

**Electronic Supplementary Information for MS:**

**Molecular chairs, zippers, zigzag and helical chains: chemical enumeration of supramolecular isomerism based on a predesigned metal-organic building-block**

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**Synthetic details:** Synthesis of  $[\text{Cu}^{\text{I}}(2\text{-pytz})]_n$ : Hydrothermal treatment of Copper (II) salts ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{Cu}_2(\text{OH})_2\text{CO}_3$  or  $\text{Cu}(\text{OH})_2$  1.0-2.0 mmol), aqueous ammonia (25%, 2.0-3.0 mL) and 2-cyanopyridine (5-20 mmol) at 100-160°C for 2-3 days yielded orange and/or red crystals (ca. 5-45% based on copper salts, or 1-35% based on 2-cyanopyridine). Optimized procedures for pure **I**:  $\text{Cu}_2(\text{OH})_2\text{CO}_3$  (0.221 g, 1.0 mmol), aqueous ammonia (25%, 2.0 mL), 2-cyanopyridine (1.04 g, 10 mmol) and water (5.0 mL) at 160 °C for 3 days (yield 0.26 g); **II**:  $\text{Cu}(\text{OH})_2$  (0.196 g, 2.0 mmol) was used to replace  $\text{Cu}_2(\text{OH})_2\text{CO}_3$  in the procedure for **I** (yield 0.22 g); **III**: benzene (3.0 mL) was used to replace water (5.0 mL) in the procedure for **I**; **IV**:  $\text{Cu}_2(\text{OH})_2\text{CO}_3$  (0.221 g, 1.0 mmol), aqueous ammonia (25%, 3.0 mL), 2-cyanopyridine (2.08 g, 20 mmol) at 160 °C for 2 days (yield 0.08 g). Powder XRD patterns of massive products of **I-IV** derived from the optimized methods fit their crystal structures.

**Additional comments:** The solvent accessible areas are ca. 9.6% volume of the unit cell of **IV** (A. L. Spek, PLATON, Utrecht University, Utrecht, The Netherlands, 2003). The empty cavities are too small for accommodation of any guest larger than a water molecule. No residual peak greater than 0.2 can be found around the centers of the cavities, and the refinement of a suggested oxygen atom at such a position gives less than 2% occupancy.

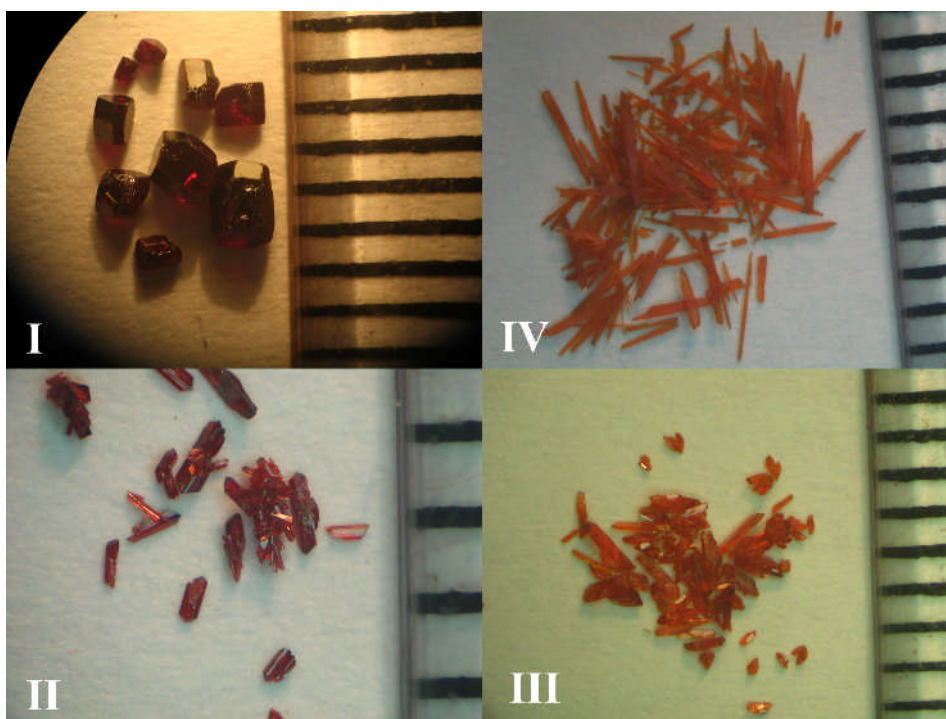


Figure S1. Photographs of **I-IV** (ruler scale: 1 mm).

