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PAPER

Co-crystals of tetrakis-1,2,3,4-(4′-carboxyphenyl)cyclobutane with dipyridyl spacers: design and serendipity†

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Tetrakis-1,2,3,4-(4′-carboxyphenyl)cyclobutane (TCCB), a tetracarboxylic acid, has been employed for making co-crystals with linear dipyridyl spacers molecules like 4,4′-bipyridine (4,4′-bpy), 1,2-bis(4′-pyridyl)ethane (4,4′-bpethane), *trans*-1,2-bis(4′-pyridyl)ethylene (4,4′-bpe) and 1,4-bis(4′-pyridyl)-2,3-diaza-1,3-butadiene (4,4′-bpdb). In the case of 4,4′-bpy, a 2 : 1 co-crystal was obtained with TCCB having a three dimensional 5-fold interpenetrated **dmp** network. The diagonal–diagonal interpenetrated isostructural (4,4)-connected 2D networks were obtained in 1 : 1 co-crystals of TCCB with 4,4′-bpe and 4,4′-bpdb. The (4,4)-connected nets in the 1 : 1 co-crystal of TCCB with 4,4′-bpethane were found to stack parallel instead of interpenetrating. 1 : 1 co-crystals were always obtained in the last three cases regardless of molar ratio during co-crystallization, indicating the influence of kinetic factors. The structural diversity and similarities in this series of co-crystals in the context of composition variation and solvent interference are discussed. The serendipitous formation of (4,4)-connected networks is critically compared with designability of the system in presence of synthon competition.

Introduction

Co-crystals,[1] the multi-component crystalline materials comprised of neutral molecules, are highly studied compounds in crystal engineering in recent times both for their solid state architectures[2,3] and pharmaceutical importance.[4] The pattern of supramolecular interactions working between the molecular components in a co-crystal is termed as 'supramolecular synthon',[5] which dictates the solid state structure of a co-crystal. The co-crystal formed by the combination of carboxylic acid and pyridyl group *via* COOH···N(py) hydrogen bonding interactions has been extensively studied in literature.[3] Co-crystals of various structural types have been generated by the combination of hydrogen bond donors (*e.g.* carboxylic acid) and acceptors (*e.g.* pyridine) of diverse geometries. For example, C_3 symmetric trimesic acid has been employed to co-crystallize with 4,4′-bipyridyl in 1 : 1.5 ratio to generate (6,3) connected honeycomb network.[6] A 'rosette' like network structure was also successfully designed by the combination two C_3-symmetric molecules like melamine and cyanuric acid acting as hydrogen bond donor and acceptor, respectively.[7] Tetrahedral symmetric nodes like NH_4^+ ion[8] and organic compounds with T_d or S_4 symmetry have been combined with linear compounds having complementary functional groups to construct three dimensional diamondoid hydrogen bonded networks.[9] Similarly, the structure directing effects of C_3-symmetric guanidinium cations have also been extensively studied for generating various organic and inorganic architectures with diverse structures with various oxyanions.[10] Therefore, by the judicious combination of hydrogen bonded nodes and linkers of varied symmetry and utilizing directional hydrogen bonding interaction have paved the way for designing co-crystals of desired structures and properties.

Another important aspect to be taken into consideration is synthon competition of homo- and hetero-synthons in the presence of multiple functional groups.[11] Many supramolecular synthons are possible by a small displacement of the position or orientation of functional groups which compete during crystallization and the most favourable synthons are found to construct in the solid state structure. The solvents used in the crystallization process also play crucial roles in the synthon formation by interfering with the hydrogen bonding.[12]

The relative orientation of the functional groups on cyclobutanes ring allows organic linkers of certain geometry to generate metal–organic compounds of desired topology. Two isomers *rctt*- and *rtct*-tetrakis-1,2,3,4-(4′-pyridyl)cyclobutane (TCCB) have been used for this purpose as 4-connected planar and tetrahedral organic linkers, respectively.[13] In this study, we have chosen *rctt*-TCCB for designing co-crystals with linear dipyridyl compounds. The geometry of this cyclobutane derived tetracarboxylic acid, *rctt*-TCCB, can be simplified as a pseudo

