Supplementary Material

Supramolecular isomerism in multivalent metal-templated assemblies with topochemical influence in the regioselective synthesis of tetrakis(2-pyridyl)cyclobutane isomers

---

Alexander Briceño,*[a] Dayana Leal,[a,b] Reinaldo Atencio,[a] and Graciela Díaz de Delgado,[b]

(a) Instituto Venezolano de Investigaciones Científicas, (IVIC), Apartado 21827, Caracas, 1020-A, Venezuela. Laboratorio de Síntesis y Caracterización de Nuevos Materiales, Centro de Química. (b) Universidad de Los Andes, Facultad de Ciencias, Departamento de Química, Laboratorio de Cristalografía. Apartado 40 La Hechicera, Mérida 5251, Venezuela.

1. Experimental Section

2. List of Figures

Figure S1. (a) ^{1}H NMR spectrum of the *rtct*-tpcb isomer obtained from the photoreaction of compound **1**. (b) ^{1}H NMR spectrum of the *rctt*-tpcb isomer obtained from the photoreaction of compound **2**

Figure S2. Experimental (red) and theoretical (blue) XRD patterns: (a) compound **1**, (b) compound **2**, and (c) compound **3**. All the patterns are affected by preferred orientation.

Figure S3. FT-IR spectra of compound **3**: (a) fresh sample, (b) sample irradiated with 302 nm using a Pyrex filter, (c) sample irradiated with unfiltered UV light at 302 nm.

Figure S4. FT-IR spectra of compound **2**: (a) fresh sample (blue line), (b) sample irradiated with unfiltered UV light at 302 nm (red line).

Figure S5. Comparative view of the building blocks found in the crystal structures of the supramolecular isomer **1** (a) and **2** (b). Hydrogen atoms of the bipyridines are omitted for clarity.

1. Experimental Section

All reagents were obtained from commercial sources and used without further purification. The elemental analyses were 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 patters were recorded on a Siemens D5005 Diffractometer with Cu(Kα) (1.5418 Å) radiation, with a scan speed of 2 deg/min. These patterns showed that compounds **1-3** were obtained as pure single-phases (Fig. S2). The ^{1}H NMR spectra of the isolated products were recorded on a Bruker AVANCE-300 Spectrometer in $CDCl_3$.

Synthesis of $Mn(NCS)_2(OH_2)_4\cdot 4(bpe)$ (1). A solution of bpe (200 mg, 1 mmol) in 20 mL of methanol was added to 40 mL of an aqueous solution of $MnCl_2\cdot 4H_2O$ (112 mg, 0.55 mmol) and NaSCN (88 mg, 1 mmol), and allowed to stir for 1 h. Slow evaporation of the resulting solutions at room temperature gave crystals of good quality for X-ray single crystal analysis. The XRD pattern showed that **1** was obtained as a highly pure single-phase (Fig. S2a). Yield based on bpe: 80% (pale yellow prisms). Anal. calcd. (%) for $C_{50}H_{48}MnN_{10}O_4S_2$: C, 61.78; H, 4.98; N, 14.41; S, 6.59. Found: C, 61.93; H, 5.83; N, 14.04; S, 6.02. IR (cm^{-1}): ν(O-H): 3600-2900, ν(NCS): 2065, ν(C-C): 1588-1560, ν(C-N): 1468-1424, ν(=C–H): 963.

Synthesis of $Mn(NCS)_2(OH_2)_4\cdot 4(bpe)$ (2). A mixture of bpe (100 mg, 0.55 mmol), $MnCl_2\cdot 4H_2O$ (112 mg, 0.55 mmol) and NaSCN (88 mg, 1 mmol) in a molar ratio of 1:1:2 were dissolved using the same amounts of solvents used for **1**. The XRD pattern showed that the bulk represents the same phase as observed in the single crystal, this phase is different to **1** (Fig S2b). Yield 72% (pale yellow plates). Anal. calcd. (%) for $C_{50}H_{48}MnN_{10}O_4S_2$: C, 61.78; H, 4.98; N, 14.41; S, 6.59. Found: C, 62.23; H, 5.12; N, 14.25; S, 6.63. IR (cm^{-1}): ν(O-H): 3600-2900, ν(NCS): 2071, ν(C-C): 1593-1564, ν(C-N): 1473-1434, ν(=C–H): 963.

