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

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This document contains Supplementary Figures, S1-S13.

1. Characterization and Supporting figures

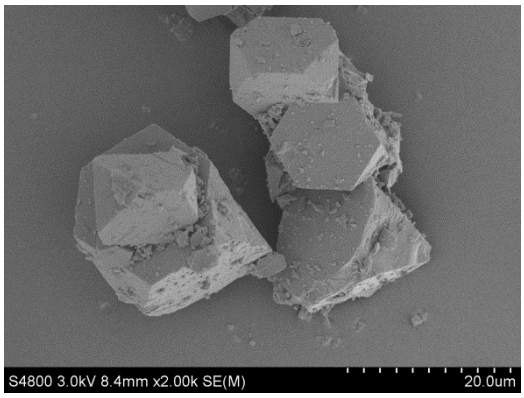

Figure S1. SEM images of quasiracemate, (**FT-RCC3**-*R*)·(**CC1**-*S*), crystallised from CH_2Cl_2/acetone.

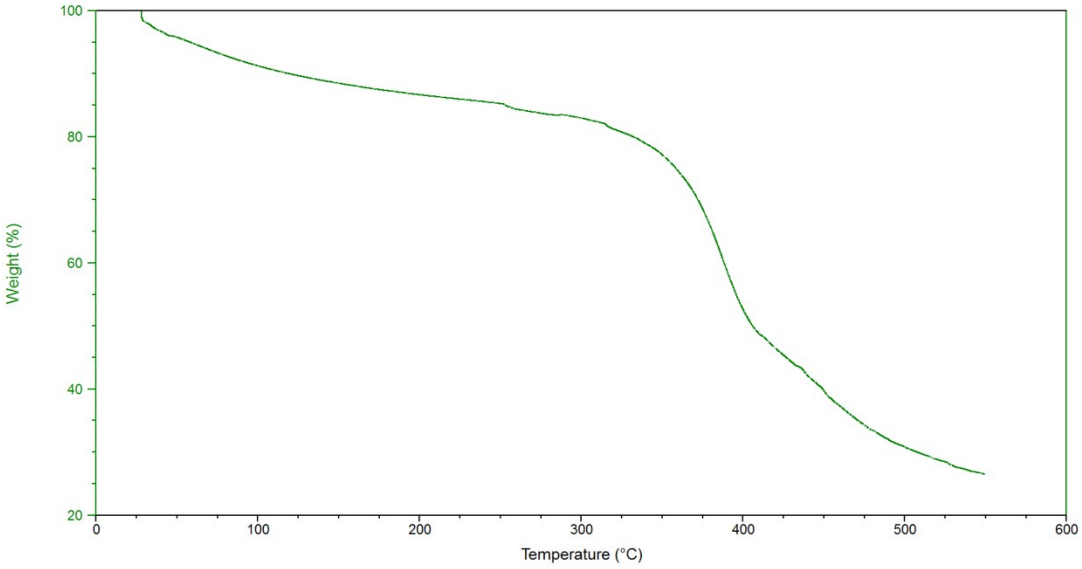

Figure S2: TGA of quasiracemate, (**FT-RCC3**-*R*)·(**CC1**-*S*), crystallised from CH_2Cl_2/acetone.