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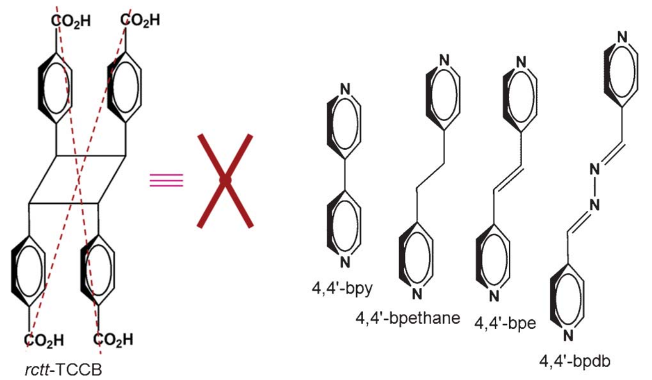
† Electronic supplementary information (ESI) available: Additional structural diagrams, hydrogen bonding parameters, ^{1}H NMR spectra and TGA plots. CCDC reference numbers 766937 and 873781–873783. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ce25513h



Scheme 1 The structures of pseudo C_4-symmetric *rctt*-TCCB and dipyridyl linkers used in this study.

C_4-symmetric 4-connected node as shown in Scheme 1. The crystal structure of four co-crystals of TCCB obtained with 4,4′-bipyridine (4,4′-bpy), 1,2-bis(4′-pyridyl)ethane (4,4′-bpethane), *trans*-1,2-bis(4′-pyridyl)ethylene (4,4′-bpe) and 1,4-bis(4′-pyridyl)-2,3-diaza-1,3-butadiene (4,4′-bpdb) are discussed and compared here in this paper in the context of designability and serendipity in the synthesis of co-crystals.

Results and discussion

Co-crystal of TCCB with 4,4′-bipyridine (1)

A co-crystal of composition (TCCB)(4,4′-bpy)$_2$·(2DMF) (**1**) using TCCB and 4,4′-bpy was synthesized by dissolving a stoichiometric amount of TCCB and 4,4′-bpy (1 : 2) in DMF and the single crystals were grown by evaporating the solution slowly. X-ray crystal structure analysis reveals that there are half a TCCB, two halves of a 4,4′-bpy and one DMF molecule in the asymmetric unit,‡ where the TCCB and DMF solvents were found to be disordered. From the observed values of C=O distances of 1.21(5) Å and corresponding C–OH distances of 1.32(5) Å for the carboxylic acid groups, it can certainly be called a co-crystal and not a salt. The four carboxylic acid groups of TCCB donates four hydrogen bonds to four different 4,4′-bpy acceptors in an $\mathbf{R}_2^2(7)$ fashion.[14] Each of the 4,4′-bpy bridges two carboxylic acid groups of two TCCB molecules *via* H–bonding (Fig. 1). The DMF molecules present in the crystal are found not to participate in H-bonding and instead fill up the void space. There are two types of crystallographically independent 4,4′-bpy molecules. One type is planar and another type is staggered (torsional angle is 30.91°) and that make up two different distances between centroids of cyclobutane rings of 26.53 Å and 25.69 Å, respectively.

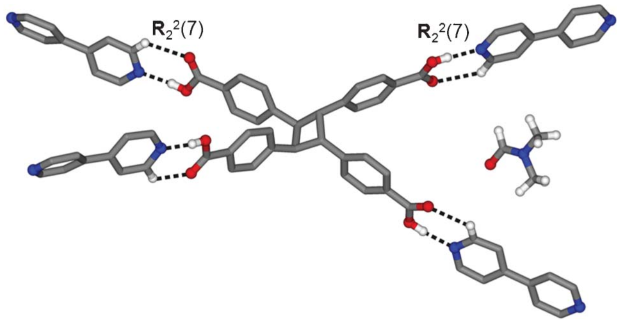


Fig. 1 The H–bonding pattern in co-crystal **1** is shown.

