Cocrystal Controlled Solid-State Synthesis of a Rigid Tetracarboxylate Ligand that Pillars both Square Grid and Kagomé Lattice Layers

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Supplementary Information

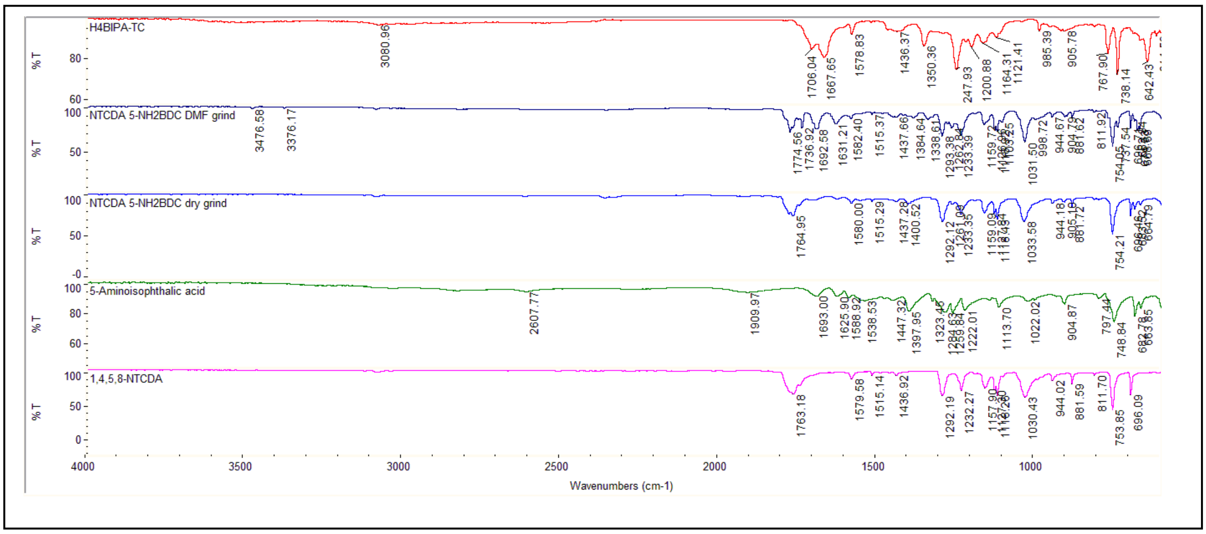

Figure S1, the FTIR specta of (bottom to top) 1,4,5,8-naphthalenetetracarboxylic dianhydride, 5-aminoisophthalic acid, dry grind of both reactants, DMF grind of both reactants, and H_4BIPA-TC

