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## Exploiting the use of hydrogen bonding and metal-coordination in the self-assembly of photoreactive multi-component networks

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## 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 patterns were recorded on a Siemens D5005 Diffractometer with Cu(K $\alpha$ ) (1.5418 Å) radiation, with a scan speed of 2 deg/min. These patterns showed that compounds **1-2** were obtained as pure single-phases (Fig. S1). The <sup>1</sup>H NMR spectra of the isolated products were recorded on a Bruker AVANCE-300 Spectrometer in CDCl<sub>3</sub>. The UV-vis spectra were recorded on a HP 8453 diode array instrument.

**Synthesis of [Mn(2,4-bpe)(OH<sub>2</sub>)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub>·2(2,4-bpe)·2H<sub>2</sub>O (**1**).** A solution of 2,4-bpe (200 mg, 1 mmol) in 20 mL of methanol was added to 30 mL of an aqueous solution of Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (126 mg, 0.5 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. S1a). Yield based on bpe: 85% (brown prisms). Anal. calcd. (%) for C<sub>48</sub>H<sub>52</sub>Cl<sub>2</sub>MnN<sub>8</sub>O<sub>14</sub>: C, 52.85; H, 4.81; N, 10.27. Found: C, 52.88; H, 4.37; N, 11;12. IR (cm<sup>-1</sup>): ν(O-H): 3600-3200, ν(C-C): 1610-1562, ν(C-N): 1470-1430, ν(Cl-O): 1083.

**Caution!** Perchlorate salts are potentially explosive and should only be handled in small quantities.

**Synthesis of [Mn(2,4-bpe)<sub>2</sub>(NCS)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>] (**2**).** A mixture of MnCl<sub>2</sub>·4H<sub>2</sub>O (98.99 mg, 0.5 mmol), NaSCN (88 mg, 1 mmol) and 2,4-bpe (200 mg, 1 mmol) in a molar ratio of 1:2:2 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 (Fig S1b). Yield 72% (Brown crystals). Anal. calcd. (%) for C<sub>26</sub>H<sub>24</sub>MnN<sub>6</sub>O<sub>2</sub>S<sub>2</sub>: C, 52.63; H, 4.23; N, 14.71; S, 11.22. Found: C, 54.15; H, 4.21; N, 14.96; S, 11.09. IR (cm<sup>-1</sup>): ν(O-H): 3600-3200, ν(NCS): 2090-2064, ν(C-C): 1608-1564, ν(C-N): 1435.