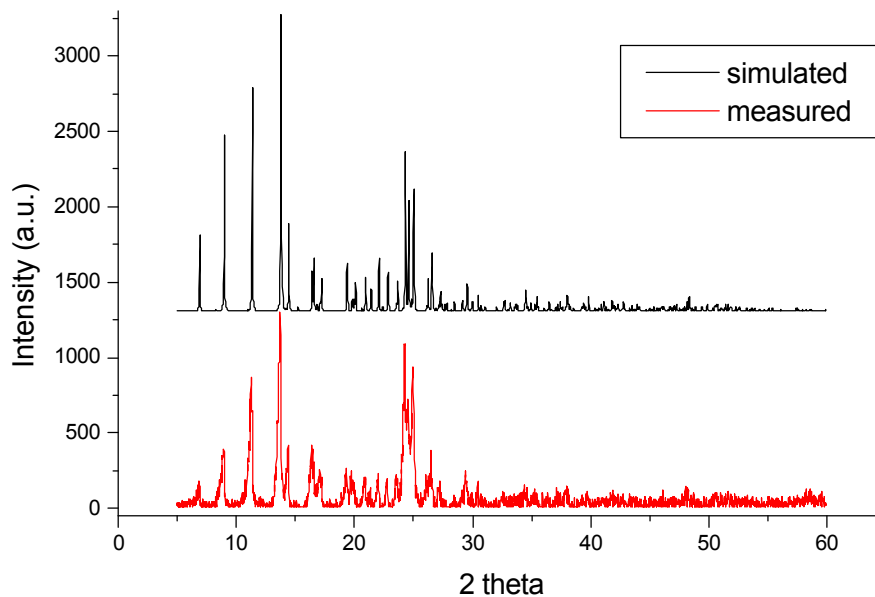


Figure S2a. X-ray powder diffraction pattern of massive product **I** synthesized by the optimized method. Simulated patterns in Figure S3 were generated by PowderCell 2.4, W. Kraus and G. Nolze

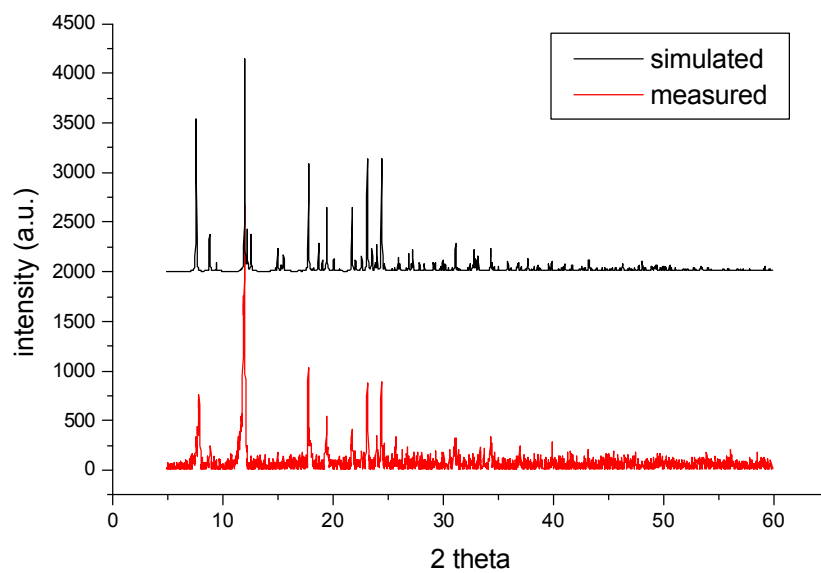


Figure S2b. X-ray powder diffraction pattern of massive product **II** synthesized by the optimized method.

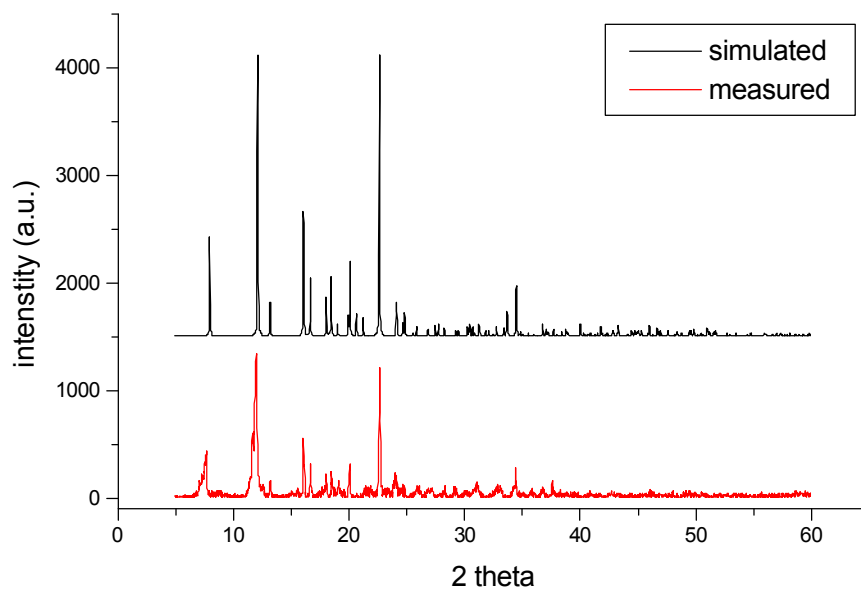


Figure S2c. X-ray powder diffraction pattern of massive product **III** synthesized by the optimized method.

