Electronic Supplementary Information for Dalton Transactions

Supplementary Material

A non photochemical route for the regioselective preparation of *rtct*-pyridylcyclobutanes via hydrothermal isomerisation promoted by polymolybdates.

Alexander Briceño,* Aaron Fulgence, Yennifer Hill and Reinaldo Atencio.

Instituto Venezolano de Investigaciones Científicas, (IVIC), Apartado 21827, Caracas, 1020-A, Venezuela. Laboratorio de Síntesis y Caracterización de Nuevos Materiales, Centro de Química.

1. Experimental Section

2. List of Figures

1. Experimental Section

All reagents were obtained from commercial sources and used without further purification. The elemental analysis was performed (C, H, N) on a model EA1108 Fisons elemental analyzer. The FT-IR spectra were recorded from KBr discs, using a Nicolet Magna-IR 560 spectrophotometer. XRPD pattern was recorded on a Siemens D5005 Diffractometer with Cu(Kα) (1.5418 Å) radiation, with a scan speed of 2 deg/min. The ^{1}H NMR spectra were recorded on a Bruker AVANCE-300 Spectrometer in $CDCl_3$.

Synthesis of *rctt*-pyridylcyclobutanes (tpcb)

The cyclobutane derivatives were prepared from controlled [2+2] cycloaddition reactions in the solid state of *trans*-bis(2-pyiridyl)ethylene, *trans*-bis(4-pyridyl)ethylene and *trans*-1-(2-pyridyl)-2-(4-pyridyl)ethylene, according to previously published procedures.[3b, 6] The different photoproducts obtained were characterised before the hydrothermal reaction by NMR spectroscopy: ***rctt*-2,2'-tpcb** ^{1}H NMR (300 MHz, $CDCl_3$), δ_H(ppm): 8.42(H_a, ddd), 7.36(H_b, td), 6.9(H_c, ddd) 7.07(H_d, dd), and 5.13(H_e, s); ***rctt*-4,4'-tpcb** (300 MHz, $CDCl_3$), δ_H(ppm): 8.45(H_a, dd), 7.00(H_b, dd), and 4.48(H_c, s); ***rctt*-2,4'-tpcb-ht** (300 MHz, $CDCl_3$), δ_H(ppm): 8.43(H_a, ddd), 8.29(H_e, ddd), 7.42(H_b, td), 7.01(H_f, dd), 6.97-6.94($H_{c,d}$ m), 4.86(H_g, td) and 4.71(H_h, td)

Synthesis of [(Mo_8O_{26})(*rtct*-2,2'-H_2tpcb)$_2$ (1). A mixtute of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (HMA) (122 mg, 0.1 mmol) and *rctt*-tetrakis(2-pyridyl)cyclobutane (*rctt*-2,2'-tpcb) (35 mg, 0.1 mmol) in a molar ratio (1:1) in 10 mL of H_2O was heated at 140 ºC for 3 days. After slow cooling to room temperature colourless crystals of **1** were obtained with a yield of 55% based on *rctt*-2,2'-tpcb. The XRD pattern showed that **1** was obtained as a highly pure single-phase (Fig. S1). Anal. calcd. (%) for $C_{48}H_{44}Mo_8N_8O_{26}$: C, 30.08; H, 2.31; N, 5.84. Found: C, 30.07; H, 2.45; N, 5.92. IR (KBr, cm^{-1}): ν(N^+-H): 3225, ν(C=C and C=N): 1644-1610 and 1485, ν(Mo=O):943-919 and ν(Mo-O-Mo): 857.

Synthesis of [(Mo_8O_{26})(*rctt*-4,4'-H_4tpcb) (2). A mixtute of HMA (122 mg, 0.1 mmol) and *rctt*-tetrakis(4-pyridyl)cyclobutane (*rctt*-4,4'-tpcb) (35 mg, 0.1mmol) in a molar ratio (1:1) in 10 mL of H_2O was heated at 140 ºC for 3 days. After slow cooling to room temperature crystals of good quality of **2** for X-ray single crystal analysis were isolated together with an

unidentified white powder with a yield of 72% based on *rctt*-4,4'-tpcb. IR (KBr, cm^{-1}): $\nu(N^+$-H): 3226, ν(C=C and C=N): 1631-1600 and 1498, ν(Mo=O):947-911 and ν(Mo-O-Mo): 851.