Synthesis of $Co(NCS)_2(OH_2)_4\cdot 4(bpe)$ (3). A mixture of bpe (200 mg, 1 mmol), $CoCl_2$ (72 mg, 0.55mmol) and NaSCN (88mg, 1mmol) using either molar ratio 2:1:2 as 1:2:1 produce exclusively **3.** These results were corroborated by XRPD (Fig S2c**).** Yield: 75% (pink plates). $C_{50}H_{48}CoN_{10}O_4S_2$: calcd (%): C, 61.53; H, 4.96; N, 14.35; S, 6.57. Found (%): C, 61.39; H, 5.07; N, 14.01; S, 6.12. IR (cm^{-1}): ν(O-H): 3600-2900, ν(NCS): 2094, ν(C-C): 1592-1564, ν(C-N): 1474-1434, ν(=C–H): 966.

Solid state reactivity.

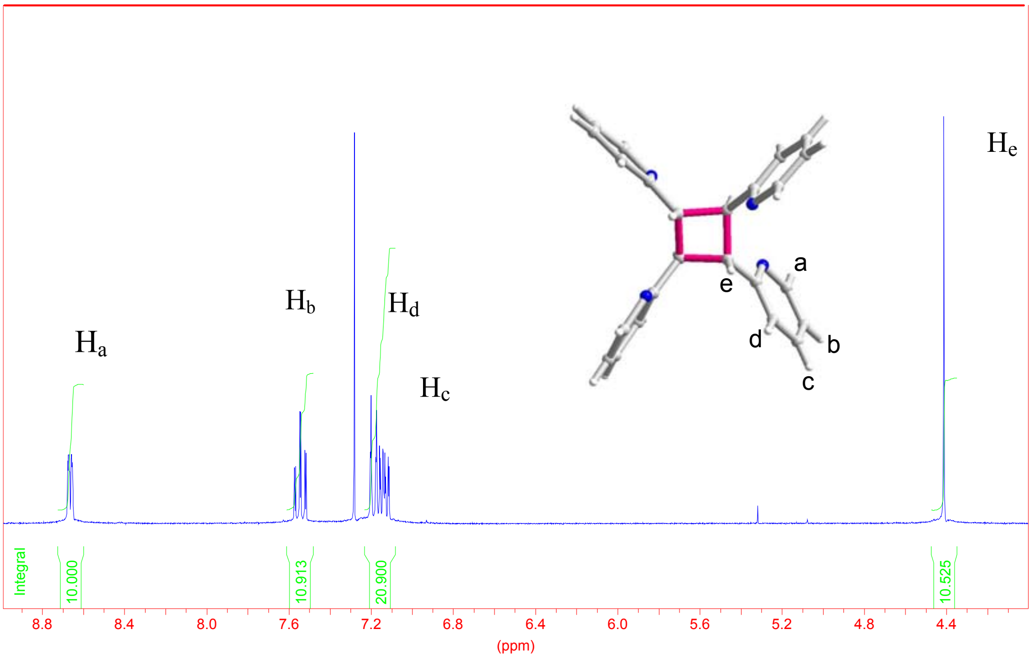
The products were isolated by fractioned crystallization process of the recrystallisation of the irradiated samples (200 mg) of **1-3** in a mixed water-methanol 3:1, respectively. The *rtct*-tetrakis(2-pyridyl)cyclobutane isomer (*rtct*-tpcb) (**4**) was obtained by topochemical reaction from compound **1**. A powdered crystalline and crystals of **1** was irradiated with a Hg lamp at 302 nm during 7 days. Recrystallisation of **4** in chloroform gives suitable crystals for single crystal analysis (**4**). Yield: 48 %. ^{1}H NMR (300 MHz, $CDCl_3$), δ_H(ppm), J (Hz): 8.66(H_a, ddd; J_{ab}= 4.9, J_{ac}= 1.6, J_{ad}= 0.9), 7.54(H_b, td; J_{bc}= 7.6, J_{bd}= 1.8), 7.13(H_c, ddd; J= 4.89, J_{cd}= 7.8), 7.19 (H_d td), and 4.41(H_e, s).