**Solid state reactivity.**

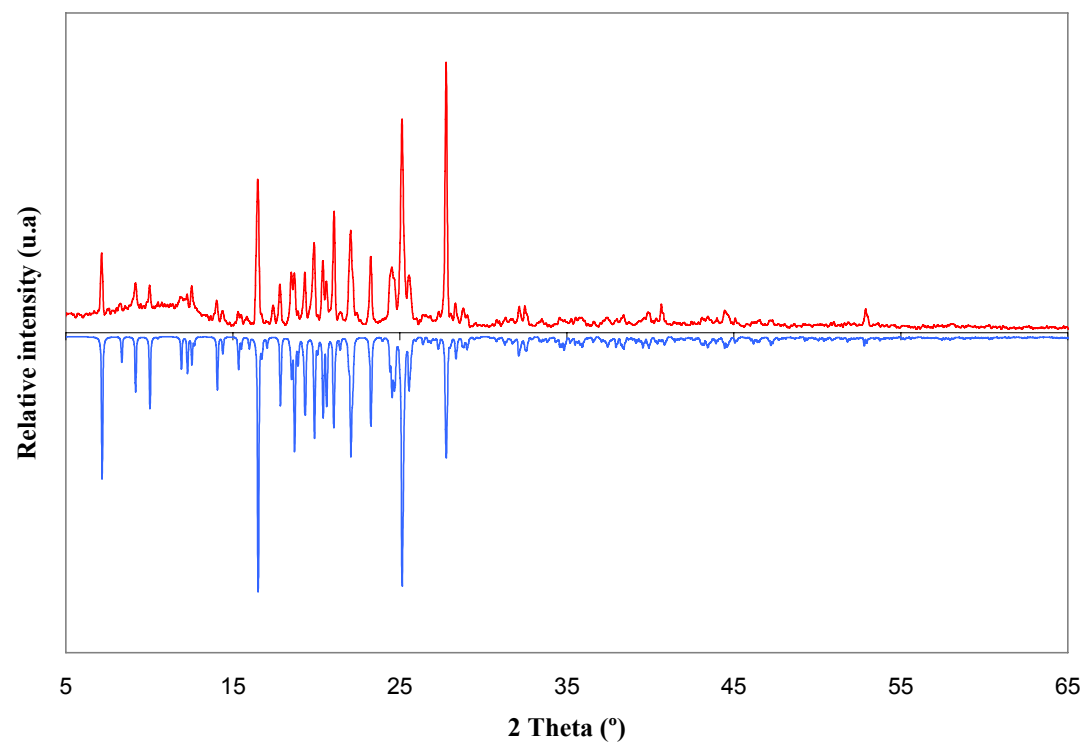
The *rctt*-1,3-bis(2-pyridil)-2,4-bis(4-pyridyl)cyclobutane [*rctt*-(2,4-tpcb-ht)] (**3**) was obtained by topochemical reaction from compound **1**. A powdered crystalline a of **1** was irradiated with a Hg lamp at 302 nm during 3 days. The product **3** was isolated from the dissolution of **1** irradiated in a mixture H<sub>2</sub>O-CH<sub>2</sub>Cl<sub>2</sub> and after extraction with CH<sub>2</sub>Cl<sub>2</sub> (Yield: 100 %). Recrystallisation of **3** in a mixture of chloroform-DMSO at 35 °C gives suitable crystals for single crystal analysis (**3**). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ<sub>H</sub>(ppm): 8.43(H<sub>a</sub>, ddd), 8.29(H<sub>e</sub>, ddd), 7.42(H<sub>b</sub>, td), 7.01 (H<sub>d</sub>, dd), 6.97(H<sub>c</sub>, ddd;), 4.86 (H<sub>g</sub>, td), 4.70(H<sub>h</sub>, td).

The *rttt*-tetrakis(2-pyridyl)cyclobutane isomer (*rttt*-tpcb-ht) (**4**) was obtained from **2** after irradiated and heated in H<sub>2</sub>O/Methanol under reflux. Yield: 40-42%. Recrystallisation of **2** in DMSO gives suitable crystals of compound [Mn(*rttt*-2,4-tpcb-ht)<sub>4</sub>(NCS)<sub>2</sub>] for single crystal analysis (**4**).