Synthesis of [(Mo_8O_{26})(*rctt*-2,4'-H_4tpcb) (3). A mixtute of HMA (122 mg, 0.1 mmol) and *rctt*-1,3-bis(2-pyridyl)-2,4-bis(4-pyridyl)cyclobutane (*rctt*-2,4'-tpcb-ht) (35 mg, 0.1 mmol) in a molar ratio (1:1) in 10 mL of H_2O was heated at 140 ºC for 3 days. After slow cooling to room temperature pale yellow crystals of good quality of **3** were isolated together with an unidentified yellow powder with a yield of 68% based on *rctt*-2,4'-tpcb. IR (KBr, cm^{-1}): $\nu(N^+$-H): 3228, ν(C=C and C=N): 1634-1605 and 1495, ν(Mo=O):948-910 and ν(Mo-O-Mo): 851.

Synthesis of [(Mo_8O_{26})(*rtct*-4,4'-H_2tpcb)$_2$] (4). A mixtute of HMA (168 mg, 0.15 mmol) and *rctt*-4,4'-tpcb (35 mg, 0.1mmol) in a molar ratio (1.5:1) in 10 mL of H_2O was heated at 160 ºC for 3 days. After slow cooling to room temperature crystals of good quality of **4** for X-ray single crystal analysis were isolated with a yield of 60% based on *rctt*-4,4'-tpcb. IR (KBr, cm^{-1}): ν(O-H): 3400, $\nu(N^+$-H): 3221, ν(C=C and C=N): 1633-1602 and 1501, ν(Mo=O):945-918 and ν(Mo-O-Mo): 850.

^{1}H NMR of the products obtained from the extraction of compounds 1-4.

The products were obtained after the dissolution of solid phases **1-4** in a NaOH solution (pH~ 12) and after the extraction with CH_2Cl_2. The compound *rtct*-tetrakis(2-pyridyl)cyclobutane isomer (*rtct*-2,2'-tpcb) (**5**) was obtained as single product from compound **1**. (***rtct*-2,2'-tpcb)**: ^{1}H NMR (300 MHz, $CDCl_3$), δ_H(ppm): 8.66(H_a, ddd), 7.54(H_b, td), 7.13(H_c, ddd), 7.19 (H_d td), and 4.41(H_e, s). From the solid **2** and **3** were identified the *rctt* and *rtct* isomers. ***rtct*-4,4'-tpcb (6):** ^{1}H NMR (300 MHz, $CDCl_3$), δ_H(ppm): 8.57(H_a, dd), 7.14(H_b, dd), and 3.69(H_c, s). ***rtct*-2,4'-tpcb-ht (7):** ^{1}H NMR (300 MHz, $CDCl_3$), δ_H(ppm): 8.67(H_a, dd), 8.46(H_e, dd), 7.64(H_b, td), 7.16-7.21($H_{c,d}$, m), 7.12(H_f, dd) 4.31(H_g, t) and 3.25(H_h, t)

Crystal structure determination. Intensity data were recorded at room temperature on a Rigaku AFC-7S diffractometer equipped with a CCD bidimensional detector using monochromated Mo(Kα) radiation (λ = 0.71073 Å). An empirical absorption correction (multi-scan) was applied using the package CrystalClear. The structures were solved by Direct Methods and refined by full-matrix least-squares on F^2 using the SHELXTL-PLUS

package. Hydrogen atoms on C and N atoms were placed at fixed positions using the HFIX instruction, except for the structure **1**, which were found from the Difference Fourier map. All the H atoms were refined with isotropic displacement parameters set to 1.2 × *U*eq of the attached atom. In the structure **4** one of the pyridyl rings (C15/C16/C17/N3/C18/C19) was refined with the SIMU and DELU instructions. The water molecules O2W to O6W were found disordered over two positions. These atoms only were refined with isotropic displacement parameters. The occupational parameters were refined. The H atoms on the water molecules were not located in the density map.

Figure S1. Experimental (red) and theoretical (blue) XRD patterns for compound **1**.