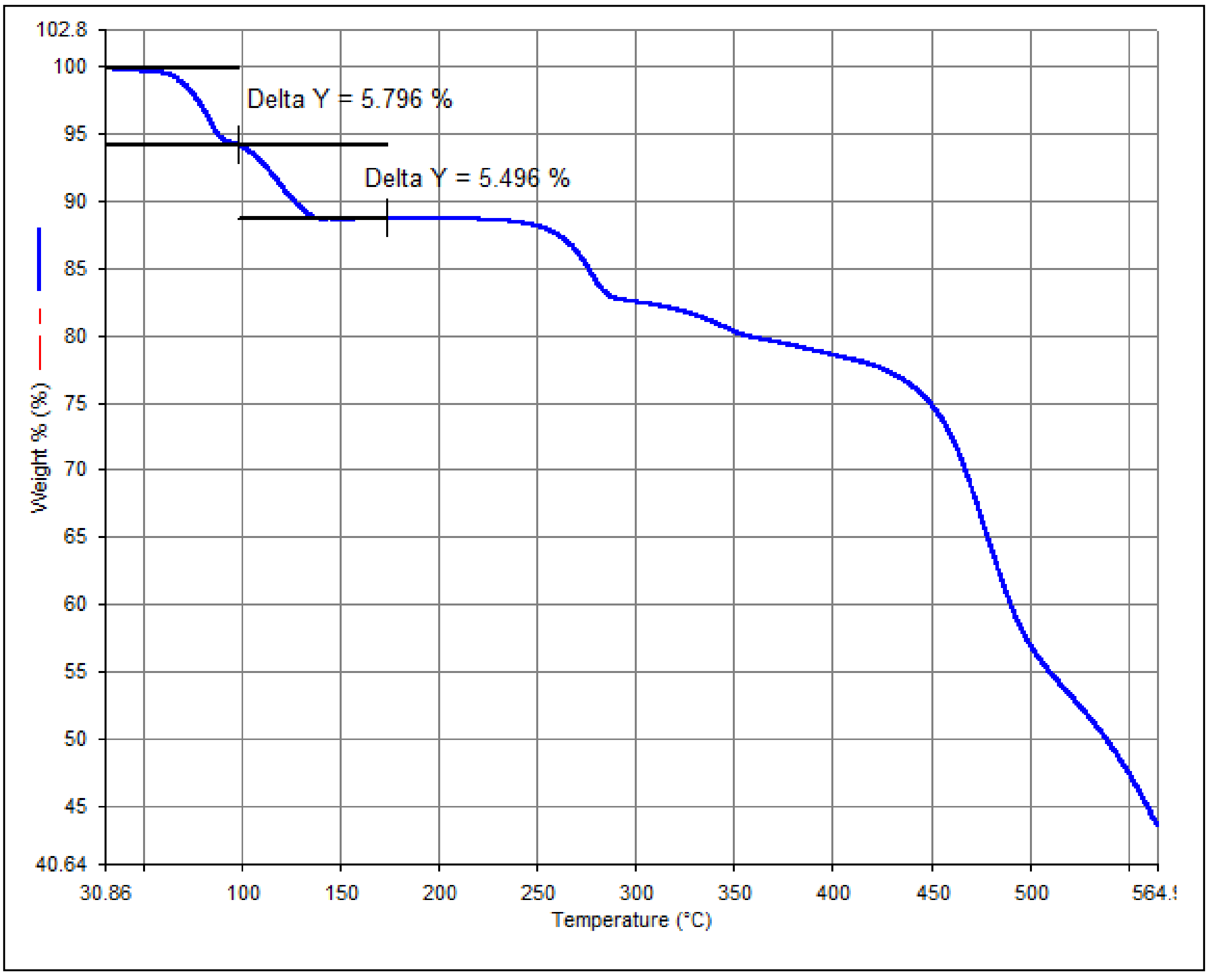

Figure S2, TGA from the DMF grind of 1,4,5,8-naphthalenetetracarboxylic dianhydride and 5-aminoisophthalic acid. The first weight loss of 5.796% corresponds well with the loss of two water molecules (calculated 5.71%) to form the diimide H_4BIPA-TC. The second weight loss ocurrs as DMF evaporates from the synthesized H_4BIPA-TC. Decomposition begins around 270°C.

