

Supplementary Material

Concomitant [2+2] cycloaddition solid state reactions from co-crystals self-assembled via mechanochemistry

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Figure S2. (a) ¹H NMR of the mixture of products obtained from the photoreaction of compound **2**, where **ca**: citraconic acid; **cbta-ma**: dimer formed from **ma**. (b) ¹H NMR spectrum of the mixture of pyridylcyclobutanes stereoisomers isolated from the irradiation of **2**. The inset shows the structures of the different isomers *rctt* (a), *rtct* (b) and *rcct* (c).

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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(K α) (1.5418 Å) radiation, with a scan speed of 2 deg/min. The ^1H NMR spectra were recorded on a Bruker AVANCE-300 Spectrometer in CDCl_3 . The UV-vis spectra were recorded on a HP 8453 diode array instrument.

Preparation of (1). A solution of *trans*-1,2-bis(2-pyridyl)ethylene (**2,2'-bpe**) (200 mg, 1 mmol) in 20 mL of methanol was added to 25 mL of a solution of fumaric acid (**fa**) (128 mg, 1 mmol) and allowed to stir for 15 min. Slow evaporation of the resulting solutions at room temperature gave crystals of good quality for X-ray single crystal analysis. Yield based on 2,2'-bpe: 85% (pale yellow prisms). The XRD pattern showed that **1** can be also obtained as a highly pure single-phase from direct co-grinding of the starting compounds for a period of 5-10 min (solvent-free) (Fig 1(a)). Anal. calcd. (%) for $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4$: C, 64.36; H, 4.69; N, 9.39. Found: C, 64.28; H, 4.22; N, 9.55. IR (cm^{-1}): $\nu(\text{C-H})$: 3068, $\nu(\text{C=O})$: 1704, $\nu(\text{C=C, C=N})$: 1600-1485, $\nu(\text{C-O})$: 1286, $\nu(\text{C-H})$: 990.

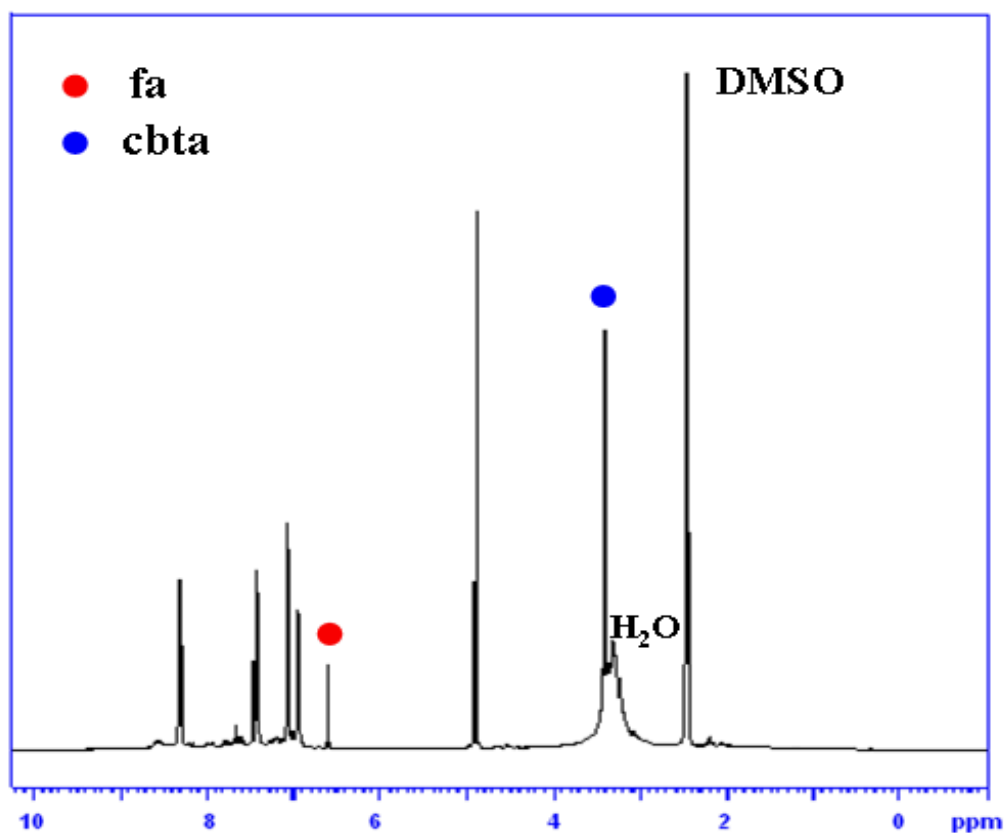
Preparation of (2). A solution of 2,2'-bpe (200 mg, 1 mmol) in 20 mL of methanol was added to 25 mL of a solution of mesaconic acid (**ma**) (143 mg, 1 mmol) and allowed to stir for 15 min. Slow evaporation of the resulting solutions at room temperature gave crystals of good quality for X-ray single crystal analysis. Yield based on 2,2'-bpe: 67% (pale yellow prisms). The XRD pattern showed that **2** can be also obtained as a highly pure single-phase via liquid-assisted grinding for a period of 5-10 min, adding water in stoichiometric proportion (Fig 1(b)). Anal. calcd. (%) for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_5$: C, 61.76; H, 5.45; N, 8.48. Found: C, 61.82; H, 5.28; N, 8.83. IR (cm^{-1}): $\nu(\text{O-H})$: 3600-2900, $\nu(\text{C=O})$: 1700, $\nu(\text{C=C})_{\text{acid}}$: 1645, $\nu(\text{C=C, C=N})_{2,2'\text{-bpe}}$: 1600-1476, $\nu(\text{C-O})$: 1244, $\nu(\text{C-H})$: 985.