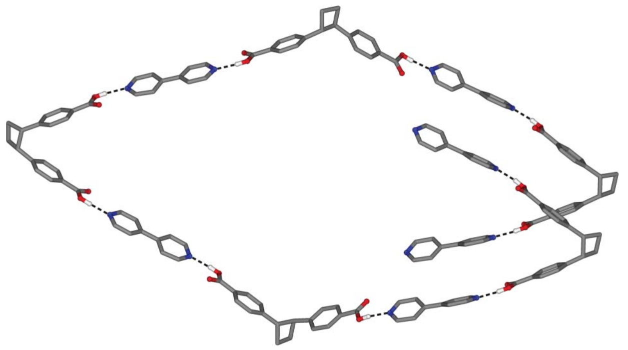


Fig. 2 Instead of forming a 4-connected square net, co-crystal **1** forms helical segments (only O–H···N hydrogen bonding is shown).

Instead of making a two dimensional sheet-like structure composed of closed circuit hydrogen bonded square nets between the 4-conntected nodes at cyclobutane rings and two-connected nodal positions between each two 4-connected nodes, the H–bonding propagates with helical segments to form an interpenetrated three dimensional network (Fig. 2). The pitch of these helical segments contains four TCCB and four 4,4′-bpy units and propagates along the *c*-direction with the pitch-length of 12.61 Å, which is also equal to the unit cell length *c*. The degree of interpenetration and the topology of the network was analysed by TOPOS[14,15] and we found it as a 5-fold interpenetrated **dmp** network (Fig. 3 and ESI†).[16] To the best of our

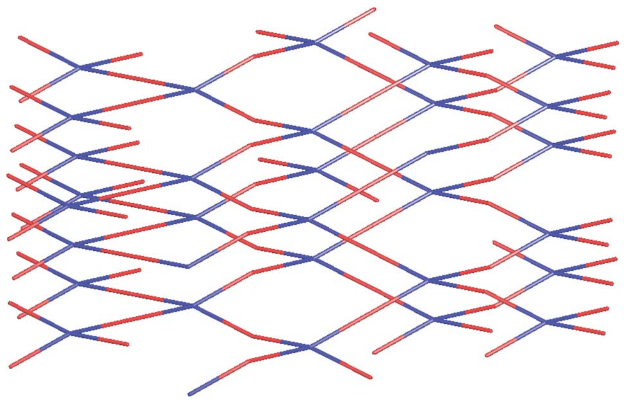


Fig. 3 A single **dmp** net, found in **1**. The figure containing all five interpenetrated nets is shown in the ESI.†

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‡ Crystal data for **1** at 100(2) K: $C_{58}H_{54}N_6O_{10}$, M = 995.07, orthorhombic, space group *Pnna*, a = 18.6545(8), b = 21.7602(9), c = 12.6058(5) Å, V = 5117.0(4) Å^3, Z = 4, D_c = 1.292 g cm^{-3}, μ = 0.089 mm^{-1}, Goof on F^2 = 1.195, final R_1 = 0.0982, wR_2 = 0.2089 [for data 3924 $I > 2\sigma(I)$]. Crystal data for **2** at 100(2) K: $C_{52}H_{56}N_4O_{11}$, M = 913.01, monoclinic, space group *C2/c*, a = 28.787(3), b = 10.7716(12), c = 14.7431(16) Å, β = 95.240(3)°, V = 4552.5(9) Å^3, Z = 4, D_c = 1.332 g cm^{-3}, μ = 0.094 mm^{-1}, Goof on F^2 = 1.087, final R_1 = 0.0729, wR_2 = 0.1804 [for 3633 data $I > 2\sigma(I)$]. Crystal data for **4** at 100(2) K: $C_{45}H_{38}N_4O_9$, M = 778.79, monoclinic, space group $P2_1/n$, a = 11.0252(9), b = 10.1233(7), c = 34.861(3) Å, β = 98.614(3)°, V = 3847.0(5) Å^3, Z = 4, D_c = 1.345 g cm^{-3}, μ = 0.095 mm^{-1}, Goof on F^2 = 1.015, final R_1 = 0.0647, wR_2 = 0.1333 [for 5855 data $I > 2\sigma(I)$].