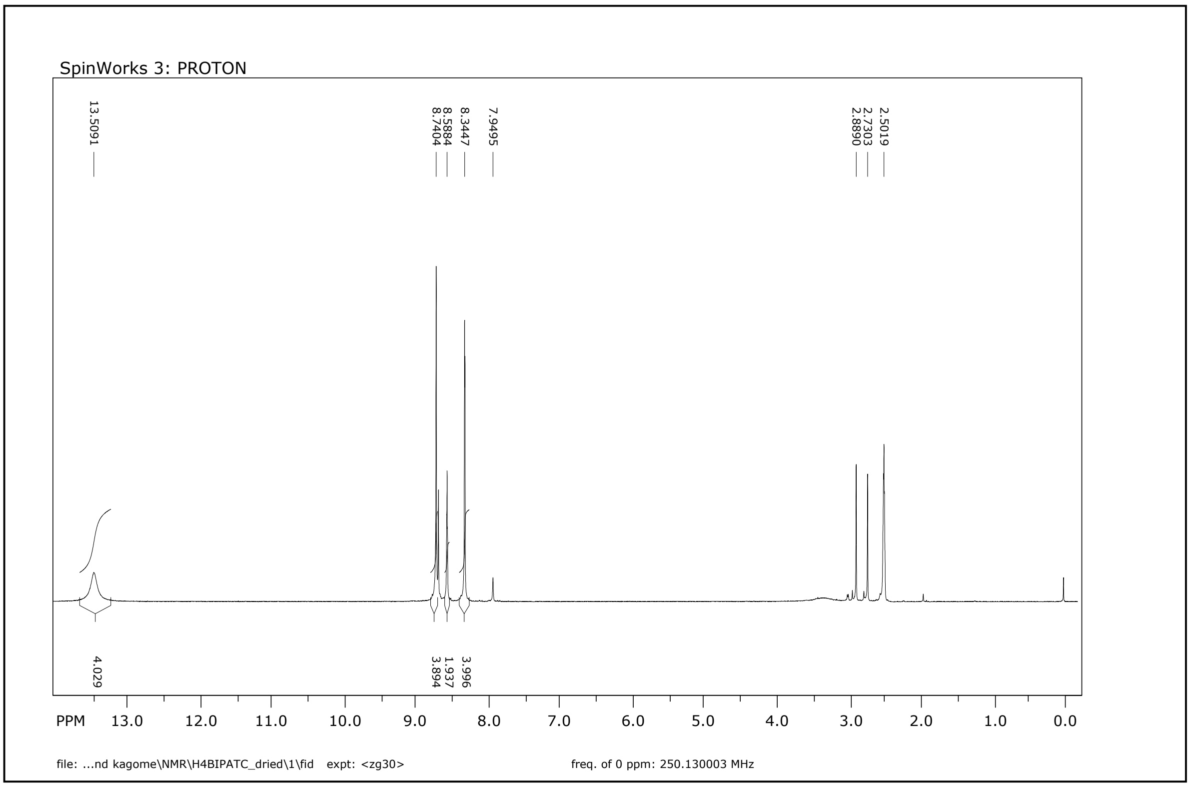

Figure S3, **H_4BIPA-TC** after heating DMF grind to 180°C and performing NMR in deuterated DMSO. Peaks from DMF and DMSO are present anlong with the proton peaks from **H_4BIPA-TC**.

Structure	**1**	**2a**	**2b**
Empirical Formula	$Cu_2C_{30}H_{10}N_2O_{14}$	$Cu_2C_{38}H_{28}N_4O_{14}$	$Cu_2C_{44}H_{28}N_4O_{12}$
Formula Weight	749.48	891.72	931.78
Temperature	100(2) K	100(2) K	183(2) K
Wavelength	0.71073 Å	1.54178 Å	0.71073 Å
Crystal system, Space Group	Monoclinic, C2/m	Orthorhombic, Imma	Orthorhombic, Imma
Unit Cell Dimensions	a = 32.461(12) Å α = 90°. b = 18.024(6) Å β = 119.964(9) ° c = 19.748(7) Å γ = 90°	a = 15.2248(3) Å α = 90°. b = 36.4392(7) Å β = 90° c = 10.3036(2) Å γ = 90°	a = 14.981(2) Å α = 90°. b = 36.371(5) Å β = 90° c = 10.922(2) Å γ = 90°
Volume	10010(6) Å^3	5716.23(19) Å^3	5951.1(16) Å^3
Z, Calculated Density	6, 0.746 Mg/m^3	4, 1.036 Mg/m^3	4, 1.040 Mg/m^3
Absorption Coefficient	0.672 mm^{-1}	1.352 mm^{-1}	0.763 mm^{-1}
F(000)	2244	1816	1896
Crystal Size	0.05 x 0.04 x 0.03 mm	0.10 x 0.10 x 0.10 mm	0.10 x 0.10 x 0.10 mm
Theta range for data collection	1.34° to 20.99°	2.42° to 65.69°	1.95° to 25.47°
Limiting indices	-31<=h<=32, -10<=k<=17, -19<=l<=19	-17<=h<=17, -41<=k<=42, -11<=l<=12	-17<=h<=18, -20<=k<=44, -12<=l<=13
Reflections collected / unique	16510 / 5453 [R(int) = 0.1855]	12420 / 2594 [R(int) = 0.0470]	15247 / 2922 [R(int) = 0.0433]
Completeness to theata	20.99° = 97.5%	65.69° = 99.1%	25.47° = 99.7%
Absorption Correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and Min. transmission	0.9801 and 0.9672	0.8766 and 0.8766	2922 / 0 / 144
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2

