

# Network Formation of Bis(2-benzimidazylmethyl)amine in Salts with Carboxylic Acids: The Structures Based on the Interplay of Strong and Weak Intermolecular Interactions

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**ABSTRACT:** Six new organic salts containing flexible and polydentate bis(2-benzimidazylmethyl)amine (BBMA) and a variety of carboxylic acids, including benzoic acid (HBA), *p*-nitrobenzoic acid (4-NHBA), 3,5-dinitrobenzoic acid (3,5-DiNHBA), terephthalic acid (H<sub>2</sub>TPA), trimesic acid (H<sub>3</sub>T-MA), and pyromellitic acid (H<sub>4</sub>PMA), formulated as (HB-BMA)  $\cdot$  (HBA)  $\cdot$  (BA) (1), (HBBMA)  $\cdot$  (4-NHBA) (2), (H<sub>2</sub>BBMA)  $\cdot$  (3,5-DiNBA)<sub>2</sub> (3), (H<sub>2</sub>BBMA)  $\cdot$  (TPA)  $\cdot$  (H<sub>2</sub>-



TPA)<sub>0.5</sub>·DMF (4),  $(H_2BBMA) \cdot (H_2TMA)_2 \cdot DMF$  (5), and  $(H_2BBMA) \cdot (H_2PMA)$  (6), have been synthesized. The salts were characterized by elemental analysis, IR, thermogravimetric analysis, powder X-ray diffraction, and single-crystal X-ray diffraction, to understand how variations in their molecular structures and intermolecular interactions influence their supramolecular assemblies. Proton transfer from the COOH to benzimidazole N acceptor (BimN) occurred in the six organic salts (1–6), leading to the ionic heterosynthon VI in all structures. Competition and cooperation between COOH, COO<sup>-</sup>, BimNH<sup>+</sup>, BimN, -NH<sub>2</sub><sup>+</sup>-, and -NH- functional groups for the observed hydrogen bond synthons are examined in the six structures. To the best of our knowledge, there are no systematic studies on hydrogen bond competition and interplay when the above six H-bonded donors or acceptors are present in the same crystal structure. It is noted that C-H···O hydrogen bonds increase the dimensionality of the supramolecular architectures of the six salts (from one-dimensional (1-D) to two-dimensional (2-D) in 1; from 1-D to three-dimensional (3-D) in 2, from zero-dimensional (0-D) to 3-D in 3, from 2-D to 3-D in 5, from 1-D to 2-D in 6).

## INTRODUCTION

Multicomponent crystals and acid—base complexes have received considerable attention over the past few years<sup>1,2</sup> not only because of their intriguing structural motifs<sup>3,4</sup> but also for their useful properties and promising applications as functional materials.<sup>5,6</sup> An advantage in fabricating cocrystals or salts is that a number of closely related X-ray crystal structures may be determined to understand the relationship among intermolecular forces, molecular shapes, and crystal structures, which represents the fundamental aspect in supramolecular chemistry.<sup>7,8</sup>

Carboxylic acids represent one of the most prevalent functional groups in crystal engineering because they possess a hydrogen bond donor and acceptor with a geometry that facilitates self-association through supramolecular homosynthons. Indeed, carboxylic acids are well-known to self-associate via centrosymmetric dimer (I) or catemer (II).<sup>9–11</sup> Furthermore, it is now recognized that carboxylic acids are ideal candidates for multicomponent crystals since they form persistent supramolecular heterosynthons with a number of different complementary functional groups such as aromatic nitrogen, phosphonyls, and sulfonyls. The identification of supramolecular synthons<sup>12</sup> between common functional groups is a first step toward crystal engineering. Strong and specific recognition of the carboxylic acid group with pyridine (acid-pyridine synthon) is well studied.<sup>13–18</sup> However, the recognition pattern between the carboxylic acid group and imidazole (acid-imidazole synthon) remains less well-explored.

Recently, we and others have made efforts to use organic salts as molecular building blocks to control molecular packing in crystalline materials.<sup>19–25</sup> In this regard, a series of salts formed by imidazoles with carboxylic acids were chosen to investigate its supramolecular synthons and provided the experimental data to validate the work toward the a priori prediction of organic salt crystal structures.<sup>19–25</sup> A survey of the Cambridge Structural Database (CSD) indicates that 79% of complexes that contain both imidazole and carboxyl groups generate imidazolium-carboxylate supramolecular heterosynthons rather than carboxyl or imidazole supramolecular homosynthons.<sup>19</sup> Moreover, there is a mix of neutral O–H···N and ionic N<sup>+</sup>–H···O<sup>-</sup>

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Scheme 1. Supramolecular Homosynthons (I, II, and III) and Heterosynthons (IV, V, and VI, VII, VIII, IX, X, XI)



Scheme 2. Two-Step Protonation Processes of BBMA



acid-imidazole synthons in these crystal structures. All these findings indicate that there is indeed a strong competition between the anion and the neutral molecule toward recognition in the available receptors. For the polybenzimidazole, except for homosynthons III, there are five variants of the acid-imidazole heterosynthon in crystal structures: neutral, one-point (IV, V, XI); and ionic, single-point (VI, VIII), as depicted in Scheme 1. The carboxylic acid OH donor is localized on the acid group, and benzimidazole N or amino N is the acceptor in neutral synthons (**IV**, **V**, **XI**). When there is a sufficient  $pK_a$  difference between the COOH and benzimidazole groups, proton transfer will occur to give an ionic hydrogen bond  $N^+$ –H···O<sup>-</sup>, which can exist as a single interaction, (VI) and (VIII). The transfer from neutral to ionic hydrogen bond as a continuum of intermediate N-H···O bond states has ever been noted.<sup>19–23,26–29</sup> The issue of whether the acid-imidazole synthon is neutral or ionic is more than a physical and structural chemistry problem, thanks to the legal and patent implications of pharmaceutical cocrystals and salts.