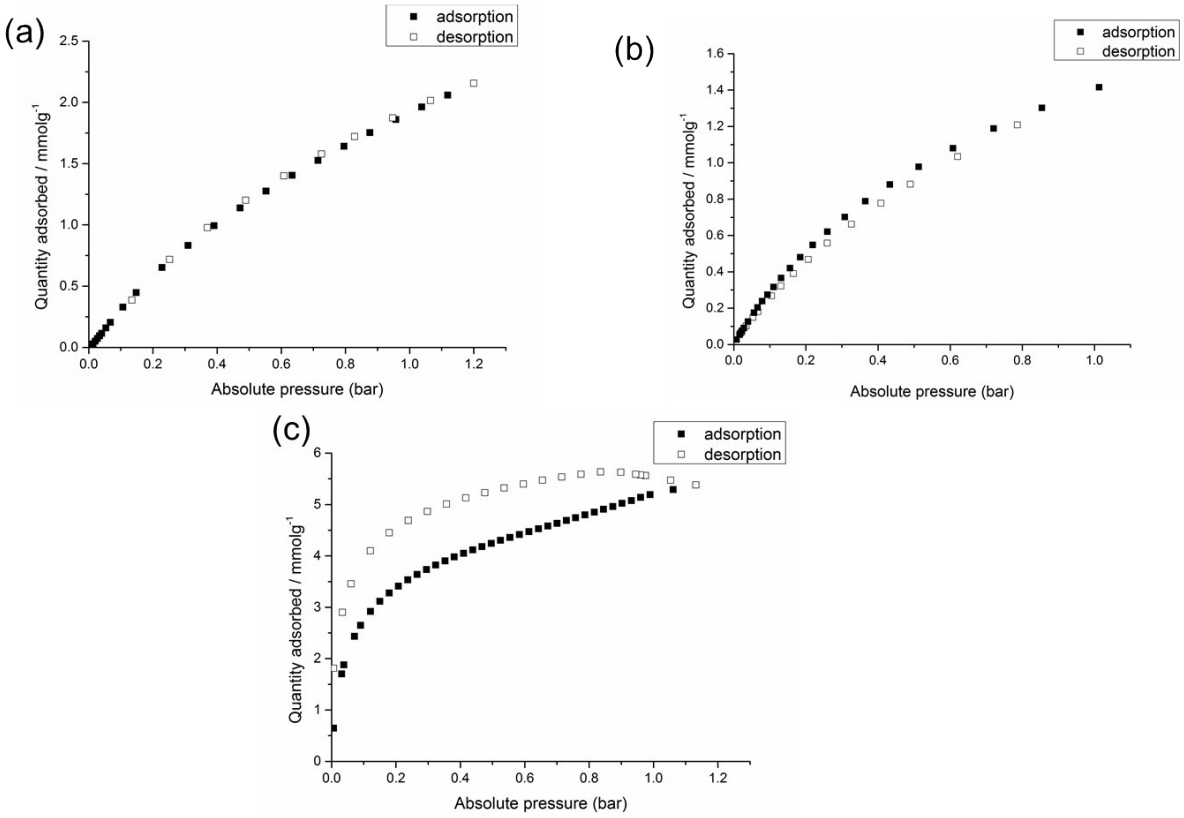

Figure S3. Gas sorption isotherms of quasiracemate, (**FT-RCC3**-*R*)·(**CC1**-*S*), (a) CO_2 at 278 K, (b) CH_4 at 278 K, and (c) H_2 at 77 K. (**FT-RCC3**-*R*)·(**CC1**-*S*) was crystallised from CH_2Cl_2/acetone and activated by heating under vacuum at 90 °C. Closed and open symbols represent adsorption and desorption curves, respectively.