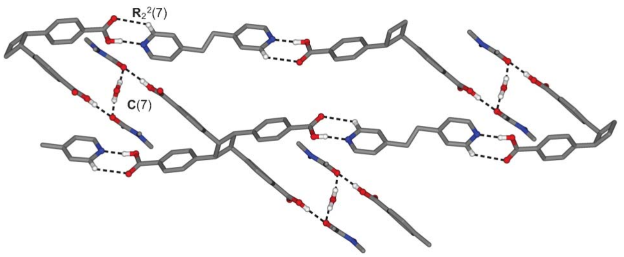


Fig. 4 The hydrogen bonded connectivity in the co-crystal **2**.

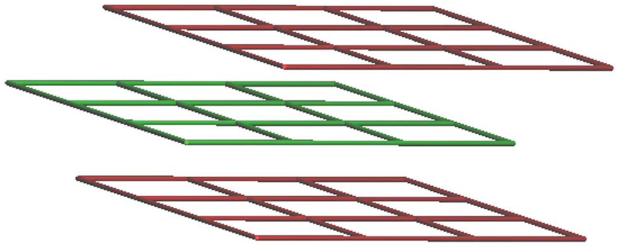


Fig. 5 The parallel stacking of (4,4) connected tetragonal nets in **2**, perpendicular to the *b*-axis.

knowledge, a maximum of 3-fold interpenetration has been reported with organic systems in **dmp** networks to date.[17] Therefore, this is the highest degree of interpenetration we have found in this co-crystal.

Co-crystal of TCCB with 4,4′-bpethane (2)

Another co-crystal of composition (TCCB)(4,4′-bpethane)·(2DMA)·H_2O (**2**) was synthesized by dissolving TCCB and 4,4′-bpethane in 1 : 2 ratio in *N*,*N*-dimethylacetamide (DMA) and then slow evaporation. The asymmetric unit of this co-crystal contains half a molecule of TCCB, half a molecule of 4,4′-bpethane, one DMA and half a water molecule.‡ From the observed values of C=O distances for two carboxylic acid groups in the asymmetric unit [C=O distances are 1.22(3) and 1.20(4) Å and corresponding C–OH distances are 1.30(3) and 1.33(4) Å, respectively], it can certainly be called a co-crystal and not a salt. Two diagonally opposite carboxylic acid groups of TCCB donate H-bonding to two 4,4′-bpethane molecules in $\mathbf{R}_2^2(7)$ fashion. The other two carboxylic acid groups donate H-bonding to DMA molecules and the H-bonding further continues to propagate *via* water and another DMA molecules to connect finally to a carboxylic acid group of another TCCB (Fig. 4). Therefore, the growth of the H-bonded network results in (4,4) connected two dimensional network. These two dimensional tetragonal sheets were found to stack parallel in an ABAB fashion, perpendicular to the *b*-axis. The two side lengths of these tetragonal nets are 16.76 and 27.47 Å and the distance of separation is 5.39 Å, which is half of the unit cell parameter *b*. We attempted to grow single crystals by slowly evaporating DMF solution as described for **1**, which has shown to be non-interfering in H–bonding and may lead to a different topology. However, the rod-like single crystals obtained were unable to diffract the X-ray beam.

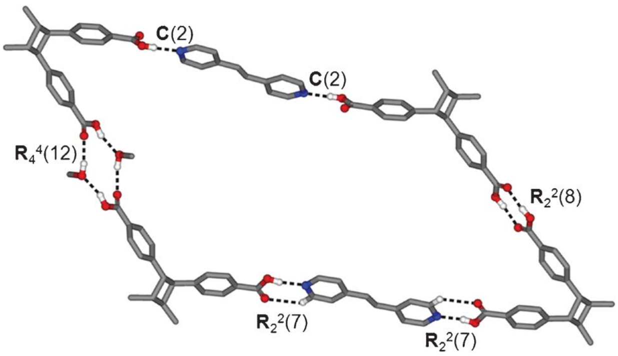


Fig. 6 The supramolecular synthons that construct the solid state architecture in co-crystal **3** and the H-bonded motifs are shown.

