

**A 1D crystalline organic polyrotaxane formed via hydrogen bond-mediated self-assembly
of a conformationally flexible tri-carboxylic acid**

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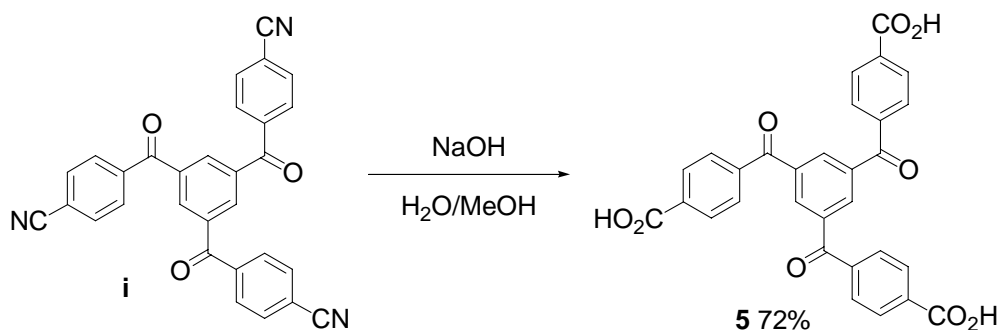
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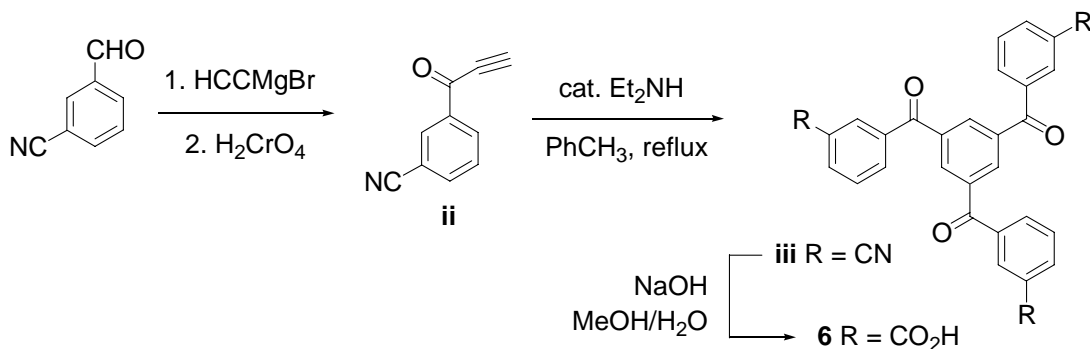
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Preparation of 1,3-5-tris(4-carboxybenzoyl)benzene (**5**).



The previously reported tris(cyano) TAB **i** (0.50 g, 1.1 mmol)¹ was combined with 0.50 g NaOH in a mixture of methanol (3 mL) and H₂O (2 mL). The reaction was heated to reflux for 12 h. After cooling to room temperature the solution was acidified with 50% aqueous HCl and the resulting precipitate was collected by vacuum filtration. This solid was dissolved in 15 mL of saturated NaHCO₃ solution and washed with ethyl acetate (2 x 15 mL). The aqueous layer was then re-acidified with 50% aqueous HCl until pH < 2, resulting in precipitation of the desired tri-acid. The precipitate was collected and dried under vacuum to give **5** (0.40 g, 72%) as a colorless solid. Mp. > 250 °C. ¹H-NMR (300 MHz, DMSO-*d*₆) δ 8.29 (s, 3H), 8.10 (d, *J* = 7.6 Hz, 6H), 7.94 (d, *J* = 7.6 Hz, 6H). ¹³C-NMR (75 MHz, DMSO-*d*₆) δ 193.7, 166.5, 139.4, 137.1, 134.6, 134.0, 129.9, 129.4. IR (thin film) ν (cm⁻¹) 3450-2600 (br.), 1660. HRMS (EI): calcd. for C₃₀H₁₈O₉ 522.0951 [M]⁺, found 522.0947.

Preparation of 1,3,5-tris(3-carboxybenzoyl)benzene (**6**).