Data / restraints / parameters	5453 / 6 / 282	2594 / 0 / 159	2922 / 0 / 144
Goodness-of-fit on F^2	0.951	1.032	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0819, wR2 = 0.1423	R1 = 0.0375, wR2 = 0.1018	R1 = 0.0429, wR2 = 0.1238
R indices (all data)	R1 = 0.1634, wR2 = 0.1568	R1 = 0.0452, wR2 = 0.1057	R1 = 0.0491, wR2 = 0.1285
Largest diff. peak and hole	0.699 and -0.420 e^{-} $Å^{-3}$	0.271 and -0.282 $e^{-}Å^{-3}$	0.580 and -0.461$e^{-}Å^{-3}$

Table S1, The X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer (CuKα, λ = 1.54178 Å or MoKα or λ = 0.71073 Å using SMART APEX). Indexing was performed using APEX2[1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01.[2] Absorption correction was performed by multi-scan method implemented in SADABS.[3]. Space groups were determined using XPREP implemented in APEX2.[1] The structure was solved using SHELXS-97 and refined using SHELXL-97 contained in APEX2[1] and WinGX v1.70.01[4-6] programs packages. Hydrogen atoms were placed in geometrically calculated positions or found in the Fourier difference map and included in the refinement process using riding model. For all structures the contribution of disordered solvent molecules was treated as a diffuse using Squeeze procedure implemented in Platon program.[7, 8]

