Electronic Supporting Information

Tetrameric Molecular Bowl Assembled from Glycoluril Building Blocks

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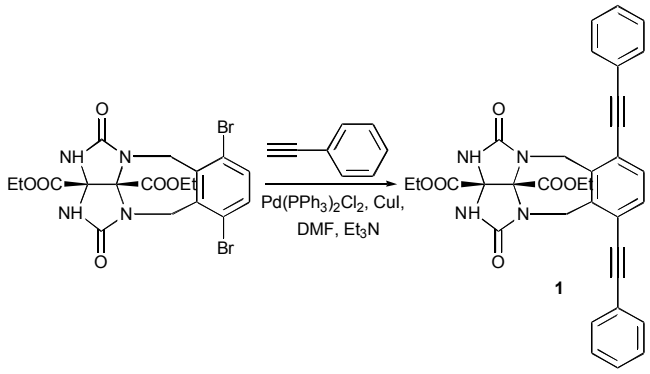


Detailed synthetic procedure for compound 1: The solvents used in the reactions were dried according to standard procedures. All reactions were performed under an inert atmosphere, under strictly anhydrous conditions. All chemicals were used as received. Preparation of **1**: To a solution of $Pd(PPh_3)_2Cl_2$ (36 mg, 0.05 mmol), CuI (19 mg, 0.10 mmol) and Diethyl 6,9-dibromo-1,4-dioxo-1,2,3,4,5,10-hexahydro-2,3,4a,10atetraazabenzo[g] cyclopenta [cd]azulene-2a,10b-dicarboxylate (273 mg, 0.50 mmol) in freshly distilled Et_3N (5 ml) and DMF (25 ml) under Ar atmosphere at room temperature, were added ethynylbenzene (204 mg, 2 mmol). The mixture was warmed to 100 ˚C for 14 h (monitored by TLC), and then the solvent was removed under reduced pressure, the solid residue was purified by flash chromatography (SiO_2, CH_2Cl_2/CH_3OH, 50:1) to give **1** (214.6 mg, 0.365 mmol, 73%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65-7.36 (m, 12H), 6.17 (s, 2H), 5.83 (d, *J* = 16.0, 2H), 4.35 (d, *J* = 16.0, 2H), 4.29 (q, *J* = 6.8, 2H), 4.16 (q, *J* = 6.8, 2H), 1.33 (t, *J* = 6.8, 3H), 1.21 (t, *J* = 6.8, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9, 165.8, 157.2, 138.6, 131.7, 131.4, 128.6, 128.4, 123.5, 122.8, 95.5, 87.0, 82.6, 73.7, 63.4, 63.2, 45.9, 41.8, 14.0, 13.7. MS (ESI): *m/z* 589 ($[M+H]^+$), 611 ($[M+Na]^+$) (calcd 588.20).

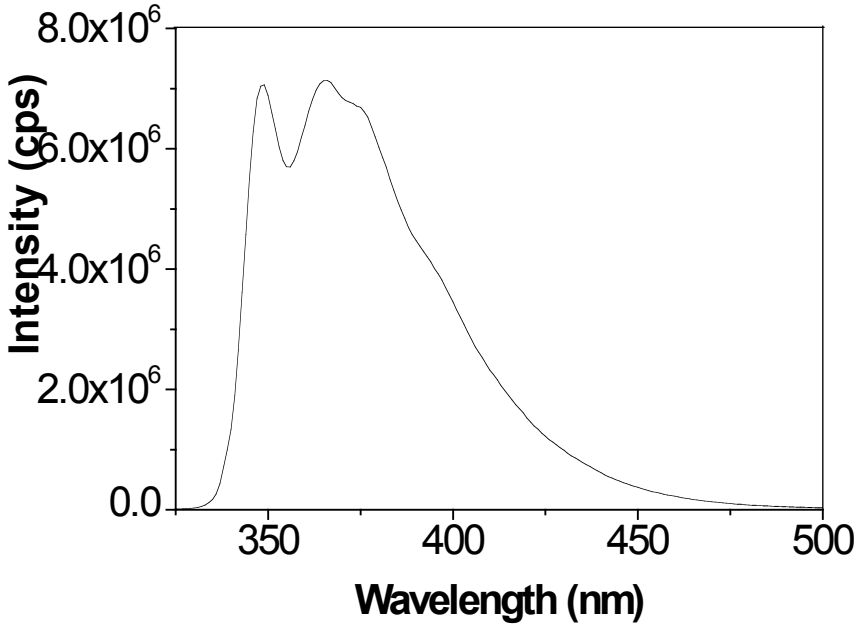


Figure S1. Fluorescence emission spectra of **1** (1×10^{-5} M) in THF. λ_{ex} = 334 nm.