On the other hand, compared to tris(2-benzimidazylmethyl)amine, the bis(2-benzimidazylmethyl)amine is a more flexible molecule, and thus conformational changes will lead to a changeable array of intermolecular interactions based on the binding sites, which probably results in a variety of crystalline architectures with desirable connectivity and metrics. Meanwhile, it is noted that the BBMA can exhibit twostep proton-transfer processes to give protonated species, HBBMA<sup>+</sup>, H<sub>2</sub>BBMA<sup>2+</sup> (i), and H<sub>2</sub>BBMA<sup>2+</sup> (ii), as shown in Scheme 2. These species exhibit a diverse directionality intrinsic to the BBMA system and construct multidimensional network structures. At this juncture, as a case study we have attempted to isolate different degrees of protonated receptors of BBMA at different experimental conditions to study the recognition pattern of anion vs cation. In this contribution, we will present a systematic investigation on such organic salts of BBMA and demonstrate the reliable supramolecular synthons. Indeed, proton transfer from carboxyl to benzimidazole is found, and crystallization of BBMA with various carboxylic acids (see Scheme 3) produce ordered lattices by supramolecular synthons II, III, IV, V, VI, VII, VIII, IX, X, and XI. A schematic representation of H-bonding synthons related to this work is summarized in Scheme 1.

## EXPERIMENTAL SECTION

**Materials and General Procedures.** Starting materials and solvents for synthesis were purchased commercially and used as received. The ligand BBMA was prepared according to reported procedures.<sup>31</sup> IR spectra were recorded as KBr pellets on a Nicolet Magna 750 FT–IR spectrometer in the 4000–400 cm<sup>-1</sup> region. Elemental analyses for C, H, and N were performed on a Flash 1112 elemental analyzer. Powder X-ray diffraction (PXRD) patterns were recorded using a Rigaku D/Max-IIIA diffractometer from 2° to 60° with a step size of 0.02° and a scan speed of 0.3 s preset time. Thermogravimetric analyses were carried out on a SDT Q600 analyzer. A platinum pan was used for heating the sample, and the analyses were carried out in nitrogen at a heating rate of 10 °C/min in the temperature range 25–700 °C.

General Procedure for the Preparation of the Compounds (1-6). A mixture of the bis(2-benzimidazylmethyl)amine and aromatic acid in a molar ratio of 1:2 was heated with gentle stirring at 60-80 °C

Scheme 3. Molecular Components Used in This Work



for 1 h in DMF and then cooled to room temperature. The undissolved materials were removed by filtration. The filtrate was set aside to crystallize. After one week, the single crystals suitable for X-ray analysis were obtained.

(HBBMA) · (BA) · (HBA) (1), the yield was 86% based on the BBMA. Mp: 253.0–255.0 °C. Anal. Calcd. for  $C_{30}H_{27}N_5O_4$ : C, 69.08; H, 5.22; N, 13.43 (%). Found: C, 68.99; H, 5.27; N, 13.31 (%). IR: 3300 (w), 1727 (s), 1667 (w), 1627 (w), 1593 (m), 1541 (s), 1514(m), 1448 (m), 1369(vs), 1312 (m), 1300 (m),1270 (m), 1151 (m), 1116 (w), 1050 (m), 1017 (w), 1003 (w), 948 (w), 903 (m), 802 (m), 752 (s), 740 (s), 713 (vs), 690 (m), 668 (s) cm<sup>-1</sup>.

(HBBMA) · (4-NBA) · (4-NHBA) (2), the yield was 77% based on the BBMA. Mp: 195.0–197.0 °C. Anal. Calcd. for  $C_{30}H_{25}N_7O_8$ : C, 58.92; H, 4.12; N, 16.03 (%). Found: C, 58.79; H, 4.20; N, 16.15 (%). IR: 3431 (w), 3293 (w), 3047 (m), 2923.7 (m), 2869 (m), 2742 (m), 1725 (s), 1628 (m), 1560 (vs), 1519 (s), 1488 (w), 1456 (m), 1375 (m), 1341 (vs), 1316 (s), 1149 (w), 1103 (w), 1059 (w), 1004 (w), 967 (w), 882 (m), 859 (w), 797 (m), 751 (s), 723 (s), 620 (w), 476(w) cm<sup>-1</sup>.

 $(H_2BBMA) \cdot (3,5-DiNBA)_2$  (3): the yield was 82% based on the BBMA. Mp: 201.0–203.0 °C. Anal. Calcd. for  $C_{30}H_{23}N_9O_{12}$ : C, 51.36; H, 3.30; N, 17.97 (%). Found: C, 51.41; H, 3.19; N, 18.05 (%).IR: 3434 (w), 3162 (w), 3113 (w), 3064 (w), 1625 (m), 1541 (vs), 1458 (m), 1446 (m), 1387 (m), 1343 (vs), 1275 (w), 1221 (m), 1124 (w), 1071 (m), 954 (w), 920 (w), 877 (w), 844 (w), 789 (w), 766 (m), 750 (m), 729 (s), 715 (s), 644 (w), 610 (m), 558 (w), 527 (w) cm<sup>-1</sup>.

 $(H_2BBMA) \cdot (TPA) \cdot (H_2TPA)_{0.5} \cdot DMF$  (4), the yield was 76% based on the BBMA. Mp: 247.0–249.2 °C. Anal. Calcd. for  $C_{31}H_{31}N_6O_7$ : C, 62.10; H, 5.21; N, 14.02 (%). Found: C, 62.31; H, 5.07; N, 13.92 (%). IR: 3305 (m), 3071 (m), 1722 (s), 1679(s), 1625 (m), 1610 (m), 1547 (s), 1440 (m), 1402 (m), 1374 (m), 1256 (s), 1210 (s), 1168 (s), 1107 (m), 1017 (w), 981 (w), 932 (w), 890 (w), 802 (w), 756 (s), 700 (w), 680 (s), 669 (s), 617 (m), 536 (w), 421 (m) cm<sup>-1</sup>.