Solid state reactivity.

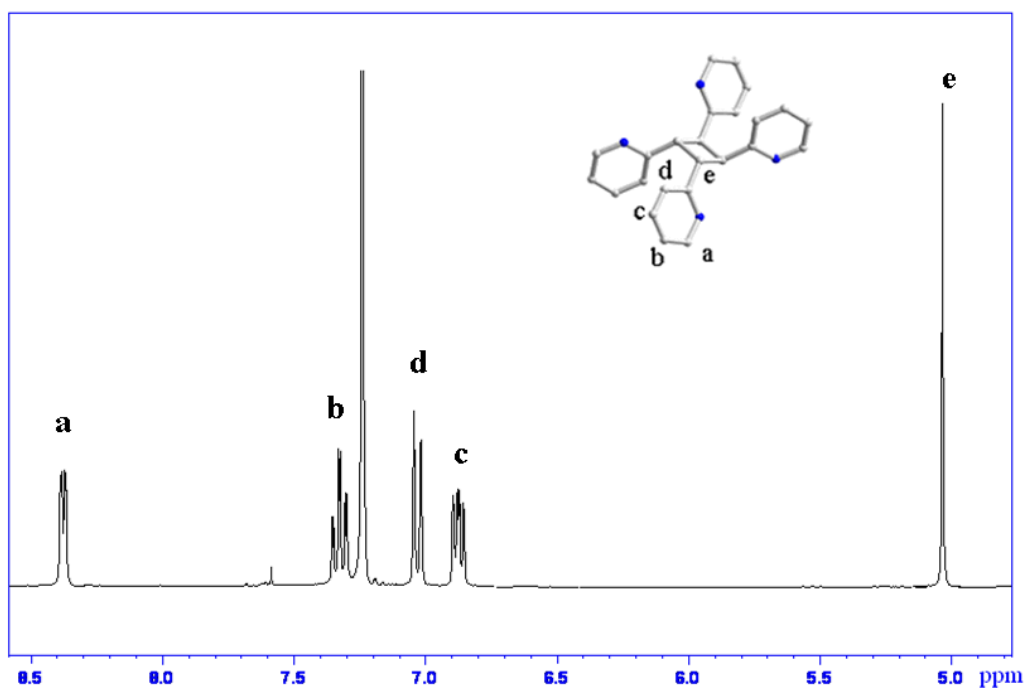
The reactivity of compounds **1-2** was studied upon irradiation with a UV light. A powdered crystalline (50 mg) and crystals of **1-2** were irradiated at different wavelengths (254, 302 and 356 nm) during 2 days. The irradiated samples were characterised by ^1H NMR spectroscopy for monitoring the respective topochemical transformations. The *rctt*-tetrakis(2-pyridyl)cyclobutane isomer (*rctt*-tpcb) was obtained by reaction from the compounds **1** or **2** in high yield (75-98%). This compound was isolated from an extraction with CH_2Cl_2 after the neutralization of the component acid with NaOH in either case. ^1H 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 $\text{Mo}(\text{K}\alpha)$ radiation ($\lambda = 0.71073 \text{ \AA}$). 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 carbon atoms were placed at fixed positions using the HFIX instruction. H-atoms on coordinated water molecules and carboxylic groups were found from the Difference Fourier map. They were refined with isotropic displacement parameters set to $1.2 \times U_{\text{eq}}$ of the attached atom. In the structure **2**, one bipyridine molecule was found to be disordered and was modelled in two sets of positions and constraining the pyridyl rings to be regular hexagons. The occupational parameters were determined to be 50:50.