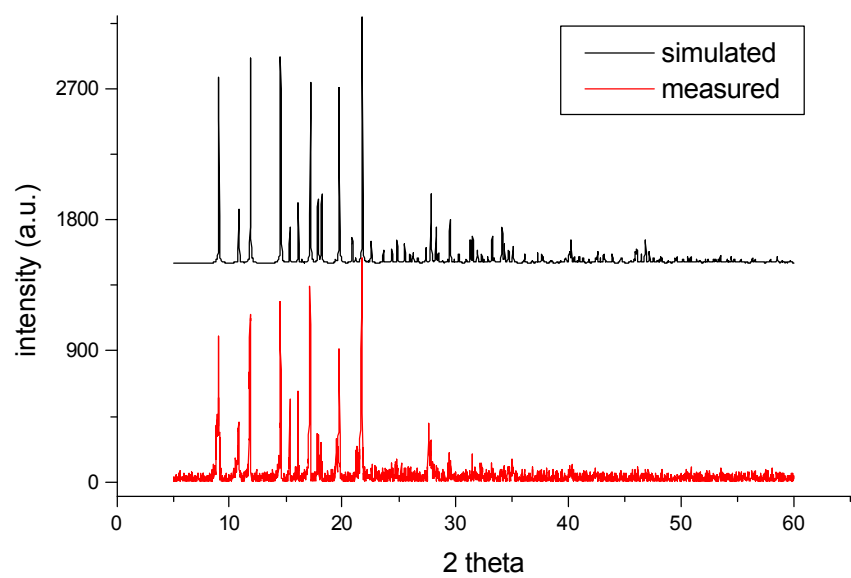


Figure S2d. X-ray powder diffraction pattern of massive product **IV** synthesized by the optimized method.

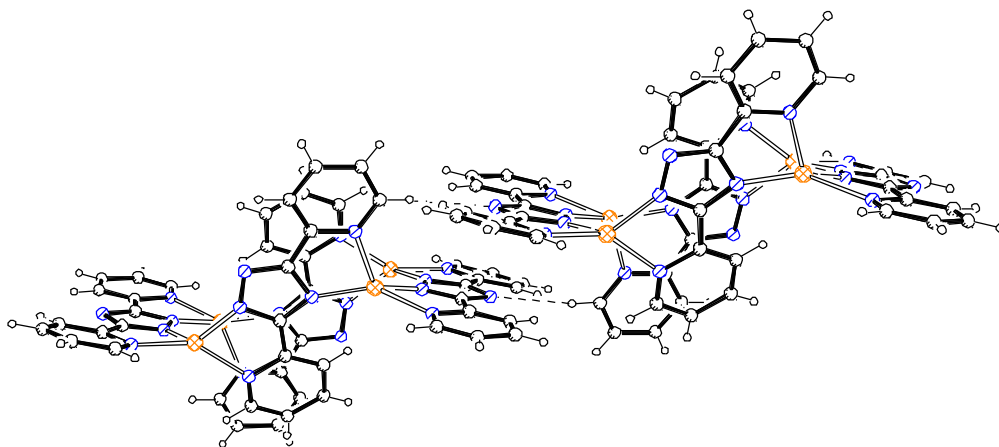


Figure S3a C-H...N ( $C\cdots N$  3.529 Å) and face-to-face  $\pi$ - $\pi$  stacking interactions (ca. 3.5 Å) between adjacent chairs in **I**.

