ca. 59% yield (Found: C, 54.14; H, 5.05; N, 7.05%. Calc. for $C_{18}H_{20}N_2O_4Cl_2$: C, 54.15; H, 5.05; N, 7.02%).

(**5**): An ethanol solution (10 mL) of Hoaba (0.274 g, 2.0 mmol) was added to a stirred solution (5 mL) of pip (0.086 g, 1.0 mmol) and the reaction mixture was stirred for 5 min. The resulting thin-red solution was allowed to stand in the dark at room temperature for 3 days, yielding colorless crystals in ca. 63% yield (Found: C, 59.95; H, 6.74; N, 15.58%. Calc. for $C_{18}H_{24}N_4O_4$: C, 59.99; H, 6.71; N, 15.55%).

(**6**): An ethanol solution (10 mL) of Hpaba (0.274 g, 2.0 mmol) was added to a stirred solution (5 mL) of pip (0.086 g, 1.0 mmol) and the reaction mixture stirred for 5 min. The resulting yellowish solution was allowed to

Table 1 Crystal data and structure parameters for compounds **1**–**6**

	1	**2**	**3**	**4**	**5**	**6**
Formula	$C_{18}H_{22}N_2O_4$	$C_{18}H_{20}Cl_2N_2O_4$	$C_{18}H_{20}Cl_2N_2O_4$	$C_{18}H_{20}Cl_2N_2O_4$	$C_{18}H_{24}N_4O_4$	$C_{18}H_{28}N_4O_6$
*F*w	330.38	399.26	399.26	399.26	360.41	396.44
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthogonal	Monoclinic	Monoclinic
Space group	*Pbca*	$P2_1/c$	$P2_1/c$	*Pccn*	$P2_1/c$	$P2_1/c$
α [Å]	8.2842(8)	10.8451(13)	13.7630(14)	8.143(2)	18.675(3)	6.5957(13)
β [Å)	8.3692(8)	8.0496(10)	8.1716(9)	26.993(6)	6.0092(11)	11.760(2)
χ [Å]	25.061(2)	11.1236(13)	8.4131(9)	8.264(2)	17.747(3)	12.613(2)
α [°]	90.00	108.979(2)	104.184(2)	90.00	116.934(3)	90.00
β [°]	1737.6(3)	918.29(19)	917.34(17)	1816.5(7)	1775.6(5)	978.3(3)
γ [°]	4	2	2	4	4	2
V [Å^3]	1.263	1.444	1.445	1.460	1.348	1.346
Z	0.090	0.380	0.380	0.384	0.097	0.102
ρ_{calcd} [g/cm^3]	0.0713	0.0455	0.0382	0.0754	0.0544	0.0461
μ [mm^{-1}]	0.1552	0.1070	0.1057	0.1914	0.1425	0.1162
$R_1[I > 2\sigma(I)]$[a]	0.0887	0.0543	0.0447	0.0950	0.0787	0.0529
wR_2(all data)[b]	0.1640	0.1123	0.1093	0.2204	0.1618	0.1215

$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2s}$

stand in the dark at room temperature for 1 week, yielding yellowish crystals in ca. 67% yield (Found: C, 54.55; H, 7.10; N, 14.18%. Calc. for $C_{18}H_{28}N_4O_6$: C, 54.53; H, 7.12; N, 14.13%).

X-Ray Crystallography

The diffraction data for **1–6** were collected at 273 K on a Bruker Smart 1000 CCD diffractometer with Mo–Kα radiation ($\lambda = 0.71073$ Å), and the data reduction was performed using Bruker SAINT [30]. The structures were solved using direct method, which yielded the positions of all or most of the non-hydrogen atoms. These were refined first isotropically and then anisotropically. All the hydrogen atoms of the ligands were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL programs [31]. The crystallographic data for **1–6** are summarized in Table 1. Hydrogen bond parameters are listed in Table 2.