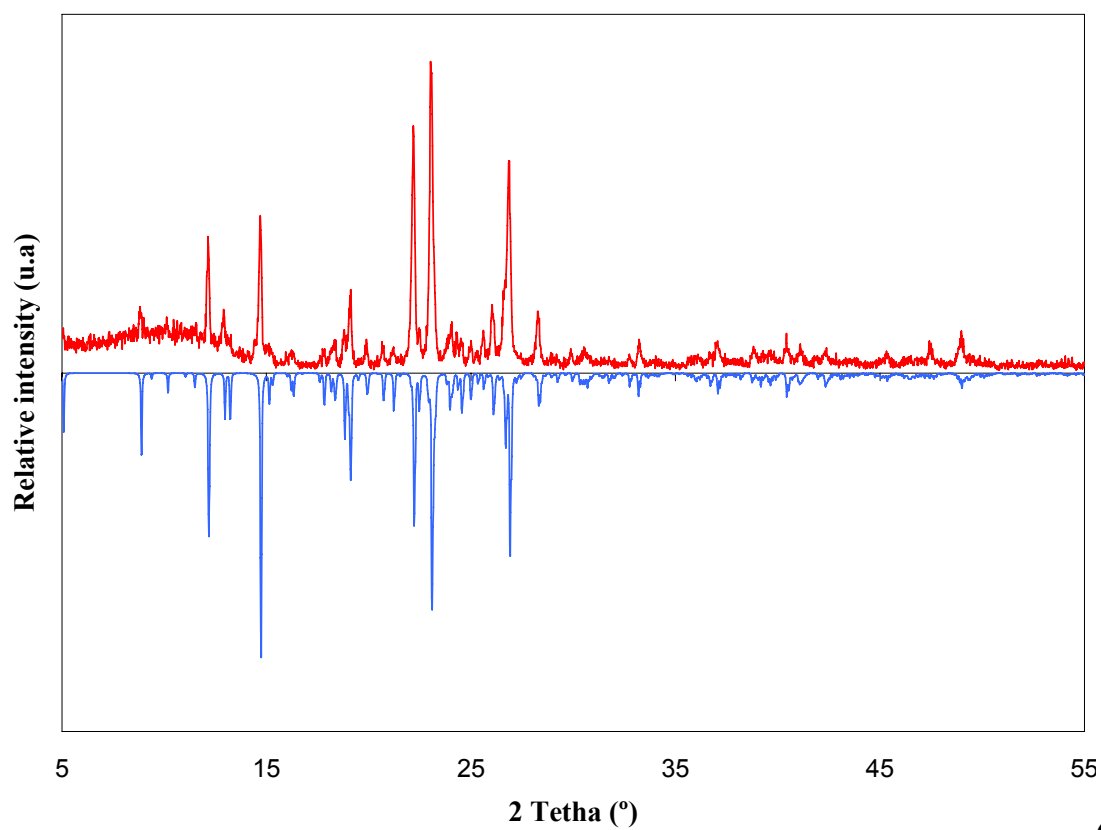
**Crystal structure determination.** Intensity data were recorded at room temperature on a Rigaku AFC-7S diffractometer equipped with a CCD bidimensional detector using monochromated Mo(Kα) radiation (λ = 0.71073 Å). An empirical absorption correction (multi-scan) was applied using the package CrystalClear. The structures were solved by Direct Methods and refined by full-matrix least-squares on *F*<sup>2</sup> using the SHELXTL-PLUS package. 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 × *U*<sub>eq</sub> of the attached atom. In the structure **1** the ClO<sub>4</sub><sup>-</sup> anion displayed highly anisotropic thermal motion and was modelled as disordered in two set of positions and these were refined isotropically constraining Cl-O distances to 1.400(3) Å. In the structure **2**, one of the bipyridine molecules was found to be disordered and was modelled in two sets of positions. The pyridyl rings were refined as rigid groups. In the structure **4**, the NCS<sup>-</sup> ligand was also found disordered in two sets of positions.

**Note:** The terms *rctt* and *rttt* are used by the IUPAC for indicating the relative orientation (*cis* o *trans*) of the substituent on the cyclobutane ring with regard to reference group (*r* = reference group, *c*= *cis* and *t*= *trans*).

**Figure S1.** Experimental (red) and theoretical (blue) XRD patterns: (a) compound **1** and (b) compound **2**. Both patterns are affected by preferred orientation.