Co-crystal of TCCB with 4,4′-bpe (3)

Another co-crystal containing TCCB of composition (TCCB)(4,4′-bpe)·MeOH (**3**) was synthesized by dissolving TCCB with 4,4′-bpe in methanol. The detailed structural description of this co-crystal was reported before.[18] Various types of graph set notations of the hydrogen bonded motifs in (4,4) connected 2D nets are shown in Fig. 6 which are **C**(2), $\mathbf{R}_2^2(7)$, $\mathbf{R}_2^2(8)$, $\mathbf{R}_4^4(12)$. These two dimensional 4-connected uninodal nets are found to stack parallel with a distance of separation 4.44 Å and then further involve in diagonal–diagonal inclined interpenetration (also known as polycatenation)[19] to generate an overall three dimensional network structure with an angle of 61.8° between inclined nets (see ESI†).

Co-crystal of TCCB with 4,4′-bpdb (4)

Another co-crystal of composition (TCCB)(4,4′-bpdb)·MeOH (**4**) was grown from methanol by dissolving TCCB and 4,4′-bpdb in 1 : 2 ratio. X-ray crystal structure analysis revealed that the asymmetric unit contains one molecule of TCCB, two halves of the compound 4,4′-bpbd and one methanol solvent molecule.‡ The observed values of C=O distances for four carboxylic acid groups [C=O distances are 1.22(3), 1.22(3), 1.22(3) and 1.22(3) Å and corresponding C–OH distances are 1.33(3), 1.33(3), 1.32(4), 1.32(2) Å, respectively] confirm it to be a co-crystal and not a salt. Three types of supramolecular synthons, *viz.* centrosymmetric carboxylic acid dimer, carboxylic acid dimer *via* methanol molecule and carboxyl–pyridyl H–bonding (Fig. 7), play a principal role to construct two dimensional nets. The graph set notations of the hydrogen bonded motifs present in this

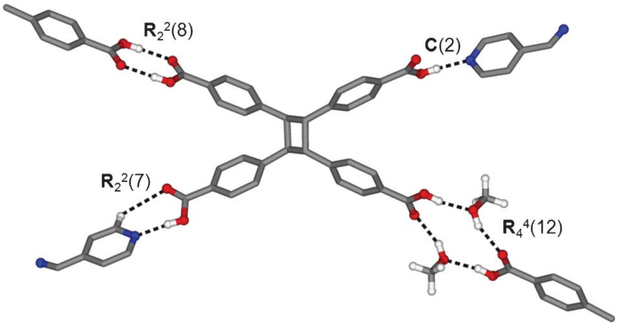


Fig. 7 Part of the connectivity in **4**, which is isostructural with **3**.

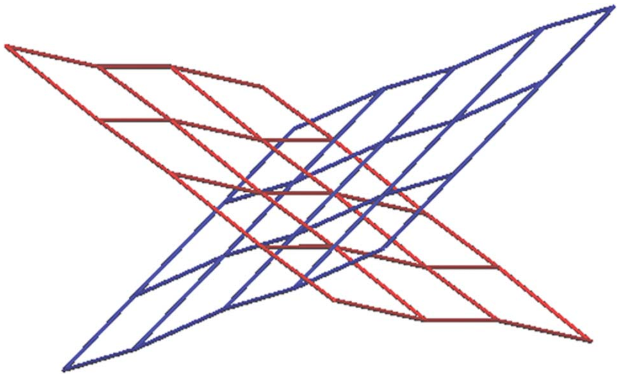


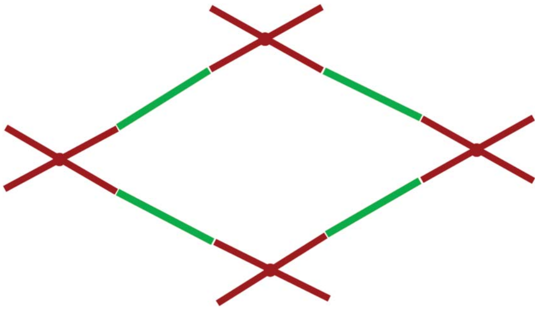
Fig. 8 Inclined interpenetration (polycatenation) of puckered (4,4) nets in **4**.

