A new ligand for metal organic framework and co-crystal synthesis: Mechanochemical route to \textit{rctt}-1,2,3,4-tetrakis-(4'-carboxyphenyl)-cyclobutane

Goutam Kumar Kole,\textsuperscript{a} Lip Lin Koh,\textsuperscript{a} So Young Lee,\textsuperscript{b} Shim Sung Lee,\textsuperscript{b} and Jagadese J. Vittal\textsuperscript{a, b}\textsuperscript{*}

\textsuperscript{a}Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore-117543. E-mail: chmjjv@nus.edu.sg; Fax: +65 6779 1691; Tel: +65 6516 2975

\textsuperscript{b}Department of Chemistry and Institute of Natural Science, Gyeongsang National University, Jinju 660-701, South Korea

Supporting Information

Experimental section:

Materials: \textit{Trans}-4,4'-stilbenedicarboxylic acid (H\textsubscript{2}SDC) was synthesized via dehydro-dimerization reaction, reported in literature.\textsuperscript{1} 1,3-Diamino propane (DAP) was purchased from Acros and was used without further purification.

The NMR spectra were recorded with a Bruker ACF 300FT-NMR spectrometer with TMS as internal reference. ESI-MS spectra were recorded for the cyclobutane derivatives in negative ion mode from methanol solution (\textless 50 \mu g.mL\textsuperscript{-1}) with Finnigan MAT LCQ Mass Spectrometer by the syringe-pump method. Thermogravimetric analyses (TGA) were carried out on a TA Instrument SDT 2960 TGA Thermal Analyzer. The samples were heated at a constant rate of 5\degree C min\textsuperscript{-1} from room temperature and the atmosphere was maintained with continuous flow of nitrogen. Elemental analyses were performed in the Micro-analytical Laboratory, Department of Chemistry, National University of Singapore. Powder X-ray diffraction (PXRD) patterns were obtained by using a D5005 Bruker X-ray diffractometer equipped with Cu K\alpha radiation (\lambda = 1.5410 \text{\AA}). The accelerating voltage and current were 40 KV and 40 mA respectively.
**UV irradiation:**

The UV irradiation experiments were conducted by using Luzchem photoreactor (wavelength 350nm, Intensity ~ 1.75 mW-cm$^{-2}$). ~ 20 mg of the finely powdered sample was packed gently between two pyrex glass slides and the UV irradiations were completed by flipping the packed glass slide pairs for each sample in half of their irradiation time interval to ensure uniform irradiation.

**X-ray Crystallography:**

Single Crystals suitable for data collection were chosen under an optical microscope, mounted on glass fibre, and frozen under a stream of cryogenic nitrogen gas before data collection. Intensity data for 1-3 were collected on a Bruker APEX diffractometer attached with a CCD detector and graphite-monochromated MoKα (λ = 0.71073 Å) radiation. On the other hand, the data for 4 were collected on a Bruker SMART APEX II ULTRA diffractometer attached with a CCD detector and graphite-monochromated MoKα (λ = 0.71073 Å) radiation. Empirical absorption corrections were applied with the data using the program SADABS$^2$ and the crystallographic package SHELXTL$^3$ was used for all calculations. In 1, the positional and isotropic thermal parameters of all the N-H and O-H hydrogens were refined in the model. One of the bpe ligand and methanol are disordered in 3. The site occupancy of the CH$_3$OH was refined to 66.4(8)%. The site occupancy of the bpe was fixed at 0.5 and only the isotropic thermal parameters of the C’s were refined. In 4, the systematic extinction was not clear. Structure was eventually solved in Pbam. Attempt to solve the structure in space groups of lower or other symmetry failed to give better solution. The asymmetric unit contains half a Zn and quarter of the anion. All groups except the Zn and carboxylate groups are disordered. In other words, the tetracarboxyphenylcyclobutane, solvent DMF and dimethylamine oxide are disordered. The large extent of disorder has resulted in difficulty in refinement. Large extent of restraints, including bond lengths and thermal parameters, were applied. But the connectivity in the structure is proved beyond any doubt despite the disordered structure in 4. The neutral ligand dimethylamine may be produced by the oxidation of DMF by H$_2$O$_2$ under hydrothermal conditions. In any case a small amount of dimethylamine is found as impurity in DMF which can be rationalized from its smell also.
Synthesis:

Synthesis for 1: \text{H}_2\text{SDC} (0.268 g, 1 mmol) was dispersed in 25 ml of water and \text{DAP} (0.074 g, 1 mmol) was added dropwise to dissolve all the \text{H}_2\text{SDC}. The clear aqueous solution was allowed to evaporate slowly. Colourless block like single crystals were separated out in 2 days. Crystals were filtered and dried in air. Yield: 0.30 g, 87%. Analysis found: C, 63.24; H, 6.60; N, 7.81, \text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_5 requires: C, 63.32; H, 6.71; N, 7.77%. \textsuperscript{1}H NMR (300 MHz, D\textsubscript{2}O, 298K): \delta = 7.83 (d, 4H, Ar-H), 7.62 (d, 4H, Ar-H), 7.32 (s, 2H, CH=CH), 3.01 (t, 4H, CH-CH), 1.97 ppm. (q, 2H, CH-CH).

Synthesis for 2: A mixture of \text{H}_2\text{SDC} (0.268 g, 1 mmol), \text{DAP} (0.074 g, 1 mmol) and few drops of water were ground well for 20 minutes on an agate mortar. The mixture was dried and packed in between two glass slides and then irradiated under UV (Luzchem photo reactor, using the wavelength 350 nm) for 30 h. After irradiation, the product was dissolved in water and acidified while hot, with dilute HCl to precipitate the dimer. The crude product was dried under reduced pressure and recrystallized from methanol. Analysis for 2: \text{C}_{32}\text{H}_{24}\text{O}_8.2\text{H}_2\text{O} (see Fig. S14) requires C, 67.12; H, 4.93; analysis found C, 66.99; H, 4.88%. \textsuperscript{1}H NMR (300 MHz, d\textsubscript{6}-DMSO, 298K): \delta = 7.70 (d, 8H, Ar-H), 7.33 (d, 8H, Ar-H), 4.71 ppm. (s, 4H, CH-CH). m/z 535.4 represents (M-1) peak in ESI-MS (Fig. S13).

Synthesis for 3: \text{TCCB} (0.268 g, 0.5 mmol) in 10 ml methanol was carefully layered over bpe (0.09 g, 0.5 mmol) in 5 ml methanol in a very long test tube. Colourless block like single crystals were separated in 2 days on the wall of the test tube. Yield: 0.22 g, 58%. Analysis for \text{C}_{45}\text{H}_{38}\text{O}_9\text{N}_2 requires C, 71.99; H, 5.10; N, 3.73; analysis found C, 71.73; H, 5.06; N, 3.71%.

Synthesis for 4: \text{TCCB} (0.0268 g, 0.05 mmol), \text{Zn(NO}_3\text{)_2.6H}_2\text{O} (0.0298 g, 0.1 mmol) and a few drops of \text{H}_2\text{O}_2 in 8ml DMF were heated at 105\degree C in a scintillation vial for 30h and then were cooled very slowly for 15h. Colourless single crystals were separated by filtration. Yield 0.032 g, 69%. Analysis found for the dried sample: C, 53.85; H, 4.61; N, 3.63, [\text{Zn}_2(\text{C}_{32}\text{H}_{20}\text{O}_8)(\text{C}_2\text{H}_7\text{NO})_2] requires C, 55.06; H, 4.33; N, 3.57%. A small discrepancy in the elemental analysis may be attributed to the incomplete removal of DMF on drying.
Fig. S1. $^1$H NMR (300 MHz, DMSO-$d_6$) spectrum of trans-4,4'-stilbenedicarboxylic acid (H$_2$SDC).