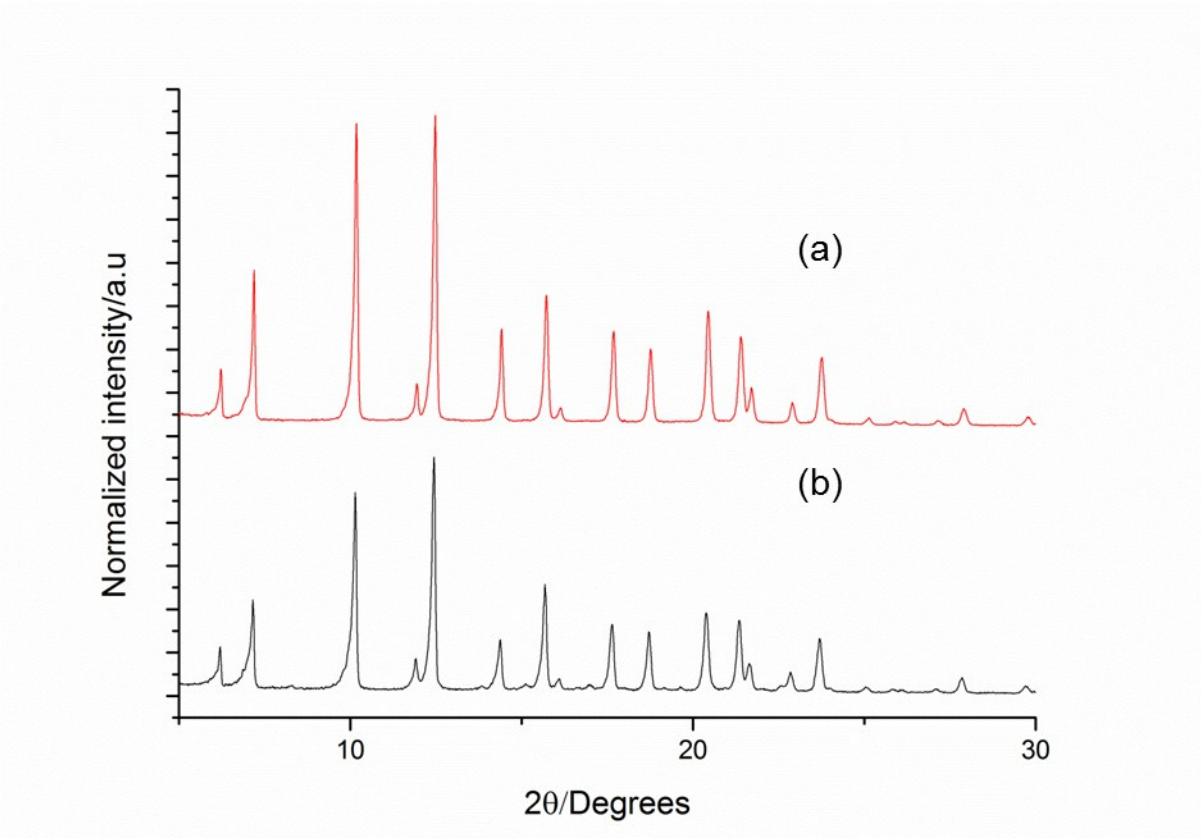

Figure S4. PXRD for quasiracemate, (**FT-RCC3**-*R*)·(**CC1**-*S*), recorded (a) before, and (b) after gas sorption. There is no phase change during gas sorption analysis indicating the materials is stable. Crystals obtained from DCM/Acetone (anti-solvent).

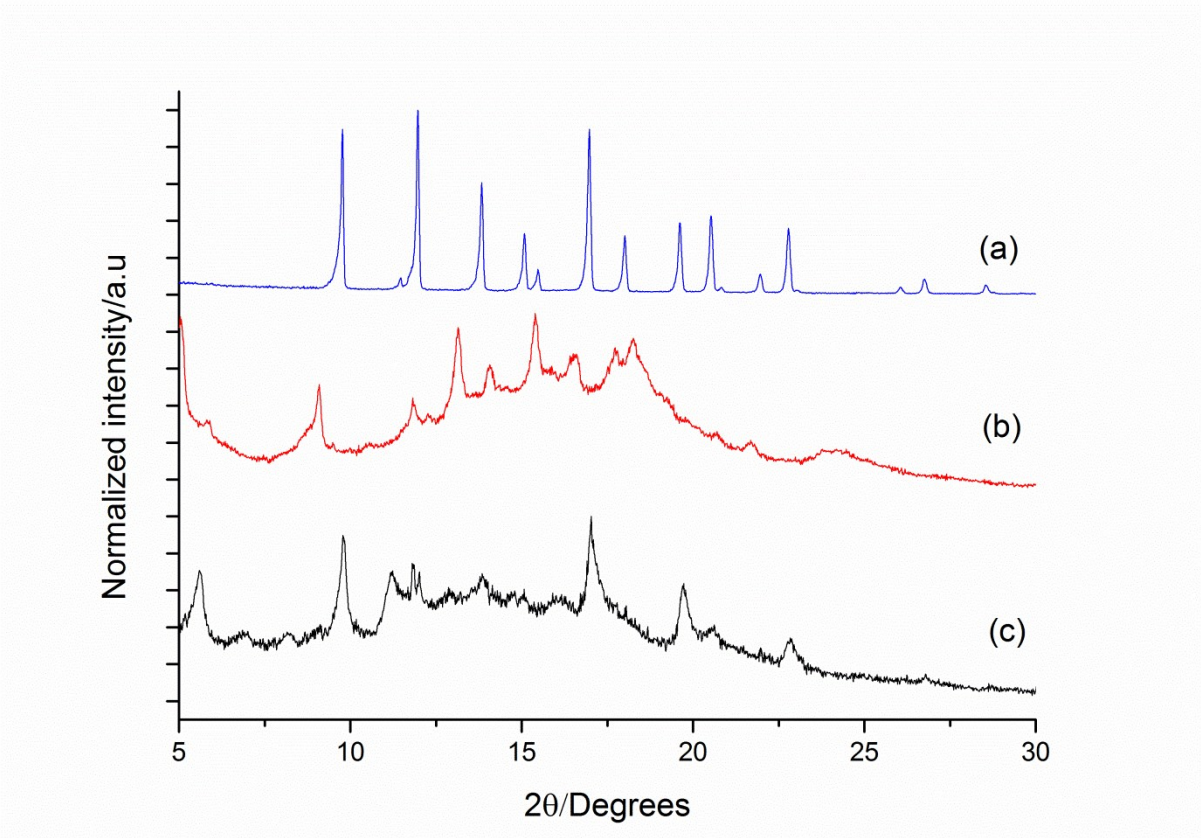

Figure S5. PXRD analysis of (a) **FT-RCC3-***R*, (b) **CC13**, and (c) a phase mixture comprising **FT-RCC3-***R* and **CC13**. All samples were crystallised from CH_2Cl_2/acetone.

