



# Mutual interplay of non-covalent interactions in modulating the geometry of organic linkers in their salts



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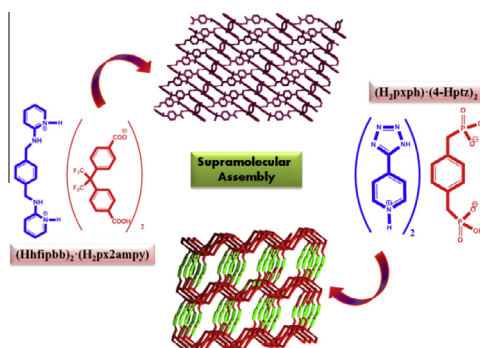
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## HIGHLIGHTS

- Synthesis and characterization of ion pair organic salts.
- Compounds have been characterized by single crystal X-ray crystallography.
- The conformational modulation by supramolecular interactions has been studied.
- Mutual interplay of non-covalent interactions has been demonstrated.
- Compounds are additionally characterized by TGA and bulk homogeneity proved by PXRD.

## GRAPHICAL ABSTRACT

The conformational modulation of flexible linkers, influenced by the mutual interplay of non-covalent interactions, has been demonstrated in two ion-pair organic salts.



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## ABSTRACT

Two ion-pair compounds  $(\text{Hhfpbb})_2 \cdot (\text{H}_2\text{px}2\text{ampy})$  (**1**) and  $(\text{H}_2\text{pxph}) \cdot (\text{4-Hptz})_2$  (**2**) have been synthesized, based on the ligands 4,4'-(hexafluoroisopropylidene)-bis(benzoic acid) ( $\text{H}_2\text{hfpbb}$ ), 1,4-bis(2-pyridylaminomethyl)benzene ( $\text{px}2\text{ampy}$ ), *p*-xylylenediphosphonic acid ( $\text{H}_4\text{pxph}$ ) and (5-(4-pyridyl) tetrazole) ( $\text{4-ptz}$ ). Both the compounds **1** and **2** are characterized by routine elemental analyses, IR-, thermogravimetric studies and unambiguously characterized by single crystal X-ray crystallography. The mutual supramolecular interactions, exhibited by the individual ligands in the organic salts, modulate their geometries to form higher dimensional supramolecular architectures in the crystals of organic salts **1** and **2**. In compound **1**, the di-cation  $\text{H}_2\text{px}2\text{ampy}^{2+}$  modulates its potential hydrogen donor sites in a *cis* conformation to form a  $R_2^2(8)$  hetero synthon with carboxylate oxygen atoms of singly deprotonated  $\text{Hhfpbb}^{1-}$  anion and thereby restricts the twisting between two benzene rings in the  $\text{Hhfpbb}^{1-}$  skeleton to form 3D intricate supramolecular architecture. The *trans*-conformations of  $\text{H}_4\text{pxph}$  (compound **2**) forms 1D chain through  $R_2^2(8)$  homo synthons, which extends to a 3D porous supramolecular network through interactions with  $\text{4-Hptz}^+$  cations (by twisting them). The ion components, that are present in both compounds, modulate their geometry from their classical geometries, displayed by them in the metal coordination architectures and inorganic salts.

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## Introduction

In the recent era, crystal engineering carries the prime theme of research for the people, working in the fields of biological chemistry,

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materials sciences, physics and most actively in the field of pharmaceuticals [1–6]. In the field of organic crystal designing, intermolecular interactions play an important role in the formation of supramolecular architectures as well as affecting the physical and chemical properties of resulting crystalline solids [7]. Supramolecular synthons, formed due to classical hydrogen bonding interactions, precisely termed as building blocks, are widely utilized tools to analyze, classify and design of existing and novel organic solids [8,9]. In the multicomponent systems of organic solid state chemistry, the functionalities, displayed by the single components, are useful for better understanding the reactivity and dynamics of the complex chemical reactions [10,11]. The strength of the intermolecular interactions between two components mutually interplay a role to modulate their geometries [12,13].

Dicarboxylic acids are largely employed as building blocks to construct the supramolecular architectures due to their tendency to form non-covalent interactions, generally through predictable synthons [14–16]. The majority of organic salts comprised of carboxylic acids with a wide variety of pyridines, azoles, amines and their related compounds [17,18]. The co-existence of phosphonic acids, tetrazoles as constituents of organic salts are very rare in this domain. Clearfield et al. reported the ion pair compounds of 1,3,5-benzene triphosphonic acid, where the protons on the phosphonic acid groups are transferred to the bipyridines and forms multi-dimensional supramolecular architectures with the aid of supramolecular interactions [19]. Tetrazole-assisted ion-pair organic compounds are less explored, whereas, tetrazole with different inorganic anions are widely studied [20–24]. In crystal engineering, flexible and bent linkers are often used to construct the extended metal coordination architectures, but their utilization as supramolecular building blocks are infrequent [25,26]. Flexible and bent linkers have different degrees of freedom and can exist in different conformations, which are often directed by diverse non covalent interactions in the pertinent crystal structure [27].