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC-672374 (**1**), -672375 (**2**), -672376 (**3**), -672377 (**4**), -672378 (**5**), -672379 (**6**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code_(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk).

Results and Discussion

Single-crystal X-ray diffraction study reveals that **1** is a hydrogen-bonded two-dimensional supramolecular network The asymmetric unit contains a half of the diprotonated $[H_2pip]^{2+}$ and a deprotonated ba^- anoin. Each diprotonated

Table 2 Hydrogen bond lengths (Å) and bond angles (°) for **1–6**

D–H···A	D–H	H···A	∠DHA	D–H···A
$[H_2pip][ba]_2$ (**1**)				
N1–H1NA···O(2)[a]	0.960	1.781	169.78	2.731
N1–H1NB···O1	1.053	1.543	177.68	2.595
$[H_2pip][ocba]_2$ (**2**)				
N1–HN1A···O(2)[b]	0.879	1.866	161.35	2.713
N1–HN1B···O1	0.958	1.710	169.10	2.657
$[H_2pip][mcba]_2$ (**3**)				
N1–H1···O(1)[c]	0.922	1.821	161.34	2.710
N1–H2···O2	1.038	1.595	173.05	2.628
$[H_2pip][pcba]_2$ (**4**)				
N1–H1A···O(2)[d]	0.900	1.826	162.98	2.700
N1–H1B···O1	0.900	1.739	175.21	2.637
$[H_2pip][oaba]_2$ (**5**)				
N3–H3A···O(2)[e]	0.976	1.714	168.95	2.679
N3–H3B···O1	0.972	1.765	165.01	2.716
N4–H1···O(4)[f]	0.958	1.695	172.46	2.647
N4–H4A···O(3)[g]	0.919	1.789	165.79	2.689
N1–H1A···O2	0.860	2.080	128.91	2.705
N2–H2A···O3	0.860	2.052	129.13	2.680
$[H_2pip][paba]_2$ (**6**)				
O1W–H1WA···O2	0.871	1.964	173.27	2.831
O1W–H1WB···O(1)[i]	0.874	1.945	171.08	2.811
N1–H1B···O(1W)[j]	0.860	2.103	165.69	2.944
N2–H2B···O1	0.971	1.748	167.47	2.703
N2–H2A···O(2)[k]	1.042	1.618	162.36	2.630

Symmetry codes: [a] $-x - 1/2, y + 1/2, z$; [b] $-x, y - 1/2, -z - 1/2$; [c] $-x + 1, -y + 1, -z + 1$; [d] $-x + 3/2, y, z - 1/2$; [e] $x, y - 1, z$; [f] $-x - 1, y - 1/2, -z - 1/2$; [g] $-x - 1, y + 1/2, -z - 1/2$; [h] $x, y - 1, z$; [j] $x - 1, -y + 1/2, z + 1/2$; [k] $-x + 1, -y + 1, -z$