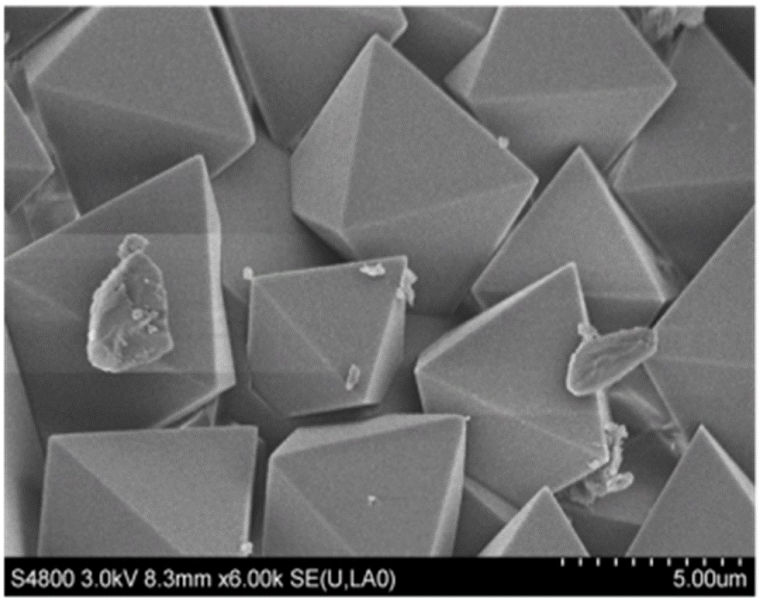

Figure S6. SEM image of ternary co-crystal, (**CC3**-$S_{0.5}$**CC4**-$S_{0.5}$)·(**CC13**-$S_{0.5}$**CC3**-$S_{0.25}$**CC4**-$S_{0.25}$), displaying octahedral crystal habit.

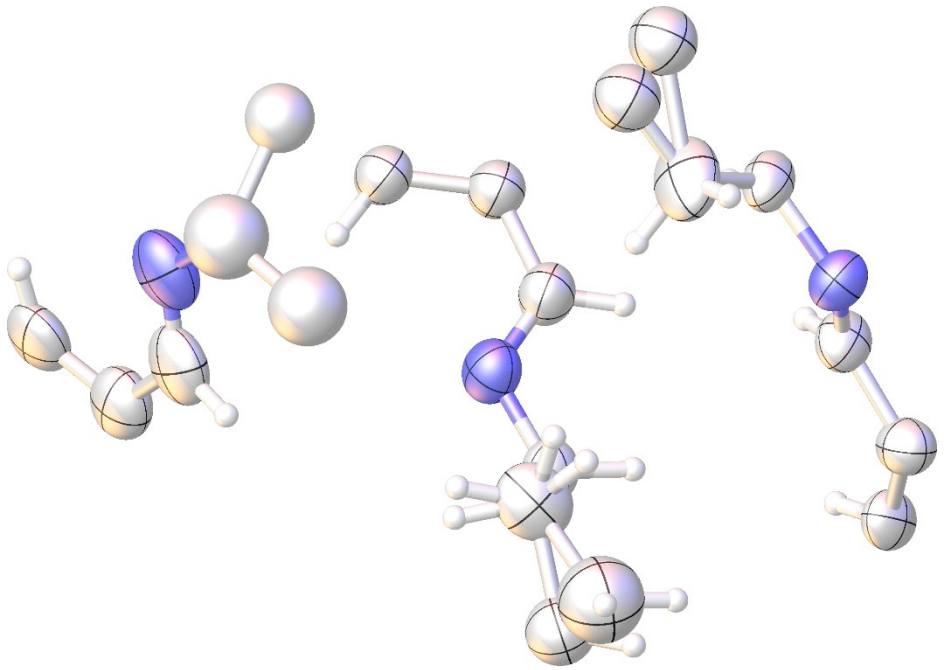

Figure S7. Displacement ellipsoid plot of the asymmetric unit from the single crystal structure, (**CC3**-$S_{0.5}$**CC4**-$S_{0.5}$)·(**CC13**-$S_{0.5}$**CC3**-$S_{0.25}$**CC4**-$S_{0.25}$)·$(H_2O)_{11.92}$; residual H_2O omitted for clarity. Ellipsoid are displayed at 50% probability level. Isotropically 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.