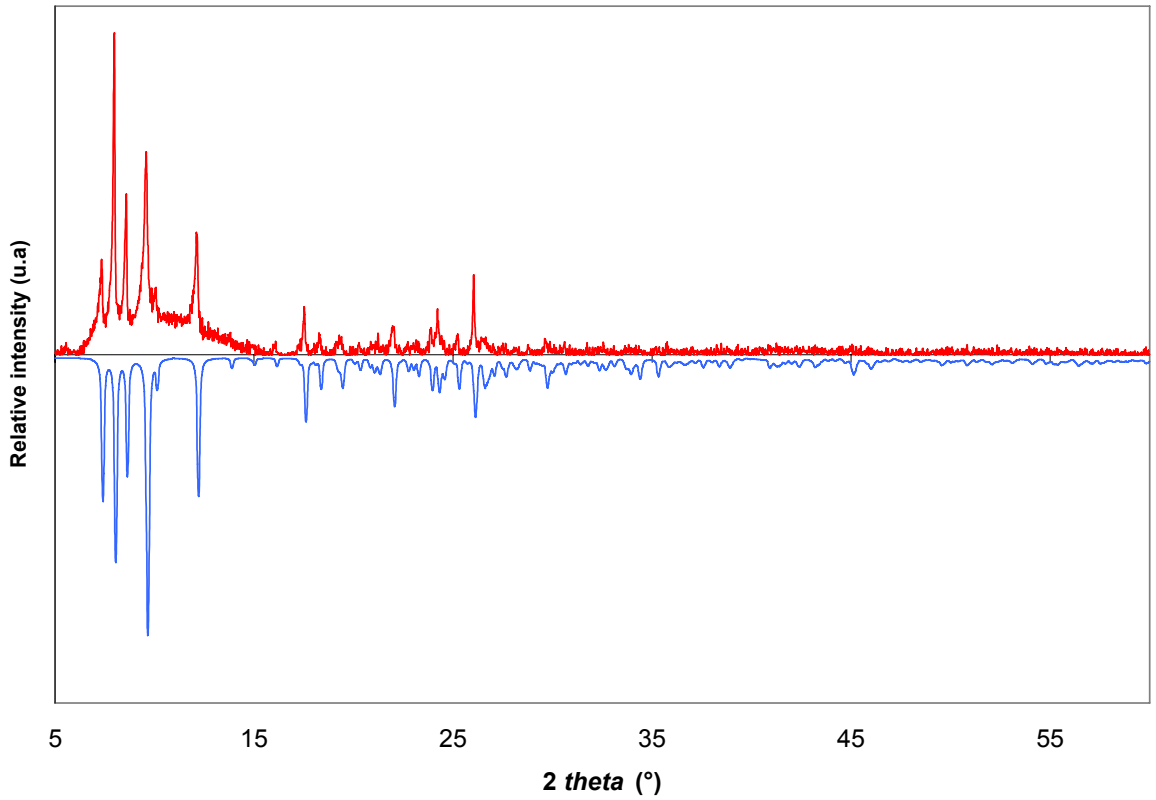


Figure S2. View of the stacking of the layers in the crystal structure of **1**, showing the pyridine rings π-π interactions along the *b* axis.