co-crystal are **C**(2), $\mathbf{R}_2^2(7)$, $\mathbf{R}_2^2(8)$, $\mathbf{R}_4^4(12)$. Each 4,4′-bpdb molecule bridges carboxylic acid groups of two TCCB molecules and the connectivity of two methanol molecules hydrogen bonded to two carboxylic acids led to the formation of (4,4) connected 2D nets. The four sides of each quadrilateral window of the net are unequal and were measured to be 30.55, 19.42, 30.55 and 16.94 Å. These two dimensional 4-connected nets are found to stack parallel with a distance of separation 4.38 Å and then further undergo diagonal–diagonal inclined interpenetration (polycatenation)[19] to result in an overall three dimensional network. The angle on inclination is 60.7° and there are two nodes of two parallel nets on each window of the interpenetrating net. The nodes of the nets are puckered, as shown in Fig. 8, and the topology of this co-crystal is found to be the same as in **3**.

Comparative discussion

Among the four co-crystals discussed above, only **1**, where TCCB is crystallized with 4,4′-bpy in 1 : 2 ratio, has hydrogen bonded three dimensional architecture. Other three co-crystals (**2–4**) where 4,4′-bpethane, 4,4′-bpe and 4,4′-bpdb co-crystallized with TCCB in 1 : 1 ratio, have two dimensional hydrogen-bonded structures. **3** and **4** have the same topology and show inclined interpenetration (polycatenation) of puckered (4,4) sheets. On the other hand, no interpenetration was found in **2**. DMF molecules present in the crystal of **1** do not participate in hydrogen bonding to form a (4,4) net. On the other hand, in each of the other three co-crystals, solvent molecules interfere with the hydrogen bonding and take part in the formation of (4,4) nets. Methanol molecules participate in hydrogen bonding and bridge two carboxylic acid groups. DMA molecules along with water also bridge between two carboxylic acid groups but in a peculiar way which is beyond any design principle. We also employed similar dipyridyl compounds pyrazine and 4,4′-dithiopyridine to co-crystallize with TCCB in various solvents. However, we have not obtained suitable single crystals from these systems and therefore are not discussed here.

From its geometry, *rctt*-TCCB can be considered as a C_4-symmetric 4-connected node. Therefore, from the knowledge of design principles in crystal engineering, one can expect the formation of a (4,4)-connected network by the combination of TCCB and dipyridyl spacers in 1 : 2 ratio as shown in Scheme 2.



Scheme 2 The expected (4,4)-connected net by combination of TCCB and dipyridyl spacers in a 1 : 2 ratio.

Although we have obtained (4,4)-connected networks in **2–4**, they are not the same as what we expected. The reasons behind this serendipitous structural diversity may be the improper ratio of TCCB and dipyridyl compounds, synthon competition and solvent interference. The formation of 1 : 1 co-crystals (in case of **2–4**), instead of 1 : 2 as supplied, may be driven by their kinetic factors under the crystallization conditions. Moreover, the formation of centrosymmetric carboxylic acid dimer and solvent assisted carboxylic acid dimer synthons might also be responsible for the occurrence of 1 : 1 co-crystals. Because of the presence of many synthons, the side lengths of the quadrilateral window of (4,4)-connected networks are not equal and hence are puckered. Solvents used in co-crystallization were also found to play important roles in the synthon formation and hence in topology. All the co-crystals were first attempted to crystallize from alcohol, however, only **3** and **4** could be grown from methanol and they are found to be isostructural. DMF in **1** did not participate in hydrogen bonding but DMA in **2** participated in hydrogen bonding to connect two carboxylic acid groups leading to the serendipitous observation in crystal structure. All the solvents used for crystallization are capable of forming hydrogen bonds; however, their participation in bonding interaction might be dictated by kinetic factors.

Another interesting and unexpected observation is the formation three dimensional **dmp** nets in **1**, although the ratio of TCCB and 4,4′-bpy was maintained 1 : 2 and no carboxylic acid dimer synthon was observed. This could be due to the dihedral angle between two pyridyl groups in 4,4′-bpy. The dihedral angles for two types of 4,4′-bpy molecules in **1** of 5.7° and 31.5° impose non-planarity at the cyclobutane node and uneven inter-nodal distances (26.53 Å and 25.70 Å), which finally led to the formation of the three dimensional **dmp** net.