The *rctt*-tetrakis(2-pyridyl)cyclobutane isomer (*rctt*-tpcb) (**5)** was obtained by topochemical reaction from the compounds **2** or **3** under similar conditions as those used for **4**. Yield: 60-65%. ^{1}H NMR (300 MHz, $CDCl_3$), δ_H(ppm), J (Hz): 8.42(H_a, ddd, J_{ab}= 4.8, J_{ac}= 1.0), 7.36(H_b, td; J_{bc}=7.7, J_{bd}= 1.84), 6.9(H_c, ddd; J_{cd}=7.8) 7.07(H_d, dd), and 5.13(H_e, s).

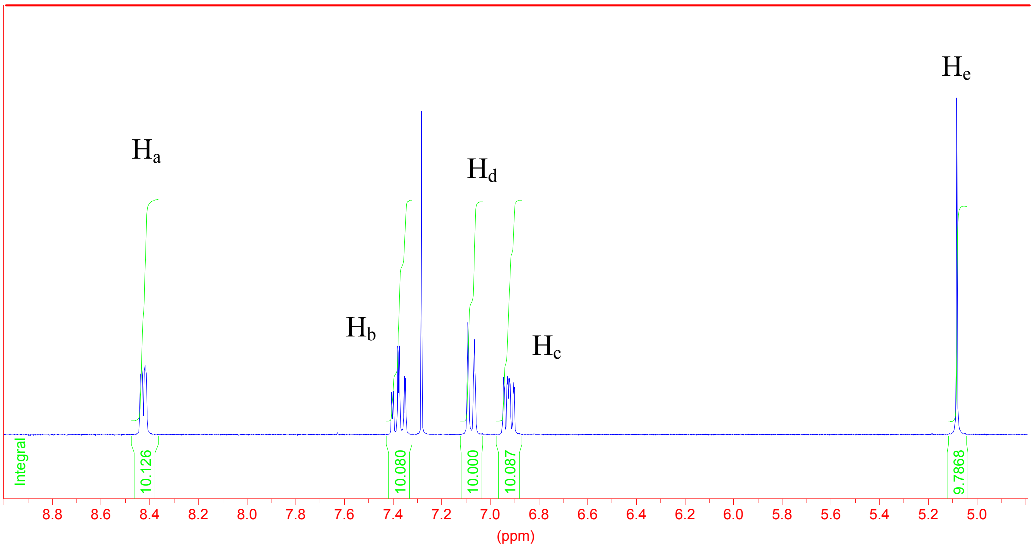
Crystal structure determination. Intensity data were recorded at room temperature on a Rigaku AFC-7S diffractometer equipped with a CCD bidimensional detector using monochromated Mo(Kα) radiation (λ = 0.71073 Å). An empirical absorption correction (multi-scan) was applied using the package CrystalClear.[20] The structures were solved by Direct Methods and refined by full-matrix least-squares on F^2 using the SHELXTL-PLUS package.[21] Hydrogen atoms on the non-disordered atoms were placed at fixed positions using the HFIX instruction. H-atoms on coordinated water molecules were found from the Difference Fourier map. They were refined with isotropic displacement parameters set to 1.2 × Ueq of the attached atom. In the structures **1-3**, at least one bipyridine molecule was found to be disordered and was modelled in two sets of positions and constraining the pyridil rings to be regular hexagons. The non-hydrogen atoms of these molecules were refined with isotropic displacement parameters.

