Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

for

A diamondoid net sustained by halogen bonds: employing a cyclobutane to generate a tetrahedral architecture

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1. Materials, General Methods and Synthesis of the Dia Net

Materials

Resorcinol (**res**) and *trans*-1,2-bis(4-pyridyl)ethylene (**BPE**) as well as the solvents ethanol, toluene, and chloroform were all purchased from Sigma-Aldrich Chemical (St. Louis, MO, USA) and used as received. The halogen bond donor 1,4-diiodoperchlorobenzene (**$C_6I_2Cl_4$**) was synthesized by a previous reported method.[1] All crystallization studies were performed in 20 mL scintillation vials.

General Methods

The photoreactive co-crystal (**res**)·(**BPE**) was prepared by a previously reported method (≈100 mg).[2] The resulting solid was then dried and placed between Pyrex glass plates for irradiation. Upon exposure to UV-radiation from a 450 W medium-pressure mercury lamp in an ACE Glass photochemistry cabinet the solid underwent a quantitative [2 + 2] cycloaddition reaction to form *rctt*-tetrakis(4-pyridyl)cyclobutane, namely 2(**res**)·(**4,4'-TPCB**), as previously reported.[2] The **res** template was removed via extraction by adding 20 mL of a 0.10 M sodium hydroxide (NaOH) base along with stirring and heating on a hot plate for 10 minutes. Pure **4,4'-TPCB** was realized after 3 washings of 25 mL of chloroform ($CHCl_3$) and subsequent loss of the solvent.

Synthesis of the Dia Net

The co-crystals (**4,4'-TPCB**)·2(**$C_6I_2Cl_4$**)·2(**toluene**) (**1**) was synthesized by dissolving 25.0 mg of **$C_6I_2Cl_4$** in 3.0 mL of toluene, which was then combined with a separate warm 1.0 mL ethanol solution of 19.4 mg of **4,4'-TPCB** (2:1 molar equivalent). The ethanol solution was heated on a hot plate until the entire solid dissolved. The resulting solution was allowed to cool and slowly evaporate and after 2 days crystals suitable for X-ray diffraction were realized.

2. Single X-ray Diffraction Information and Data Table

A suitable crystal was mounted on a MiTeGen cryoloop in random orientations for data collection. Data collections were performed using a Bruker Venture Duo Photon-II single crystal X-Ray diffractometer equipped with an Oxford Cryostream device and operated at 1500 W (50kV, 30 mA) to generate graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). Apex II and SAINT software packages were used for data collection and integration. Data collected were corrected for systematic errors using SADABS based on the Laue symmetry using equivalent reflections. Structure solution and refinement were accomplished using ShelXT[3] and ShelXL[4], respectively. The structure was solved using direct methods. Toluene molecules disordered over a mirror plane of symmetry were fixed at a 0.5 occupancy and corresponding disordered atoms flanked with Part -1 and Part 0. All non-hydrogen atoms were identified from the difference Fourier map and refined anisotropically. All hydrogen atoms were placed in their calculated positions and were refined using isotropic thermal parameters.

Table S1. Crystallographic and refinement data for **1**

CCDC code	**1996696**
Formula	$C_{50}H_{36}Cl_8I_4N_4$
Formula mass	1484.03
Temperature	100(2)
Space group	*Aba2*
a, Å	11.0411(4)
b, Å	16.8624(7)
c, Å	28.2059(7)
α, °	90
β, °	90
γ, °	90
volume, Å^3	5251.4(3)
Z	4
Density (calculated), g/cm^3	1.877
μ, mm^{-1}	2.820
Scan	ω scan

θ range for data collection, °	4.64-56.574
Reflections measured	55382
Independent observed reflections	6505
Data/restraints/parameters	6505/133/309
R_{int}	0.0309
Final R Indices [I>2σ]	R_1 = 0.0140
	$wR2$ = 0.0320
R Indices (all data)	R_1 = 0.0140
	$wR2$ = 0.0323
Goodness-of-fit on F^2	1.040