A solution of 3-cyanobenzaldehyde (1.18 g, 9.0 mmol) in ~ 5 mL of THF was cooled to 0 °C under nitrogen. A solution of ethynyl magnesium bromide (0.5 M in THF, 20 mL, 10.0 mmol) was added via syringe. The reaction mixture was allowed to warm to room temperature over 4 h and then quenched by addition of 10 mL saturated aqueous NH₄Cl solution. The mixture was diluted with ether and the layers were separated. The aqueous phase was re-extracted with an additional aliquot of ether and the combined organic layer was dried over anhydrous MgSO₄. Filtration and evaporation of the solvent gave the desired alcohol as a pale yellow oil (1.24 g, 88%) which was used directly in the next step. The alcohol was dissolved in ~15 mL of acetone. A solution of H₂CrO₄ (Jones reagent) was added via pipet until the red color indicative of excess Cr(VI) persisted. The reaction was stirred at room temperature an additional 15 min, then was quenched by addition of isopropanol (~5 mL). The chromium salts were removed by filtration through Celite and washed thoroughly with ether. The filtrate was transferred to a separatory funnel and washed sequentially with H₂O, saturated aqueous NaHCO₃ solution, and H₂O. Drying over anhydrous MgSO₄, filtration, and evaporation of the solvent gave a yellow solid that was purified by flash column chromatography (2:1 Hexanes:EtOAc) to afford **ii** (1.00 g, 82%).

¹H-NMR (300 MHz, CDCl₃) δ 8.44 (t, *J* = 1.4 Hz, 1H), 8.37 (dt, *J* = 7.9, 1.4 Hz, 1H), 7.92 (dt, *J* = 7.9, 1.4 Hz, 1H), 7.68 (t, *J* = 7.9 Hz, 1H), 3.60 (s, 1H). ¹³C-NMR (75 MHz, CDCl₃) δ 175.3, 137.4, 137.0, 133.5, 133.4, 130.0, 117.8, 113.6, 82.8, 79.6.

Without further characterization this material was subjected to cyclotrimerization.² To a solution of **ii** (0.30 g, 1.90 mmol) in toluene (~10 mL) was added two drops of Et₂NH. The yellow reaction mixture was heated to reflux for 18 h. After cooling the toluene was evaporated and the solid residue was purified by flash column chromatography (EtOAc). The desired TAB derivative **iii** was obtained as a off-white solid. Mp. 187-190 °C. ¹H-NMR (300 MHz, CDCl₃) δ

8.39 (s, 3H), 8.14 (br. s, 3H), 8.09 (d, $J = 8.5$ Hz, 3H), 7.95 (d, $J = 8.5$ Hz, 3H), 7.73 (t, $J = 8.5$ Hz, 3H). ^{13}C -NMR (75 MHz, CDCl_3) δ 192.3, 137.7, 137.3, 136.0, 134.6, 133.7, 133.6, 130.2, 116.1, 113.8. HRMS (EI) calcd for $\text{C}_{30}\text{H}_{15}\text{N}_3\text{O}_3$ 465.1114 $[\text{M}]^+$, found 465.1115.

Tris(cyano) TAB **iii** (0.50 g, 1.1 mmol) was converted to tri-acid **6** (isolated yield: 0.37 g, 66%) using the procedure given for the preparation of **5**. Mp. 150-152 °C. ^1H -NMR ($\text{DMSO}-d_6$) δ 13.41 (br. s, 3H), 8.37 (br. s, 3H), 8.31 (s, 3H), 8.23 (d, $J = 7.7$ Hz, 3H), 8.10 (d, $J = 7.7$ Hz, 3H), 7.71 (t, $J = 7.7$ Hz, 3H). ^{13}C -NMR (75 MHz, $\text{DMSO}-d_6$) δ 193.8, 166.7, 137.4, 136.6, 134.2, 134.1, 133.8, 131.9, 130.5, 129.3. IR (DMSO) ν (cm^{-1}) 3650-3200 (br.), 1664. HRMS (EI) calcd for $\text{C}_{30}\text{H}_{18}\text{O}_9$ 522.0951 $[\text{M}]^+$, found 522.0966.