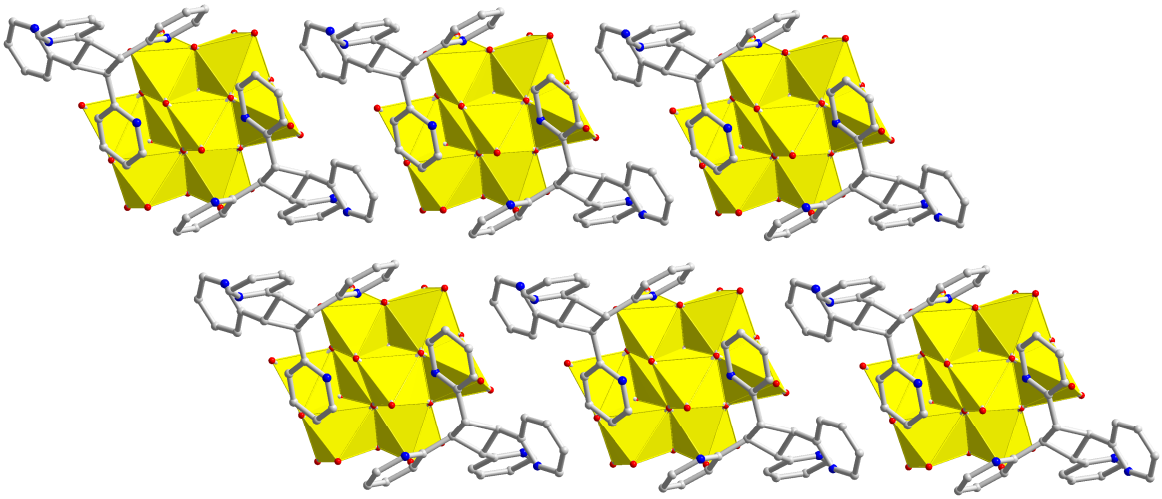
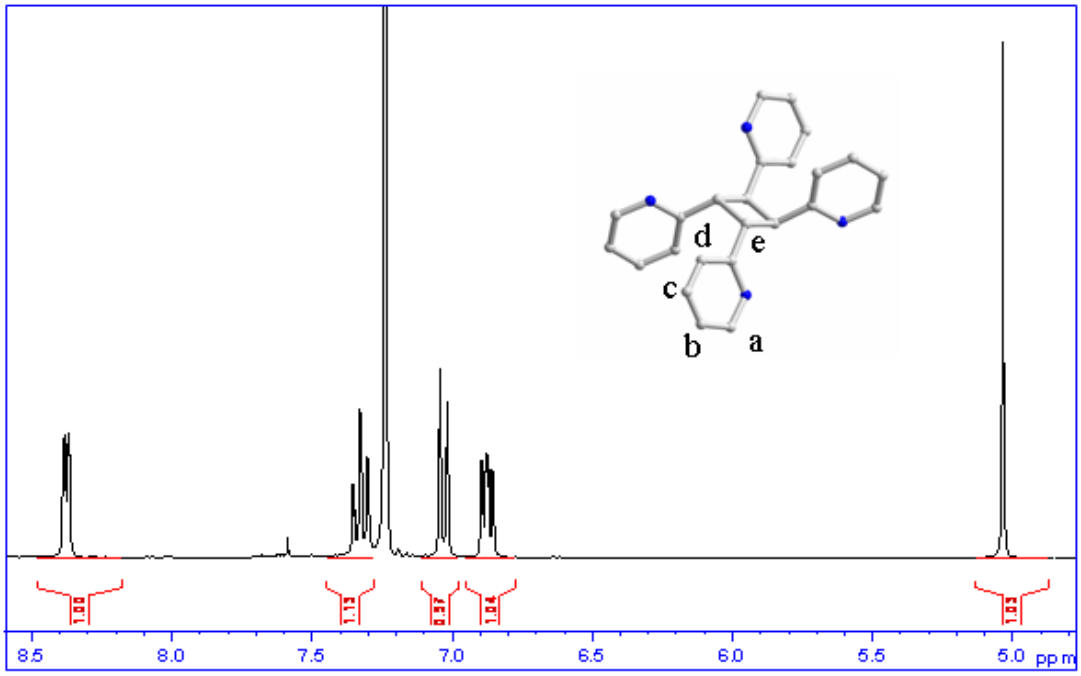
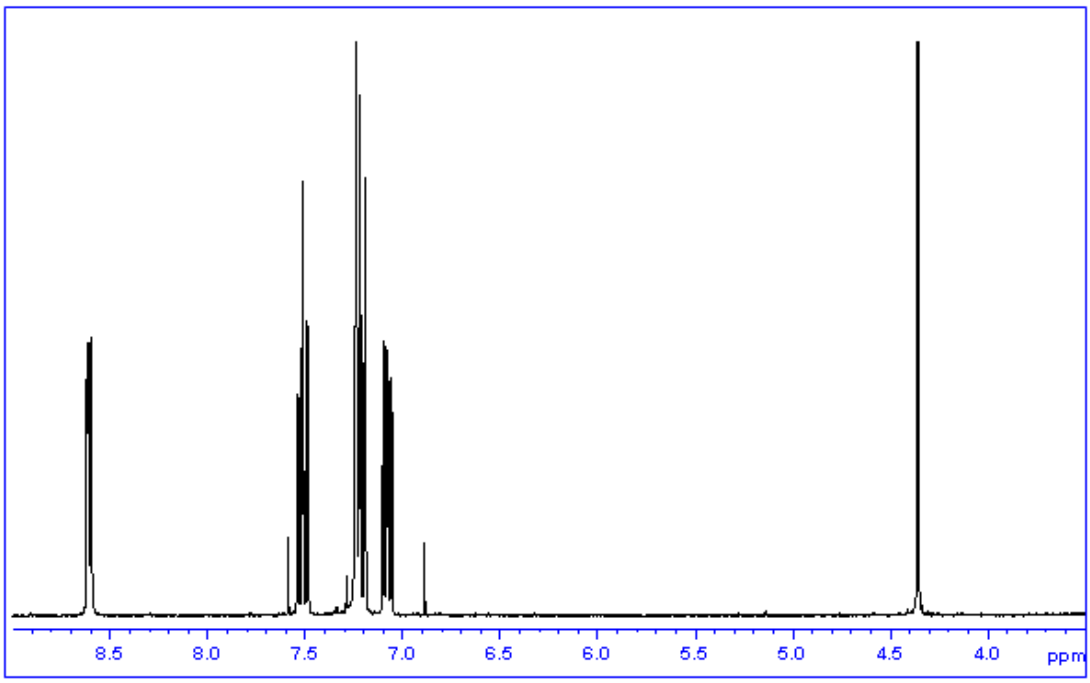