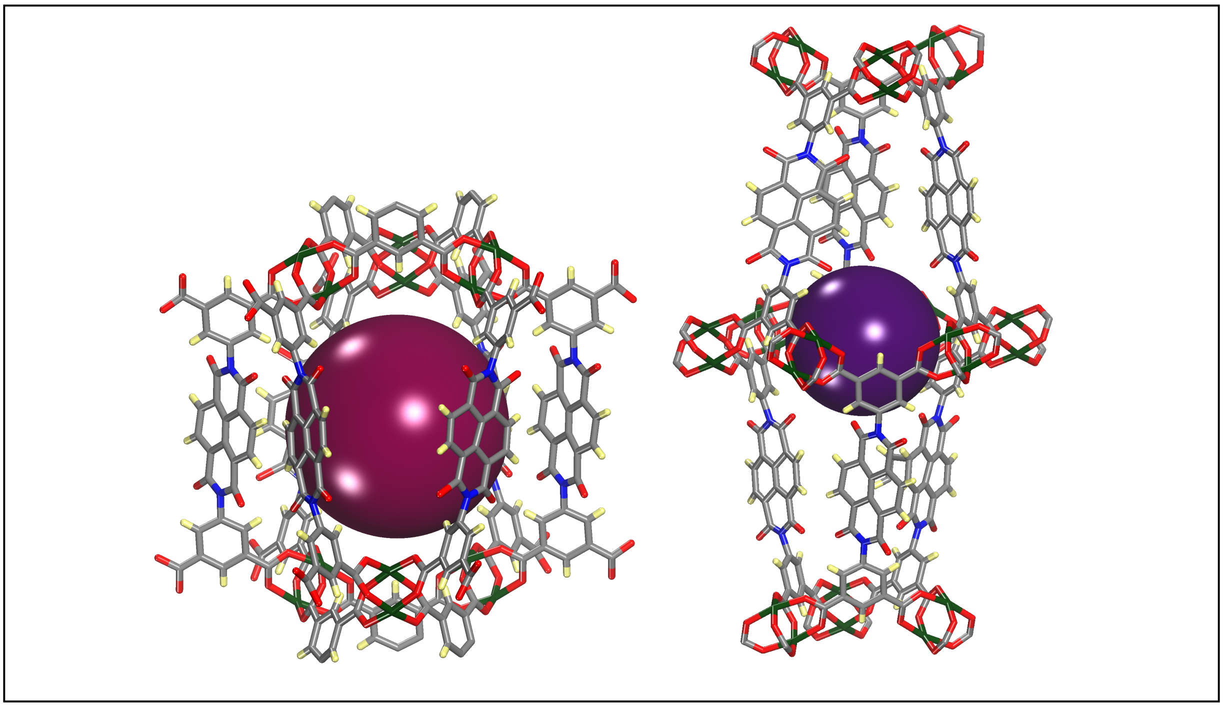

Figure S4, Cavities present in **1** from the pillared Kagomé lattice net.

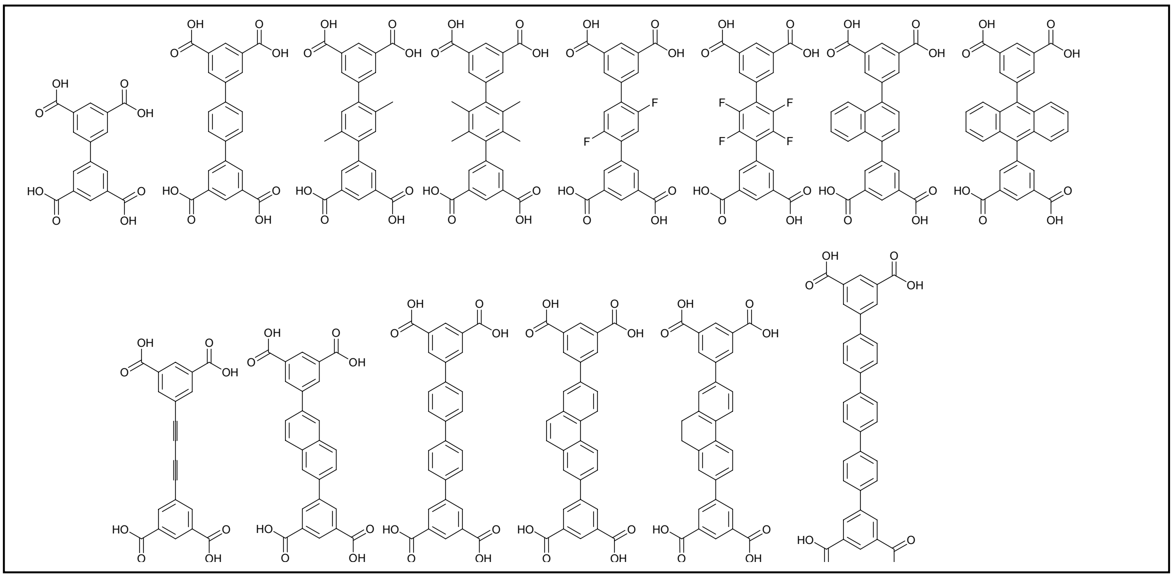

Figure S5. Linked 1,3-BDC ligands that have thus far been used to pillar Kagomé lattices or square grids (only one supramolecular isomer has been observed for each ligand).[9-12]

Supplementary References

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