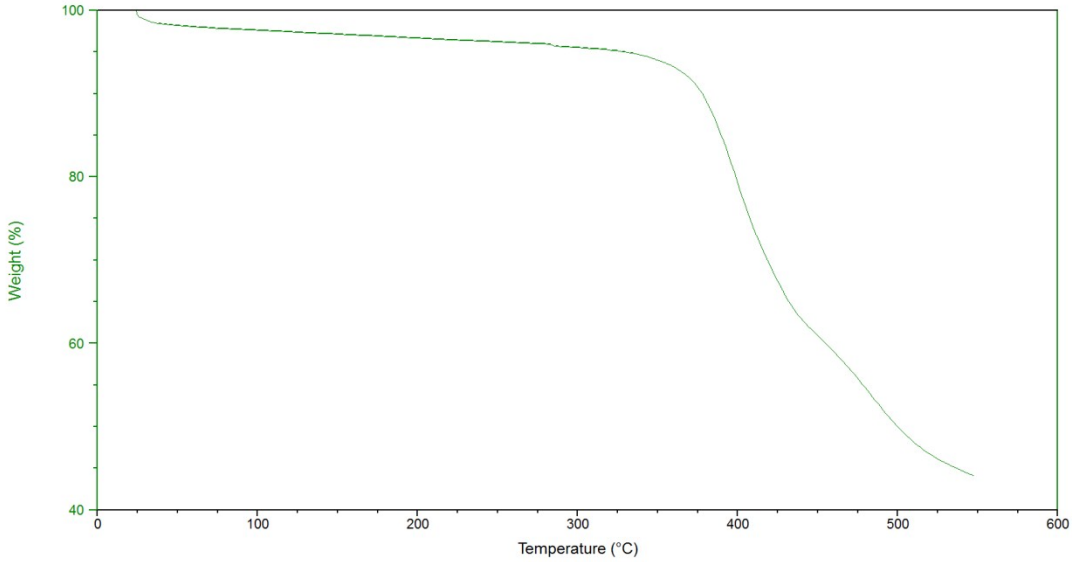

Figure S8. TGA for ternary co-crystal, (**CC3**-$S_{0.5}$**CC4**-$S_{0.5}$)·(**CC13**-$S_{0.5}$**CC3**-$S_{0.25}$**CC4**-$S_{0.25}$) , crystallised from CH_2Cl_2/acetone.