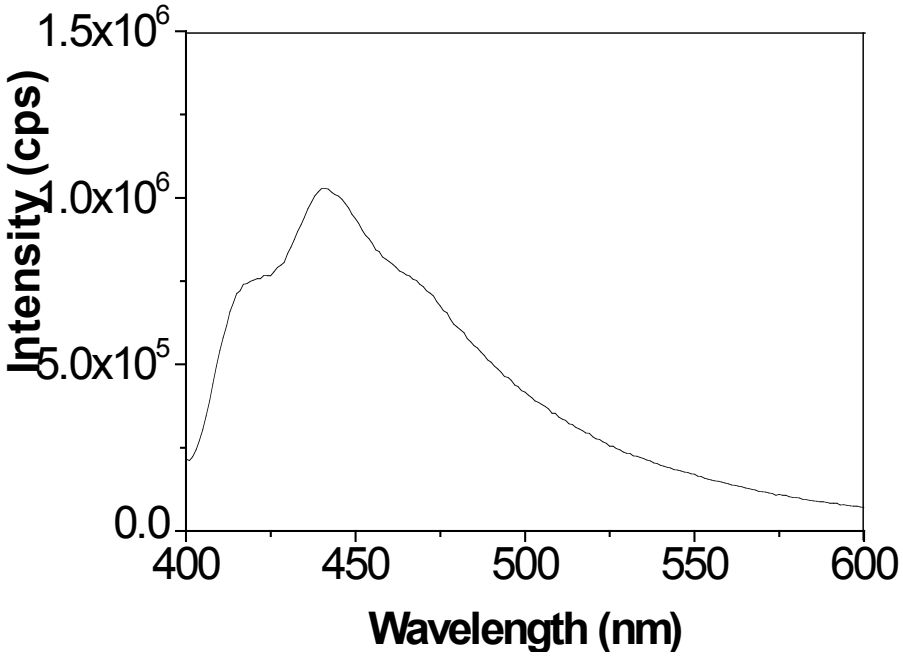
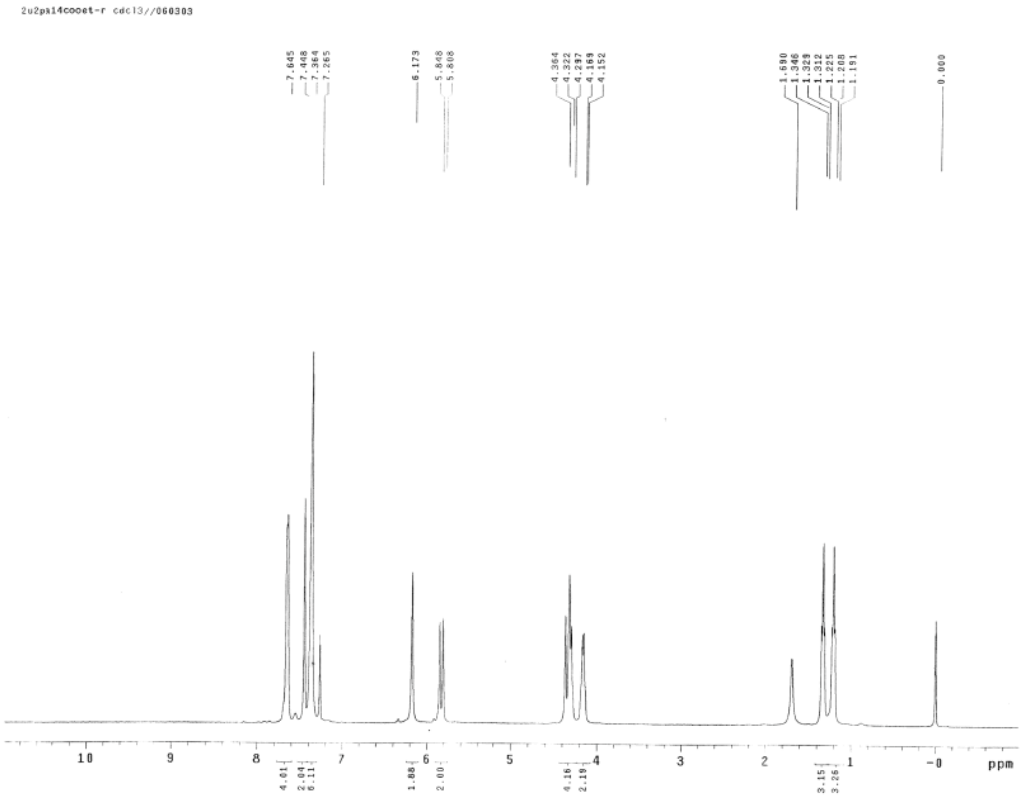
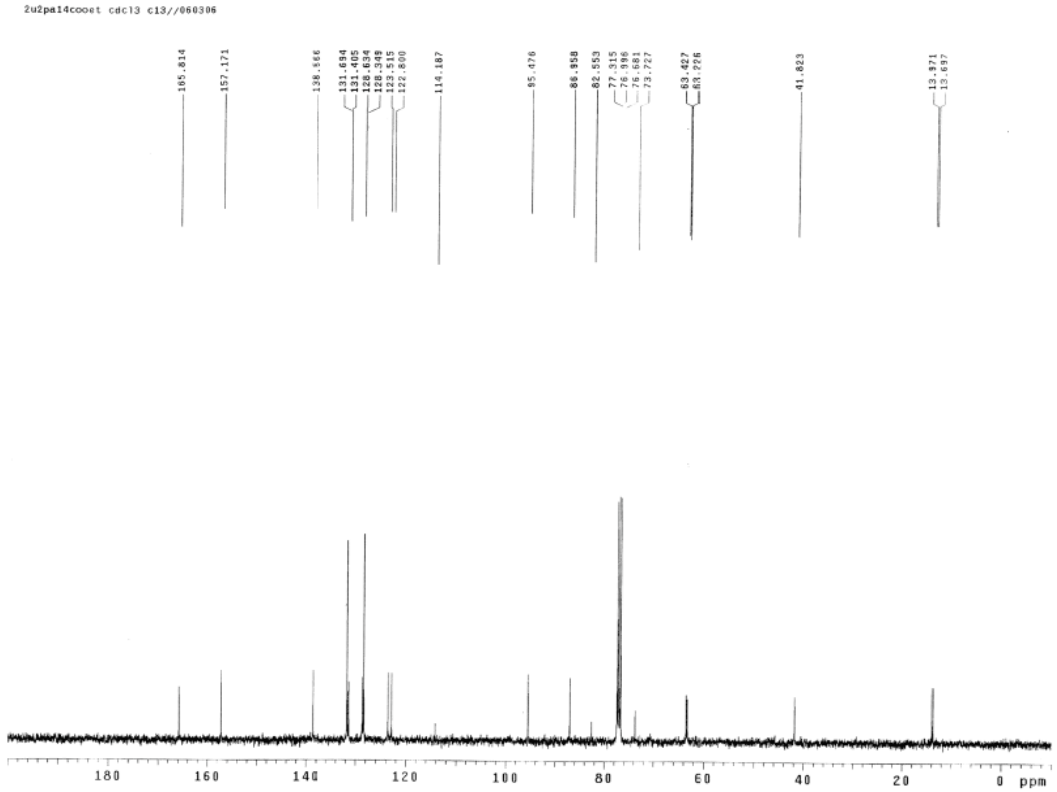