 $\begin{array}{l} (H_2BBMA) \cdot (H_2TMA)_2 \cdot DMF \ (\textbf{5}): \ the \ yield \ was \ 63\% \ based \ on \ the \ BBMA. \ Mp: \ 245.8-247.2 \ ^{\circ}C. \ Anal. \ Calcd. \ for \ C_{37}H_{34}N_6O_{13}: \ C, \ 57.66; \ H, \ 4.45; \ N, \ 10.90 \ (\%). \ Found: \ C, \ 57.81; \ H, \ 4.60; \ N, \ 10.72 \ (\%). \ IR: \ 3384 \ (m), \ 3064 \ (m), \ 2609 \ (m), \ 1721 \ (s), \ 1678 \ (s), \ 1628 \ (m), \ 1607 \ (m), \ 1545 \ (s), \ 1440 \ (m), \ 1409 \ (m), \ 1371 \ (m), \ 1257 \ (s), \ 1208 \ (s), \ 1170 \ (s), \ 1104 \ (m), \ 1012 \ (w), \ 989 \ (w), \ 936 \ (w), \ 893 \ (w), \ 800 \ (w), \ 749 \ (s), \ 699 \ (w), \ 682 \ (s), \ 667 \ (s), \ 619 \ (m), \ 530 \ (w), \ 409 \ (m) \ cm^{-1}. \end{array}$ 

(H<sub>2</sub>BBMA) · (H<sub>2</sub>PMA) (6): the yield was 75% based on the BBMA. Mp: 229.0–232.0 °C. Calcd. for  $C_{26}H_{21}N_5O_8$ : C, 58.76; H, 3.98; N, 13.18 (%). Found: C, 58.91; H, 4.10; N, 12.95 (%). IR: 3373 (w), 3068 (m), 2922 (m), 2755(m), 2632 (m), 2515 (m), 1729 (s), 1624 (m), 1578 (s), 1461 (vs), 1405 (s), 1361 (vs), 1293 (m), 1223 (m), 1142 (s), 1092 (m), 1014 (m), 890 (m), 763 (m), 752 (m), 680 (m), 615 (m) cm<sup>-1</sup>.

X-ray Crystallographic Measurements. Suitable single crystals of 1–6 were selected and mounted in air onto thin glass fibers. Accurate unit cell parameters were determined by a least-squares fit of  $2\theta$  values, and intensity data were measured on a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromatized Mo–K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at room temperature. The intensities were corrected for Lorentz and polarization effects as well as for empirical absorption based on a multiscan technique. The structures were solved by direct methods and refined by full-matrix least-squares (SHELXTL-97)<sup>32,33</sup> with anisotropic thermal parameters for all non-H atoms. The H atoms were introduced in calculated positions and

H atoms. The H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. Details of crystal data, data collection, and refinement parameters are given in Table 1.

### RESULTS AND DISCUSSION

IR Spectral Studies. Compared with the IR spectra of organic salts 1-6, it was found that the asymmetric C=O stretches for 1, 2, 3, 4, 5, and 6 occur at 1541, 1560, 1541, 1547, 1547, and 1578 cm<sup>-1</sup>, while the symmetric C=O stretches for 1, 2, 3, 4, 5, and 6 appear at 1369, 1341, 1343, 1374, 1371, and 1361 cm<sup>-1</sup>, respectively. The positions of these stretches clearly show the presence of carboxylate groups. It is pointed out that the IR spectra of 4 and 5 also display the C=O stretching vibration of DMF at 1677.6 cm<sup>-1</sup>, indicating the presence of DMF. This can be further confirmed by the crystal structure analyses of 4 and 5.

**Description of Structures.** In DMF, cocrystallization of BBMA with each of the acid coformers (Scheme 3) led to salt solid forms (1-6) as confirmed by single crystal X-ray diffraction experiments. In all cases, the 1:2 or 1:1 (cation/anion) stoichiometry expected<sup>30</sup> from the ratio of hydrogen bond donors to acceptors was found in the salts. It must be pointed out that crystals suitable for single crystal X-ray diffraction experiments could not be grown when BBMA was cocrystallized with phthalic acid or isophthalic acid. In addition, as a consequence of the low solubility of the base and acid species in other organic solvents such as methanol, acetone, acetonitrile, benzene, and toluene, the combination of them only led to the formation of a lot of precipitates. The crystallographic data for the novel crystal structures are reported in Table 1, and the hydrogen bond parameters for all solid forms are given in Table 2.

Salt of Bis(2-benzimidazylmethyl)amine Benzoic Acid (1:2) (1). The structure has the space group P2(1)/c with one monoprotonated HBBMA<sup>+</sup> cation, one benzoate anion (BA), and one HBA within the asymmetric unit. The carboxylic acid proton is transferred to the benzimidazole nitrogen. In the crystal structure, the HBBMA<sup>+</sup> cations are bridged by benzoate anions via N-H···O hydrogen bonds (synthon VI: N···O = 2.637(3) Å; synthon VII:  $N \cdot \cdot \cdot O = 2.863(2)$  and 2.761(2) Å; synthon X:  $N \cdot \cdot \cdot O = 3.292(2)$  Å) to form a one-dimensional (1-D) chain, as shown in Figure 1a. Along the hydrogen-bonded 1-D chain, each HBA is anchored to benzimidazole N atom via  $O-H \cdots N$  bonds (synthon IV:  $O \cdots N = 2.559(3)$  Å). The neighboring hydrogen-bonded chains are held together via additional C-H···O interactions to form a two-dimensional (2-D) layer (C···O = 3.348(4) and 3.395(3) Å, respectively), as shown in Figure 1b.

Salt of Bis(2-benzimidazylmethyl)amine 4-Nitrobenzoic Acid (1:2) (2). Bis(2-benzimidazylmethyl)amine with 4-nitrobezoic acid form 1:2 salt 2 through the monoproton transfer in the space group P2(1)/c. The asymmetric unit of 2 contains one

| Table 1. | Crystallogra | phic and I | Experimental | Data for | Organic Salts | s 1- | 6 |
|----------|--------------|------------|--------------|----------|---------------|------|---|
|----------|--------------|------------|--------------|----------|---------------|------|---|