Crystallization of $\mathbf{6}_{\text{polyrot}}$.

Tri-acid **6** (50 mg) was combined with 30 mg of CoCl_2 in ~15 mL of 1:1 acetone:MeOH solution. Slow evaporation at room temperature gave X-ray quality single crystals of $\mathbf{6}_{\text{polyrot}}$ after ~ 2 months. Crystallization yield was not determined.

Crystallization of $\mathbf{6}_{\text{DMF}}$.

Tri-acid **6** (50 mg) was dissolved in ~ 5 mL of DMF in a 20 mL sample vial and placed in a toluene diffusion chamber. Colorless plates of $\mathbf{6}_{\text{DMF}}$ formed along the sides of the vial after several months. Crystallization yield was not determined.

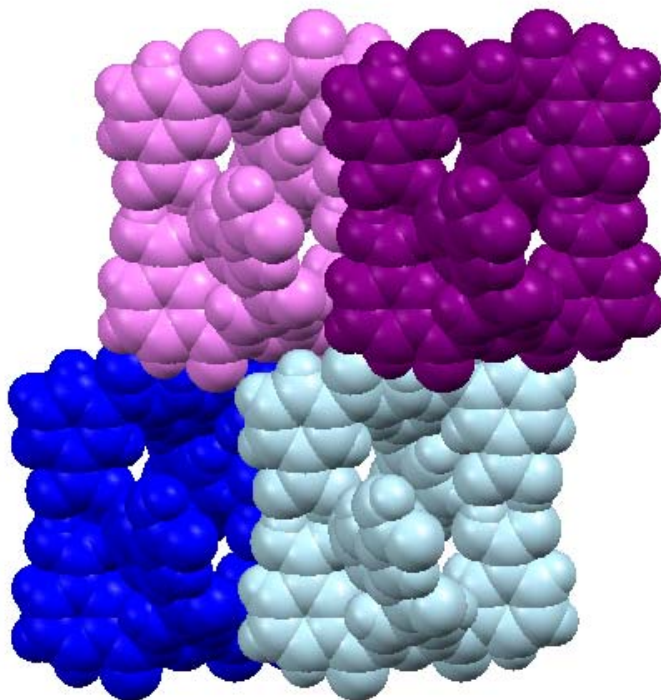


Fig. S1a Extended packing down a in $\mathbf{6}_{\text{polyrot}}$ illustrating the relationship of four independent 1D polyrotaxane chains (individual polyrotaxane chains color coded for clarity).

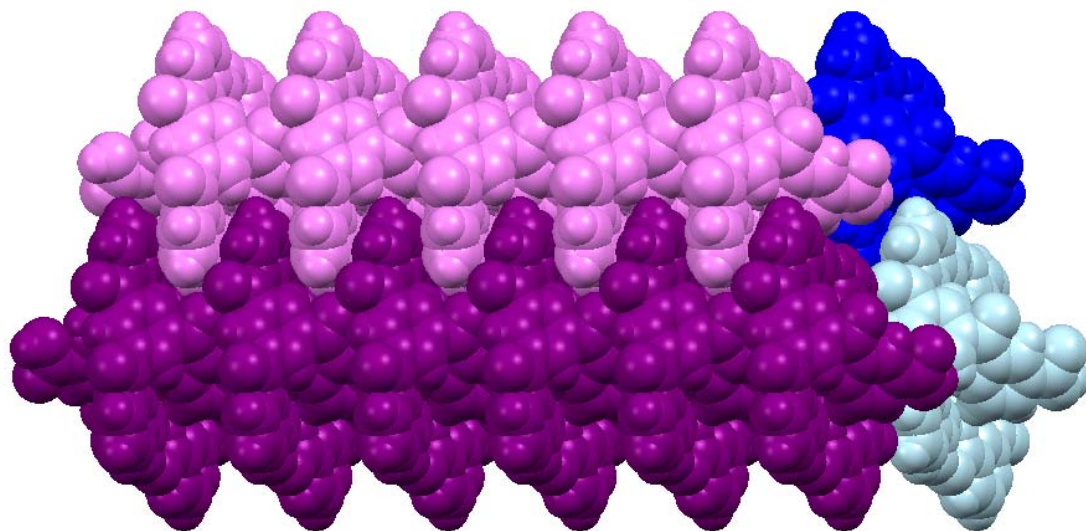


Fig S1b Extended packing of $\mathbf{6}_{\text{polyrot}}$ down c .