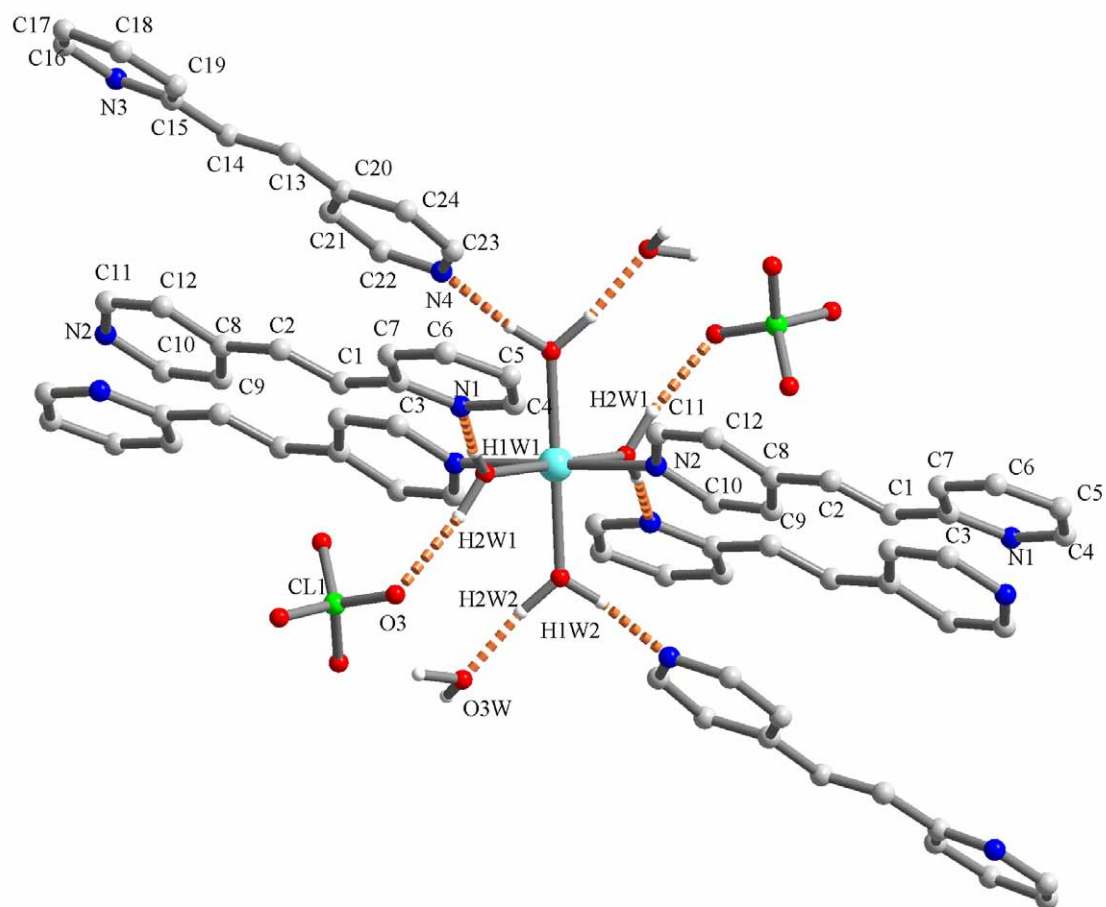


(a)

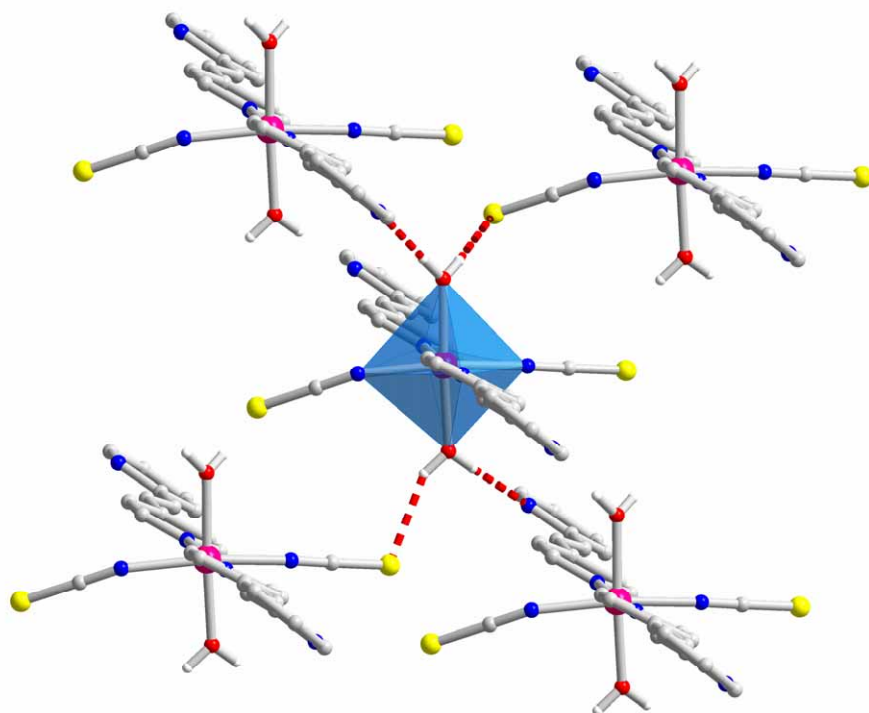


(b)