| organic salts                 | 1                    | 2                    | 3                       | 4                    | 5                       | 6                    |
|-------------------------------|----------------------|----------------------|-------------------------|----------------------|-------------------------|----------------------|
| CCDC number                   | 820586               | 820587               | 820591                  | 820588               | 820589                  | 820590               |
| formula                       | $C_{30}H_{27}N_5O_4$ | $C_{30}H_{25}N_7O_8$ | $C_{30}H_{23}N_9O_{12}$ | $C_{31}H_{31}N_6O_7$ | $C_{37}H_{34}N_6O_{13}$ | $C_{26}H_{22}N_5O_8$ |
| M                             | 521.57               | 611.57               | 701.57                  | 599.62               | 770.70                  | 532.49               |
| crystal system                | monoclinic           | monoclinic           | orthorhombic            | triclinic            | triclinic               | triclinic            |
| space group                   | P2(1)/c              | P2(1)/c              | P2(1)/c                 | $P\overline{1}$      | $P\overline{1}$         | $P\overline{1}$      |
| a/Å                           | 17.5925(19)          | 18.793(3)            | 8.5018(11)              | 10.1284(12)          | 8.583(2)                | 7.431(2)             |
| b/Å                           | 9.5612(11)           | 9.4762(15)           | 28.411(4)               | 11.7095(14)          | 13.886(3)               | 8.113(2)             |
| c/Å                           | 16.7805(19)          | 16.807(3)            | 12.7009(16)             | 14.5623(17)          | 14.780(4)               | 10.178(3)            |
| $\alpha/^{\circ}$             | 90                   | 90                   | 90                      | 72.0820(10)          | 83.222(3)               | 101.341(4)           |
| $\beta/^{\circ}$              | 111.7930(10)         | 107.759(2)           | 90                      | 70.2570(10)          | 88.057(3)               | 90.255(4)            |
| $\gamma/^{\circ}$             | 90                   | 90                   | 90                      | 69.1370(10)          | 89.200(3)               | 103.227(4)           |
| $volume/Å^3$                  | 2620.8(5)            | 2850.5(8)            | 3067.9                  | 1484.1(3)            | 1748.2(7)               | 584.9(3)             |
| Ζ                             | 4                    | 4                    | 4                       | 2                    | 2                       | 1                    |
| $D_{\rm calc}/{ m g~cm}^{-3}$ | 1.322                | 1.425                | 1.519                   | 1.342                | 1.464                   | 1.512                |
| $\mu/\mathrm{mm}^{-1}$        | 0.090                | 0.106                | 0.121                   | 0.097                | 0.113                   | 0.115                |
| T/K                           | 296(2)               | 291(2)               | 291(2)                  | 296(2                | 291(2)                  | 293(2)               |
| reflns collected              | 15707                | 20622                | 22387                   | 11380                | 13032                   | 3803                 |
| unique reflns                 | 4878                 | 5303                 | 5712                    | 5483                 | 6436                    | 2110                 |
| $R_1(I>2\sigma)$              | 0.0470               | 0.0433               | 0.0411                  | 0.0575               | 0.0662                  | 0.0516               |
| $wR_2(I>2\sigma)$             | 0.1123               | 0.1074               | 0.1066                  | 0.1561               | 0.1759                  | 0.1136               |

deprotonated 4-nitrobenzoate anion (4-NBA), one 4-NHBA, and one HBBMA<sup>+</sup> cation. As observed in 1, the HBBMA<sup>+</sup> cations are bridged by 4-nitrobenzoate anions via N-H···O hydrogen bonds (synthon VI: N···O = 2.656(2) Å; synthon VII: N···O = 2.811(2) and 2.9062(19) Å) to form a 1-D chain, as shown in Figure 2a. Along the hydrogen-bonded 1-D chain, each 4-NHBA is anchored to benzimidazole N atom via O-H···N bonds (synthon IV: O···N = 2.561(2) Å). In addition, the 4-NHBA molecules also function as a bridge to link the adjacent 1-D chains via N-H···O bonds (synthon XI: N···O = 2.980(2) Å), resulting in a 2-D layer, as shown in Figure 2b. Moreover, the layers are connected by weak C-H···O hydrogen bonds between 4-NBA anions and HBBMA<sup>+</sup> cations, forming a three-dimensional (3-D) network, as depicted in Figure 2c.

Salt of Bis(2-benzimidazylmethyl)amine 3,5-Dinitrobenzoic Acid (1:2) (3). Bis(2-benzimidazylmethyl)amine and 3,5dinitrobenzoic acid afforded a crystalline organic salt 3, in a 1:2 ratio, which has a 3-D framework. In the asymmetric unit of 3, there are two 3,5-DiNBA anions and one  $H_2BBMA^{2+}$  (ii). Synthons III, VI, VII, VIII, and IX can be formed in the supramolecular assembly of 3. Two  $H_2BBMA^{2+}$  (ii) cations are connected in a head-to-head pattern via two N-H···N hydrogen bonds (synthon III:  $N \cdots N = 2.808(2)$  Å), creating a centrosymmetric dimer. This structure is different from that observed in 1 and 2, maybe due to the different protonated sites of bis(2-benzimidazylmethyl)amine. In 1 and 2, the site only situates the benzimidazole N atoms, while in 3, one site is one benzimidazole N atom, and the other one is amine N atom. As depicted in Figure 3a, each dimer links four 3,5-DiNBA anions through the formation of  $N-H \cdots O$  hydrogen bonds between the 3,5-DiNBA anion and  $H_2BBMA^{2+}$  (ii) cation (synthon VI:  $N \cdots O = 2.667(2)$  Å; synthon VII:  $N \cdots O = 2.742(2)$  Å; synthon VIII:  $N \cdots O = 2.561(2)$  Å; synthon IX:  $N \cdots O =$ 2.755(2) Å), leading to a 0-D six-component aggregate. It should be noted that no nitro groups are involved in strong hydrogen

bonding regardless of possessing the potential to act as hydrogen bond acceptors. The results indicate that the strong hydrogen bond-directed network in this salt is in such a way as to match the strongest donor and the strongest acceptor first. Meanwhile, it must be pointed out that all N atoms in the H<sub>2</sub>BBMA<sup>2+</sup> (ii) cations participate in hydrogen bonding. Further analysis of the crystal packing reveals that the 0-D six-component aggregates are further connected by weak C–H···O hydrogen bonds between 3,5-DiNBA anions and H<sub>2</sub>BBMA<sup>2+</sup> (ii) cations, leading to a 3-D network, as depicted in Figure 3b.