Fig. S2. $^1$H NMR spectrum (300 MHz, D$_2$O) of the ground powder of 1 before UV irradiation.
Fig. S3. $^1H$ NMR spectrum (300 MHz, D$_2$O) of the same ground powder after 30 h of irradiation showing quantitative dimerization.
Fig. S4. $^1$H NMR spectrum (300 MHz) of the ground powder of 1 in D$_2$O after 12 h of irradiation in solution phase showing a mixture of products formation.

Fig. S5. Thermogravimetric analysis for the salt 1. 5.2% wt. loss above 100 °C shows strong hydrogen bonding interactions present in the lattice.
Fig. S6. Supramolecular synthons that play the key role to construct the solid-state architecture in 1 and hence the parallel orientation of SDC anions.

Fig. S7. H-bonded motifs in the crystal structure of 1.

Fig. S8. A view of packing along b-axis shows that the components are packed in zigzag manner in 1.
Fig. S9. PXRD patterns of the ground powder of 1: before and after UV irradiation. Considerable loss of crystalinity was observed.

Fig. S10. Percentage conversion vs. time (kinetics) plots for single crystals and ground powder of 1. Slight faster kinetics for the ground powder might be due to the smaller particle size and hence larger surface area.
Fig. S11. $^1$H NMR (300 MHz, DMSO-$d_6$) spectrum of the dimerized product, $rctt$-TCCB.

Fig. S12. $^{13}$C NMR (300 MHz, DMSO-$d_6$) spectrum of the dimerized product, $rctt$-TCCB.
Fig. S13. ESI-Ms spectrum of TCCB [m/z 535.4 represents (M-1) peak].

Fig. S14. Thermogravimetric analysis (TGA) of TCCB shows the presence water molecule with dimerized product. 6.7% water loss below 100°C proves the co-existence of two water molecules with each dimer molecule and hence it supports for the correct elemental analysis.
Fig. S15. This picture shows the supramolecular synthons that construct the solid state architecture in the co-crystal 3 and the H-bonded motifs are also identified.

Fig. S16. (4, 4) Connected puckered nets showing diagonal/diagonal inclined interpenetration in the co-crystal 3.

Figure S17. TGA plot of the dried co-crystal 3.
Fig. S18. $\text{^1}H$ NMR (300 MHz, DMSO-$d_6$) spectrum of the co-crystals 3. Integral values show the ratio of TCCB and bpe is 1:1.

Fig. S19. Secondary building unit (SBU) in 4.
Fig. S20. Two-dimensional planar structure of the compound 4. Disordered tetracarboxylate ligand is shown in two different colours and the disorder in DMF and dimethylamine oxide are not shown for clarity.

Fig. S21. Binodal (4,4) connected two dimensional nets found in 4. The length of the sides each window is 9.185 Å and the distance between these parallel nets is 7.077 Å.
Fig. S22. Experimental and simulated PXRD pattern of 4. Slight variation was observed due to the solvent loss during grinding.

Fig. S23. TGA plot of the dried (lattice solvent, DMF is removed) sample of metal complex 4. Calculated weight loss for the composition Zn$_2$(C$_{32}$H$_{20}$O$_8$)(C$_2$H$_7$NO)$_2$ is 15.4%; found 16.3%. The removal of dimethylamine oxide occurs after 180 °C as they are strongly coordinated to Zn(II) centres. The weight loss also indicates incomplete removal of DMF on drying.
Fig. S24. FT-IR spectrum of H₂SDC.

Fig. S25. FT-IR spectrum of TCCB shows considerable differences with the monomer in the finger print region.
Fig. S26. UV absorption spectra of SDCA and TCCB; \( \lambda_{\text{max}} \) for TCCB is shifted to the shorter wavelength (267 nm) than SDCA (330 nm).

Fig. S27. Photoluminescence spectra of SDCA and TCCB. The dimer emits at shorter wavelength than the monomer.

References