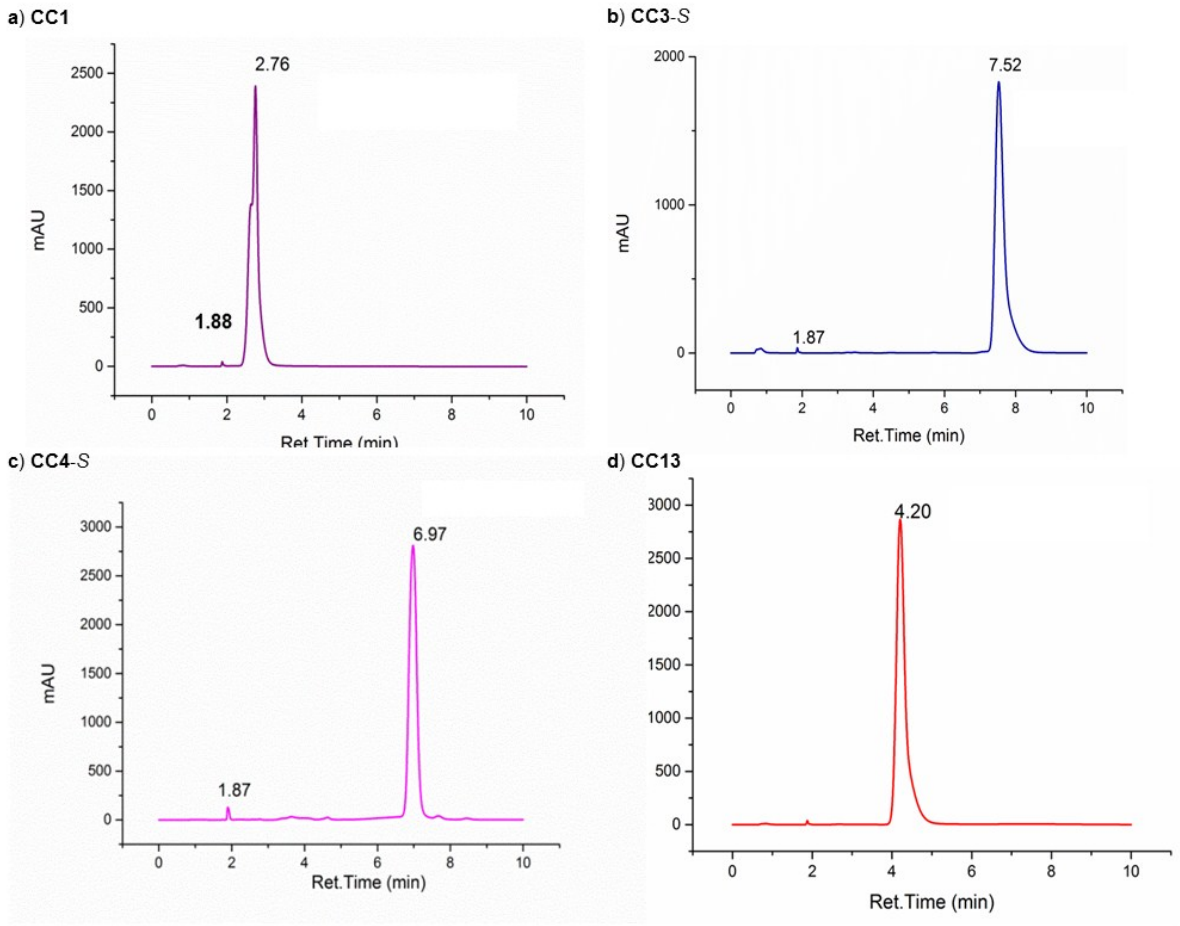

Figure S9. HPLC analysis for the single componnet cages **CC1** (retention time: 2.76 mins.), **CC3**-*S* (7.52 mins.), **CC4**-*S* (6.97 mins.), **CC13** (4.2 mins.) dissolved in CH_2Cl_2 (1.87 min)**.** Column: Syncronis C8; 3 µm; 4.6 ×150 mm; mobile phase: isocratic MeOH; flow: 1.0 mL/min; oven temperature = 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.

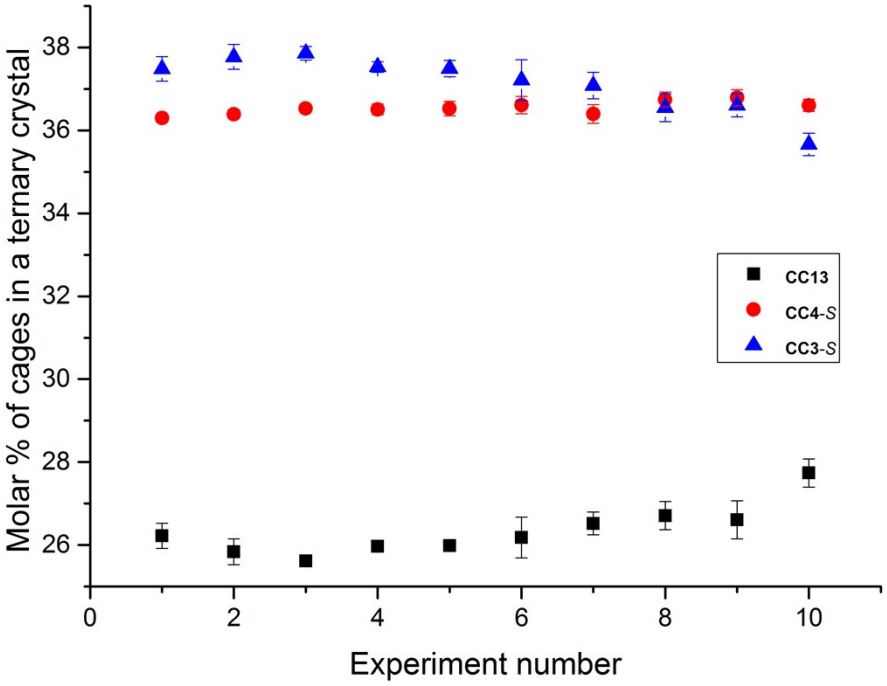

Figure S10. Quantitative HPLC analysis of ten single crystals of the ternary organic crystal, (**CC3**-$S_{0.5}$**CC4**-$S_{0.5}$)·(**CC13**-$S_{0.5}$**CC3**-$S_{0.25}$**CC4**-$S_{0.25}$), crystallised from CH_2Cl_2/acetone. Triangles, circles, and squares represent percentage composition of **CC3**-*S*, **CC4**-*S*, and **CC13** respectively in the single crystals. The quantitative percentage composition of **CC3**-*S*, **CC4**-*S*, and **CC13** in the ternary crystals determined by HPLC analysis and is in good agreement with the refined single crystal structure.