Salt of Bis(2-benzimidazylmethyl)amine Terephthalic Acid (1:2) (4). Bis(2-benzimidazylmethyl)amine and terephthalic acid afforded a crystalline organic salt 4, in a 1:2 ratio, which has a 3-D framework with 1-D channels that are filled with DMF molecules. In the asymmetric unit of 4, there are one dideprotonated terephthalate anion (TPA), half of one  $H_2$ TPA molecule, one  $H_2BBMA^{2+}$  (i), and one DMF molecule. Synthons II, V, VI, and VII can be formed in the supramolecular assembly of 4, as shown in Figure 4a. In 4, two carboxylic groups in each H<sub>2</sub>TPA and two carboxylate groups in each TPA anion take part in different hydrogen-bonding modes. First, each -COOH group of a H<sub>2</sub>PA not only connects the adjacent -COO<sup>-</sup> group of the terephthalate anion via  $O-H\cdots O$  hydrogen bonds to give synthon II  $(O \cdot \cdot \cdot O = 2.456(2) \text{ Å})$  but also links the adjacent  $H_2BBMA^{2+}$  (i) via N-H···O hydrogen bonds (synthon VII:  $N \cdots O = 2.674(3)$  Å). Second, one  $-COO^$ group of a PA anion connects the adjacent H<sub>2</sub>TPA and  $H_2BBMA^{2+}$ , forming one O-H···O and one N-H···O hydrogen bond, respectively, synthon VI:  $N \cdot \cdot \cdot O = 2.692(3)$  Å. The other one connects the neighboring  $H_2BBMA^{2+}$  (i) via  $N-H\cdots O$  hydrogen bond (synthon VI:  $N\cdots O = 2.550(3)$ ; synthon VII:  $N \cdots O = 2.734(3)$  Å). As a result, these hydrogen bonds extend the acid-base subunits to form a 3-D framework with 1-D channels that are occupied by DMF molecules. Furthermore, C-H···O hydrogen bond is

Table 2. Geometrical Parameters of Hydrogen Bonds

| salts | D-H···A           | $H \cdots A$ (Å) | $D \cdots A$ (Å) | $D-H\cdots A$ (deg) | symmetry codes              |
|-------|-------------------|------------------|------------------|---------------------|-----------------------------|
| 1     | N1-H104           | 1.99             | 2.846(2)         | 171.3               | -x + 1, y + 1/2, -z + 1/2   |
|       | N1-H1O3           | 2.61             | 3.105(3)         | 117.9               | -x + 1, y + 1/2, -z + 1/2   |
|       | N3-H304           | 2.01             | 2.863(2)         | 169.7               | -x + 1, y + 1/2, -z + 1/2   |
|       | N4-H4AO3          | 1.80             | 2.637(3)         | 165.3               | x + 1, -y, -z + 1           |
|       | N5-H5A04          | 2.59             | 3.292(2)         | 139.8               | -x + 1, y + 1/2, -z + 1/2   |
|       | $O2-H2\cdots N2$  | 1.76             | 2.560(3)         | 165.9               | x, y + 1, z                 |
| 2     | N5-H5DO2          | 2.64             | 3.160(2)         | 119.7               | x, y - 1, z                 |
|       | N5-H5D01          | 1.96             | 2.8111(18)       | 171.4               | x, y - 1, z                 |
|       | N3-H3D06          | 2.19             | 2.980(2)         | 144.6               | x, -y + 1/2, z + 1/2        |
|       | $N2-H2D\cdots O2$ | 1.80             | 2.656(2)         | 170.7               | x, -y + 3/2, z + 1/2        |
|       | $N1-H1D\cdots O1$ | 2.06             | 2.9062(19)       | 167.9               | x, y - 1, z                 |
|       | O5-H5C···N4       | 1.75             | 2.5614(19)       | 167.9               | -x, y - 1/2, -z + 1/2       |
| 3     | N5-H5D···N1       | 1.95             | 2.808(2)         | 175.7               | -x + 1, -y + 1, -z + 1      |
|       | N4-H4D07          | 1.82             | 2.667(2)         | 167.8               | -x + 1, -y + 1, -z          |
|       | N3-H3AO8          | 1.88             | 2.775(2)         | 163.7               | -x + 1, -y + 1, -z          |
|       | N3-H3BO2          | 1.67             | 2.561(2)         | 168.2               |                             |
|       | N2-H2D08          | 1.97             | 2.742(2)         | 148.7               | -x + 1, -y + 1, -z          |
| 4     | $N1-H1\cdots O2$  | 1.96             | 2.734(2)         | 149.4               |                             |
|       | N2-H205           | 1.83             | 2.674(3)         | 165.6               | -x, -y, -z + 1              |
|       | N4-H4A01          | 1.75             | 2.550(2)         | 152.9               |                             |
|       | N5-H5AO3          | 1.84             | 2.691(2)         | 171.8               | x, y, z-1                   |
|       | 06-H6···O4        | 1.66             | 2.456(2)         | 162.9               | x, y, z-1                   |
| 5     | N5-H5D012         | 2.54             | 2.991(4)         | 114.0               | -x + 1, -y + 1, -z + 1      |
|       | N5-H5D013'        | 2.67             | 2.199(3)         | 121.3               | -x + 2, -y + 1, -z + 1      |
|       | N5-H5D08          | 2.14             | 2.889(3)         | 145.8               | -x + 2, -y + 1, -z + 1      |
|       | N4-H4D···O2       | 1.83             | 2.690(3)         | 175.9               |                             |
|       | N3-H3DO10         | 2.56             | 2.383(3)         | 161.3               | x + 1, y, z - 1             |
|       | N2-H2D···O3       | 2.03             | 2.843(3)         | 156.4               | -x + 2, -y, -z + 1          |
|       | N1-H1D09          | 1.86             | 2.708(3)         | 169.6               | x, y, z - 1                 |
|       | 011-H1109         | 1.85             | 2.590(3)         | 149.6               | x - 1, y, z                 |
|       | O7−H7··O1         | 1.78             | 2.594(3)         | 168.6               | -x + 1, -y + 1, -z + 1      |
|       | O6−H6···O2        | 1.91             | 2.633(3)         | 147.4               | x - 1, y, z                 |
|       | O4-H4···O10       | 1.81             | 2.612(3)         | 164.4               | -x + 1, -y, -z + 2          |
| 6     | $N1-H1\cdots O1$  | 1.80             | 2.651(10)        | 170.2               | -x + 1, -y + 1, -z + 1      |
|       | N2-H2···O3        | 1.83             | 2.688(12)        | 173.3               | x + 1, y + 1, z + 1         |
|       | N4-H4A····O1      | 1.91             | 2.738(10)        | 160.7               | x + 1, y + 1, z + 1         |
|       | N5-H5O3           | 1.83             | 2.688(10)        | 177.5               | -x + 1, $-y + 1$ , $-z + 1$ |
|       | O4-H4···O2        | 1.57             | 2.385(3)         | 172.8               | -x+1, -y, -z+1              |

observed in the structure, which further consolidates the crystal packing.