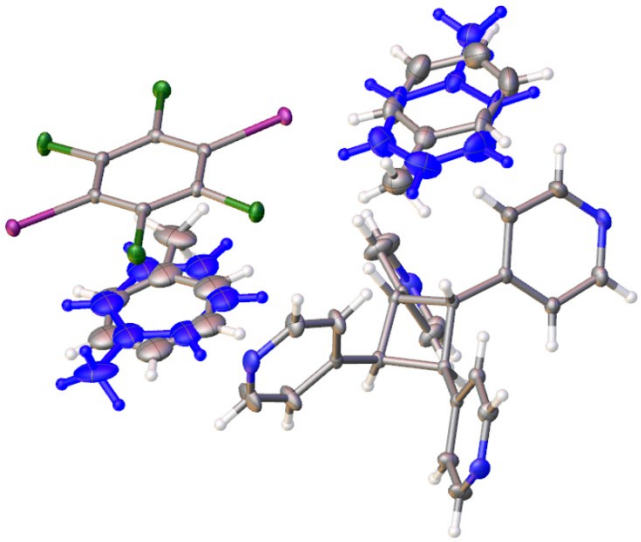

Figure S1. ORTEP with thermal ellipsoids set at 50 % probability for **1**. Toluene molecules disordered over a symmetry element shown in blue.

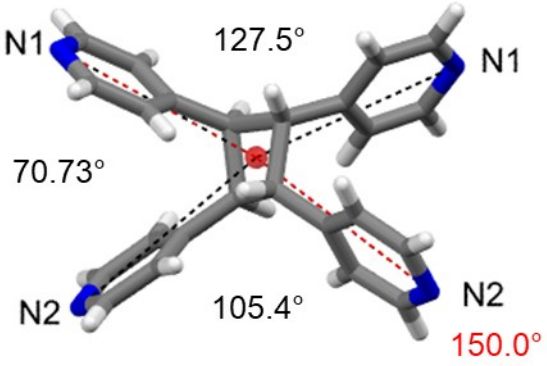

Figure S2. Corresponding geometries between 1,2-*cis* (black, 70.73°), 1,4-*trans* (black, 127.5° and 105.4°), and 1,3-*trans* (red, 150.0°) 4-pyridyl groups. Measurements are recorded from the centroid of the cyclobutane ring of **4,4'-TPCB** (red sphere) to corresponding N-atom halogen-bond acceptors.

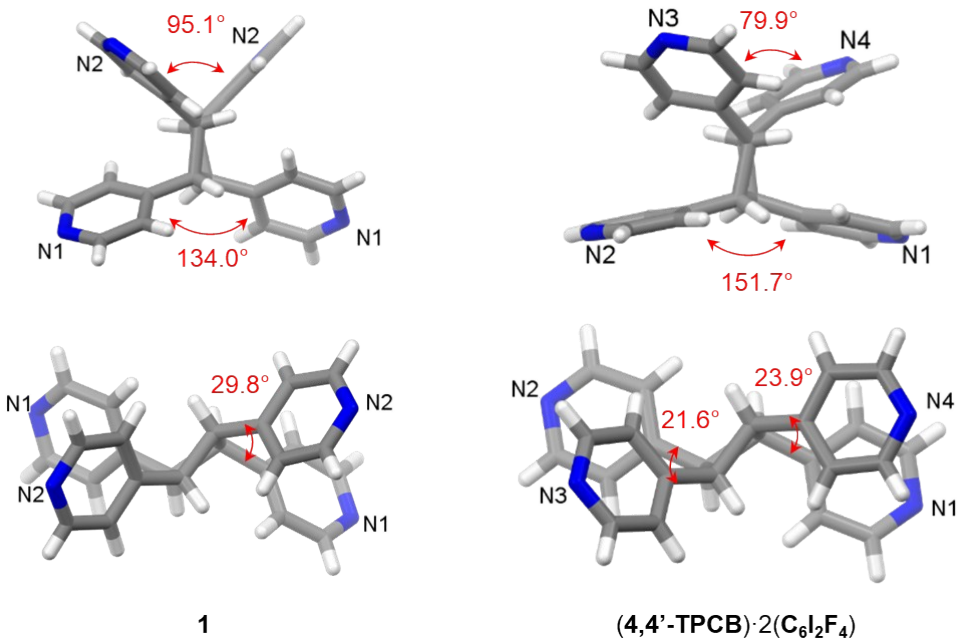

Figure S3. Dihedral angles between gauche *trans*-pyridyl (top) and *cis*-pyridyl groups (bottom) of **4,4'-TPCB** of the **dia** net of **1** (left) compared to the **sql** net of (**4,4'-TPCB**)·2(**$C_6I_2F_4$**) (right). Dihedral angles determined in reference to pairs of C-C bonds within the cyclobutane covalently connected to corresponding 4-pyridyl group.