Figure S1. (a) ^{1}H NMR spectrum of the *rtct*-tpcb isomer obtained from the photoreaction of compound **1**. (b) ^{1}H NMR spectrum of the *rctt*-tpcb isomer obtained from the photoreaction of compound **2**

(a)



(a)



(b)

Figure S2. Experimental (red) and theoretical (blue) XRD patterns: (a) compound **1**, (b) compound **2**, and (c) compound **3**. All the patterns are affected by preferred orientation

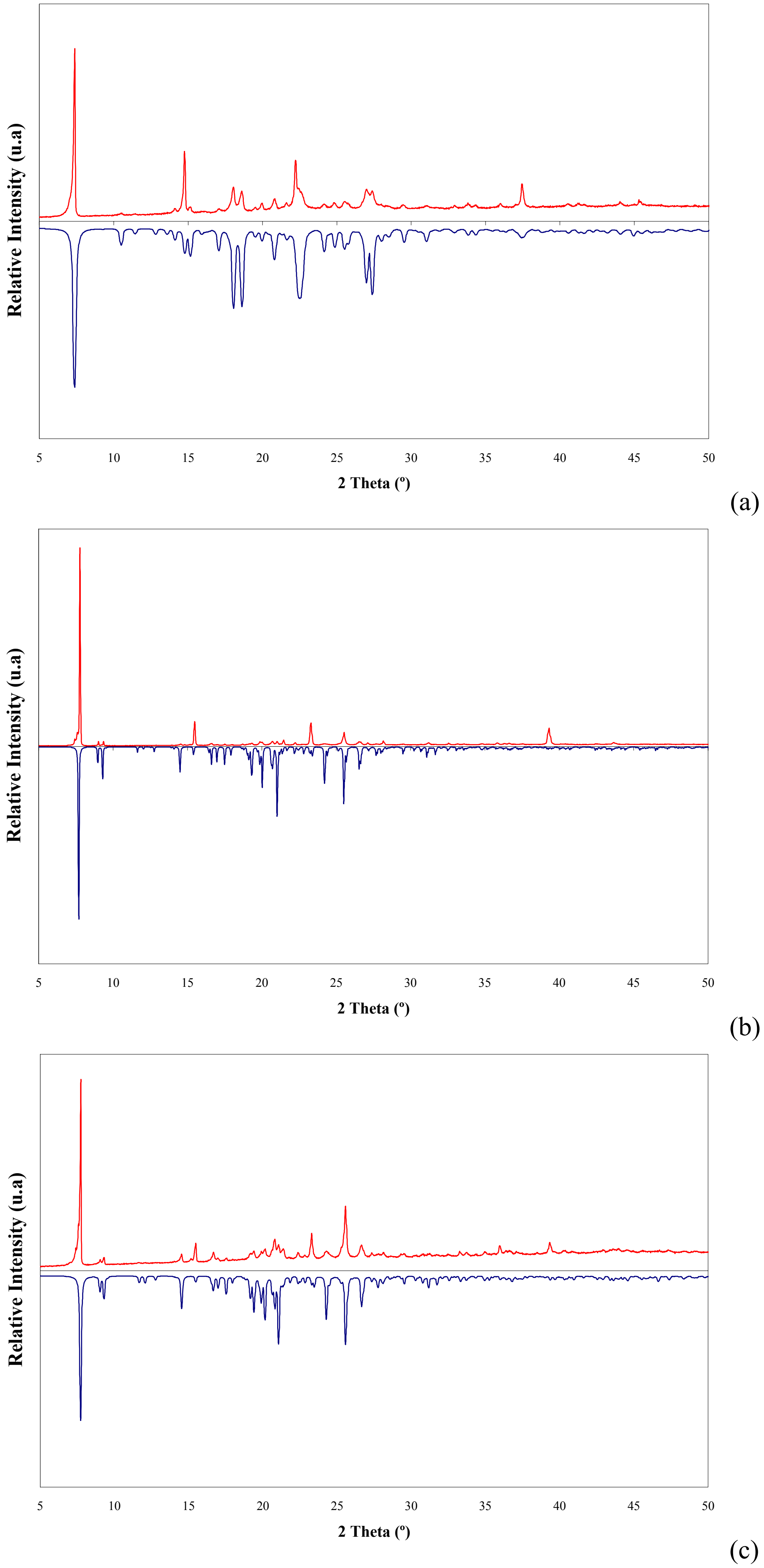


Figure S3. FT-IR spectra of compound **3**: (a) fresh sample, (b) sample irradiated with 302 nm using a Pyrex filter, (c) sample irradiated with unfiltered UV light at 302 nm.