Conclusion

We described and compared the solid state structures of various co-crystals obtained from a pseudo C_4-symmetric tetracarboxylic acid and linear dipyridyl compounds. When the desired 1 : 2 composition of tetracarboxylic acid and dipyridyl compounds was obtained, the structure of that co-crystal was serendipitous, not as we expected. However, (4,4)-connected nets were obtained due to solvent participation from unexpected ratio (1 : 1) of the molecular components. Therefore, the serendipity and designability interplay in this system and structures were governed by the solvent effect as well as other kinetic factors (ratio of molecular components). In addition, we report a 5-fold interpenetrated **dmp** net which should be highest degree of interpenetration reported in **dmp** topology to the best of our knowledge.

Experimental section

Materials and methods

TCCB was synthesized according to the method developed by us.[18] 4,4′-bpy, 4,4′-bpethane, 4,4′-bpe were purchased from common commercial sources and were used as received. 4,4′-bpdb was synthesized by reacting 4-carboxaldehyde pyridine with hydrazine. A mixture of 4-carboxaldehyde pyridine and hydrazine in 2 : 1 molar ratio was refluxed in ethanol in presence of acetic acid. The yellow solid obtained was recrystallized from ethanol and was used.

Physical measurements

The ^{1}H NMR spectra were recorded with a Bruker ACF 300 FT-NMR spectrometer with TMS as internal reference. Thermogravimetric analyses (TGA) were recorded on a TA Instrument SDT 2960 TGA Thermal Analyzer. The samples were heated at a constant rate of 5 °C min^{-1} from room temperature and the atmosphere was maintained with continuous flow of nitrogen gas. The FT-IR spectra were recorded using Varian Excalibur 3100 spectrometer with KBr pellets. Elemental analyses were performed in the Micro Analytical Laboratory, Department of Chemistry, National University of Singapore.

X-ray crystallography

Suitable single crystals were chosen under an optical microscope, mounted on glass fibre, and frozen under a stream of cryogenic nitrogen gas before data collection. Intensity data were collected on a Bruker APEX diffractometer attached with a CCD detector and graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. Empirical absorption corrections were applied using the program SADABS[20] and the crystallographic package SHELXTL[21] were used for all calculations.

In the structure refinement for **1**, there was an ambiguity in the space group. The structure could be solved and refined in the space groups $Pna2_1$ and *Pnna*. The quality of the model in terms of agreement factors, thermal parameters, bond parameters, *etc.* was better for *Pnna*, but the acid component (TCCB) had to be disordered and the solvent DMF could not be resolved. Being the higher symmetry space group *Pnna* (no. 52), the asymmetric unit is half of that in $Pna2_1$ (no. 33) and the variables were also half. The phenyl rings were refined as fixed hexagons. Since the H atoms of the CO_2H groups were assigned by calculation, the OHN angles in these H bonds were artificial. However, this would not affect the overall structure and topology of this compound. In **2**, all the hydrogen atoms were placed in the calculated position except the hydrogen atom bonded to water oxygen, which was placed using DFIX option. In **4**, all the hydrogen atoms were placed in the calculated positions.

Synthesis

We were unable to grow single crystals using the same solvent combinations for all the co-crystals for comparison purposes. Each single crystal was grown using a unique combination of solvent mixture and experimental conditions.

(TCCB)(4,4′-bpy)$_2$·2DMF (1)

TCCB (27 mg, 0.05 mmol) and 4,4′-bipyridyl (16 mg, 0.1 mmol) were dissolved in 4 mL DMF and the resulting solution was kept for slow evaporation. Diffraction quality block shaped single crystals were obtained after a week. Yield 72%.