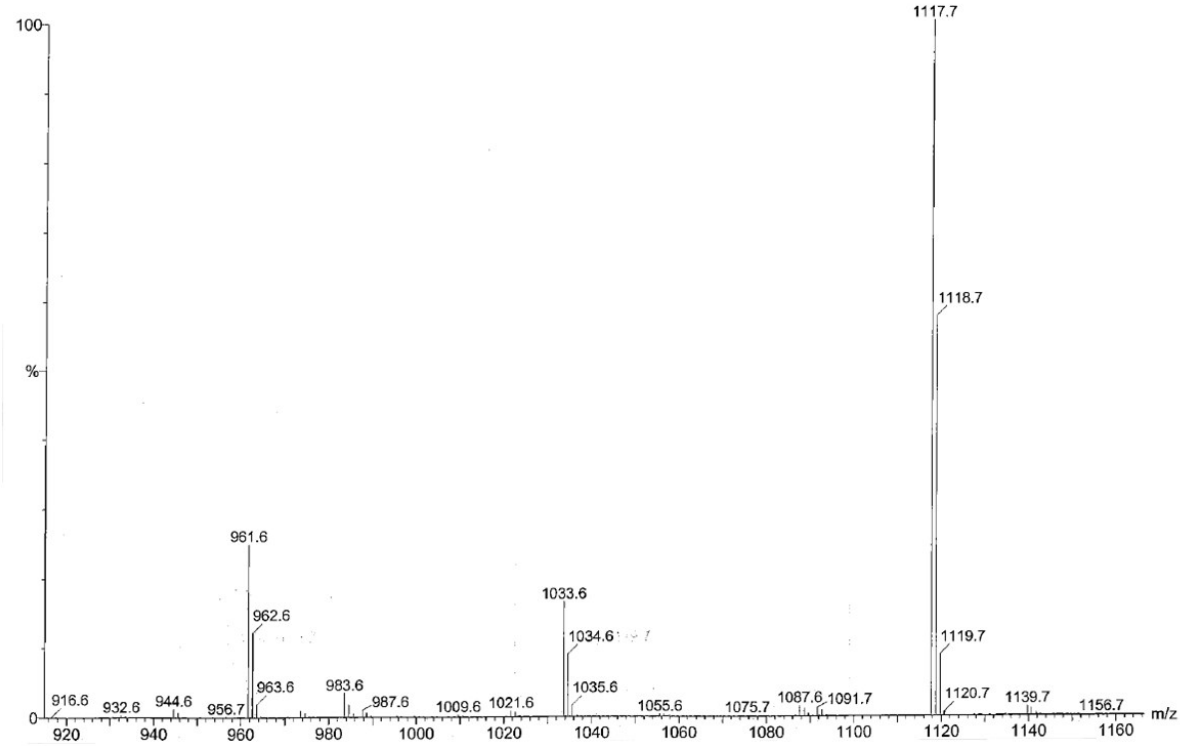

Figure S11. Mass spectrum for a single crystal of the ternary organic solid, (**CC3**-$S_{0.5}$**CC4**-$S_{0.5}$)·(**CC13**-$S_{0.5}$**CC3**-$S_{0.25}$**CC4**-$S_{0.25}$) crystallised from CH_2Cl_2/acetone. m/z ratios correspond to: 961.6 [**CC13**+H]$^+$, 1033.6 [**CC4**-*S*+H]$^+$ and 1117.7 [**CC3**-*S*+H]$^+$.