Salt of Bis(2-benzimidazylmethyl)amine Trimesic Acid (1:2) (5). Trimesic acid crystallizes readily with 0.5 equiv of bis(2-benzimidazylmethyl)amine, yielding organic salts 5. The asymmetric unit of 5 consists of two mono-deprotonated trimesic acid anions, one diprotonated bis(2-benzimidazylmethyl)amine cation, and one DMF molecule. Analysis of the intermolecular interactions reveals that trimesic acid does not introduce a typical extended honeycomb topology;<sup>34</sup> two carboxylic groups and one carboxylate group in each H<sub>2</sub>TMA anion are involved in different hydrogen-bonding modes. First, one  $-COO^-$  group in a trimesic acid unit connects one adjacent H<sub>2</sub>BBMA<sup>2+</sup> (i) cation and two neighboring H<sub>2</sub>TMA anions, forming one bifurcated N<sup>+</sup>-H···O<sup>-</sup> and one O-H···O hydrogen bond (synthon VI: N···O = 2.690(3) Å,

synthon II:  $O \cdots O = 2.633(3)$  Å), as well as one  $O - H \cdots O$ hydrogen bond (synthon II:  $O \cdots O = 2.594(3)$  Å). Second, unlike the  $-COO^-$  group, one of two -COOH groups links two adjacent  $H_2BBMA^{2+}$  (i) cations and one neighboring  $H_2TMA$  anion, creating one  $O-H\cdots N$  and one  $O-H\cdots O$ hydrogen bond (synthon VII:  $N \cdot \cdot \cdot O = 2.889(4)$  Å, synthon II:  $O \cdots O = 2.611(3)$  Å). Finally, the other one -COOH group links adjacent H<sub>2</sub>TMA anion to construct one O-H···O hydrogen bond (synthon II:  $O \cdots O = 2.590(3)$  Å). These synthons are depicted in Figure 5a. As a consequence, these hydrogen bonds extend the acid-base subunits to develop a 2-D layer structure in the bc-plane, as shown in Figure 5b. It is interesting to note that, with this assembly, each layer contains two 2-D sheets, which are furnished with trimesic acid anion through the formation of  $O-H \cdots O$  hydrogen bond, as depicted in Figure 5c. Furthermore, via bifurcated C-H···O



**Figure 1.** View of **1**. (a) View down the *b* axis, 1-D infinite chain. (b) Viewed along the *b* axis, 2-D layered structure. The broken lines represent the hydrogen bonds  $[N-H\cdots O \text{ (red)}, O-H\cdots N \text{ (red)}, C-H\cdots O \text{ (blue)}]$ .



**Figure 2.** View of **2**. (a) View down the *b* axis, 1-D infinite chain. (b) View along the *b* axis, 2-D layered structure. (c) View of 3-D arrangement. The broken lines represent the hydrogen bonds  $[N-H\cdots O \text{ (red)}, O-H\cdots N \text{ (red)}, C-H\cdots O \text{ (blue)}]$ .

interactions with  $H_2BBMA^{2+}$  (i) cation, the solvents (DMF) are captured to locate in the interlayer of the framework and function as a bridge to connect the neighboring layer, resulting in a 3-D network as depicted in Figure 5d.

Salt of Bis(2-benzimidazylmethyl)amine Pyromellitic Acid (1:1) (6). Crystallization of bis(2-benzimidazylmethyl)amine with 1,2,4,5-tetracarboxylic acid produced a proton-transfer organic salt, 6, in the space group  $P\overline{1}$ . The asymmetric unit of 6 contains one di-deprotonated H<sub>2</sub>PMA anion and one diprotonated H<sub>2</sub>BBMA (i) cation. With respect to the tetracarboxylate component, two of the four carboxylic acids are deprotonated and hydrogen-bond with diprotonated  $H_2BBMA$  (i) cation forming two N<sup>+</sup>-H···O<sup>-</sup> hydrogen bonds, resulting in synthon VI (N···O = 2.651(10) and 2.688(10) Å), while the remaining two COOH moieties are oriented longitudinally (*z*-axis) facilitating the H-bonding (synthon V: N···O = 2.688(10) and 2.738(10) Å) that promotes the 1-D polar tapes along the crystallographic *c*axis, as shown in Figure 6a. These 1-D polar tapes are further linked through the formation of C-H···O interactions, leading to 2-D sheets as depicted in Figure 6b. Two kinds of intramolecular hydrogen bonds are observed in this assembly; namely, one is formed between one -COOH and one -COO<sup>-</sup> group situated at an ortho position to each other,



Figure 3. View of 3. (a) View of 0-D six-component aggregate. (b) View of 3-D arrangement. The broken lines represent the hydrogen bonds  $[N-H\cdots O \text{ (red)}, C-H\cdots O \text{ (blue)}].$ 



**Figure 4.** View of 4. (a) View of the synthons II, V, VI, and VII. (b) 3-D arrangement with 1-D channels viewed along the *a* axis (DMF molecules are omitted for clarity). The broken lines represent the hydrogen bonds  $[N-H\cdots O \text{ (red)}, O-H\cdots N \text{ (red)}, C-H\cdots O \text{ (blue)}]$ .

and the other one is generated between an adjacent pair of N atoms of H<sub>2</sub>BBMA (i). Because these hydrogen bonds consolidate the molecular geometry, the two -COOH groups and two  $-COO^-$  groups of H<sub>2</sub>PMA anion are almost coplanar with the torsional angles being 3.81°, 3.81°, 7.78°, and 7.78°, respectively, and each the benzimidazole ring is also planar within 0.01 Å of deviations and the dihedral angles between them are 3.65°. Moreover, it is interesting to observe that the 2-D sheets stack with notable aromatic  $\pi \cdots \pi$  interactions with the distance being ca. 3.30 Å, which generates 3-D layers, as illustrated in Figure 6c.