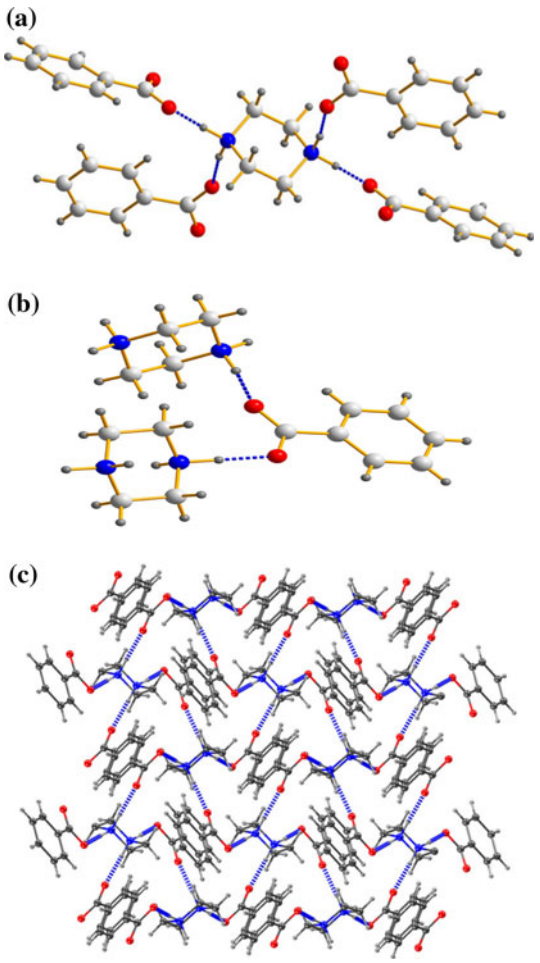

Fig. 1 Hydrogen-bonding environment around $[H_2pip]^{2+}$ cation (**a**), ba^- anion (**b**) and view of the hydrogen-bonded two-dimensional supramolecular layer (**c**) in **1**

piperazine cation $[H_2pip]^{2+}$ connects four ba^- anions through the N–H···O hydrogen bonds, while each ba^- anion is connected to two $[H_2pip]^{2+}$ cations via the carboxylate group (Fig. 1a, b). Among the N–H···O hydrogen bonds, those associated with the carboxylic groups in the *syn* mode are strong (N1···O1 = 2.595(2) Å), whereas those associated with the carboxylic groups in the *anti* mode are moderate (N1···O2 = 2.731 Å). Consequently, a two-dimensional supramolecular layer is thus generated by N–H···O hydrogen-bonds (Fig. 1c).

When one of the H atoms of the benzene ring was replaced by the Cl atoms on different position, crystals of compounds **2**, **3** and **4** are obtained. In the crystal structure of **2**, each $[H_2pip]^{2+}$ cation is hydrogen-bonded to four $ocba^-$ anions (Fig. 2a), resulting a N–H···O hydrogen-bonded two-dimensional layer, in which the N–H···O hydrogen bond associated with carboxylic group in the *syn* mode (2.657 Å) only slightly shorter than that associated with the carboxylic group in the *anti* mode (2.713 Å). Differently, there are existing intramolecular Cl···O contacts between the Cl atom and carboxylic O atom (3.069(2) Å) (Fig. 2b), and intermolecular Cl···O contacts (3.179(2) Å) to form two $ocba^-$ anions dimer (Fig. 2c), both of which are less than their respective van der Walls radius sums (3.27 Å) [32–35]. Notably, the structures of compound **3** and **4** with Cl atom on the *m*- and *p*- position, respectively, are similar to compound **1**, though crystallizing in different space groups, indicating that the Cl atom on the *m*- and *p*- position with long distance from carboxylate group has no effect on the molecular packing.

When the Cl atom was replaced by amino group, a one-dimensional chain-based structure was formed in compound **5**. There are two halves of centrosymmetric $[H_2pip]^{2+}$ cations and two $oaba^-$ anions in a crystallographically independent unit, in which each $[H_2pip]^{2+}$ cation is located around an inverse center. Each diprotonated piperazine cation $[H_2pip]^{2+}$ connects four $oaba^-$ anions through the N–H···O hydrogen bonds, while each $oaba^-$ anioin is connected to two $[H_2pip]^{2+}$ cations via the carboxylate group in the *syn-anti* mode (O···N = 2.647–2.716 Å) (Fig. 3a, b), and then a one-dimensional