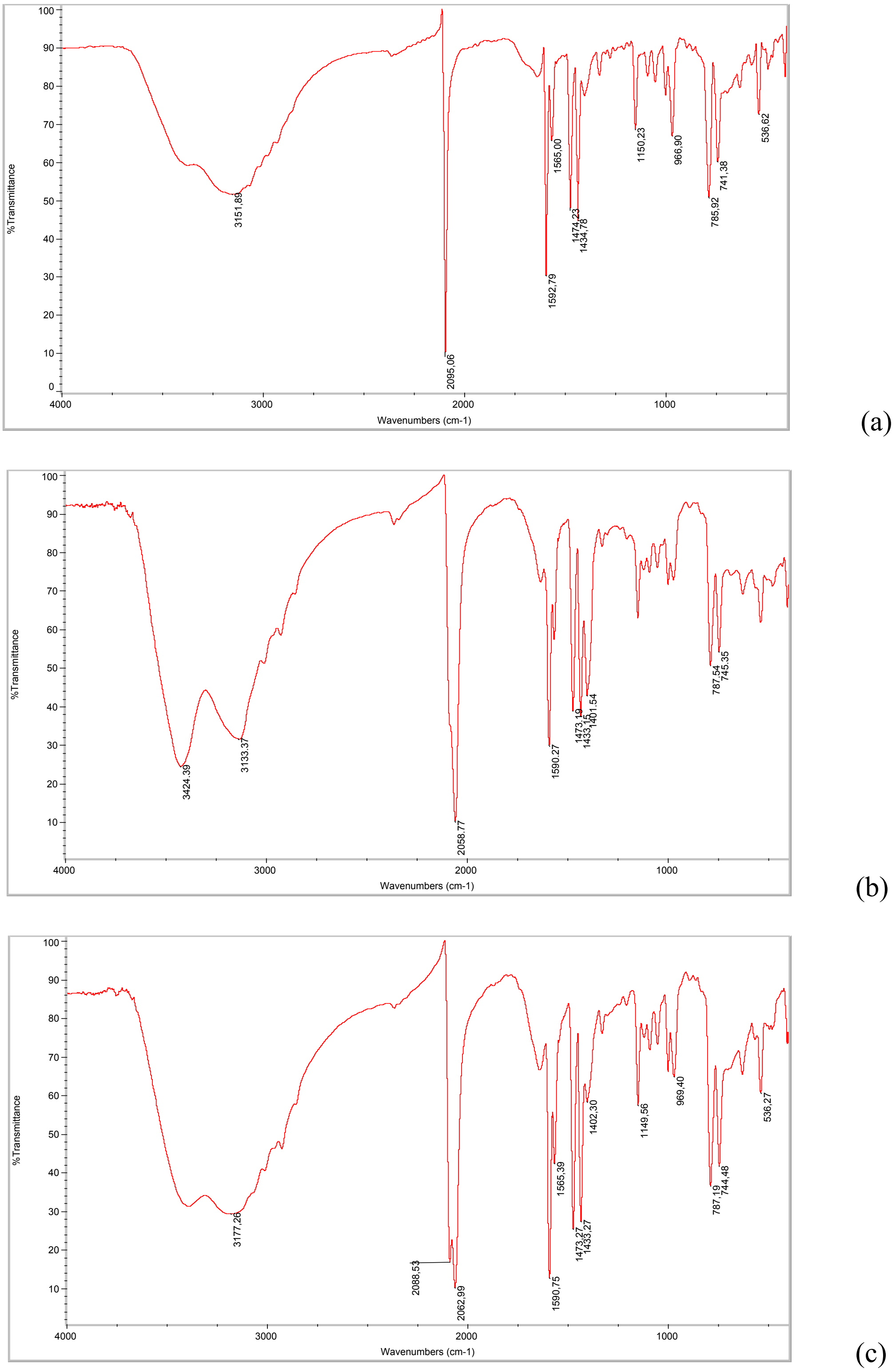


Figure S4. FT-IR spectra of compound **2**: (a) fresh sample (blue line), (b) sample irradiated with unfiltered UV light at 302 nm (red line).

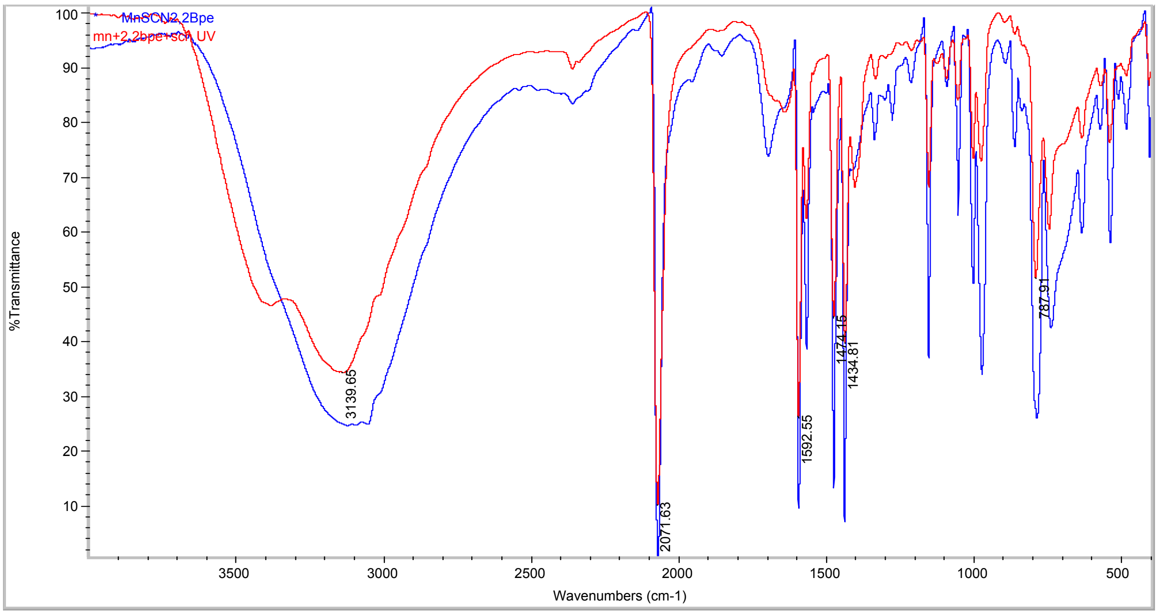


Figure S5. Comparative view of the building blocks found in the crystal structures of the supramolecular isomer **1** (a) and **2** (b). Hydrogen atoms of the bipyridines are omitted for clarity.