Structural Features and Synthon Evaluation. Variation of the carboxylic acid elements along with flexible and polydentate bis(2-benzimidazylmethyl)amine compound is envisioned to produce ionic N<sup>+</sup>-H···O<sup>-</sup> hydrogen bond as well as weaker C-H···O and aromatic  $\pi \cdot \cdot \pi$  interactions. A systematic comparison of these intermolecular interactions in the six salts reveals the following characteristics: (1) all NH functions in the protonated bis(2-benzimidazylmethyl)amine serve as H-bond donors to anions; (2) proton transfer from the carboxylic acid to BimN is present in all cases, leading to form single-point ionic synthons (VI and VIII); (3) as a consequence of competition and cooperation between COOH, COO<sup>-</sup>, BimNH<sup>+</sup>, BimN, -NH<sub>2</sub><sup>+</sup>-, and -NH- functional groups, other synthons, such as III, IV, V, VII, IX, X, and XI, can be formed in the six structures; (4) as is observed in previous studies,  $^{19-25}$  the ionic hydrogen bonds of salts 1-6 also have smaller N···O distances (2.67–2.68) than the interactions for the neutral bond (>2.88 Å) (Table 2); (5) the formation of C–H···O hydrogen bonds influences molecular packing in 1-3, 5, and 6.

In the six salts, the site of protonation (on BBMA) or deprotonation (of organic acid) is variable and thus provide unique opportunities for the discovery of new synthons. As a result, new synthons **VIII**, **IX**, and **XI** were first found in the acid-imdazole system. In the crystal structure, whether the COOH and imidazole group is neutral or ionized was ascertained by C–O, C=O bond distances and C–N–C, C–N<sup>+</sup>–C angles. For example, bond distances of 1.30, 1.20 Å and angles of 117–118° indicate a neutral synthon, whereas an intermediate distance of 1.25 Å and a slightly obtuse angle of 120–121° mean an ionized imidazole state. The C–O distance parameter is restated as  $\Delta r < 0.03$  Å for ionic COO<sup>-</sup> and  $\Delta r > 0.08$  Å for neutral COOH.

In the six salts, the formation of  $C-H\cdots O$  hydrogen bonds can influence molecular packing. This is not surprising since we examined all intermolecular contacts between C-H protons on six crystallographically unique bis(2-benzimidazylmethyl)amine cations and neighboring oxygen atoms. Most of these interactions had  $H\cdots O$  distances less than 2.72 Å (the sum of the van



**Figure 5.** View of **5**. (a) View of the synthons **II**, **VI**, and **VII**. (b) 2-D layer structure,  $H_2BBMA^{2+}$  (i) cations connecting two carboxylate sheets (DMF molecules are omitted for clarity). (c) 2-D sheets are formed with trimesic acid anion. (d) 3-D arrangement. The broken lines represent the hydrogen bonds [N-H···O (red), O-H···N (red), C-H···O (blue)].

der Waals radii for hydrogen (1.20 Å) and oxygen (1.52 Å)) and  $C-H\cdots O$  angles greater than 90°. The  $H\cdots O$  distances rather than the  $C \cdot \cdot \cdot O$  distances were examined because most of the  $C{-}H{\cdots}O$  interactions were bent instead of linear. The  $H \cdots O$  bond lengths ranged between 2.29 and 2.60 Å with an average length of 2.51 Å. The C-H···O bond angles ranged between 118 and 172° with an average angle of 147°. The C-H···O hydrogen bond parameters for salts 1-6 are given in Table 3. The fact that most of the  $C-H\cdots O$ interactions deviated significantly from linearity is not surprising, considering that formation of stronger  $N^+-H\cdots O^$ hydrogen bonds is one of the principal organizational forces involved in determining the orientation of bis(2-benzimidazylmethyl)amine cations during crystal packing. Meanwhile, it is noted that the bis(2-benzimidazylmethyl)amine cations generally form C-H···O interactions between layers instead of within layers. One reason the cations may twist out of the layers in these structures is to maximize the number of  $C-H\cdots O$  contacts that form. Consequently, fewer  $C-H\cdots O$ interactions would occur if the cations were coplanar with the layers in these structures. The structural analyses demonstrate that the formation of weak  $C-H \cdots O$  hydrogen bonds controls the dimensionality of the H-bonding.

Thermal Stability and Powder X-ray Diffraction. To study the stability of 1-6, thermogravimetric analyses (TGA) of these salts were performed (Figure 7). The TGA curves of 1 and 4 indicate that pyrolysis occurs at ca. 170 °C, while 2, 3, 5, and 6 are more stable up to 248, 262, 287, and 280 °C, respectively, where the decomposition of the framework starts. For 1, the weight loss of 46.75% from 170 to 243 °C (calcd 46.6%) corresponds to the loss of one BA anion and one HBA molecule per formula. The second weight loss of 35.8% (calcd for 53.3%) can be detected from 256 to 490 °C, which is attributed to partial decomposition of HBBMA cations. In compound 2, two mass loss steps were observed. A mass loss of 53.9% (calcd for 54.7%) over the range 248-390 °C corresponded to the loss of 1 equiv of 4-NBA anions and 1 equiv of 4-NHBA molecules. However, the latter mass losses of 20.2% corresponded to partial decomposition of HBBMA cations. Salt 3 displays the same thermogravimetric properties as 1 and 2. Two mass loss steps were also observed. A mass loss of 58.2% (calcd for 60.5%) over the range 262-470 °C corresponded to the loss of approximately 2 equiv of 3,5-diNBA anions. The second mass losses of 8.3% corresponded to partial decomposition of HBBMA cations. In 4, the first mass losses represented the loss of approximately 1 equiv of DMF (calcd: 12.2%, found: 12.3%). The second mass losses of 41.9% (calcd for 41.6%), over the range 258–590 °C, corresponded to the loss of approximately 1.5 equiv of TPA anions. In 5, the first mass losses represented the loss of approximately 1 equiv of DMF (calcd: 9.5%, found: 9.9%). The second mass losses of 54.9% (calcd for 54.5%), over the range 315-410 °C, corresponded to the loss of approximately 2 equiv of H<sub>2</sub>TMA anions. The last mass loss represented the partial decomposition of H<sub>2</sub>BBMA (i) cations. In 6, two mass loss steps were observed. A mass loss of 15% over the range 280–360  $^\circ \text{C}$ 