Figure S3. (a) ^{1}H NMR spectrum of the starting *rctt*-2,2'-tpcb isomer used for the synthesis of **1**. (b) ^{1}H NMR spectrum of the *rtct*-2,2'-tpcb isomer obtained from the extraction of compound **1.**



(a)



(b)

Figure S4. View of the hydrogen bonded 2D network found in the crystal structure of **3**. Hydrogen atoms of the 2,4'-tpcb-ht are omitted for clarity.

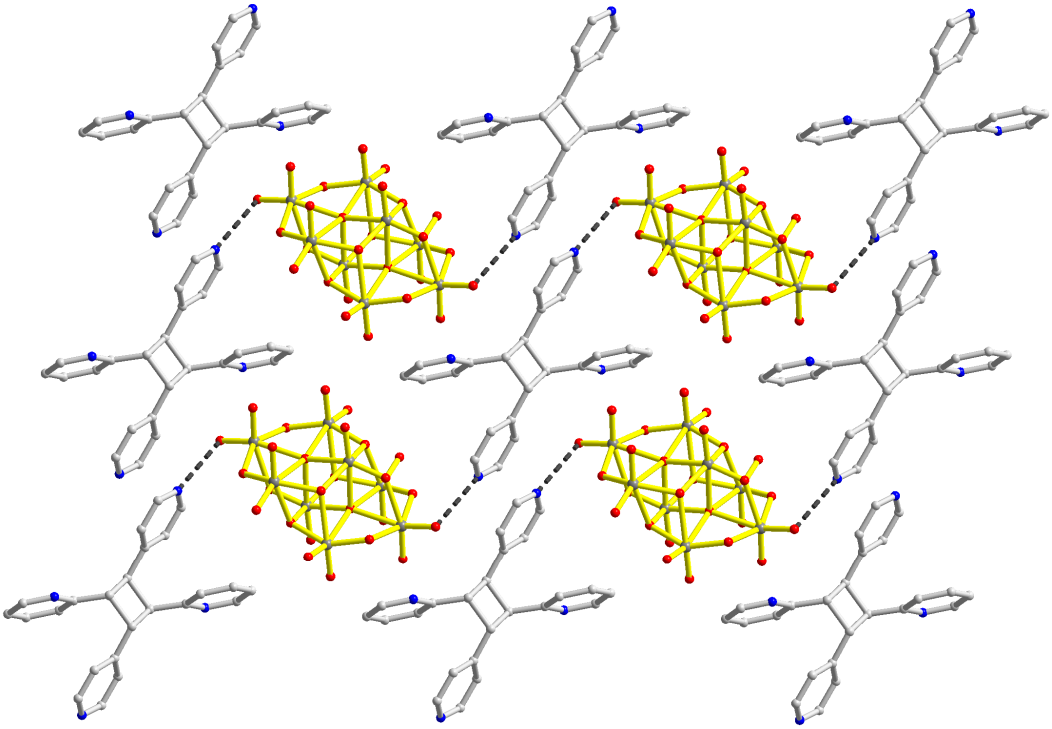
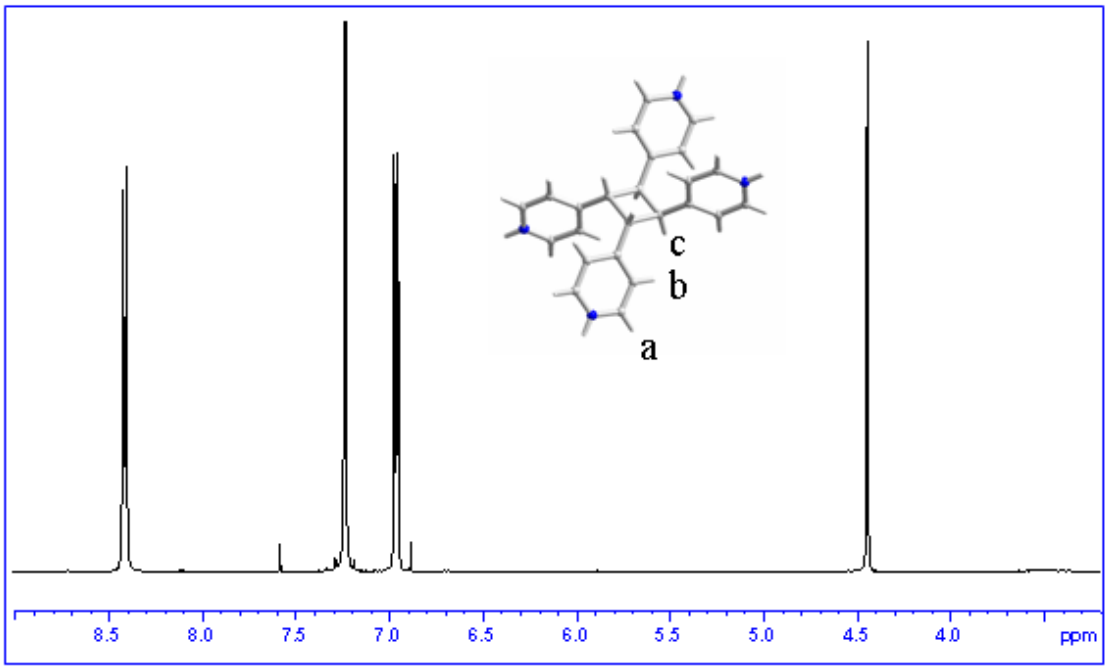
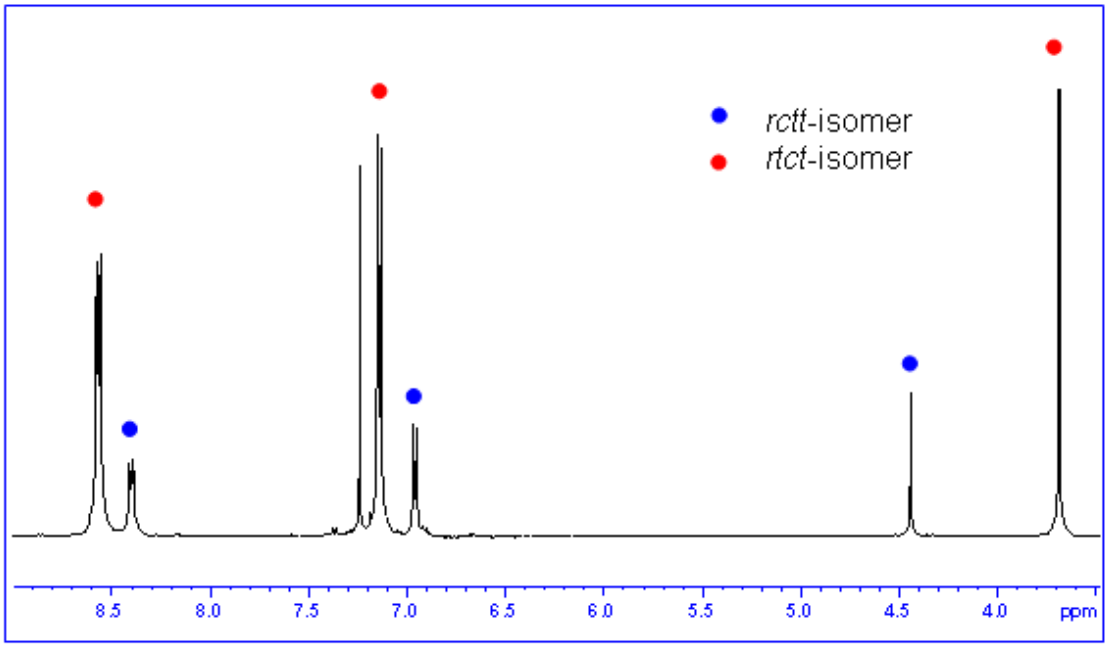