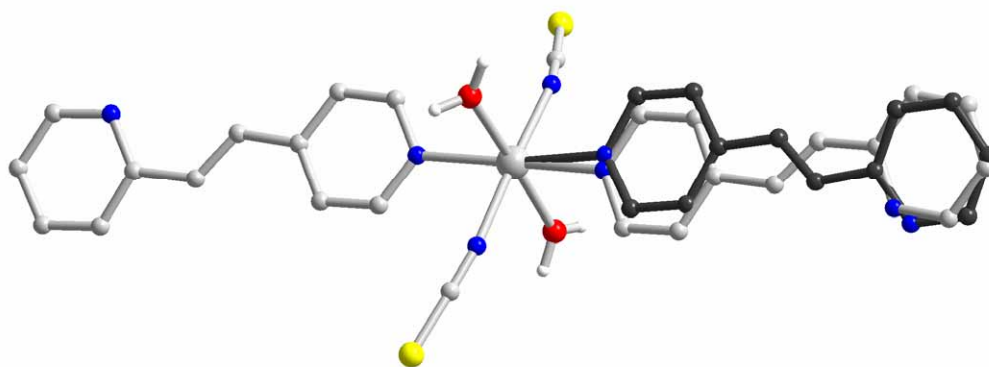
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**Figure S3.** View of the hydrogen bonding interactions around metal complex  $[\text{Mn}(2,4\text{-bpe})_2(\text{NCS})_2(\text{OH}_2)_2]$  in the crystal structure of **2**. (b) Molecular structure of **2**, showing disordered coordinated 2,4-bpe molecule. Hydrogen atoms of the bipyridines are omitted for clarity.

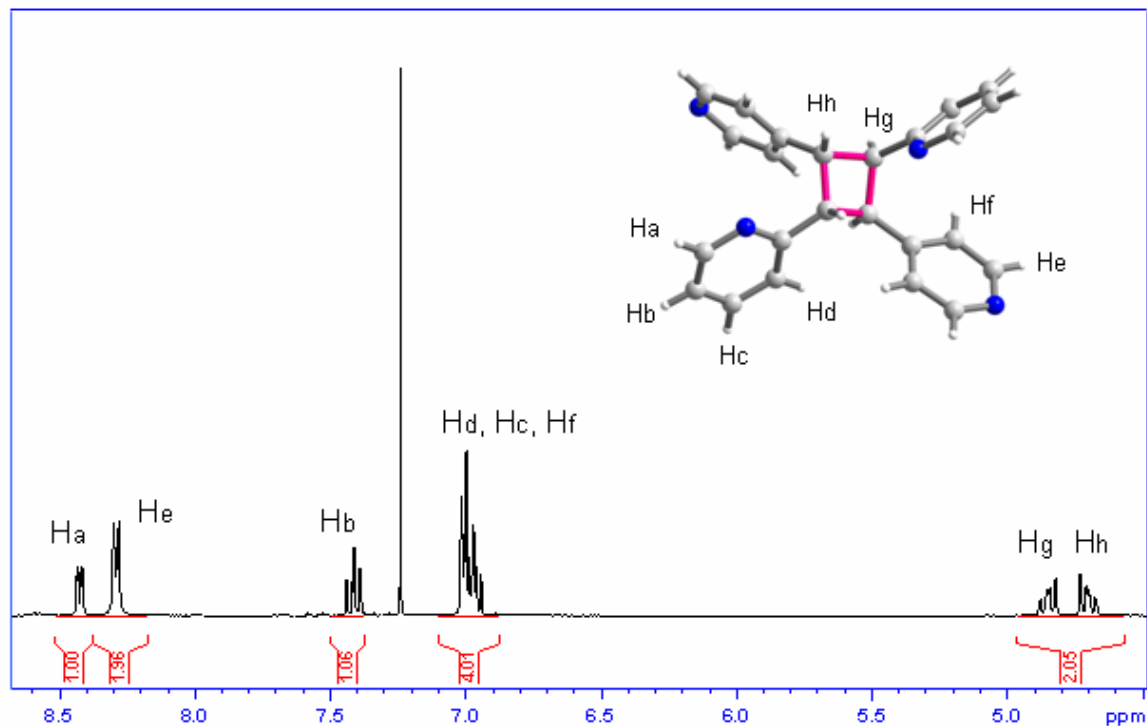


(a)