Based on aforementioned considerations, we have chosen bent carboxylic acid  $H_2hfpbb$  and double ordered long flexible linker  $px2ampy$  as one pair and flexible bisphosphonic acid  $H_4pxph$  and rigid tetrazole 4-ptz as another pair to synthesize ion pair compounds  $(Hhfpbb)_2 \cdot (H_2px2ampy)$  (**1**) and  $(H_2pxph) \cdot (4-Hptz)_2$  (**2**). These linkers are well explored to synthesize the metal coordination architectures and our attempt in this article is to study their singular functionalities in terms of modulating the geometry, supramolecular interactions in the resulting binary ion pair compounds. Both compounds **1** and **2** are characterized by single crystal X-ray crystal structure determination and through supramolecular interactions leading to the formation of higher dimensional architectures. A brief comparison of the linkers, employed in these organic salts (present study) with their corresponding reported metal coordination architectures and inorganic salts demonstrates a mutual interplay of interactions in modulating the geometry of the linkers.

## Synthesis

### Materials and methods

All the chemicals were received as reagent grade and used without any further purification. The ligands  $H_4pxph$  and  $px2ampy$  were prepared according to the literature procedures [28,29]. Elemental analyses were determined by FLASH EA series 1112 CHNS analyzer. Infra-red spectra of solid samples were obtained as KBr pellets on a JASCO – 5300 FT – IR spectrophotometer. Thermogravimetric analyses were carried out on a STA 409 PC analyzer and corresponding masses were analyzed by QMS 403 C mass analyzer, under flow of  $N_2$  gas with a heating rate of  $5^\circ C \text{ min}^{-1}$ , in the

temperature range of 30–1000 °C. Both the compounds were synthesized in 23 mL Teflon-lined stainless vessels (Thermocon, India).

### Synthesis

#### Synthesis of $(Hhfpbb)_2 \cdot (H_2px2ampy)$

A mixture of  $H_2hfpbb$  (0.25 mmol, 98.0 mg) and  $px2ampy$  (0.25 mmol, 72.5 mg) in  $H_2O$  (10.0 mL) and DMF (2.0 mL) was stirred for 30 min. The reaction mixture was placed in a 23 mL Teflon-lined stainless steel autoclave, sealed and heated at 120 °C for 72 h. The autoclave was allowed to cool to room temperature for 48 h. Small block-shaped colorless crystals of compound **1** were obtained in 42.5% yield (based on  $H_2hfpbb$ ). Anal. Calcd. for  $C_{26}H_{19}F_6N_2O_4$  (MW = 537.43) : C, 58.08; H, 3.56; N, 5.21 Found: C, 59.10; H, 3.12; N, 5.67. IR (KBr pellet,  $cm^{-1}$ ): 3326, 3271, 2953, 1704, 1676, 1550, 1391, 1260, 1260, 1216, 1178, 975, 854, 728.

#### Synthesis of $(H_2pxph) \cdot (4-Hptz)_2$

Compound **2** was synthesized by the procedure as described in the synthesis of **1**, by heating reaction mixture  $H_4pxph$  (0.66 g, 0.25 mmol) and 4-ptz (0.36 g, 0.25 mmol) in a solvent ratio of 8:2 (v/v,  $H_2O/MeOH$ ), at 120 °C in a Teflon lined stainless vessel for 3 days to yield a large colorless block-shaped crystals (yield: 0.446 g 72% based on  $H_4pxph$ ). Anal. Calcd. for  $C_{20}H_{22}N_{10}O_6P_2$  (MW = 560.42): C, 42.84; H, 3.95; N, 25.00 Found: C, 42.34; H, 3.48; N, 25.32. IR (KBr pellet,  $cm^{-1}$ ): 3084, 3042, 2484, 2154, 2046, 1944, 1639, 1508, 1267, 1093, 923, 841, 746, 680, 567.

### Single crystal X-ray structure determination of the compounds 1–2

Single-crystals suitable for structural determination of all the compounds (**1–2**) were mounted on a three circle Bruker SMART-APEX CCD area detector system under  $Mo-K\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) graphite monochromated X-ray beam, crystal to detector distance 60 mm, and a collimator of 0.5 mm. The scans were recorded with an  $\omega$  scan width of  $0.3^\circ$ . Data reduction was performed by SAINT-PLUS [30], empirical absorption corrections were performed using equivalent reflections by program SADABS [31]; structure solution was done using SHELXS-97 [32] and full-matrix least-squares refinement was performed using SHELXL-97 [33] for both compounds. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms on the C atoms were introduced on calculated positions and were included in the refinement riding on their respective parent atoms. Hydrogen atoms on the nitrogen atoms (NH groups) and oxygen atoms (hydroxyl groups) were located by Fourier electron density map. Crystal data, structure refinement parameters for both compounds are summarized in Table 1 and hydrogen bonding parameters are given in Table 2. Selected bond lengths and bond angles for compounds **1** and **2** are presented in the section of Supporting Information.

## Results and discussion

### Synthesis

Both the compounds are synthesized under hydrothermal conditions at 120 °C in the mixed solvent system of  $H_2O$ : DMF in case of **1** and  $H_2O$ : MeOH in case of compound **2** (Scheme 1). Initially attempts were made to synthesize at room temperature using conventional layering and crystallization techniques, but unfortunately those attempts were always ended up with amorphous powders. DMF was added in case of compound **1** to dissolve  $H_2hfpbb$  and MeOH in **2** to dissolve  $H_4pxph$ . The pH of reaction mixture was not disturbed by adding external acids or bases, but the compounds are obtained with different protonation states.

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