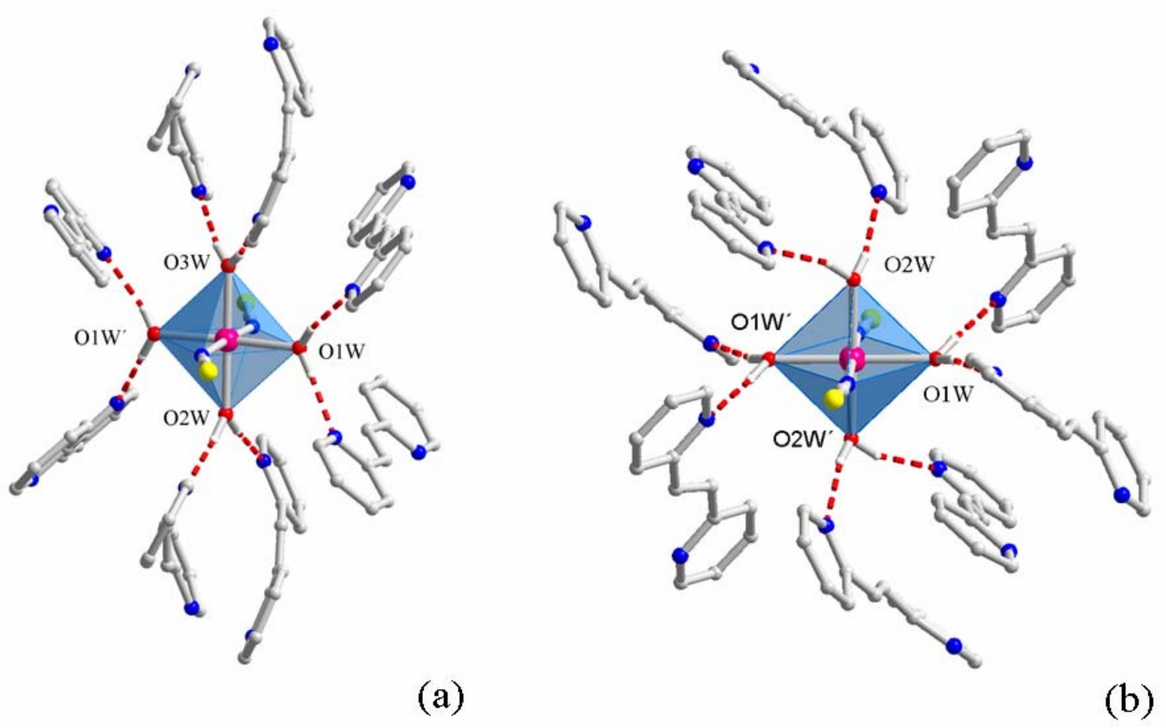
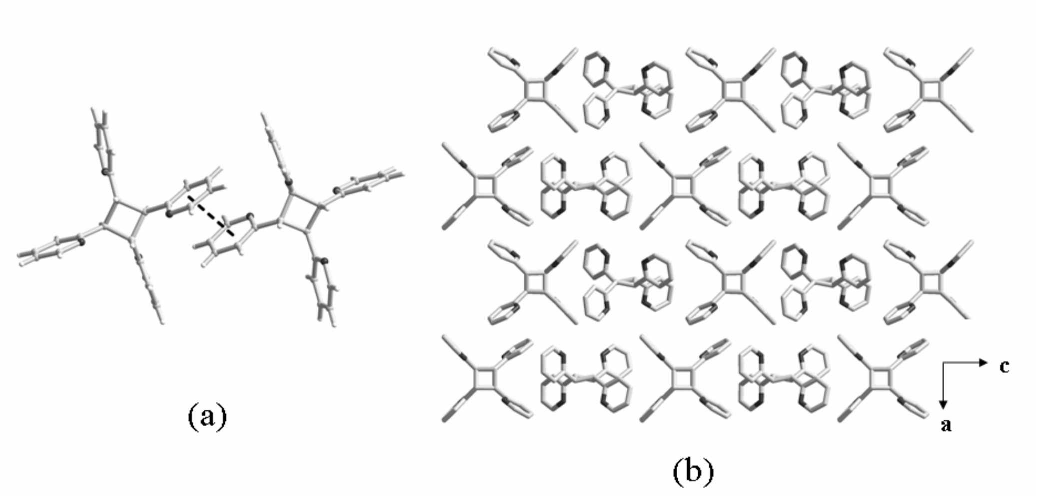


Figure S6. (a) Interaction between the molecules of the *rtct*-tpcb isomer in the crystal structure of **4**. (b) View of the crystal structure in the *ac* plane.



(a)

(b)