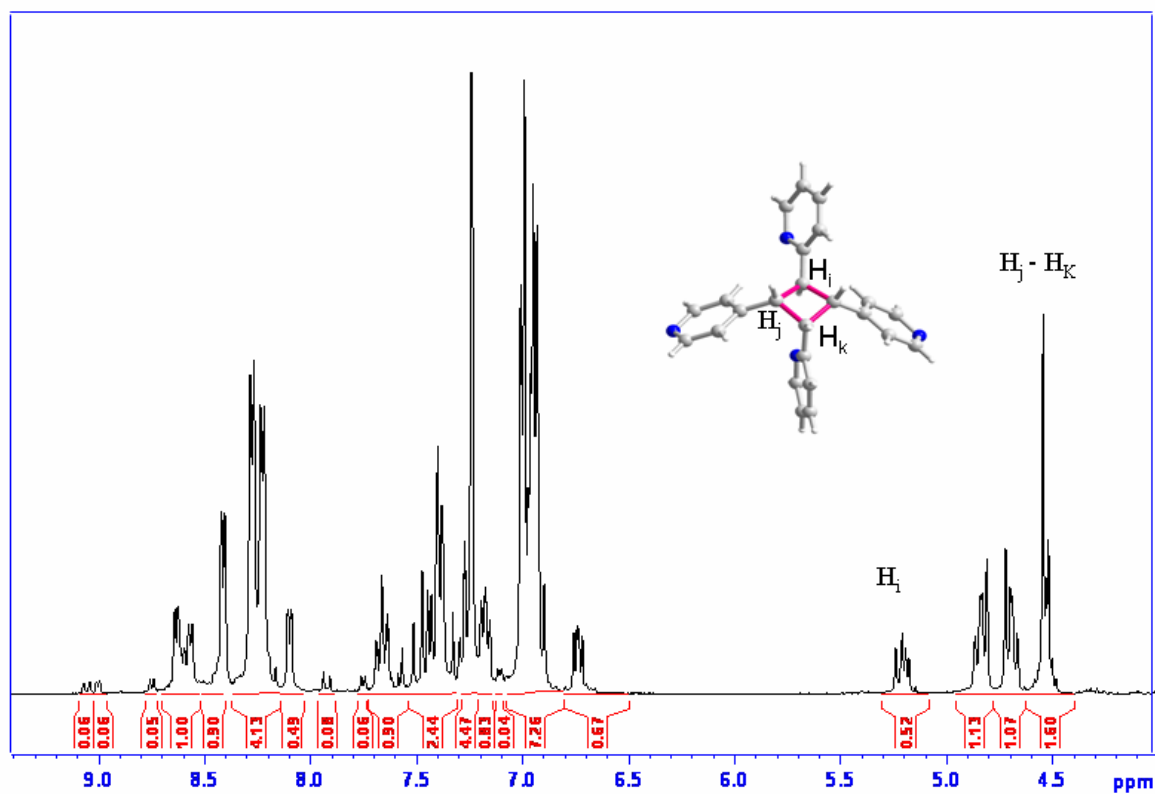


(b)

**Figure S4.** (a)  $^1\text{H}$  NMR spectrum of the *rc*tt-2,4-tpcb-ht isomer obtained from the photoreaction of compound **1**. (b)  $^1\text{H}$  NMR spectrum of the mixture of *rc*tt-2,4-tpcb-ht and *rt*tt-2,4-tpcb-ht isomers obtained from the photoreaction of compound **2** when heated in  $\text{H}_2\text{O}/\text{Methanol}$ .

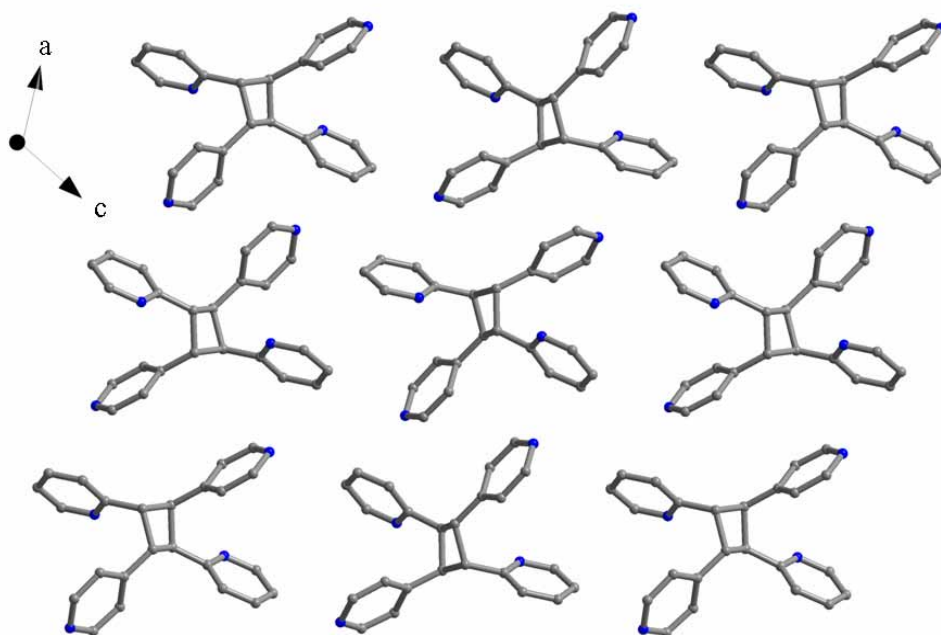


(a)