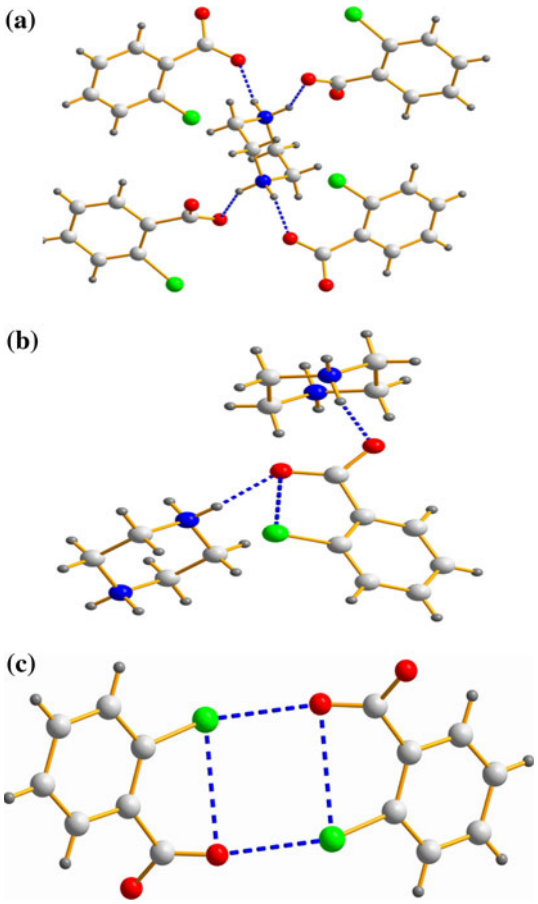

Fig. 2 Hydrogen-bonding environment around $[H_2pip]^{2+}$ cation (**a**), $ocba^-$ anion (**b**) and intermolecular Cl···O contacts (**c**) in **2**

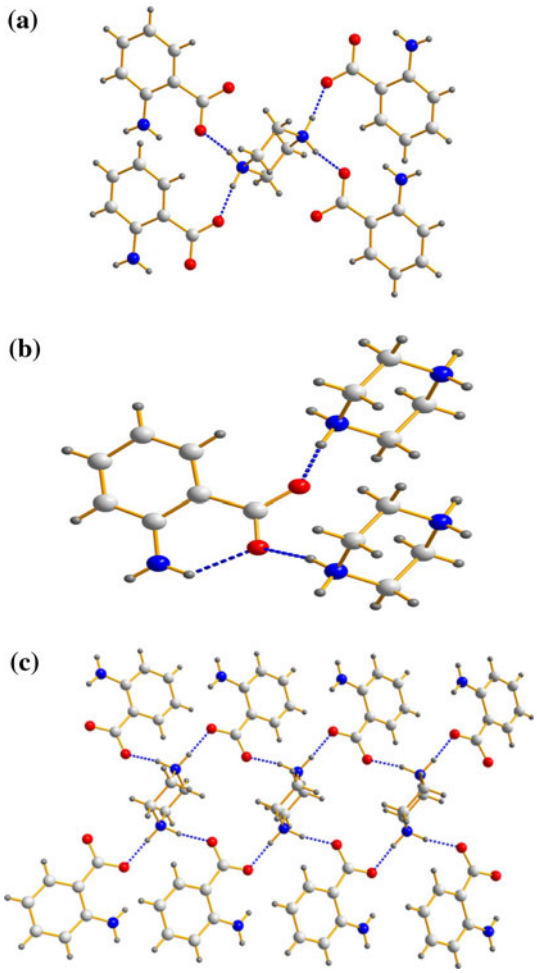

Fig. 3 Hydrogen-bonding environment around $[H_2pip]^{2+}$ cation (**a**), ba^- anion (**b**) and view of the hydrogen-bonded one-dimensional ribbon (**c**) in **5**

ribbon is formed, in which the $[H_2pip]^{2+}$ cations are located in the center while the oaba$^-$ anions are attached on its both sides (Fig. 3c).