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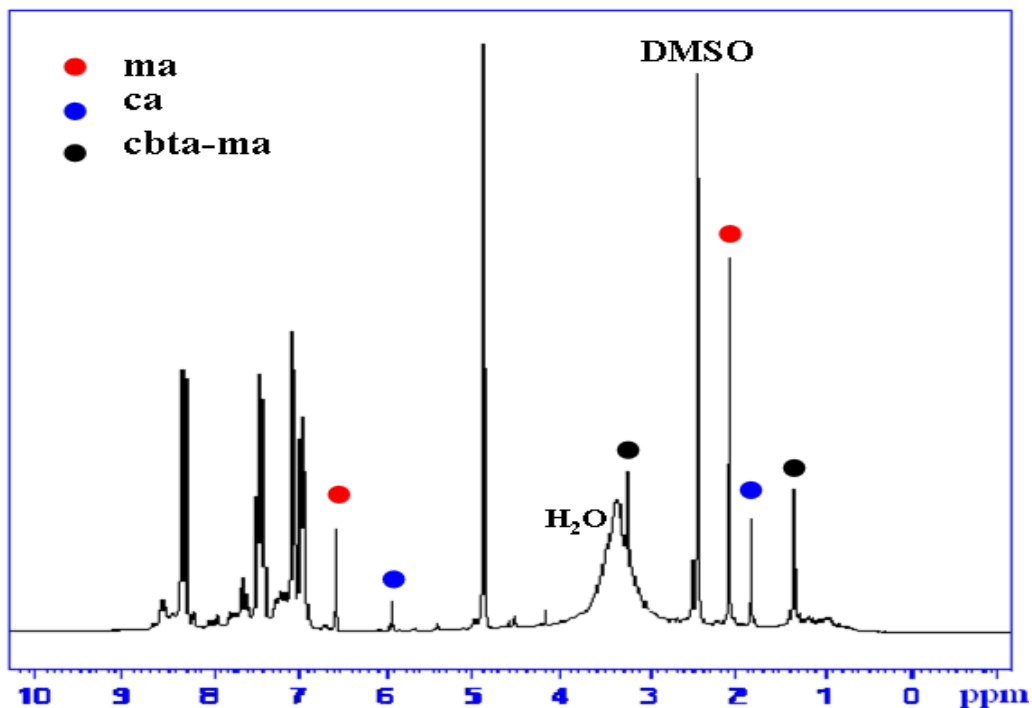


(a)

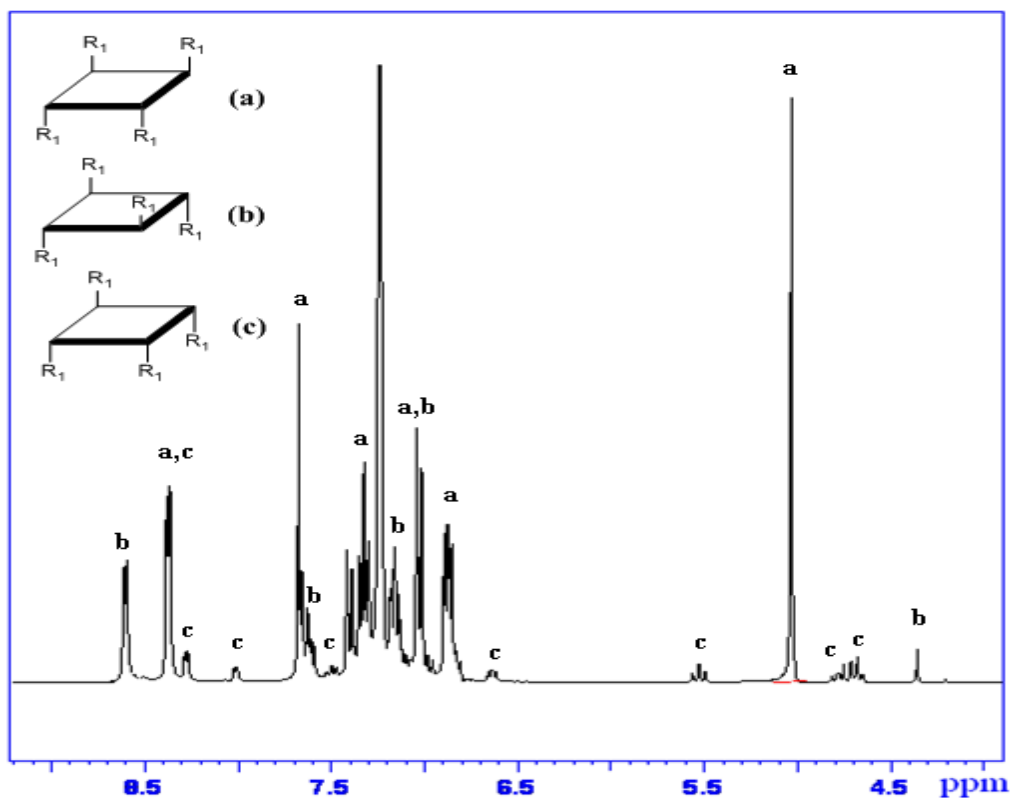


(b)

Figure S2. (a) ^1H NMR of the mixture of products obtained from the photoreaction of compound **2**, where **ca**: citraconic acid; **cbta-ma**: dimer formed from **ma**. (b) ^1H NMR spectrum of the mixture of pyridylcyclobutanes stereoisomers isolated from the irradiation of **2**. The inset shows the structures of the different isomers *rect* (a), *rtct* (b) and *recc* (c).



(a)



(b)

Figure 3. UV-visible absorption spectra in Methanol for fumaric, mesaconic and 2,2'-bpe.