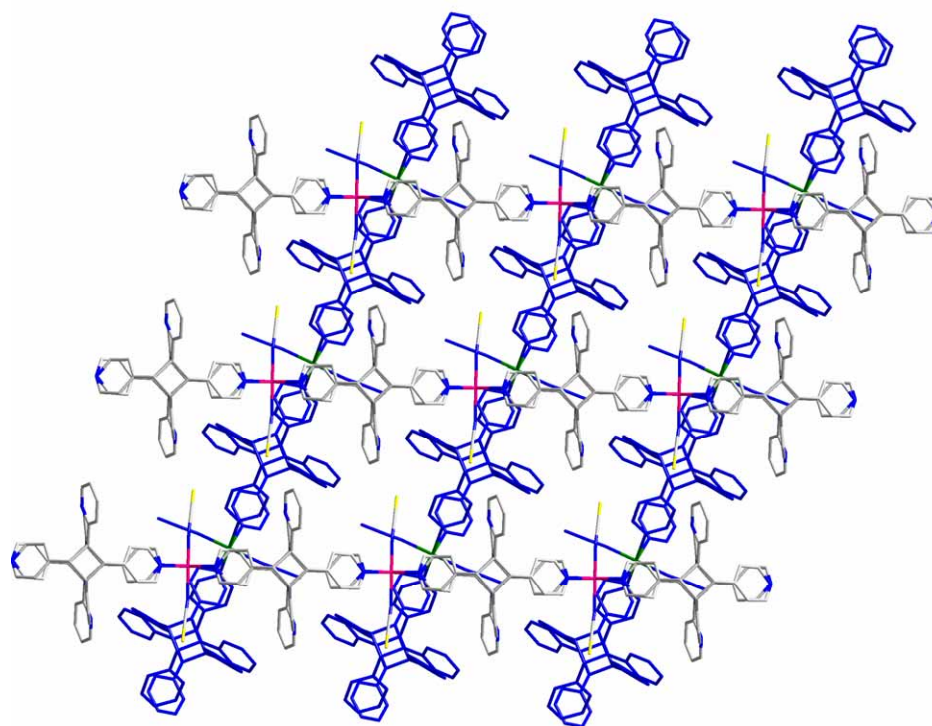


(b)