Different from compound **5**, there are one half $[H_2pip]^{2+}$ cation, one paba$^-$ anion and one lattice water molecule in the asymmetric unit. Similarly, each $[H_2pip]^{2+}$ cation links four paba$^-$ anions through strong N–H···O hydrogen bonding interactions (N···O 2.630 and 2.703 Å), while each paba$^-$ anion links two neighboring $[H_2pip]^{2+}$ cations, as well as four water molecules (Fig. 4a, b). The existence of lattice water molecules make rich hydrogen bonds among the three parts. Firstly, the water molecule acts as hydrogen donors to form hydrogen bonds with adjacent carboxylic oxygen atoms from paba$^-$ anions (O···O = 2.830(5) and 2.811(5) Å). Secondly, it also acts as a hydrogen acceptor to form a hydrogen bond with an adjacent amino group from paba$^-$ anion (N···O = 2.943(5) Å). Through these two kinds of hydrogen bonding interactions, the one-dimensional $[H_2pip]^{2+}$–[paba]$^-$ ribbons (Fig. 4c) are assembled into a three-dimensional supramolecular network.

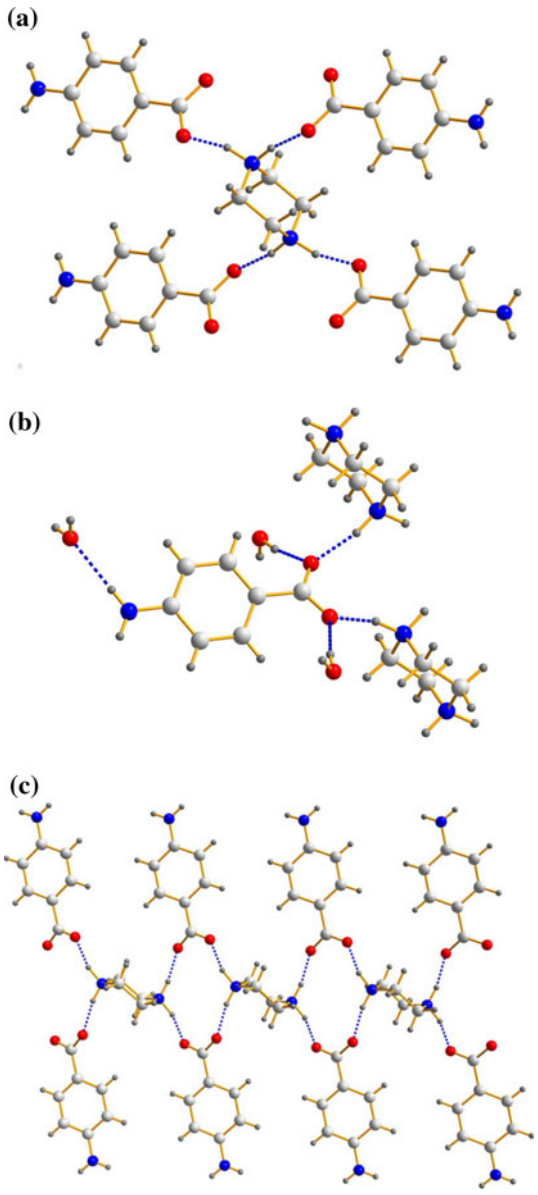

Fig. 4 Hydrogen-bonding environment around $[H_2pip]^{2+}$ cation (**a**), ba$^-$ anion (**b**) and view of the hydrogen-bonded one-dimensional ribbon (**c**) in **6**

Conclusion

The flexible and easily protonated pip molecule is be chosen as the hydrogen donor and different substituted benzoic acids as the hydrogen acceptor to construct six different compounds **1**–**6**. For different substituents of the benzoic group, similar two-dimensional hydrogen-bonded networks are formed in **1**–**4**, indicating that the introduction of chlorine has no obvious effect on the hydrogen-bonded network, including the intramolecular and intermolecular Cl···O contacts. However, when a amino group is introduced, one-dimensional supramolecular ribbons are generated in **5**–**6**, suggesting a significant effect of the amino group on the hydrogen-bonding behavior between of the $[H_2pip]^{2+}$ cations and substituted benzoic groups. As is expected, the amino group of the benzoic acids and lattice water molecules also play a vital role in formation of network.

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