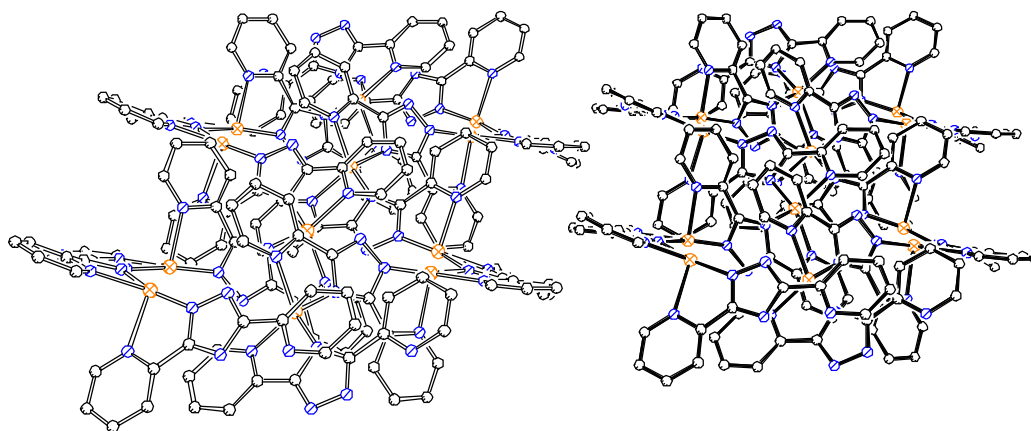


Figure S3b adjacent zipper-like double chains of **II** viewed along the  $c$ -axis showing no significant  $\pi$ - $\pi$  overlap (hydrogens are omitted for clarity).

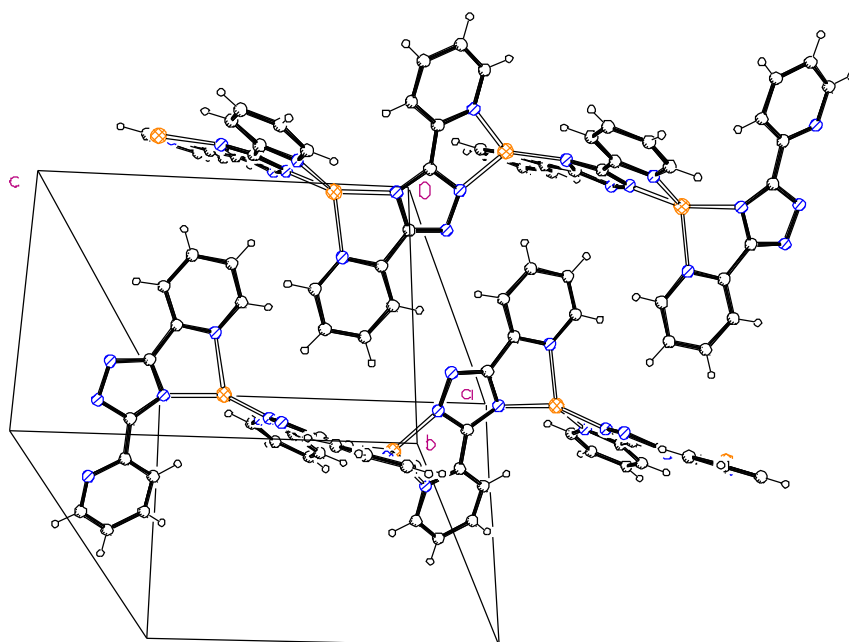


Figure S3c two adjacent zigzag chains in **III** with opposite polarities.

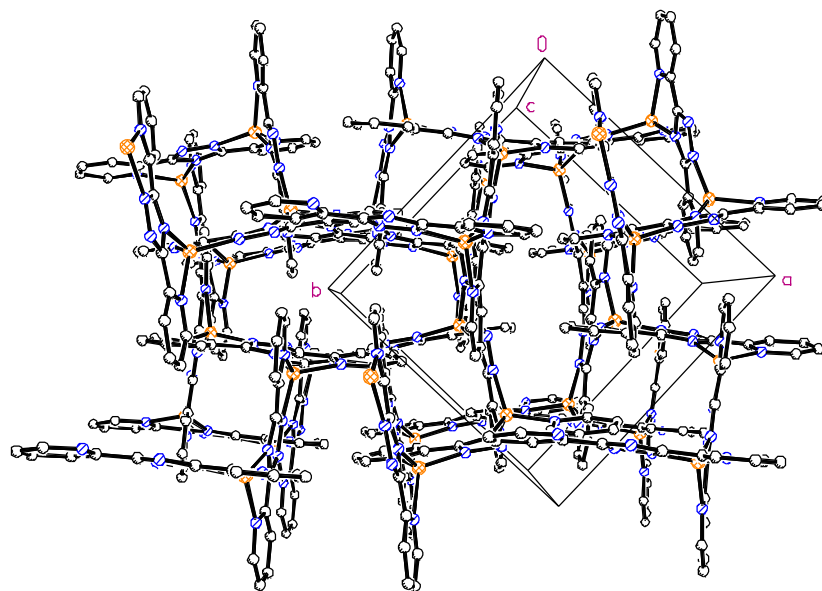


Figure S3d packing pattern of **IV** viewed along *c*-axis (hydrogens are omitted for clarity).