**Fig. S5.** View of the crystal structure of **3** in the *ac* plane

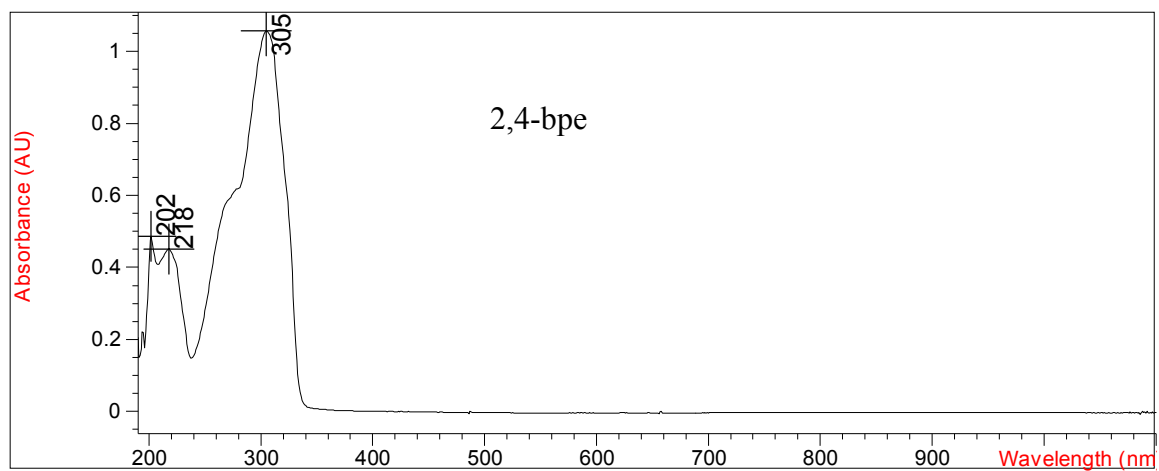


**Figure S6.** View of the relative orientation and stacking of neighboring 1D chains in the crystal structure of **4**

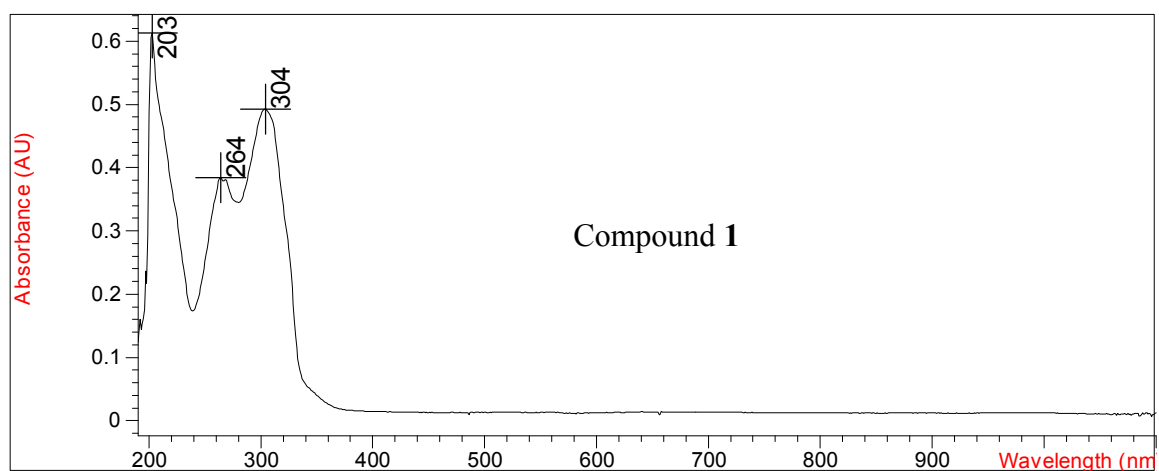




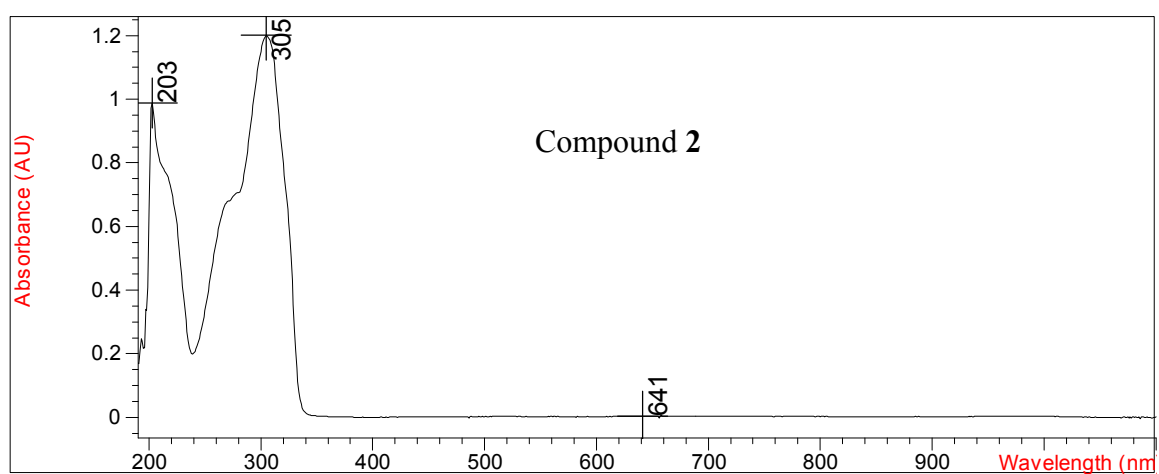
**Figure S7.** UV-vis absorption spectra in Methanol: 2,4-bpe (a), Compound **1** (b) and Compound **2**.



(a)



(b)



(c)