Figure S5. (a) ^{1}H NMR spectrum of the starting *rctt*-4,4'-tpcb used for the synthesis of **2**. (b) ^{1}H NMR spectrum of the *rctt-rtct* isomer mixture obtained from the extraction of compound **2**.

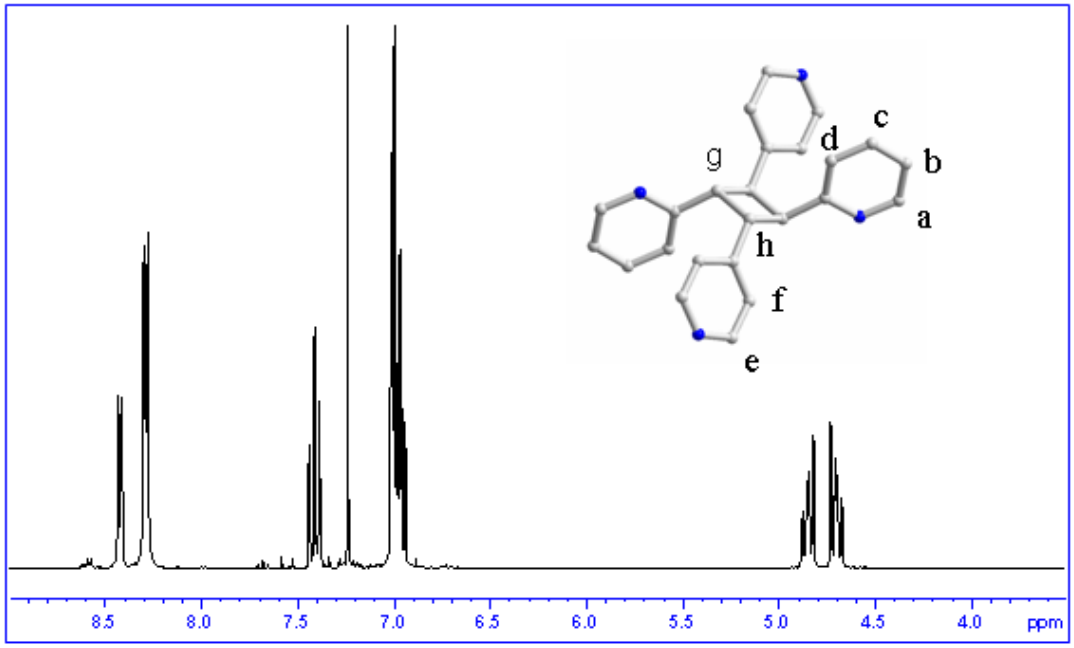


(a)