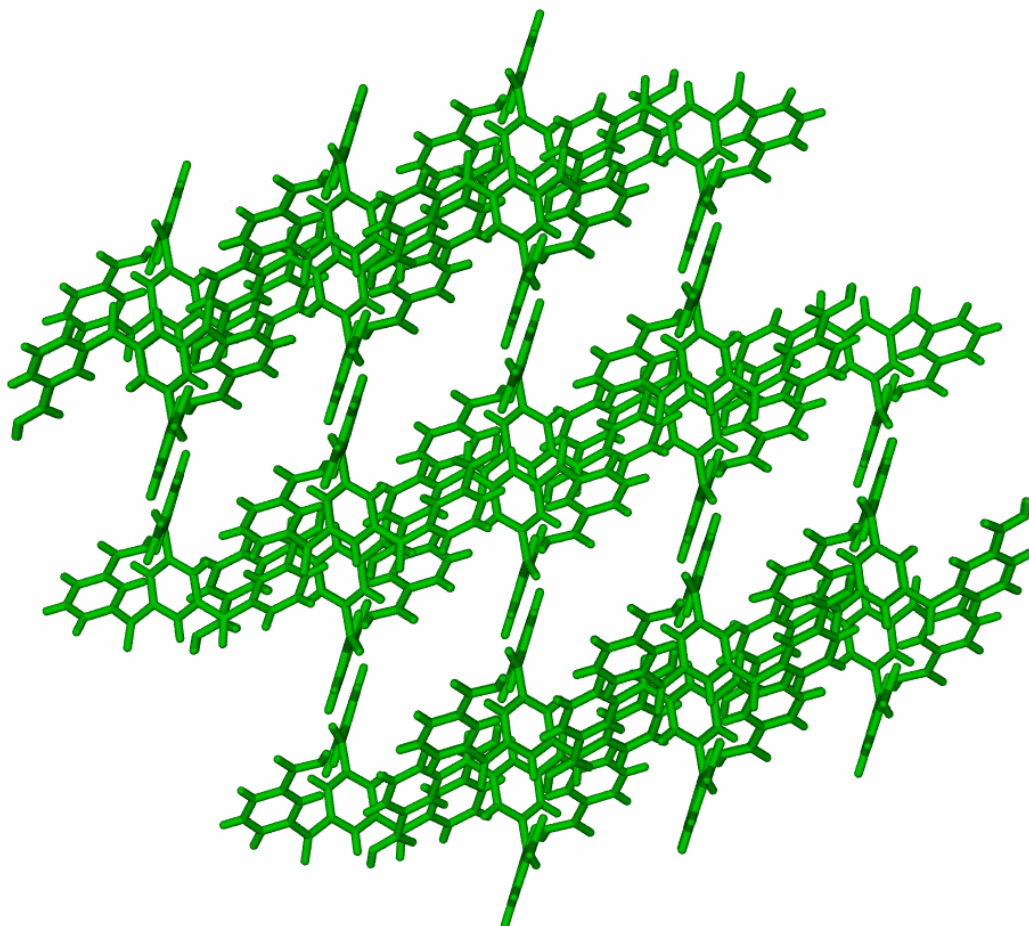


Fig. S2 Extended packing in $\mathbf{6}_{\text{DMF}}$ (down b) illustrating the channels occupied by DMF and H_2O solvates. Guest solvates and dimethyl ammonium cations have been removed for clarity.

References

1. F. C. Pigge, M. D. Burgard and N. P. Rath, *Cryst. Growth Des.*, 2003, **3**, 331.
2. K. K. Balasubramanian, S. Selvaraj and P. S. Venkataramani, *Synthesis*, 1980, 29.