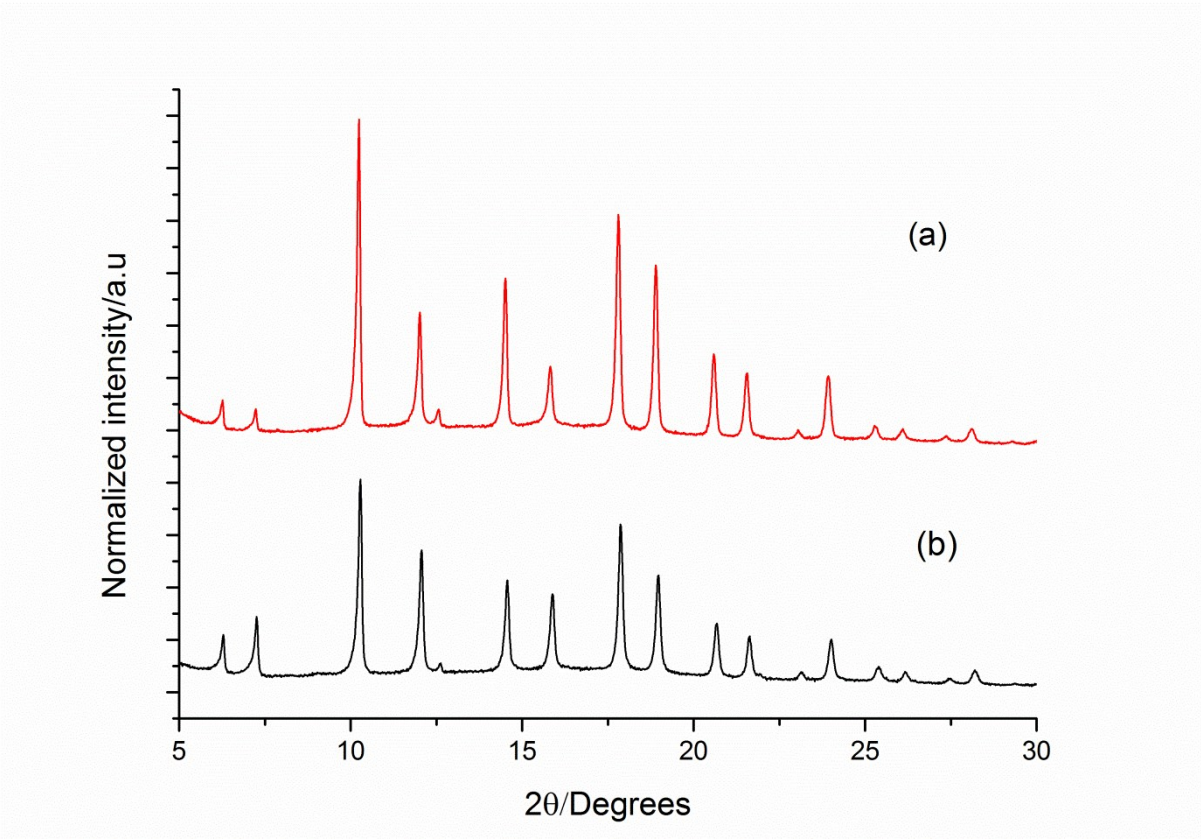

Figure S12. PXRD of ternary organic cocrystal, (**CC3**-$S_{0.5}$**CC4**-$S_{0.5}$)·(**CC13**-$S_{0.5}$**CC3**-$S_{0.25}$**CC4**-$S_{0.25}$), crystallised from CH_2Cl_2/acetone, recorded (a) before and (b) after gas sorption analysis.

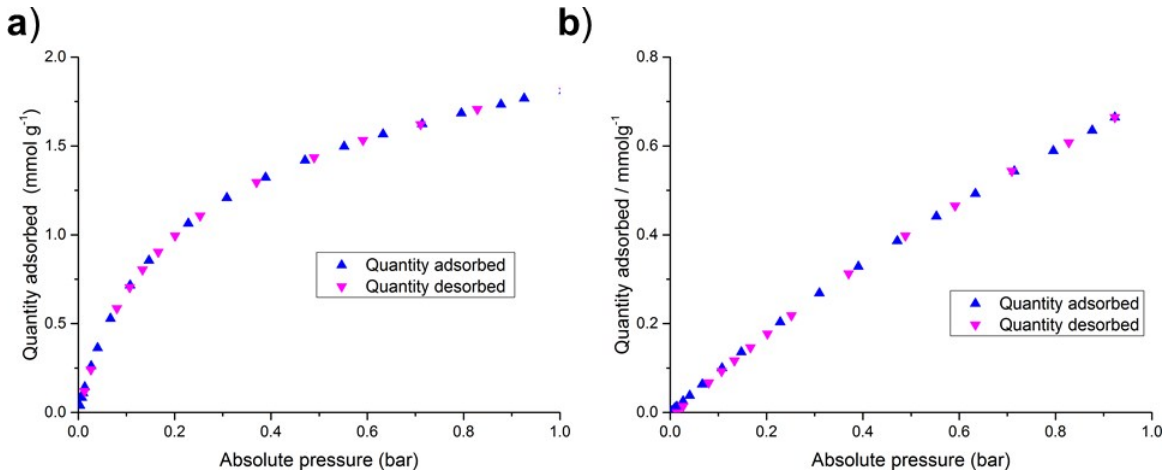

Figure 13. (a) Gas sorption analysis of ternary organic cocrystal, (**CC3**-$S_{0.5}$**CC4**-$S_{0.5}$)·(**CC13**-$S_{0.5}$**CC3**-$S_{0.25}$**CC4**-$S_{0.25}$), crystallised from CH_2Cl_2/acetone for (a) Xe, and (b) Kr.