Modular assembly of porous organic cage crystals: Isoreticular quasiracemates and ternary co-crystal

Srinu Tothadi, Marc A. Little, Tom Hasell, Michael E. Briggs, Samantha Y. Chong, Ming Liu, and Andrew I. Cooper*

This document contains Supplementary Figures, S1-S13.
1. Characterization and Supporting figures

![SEM Image](image1.png)

**Figure S1.** SEM images of quasiracemate, (FT-RCC3-R)-(CC1-S), crystallised from CH$_2$Cl$_2$/acetone.

![TGA Graph](image2.png)

**Figure S2:** TGA of quasiracemate, (FT-RCC3-R)-(CC1-S), crystallised from CH$_2$Cl$_2$/acetone.
Figure S3. Gas sorption isotherms of quasaracemate, (FT-RCC3-R)-(CC1-S), (a) CO₂ at 278 K, (b) CH₄ at 278 K, and (c) H₂ at 77 K. (FT-RCC3-R)-(CC1-S) was crystallised from CH₂Cl₂/acetone and activated by heating under vacuum at 90 °C. Closed and open symbols represent adsorption and desorption curves, respectively.
Figure S4. PXRD for quasiracemate, (FT-RCC3-R)-(CC1-S), recorded (a) before, and (b) after gas sorption. There is no phase change during gas sorption analysis indicating the materials is stable. Crystals obtained from DCM/Acetone (anti-solvent).
Figure S5. PXRD analysis of (a) **FT-RCC3-R**, (b) **CC13**, and (c) a phase mixture comprising **FT-RCC3-R** and **CC13**. All samples were crystallised from CH$_2$Cl$_2$/acetone.

Figure S6. SEM image of ternary co-crystal, (**CC3-S$_{0.3}$CC4-S$_{0.3}$**(CC13-S$_{0.5}$CC3-S$_{0.25}$CC4-S$_{0.25}$)), displaying octahedral crystal habit.
**Figure S7.** Displacement ellipsoid plot of the asymmetric unit from the single crystal structure, (CC3-S0.5CC4-S0.5)(CC13-S0.5CC3-S0.25CC4-S0.25)(H2O)11.92; residual H2O omitted for clarity. Ellipsoid are displayed at 50% probability level. Isotropically refined C atoms shown as spheres. H-atoms for the severely disordered C-H groups were not all refined as part of the asymmetric unit but the appropriate number of H atoms were included in the refined formula unit.
Figure S8. TGA for ternary co-crystal, \((\text{CC3-S}_{0.5}\text{CC4-S}_{0.5})\cdot(\text{CC13-S}_{0.5}\text{CC3-S}_{0.25}\text{CC4-S}_{0.25})\), crystallised from \(\text{CH}_2\text{Cl}_2/\text{acetone}\).
Figure S9. HPLC analysis for the single component cages CC1 (retention time: 2.76 mins.), CC3-S (7.52 mins.), CC4-S (6.97 mins.), CC13 (4.2 mins.) dissolved in CH$_2$Cl$_2$ (1.87 min). Column: Syncronis C8; 3 μm; 4.6 ×150 mm; mobile phase: isocratic MeOH; flow: 1.0 mL/min; oven temperature = 30 °C; detection λ = 254 nm. (For all single component and co-crystals same conditions are used). For quantitative analysis, 0.047 M solutions of CC1, CC13, CC4-S and CC3-S were prepared. Each cage solution was diluted to X/2, X/3, X/4, X/5 and X/6 and HPLC analysis was collected. Peak areas were used to calculate calibration curves which were used to calculate the relative concentration of each cage in a crystalline solid.
Figure S10. Quantitative HPLC analysis of ten single crystals of the ternary organic crystal, \((\text{CC}3\text{-}S_{0.5}\text{CC}4\text{-}S_{0.5})\cdot(\text{CC}13\text{-}S_{0.25}\text{CC}3\text{-}S_{0.25}\text{CC}4\text{-}S_{0.25})\), crystallised from \(\text{CH}_2\text{Cl}_2/\text{acetone}\). Triangles, circles, and squares represent percentage composition of \(\text{CC}3\text{-}S\), \(\text{CC}4\text{-}S\), and \(\text{CC}13\) respectively in the single crystals. The quantitative percentage composition of \(\text{CC}3\text{-}S\), \(\text{CC}4\text{-}S\), and \(\text{CC}13\) in the ternary crystals determined by HPLC analysis and is in good agreement with the refined single crystal structure.
Figure S11. Mass spectrum for a single crystal of the ternary organic solid, $(CC3-S_{0.5}CC4-S_{0.5})\cdot(CC13-S_{0.5}CC3-S_{0.25}CC4-S_{0.25})$ crystallised from CH$_2$Cl$_2$/acetone. m/z ratios correspond to: 961.6 [CC13+H]$^+$, 1033.6 [CC4-S+H]$^+$ and 1117.7 [CC3-S+H]$^+$. 
Figure S12. PXRD of ternary organic cocrystal, \((\text{CC}3-S_{0.5}\text{CC}4-S_{0.5})\cdot(\text{CC}13-S_{0.25}\text{CC}3-S_{0.25}\text{CC}4-S_{0.25})\), crystallised from \(\text{CH}_2\text{Cl}_2/\text{acetone}\), recorded (a) before and (b) after gas sorption analysis.
Figure 13. (a) Gas sorption analysis of ternary organic cocrystal, (CC3-S0.5CC4-S0.5)(CC13-S0.5CC3-S0.25CC4-S0.25), crystallised from CH2Cl2/acetone for (a) Xe, and (b) Kr.