^{1}H NMR (300 MHz, d_6-DMSO, 298 K): δ_H = 12.78 (s, 4H, –CO_2H), 8.72 (d, 8H, Ar–H), 7.95 (s, 2H, alde-DMF), 7.83 (d, 8H, Ar–H), 7.72 (d, 8H, Ar–H), 7.33 (d, 8H, Ar–H), 4.71 (s, 4H, CH–CH), 2.89 (s, 6H, CH_3–DMF), 2.73 (s, 6H, CH_3–DMF). FT IR (KBr, cm^{-1}): ν = 3447, 3057, 2930, 2854, 2793, 2455, 2368, 1891, 1676, 1603, 1539, 1508, 1409, 1383, 1282, 1178, 1095, 1074, 1003, 858, 808, 742, 711, 626, 555, 520, 459. Analysis found (%): C 69.87, H 5.36, N 8.35; $C_{58}H_{54}N_6O_{10}$ requires C 70.01, H 5.47, N 8.45. The observed solvent (DMF) loss 15.8% in TGA experiment compared with the calculated value 14.7%.

(TCCB)(4,4′-bpethane)·(2DMA)·H_2O (2)

The mixture of 4,4′-bpethane (20 mg, 0.1 mmol) and TCCB (27 mg, 0.05 mmol) were dissolved in 3 mL DMA and the resulting solution was allowed to evaporate slowly. Block shaped diffraction quality single crystals were obtained after a week. Regardless the ratio of 4,4′-bpethane and TCCB in the mixture, co-crystal of composition 1 : 1 was obtained every time. Yield 60%.

^{1}H NMR (300 MHz, d_6-DMSO, 298 K): δ_H = 12.8 (s, 4H, –CO_2H), 8.44 (d, 4H, Ar–H), 7.71 (d, 8H, Ar–H), 7.33 (d, 8H, Ar–H), 7.25 (d, 4H, Ar–H), 4.71 (s, 4H, CH–CH), 2.94 (s, 10H, CH–CH of 4,4′-bpethane and CH_3 of DMA together), 2.78 (s, 6H, CH_3 DMA), 1.95 (s, 6H, CH_3 DMA). FT IR (KBr, cm^{-1}): ν = 3507, 3054, 2932, 2781, 2468, 2369, 1944, 1704, 1607, 1508, 1418, 1268, 1115, 1029, 917, 824, 710, 609, 551, 481. Analysis found (%): C 68.85, H 6.18, N 6.05; $C_{52}H_{56}N_4O_{11}$ requires: C 68.41, H 6.18, N 6.14. The weight loss observed at 285 °C in the TGA experiment is 40.7% which can be matched with the sum of solvent loss (21.1%) and weight loss due to decarboxylation of TCCB (19.3%).

(TCCB)(4,4′-bpdb)·MeOH (4)

4,4′-bpdb (21 mg, 0.1 mmol in 3 mL methanol) was layered over of TCCB (27 mg, 0.05 mmol in 5 mL methanol). Diffraction quality single crystals were obtained after two days. Although 4,4′-bpdb and TCCB were mixed in 2 : 1 ratio, the co-crystal of composition 1 : 1 resulted. The same co-crystal was also resulted by slowly evaporating the above methanolic solution. Yield 85%.

^{1}H NMR (300 MHz, d_6-DMSO, 298 K): δ_H = 12.78 (s, 4H, –CO_2H), 8.75 (d, 4H, Ar–H), 8.70 (s, 2H, C–H, 4,4′-bpdb), 7.81 (d, 4H, Ar–H), 7.71 (d, 8H, Ar–H), 7.34 (d, 8H, Ar–H), 4.72 (s, 4H, CH–CH), 4.1 (s, MeOH), 3.17 (s, CH_3OH). FT IR (KBr, cm^{-1}): ν = 3423, 3040, 2920, 2789, 2601, 2509, 2375, 1911, 1694, 1606, 1572, 1509, 1415, 1313, 1278, 1180, 1119, 1061, 1013, 972, 954, 924, 854, 817, 778, 736, 709, 689, 635, 560, 515, 459. Analysis found (%): C 69.80, H 5.13, N 7.46; $C_{45}H_{38}N_4O_9$ requires C 69.40, H 4.92, N 7.19. The observed weight loss in TGA experiment is 5.1%, whereas the calculated value is 4.1%.

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