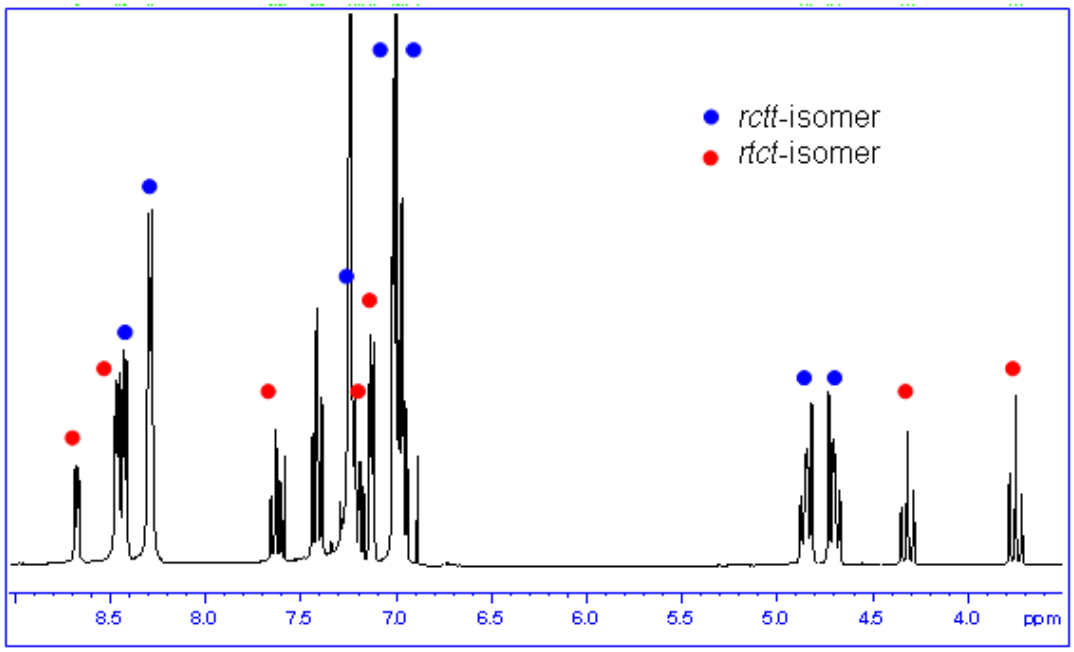


(b)

Figure S6. (a) ^{1}H NMR spectrum of the starting *rctt*-2,4'-tpcb-ht used for the synthesis of **3**. (b) ^{1}H NMR spectrum of the *rctt-rtct* isomer mixture obtained from the extraction of compound **3.**



(a)



(b)

Figure S7. Packing diagram of compound **4** along the *a*-axis, showing the cavities generated by stacking of the cyclobutanes *via* π-π interactions. Crystallisation water molecules are omitted for clarity.

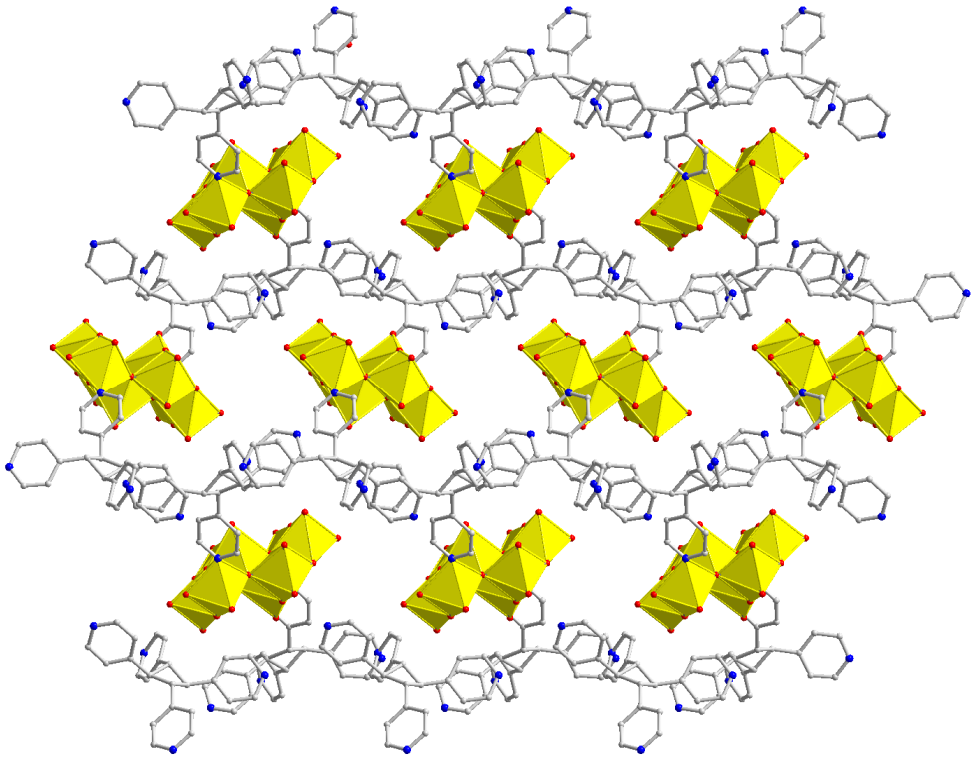


Figure S8. Comparative view of the inorganic building blocks found in the crystal structures of **1** (a) **2-3** (b) and **4** (c).