**Figure 6.** View of 6. (a) View down the *c* axis, 1-D infinite chain. (b) View of 2-D sheet. (c) Three dimensional stacking of neighboring sheets. The broken lines represent the hydrogen bonds  $[N-H\cdots O \text{ (red)}, N-H\cdots N \text{ (red)}, O-H\cdots O \text{ (red)}, C-H\cdots O \text{ (blue)}, \pi\cdots\pi \text{ (blue)}]$ .

| Table 3. Geometrical Parameters of C $-H\cdots$ O Hydrogen Bonds (Å, °) for | : 1-6 |
|---|-------|
|---|-------|

|   | D-H···A          | Н••••А (Å) | $D \cdots A(Å)$ | D-H···A (deg) | symmetry codes                |
|---|------------------|------------|-----------------|---------------|-------------------------------|
|   | 2                |            |                 |               | symmetry codes                |
| 1 | $C1-H1\cdots O4$ | 2.60       | 3.395(3)        | 140           | x, 1/2 - y, 1/2 + z           |
|   | С6-Н601          | 2.55       | 3.348(4)        | 144           | x, 3/2 - y, 1/2 + z           |
| 2 | C4-H4O7          | 2.57       | 3.490(3)        | 170           | 1 - x, -y, 1 - z              |
|   | С9-Н9ВО1         | 2.56       | 3.384(2)        | 143           | -x, 1 - y, 1 - z              |
|   | C13-H13O6        | 2.55       | 3.318(2)        | 140           | -x, -y, -z                    |
| 3 | С3-Н3СО4         | 2.49       | 3.389(3)        | 163           | 1 + x, $3/2 - y$ , $-1/2 + z$ |
|   | С5-Н5О9          | 2.58       | 3.500(3)        | 170           | 1 - x, 1 - y, -z              |
|   | C8-H8A01         | 2.43       | 3.034(2)        | 120           | 1 - x, 1 - y, 1 - z           |
|   | С9−Н9АО2         | 2.46       | 3.317(2)        | 147           | -x, 1-y, 1-z                  |
|   | C27-H27O2        | 2.29       | 3.218(2)        | 172           | 1 + x, y, z                   |
| 4 | С5-Н5О4          | 2.59       | 3.374(4)        | 142           | -x, -y, 2-z                   |
|   | C8-H8B07         | 2.52       | 3.273(6)        | 135           | -1 + x, y, z                  |
|   | C18-H18O6        | 2.60       | 3.377(3)        | 142           | -x, 1-y, 1-z                  |
| 5 | С5-Н5013         | 2.38       | 3.228(8)        | 152           | 2 - x, -y, 1 - z              |
|   | C8-H8A011'       | 2.49       | 3.329(4)        | 144           | 1 + x, y, -1 + z              |
|   | C12-H12O13       | 2.46       | 3.374(8)        | 167           | 2 - x, 1 - y, 1 - z           |
| 6 | С8-Н8••••О4      | 2.45       | 3.338(14)       | 160           | 3 - x, 2 - y, 1 - z           |
|   | C10-H10O2        | 2.48       | 3.311(15)       | 148           | 1 - x, 1 - y, 1 - z           |
|   | C13-H13AO1       | 2.52       | 3.059(11)       | 115           | 1 + x, 1 + y, 1 + z           |
|   | C16-H16O4        | 2.39       | 3.252(16)       | 154           | -1 + x, y, 1 + z              |
|   | C21-H21A···O1    | 2.58       | 3.158(15)       | 118           | 1 - x, 1 - y, 1 - z           |

corresponded to the partial loss of  $H_2PMA$  anions. The last mass loss represented the partial decomposition of  $H_2PMA$  anions and  $H_2BBMA$  (i) cations.

The identity of the single-crystal sample and as-synthesized bulk material has also been confirmed by a comparison of the simulated and experimental powder X-ray diffraction (PXRD)



Figure 7. TGA curves of 1-6.



**Figure 8.** Comparison of the experimental and simulated PXRD patterns. In each group, the bottom is the experimental pattern and the top is the simulated one.

patterns. As shown in Figure 8, the PXRD patterns of 1-6 are almost the same as that simulated from the single-crystal data, revealing the phase purity of the bulk samples.

#### CONCLUSIONS

In the present contribution for molecular tectonics, we describe the supramolecular synthesis and rational analysis of six binary salts based on carboxylic acids and polydentate bis-(2-benzimidazylmethyl)amine ligand. It is evident that the polycarboxylic acids have robust and ionic hydrogen-bonding donors/acceptors to fulfill the diversiform motifs. This work also demonstrates that bis(2-benzimidazylmethyl)amine is an excellent supramolecular reagent that can produce bimolecular salts via various synthons. In salts 1-6, the ionic N-H···O hydrogen bond is successfully applied in the design of supramolecular structures between carboxylic acids and bis(2-benzimidazylmethyl)amine. Meanwhile, the formation of weak  $C-H\cdots O$ increases the dimensionality of the supramolecular architectures. Additionally, the relative orientation and the nature of the different carboxylic acids also have a significant effect on forming the final diverse networks from 2-D in 1 to 3-D in 2-6. Therefore, the results presented here reveal that assemblies for such supramolecular systems are variable, and subtle differences of the building components will account for their structural

diversification. Further studies on such flexible building blocks are desirable to understand the crystal engineering of ionic hydrogen-bonded solids, and related exploration on this perspective is underway.

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