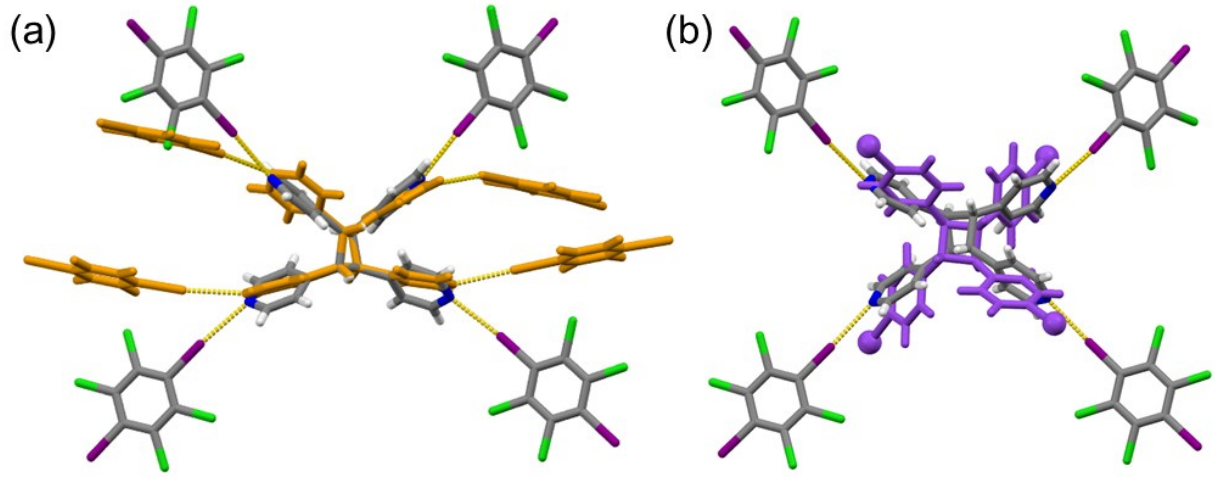

Figure S4. Overlay views comparing: (a) the **dia** net of **1** (full element colors) compared to the **sql** net of (**4,4'-TPCB**)·2(**$C_6I_2F_4$**) (orange) and (b) 3D nets constructed from the *rctt*-**4,4'-TPCB** of **1** (full element colors) compared to *rtct*-**4,4'-TPCB** (purple) of [CoF_2(*rtct*-**4,4'-TPCB**)]·$5H_2O$ with Co(II) metal centers shown as spheres.[5]

3. Topology Output

ToposPro calculations:

A net simplification of **1** was performed using ToposPro software.[6] The *Auto CN* [7] and *ADS* [8,9] commands upon choosing **4,4'-TPCB** as nodes provided a simplified net with 6^6 **dia** topology. ToposPro also indicated **dia** net related by inversion centers (-1). The following includes part of the ToposPro output, where ZA1 represents the center **4,4'-TPCB**:

```
Atom ZA1 links by bridge ligands and has
Common vertex with                    R(A-A)
ZA 1   -0.5000   -0.5000    0.7609   (-1-1 0)    22.665A        1
ZA 1    0.5000    1.5000    0.7609   ( 0 1 0)    22.665A        1
ZA 1    0.5000   -0.5000   -0.2391   ( 0-1-1)    22.665A        1
ZA 1   -0.5000    1.5000   -0.2391   (-1 1-1)    22.665A        1
-------------------------
Structural group No 1
-------------------------
Structure consists of 3D framework with ZA
There are 8 interpenetrating nets
FIV: Full interpenetration vectors
---------------------------------
[0,1/2,1/2] (16.43A)
[0,1/2,-1/2] (16.43A)
---------------------------------
PIC: [0,4,-4][1,0,1][0,2,-1] (PICVR=8)
Zt=8; Zn=1
Class Ia  Z=8
Coordination sequences
----------------------
ZA1:  1  2  3  4   5   6   7   8   9  10
Num   4 12 24 42  64  92 124 162 204 252
Cum   5 17 41 83 147 239 363 525 729 981
----------------------
TD10=981
Vertex symbols for selected sublattice
--------------------------------------
ZA1 Point symbol:{6^6}
Extended point symbol:[6(2).6(2).6(2).6(2).6(2).6(2)]
--------------------------------------
Point symbol for net: {6^6}
4-c net; uninodal net
Topological type: dia Diamond; 4/6/c1; sqc6 (topos&RCSR.ttd) {6^6} - VS
[6(2).6(2).6(2).6(2).6(2).6(2)] (76520 types in 11 databases)
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4. References

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