Figure S2. Fluorescence emission spectra of **1** in the solid state. λ_{ex} = 394 nm.

^{1}H NMR of Compound 1



^{13}C NMR of Compound 1



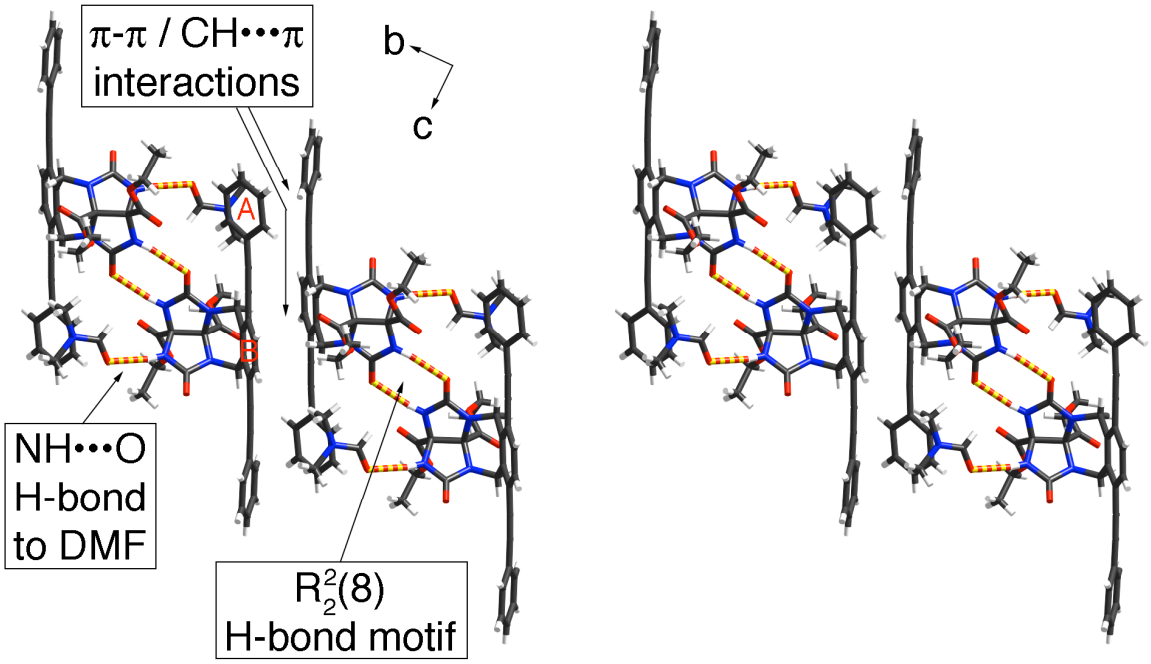


Figure 3. Cross-eyed stereoview of the packing of **1** in the crystals obtained from DMF highlighting H-bonds, π-π and CH-π interactions. Color code: C, grey; H, white; N, blue; O, red; H-bonds, red-yellow striped. Centroids of aromatic rings A and B are labelled in red.

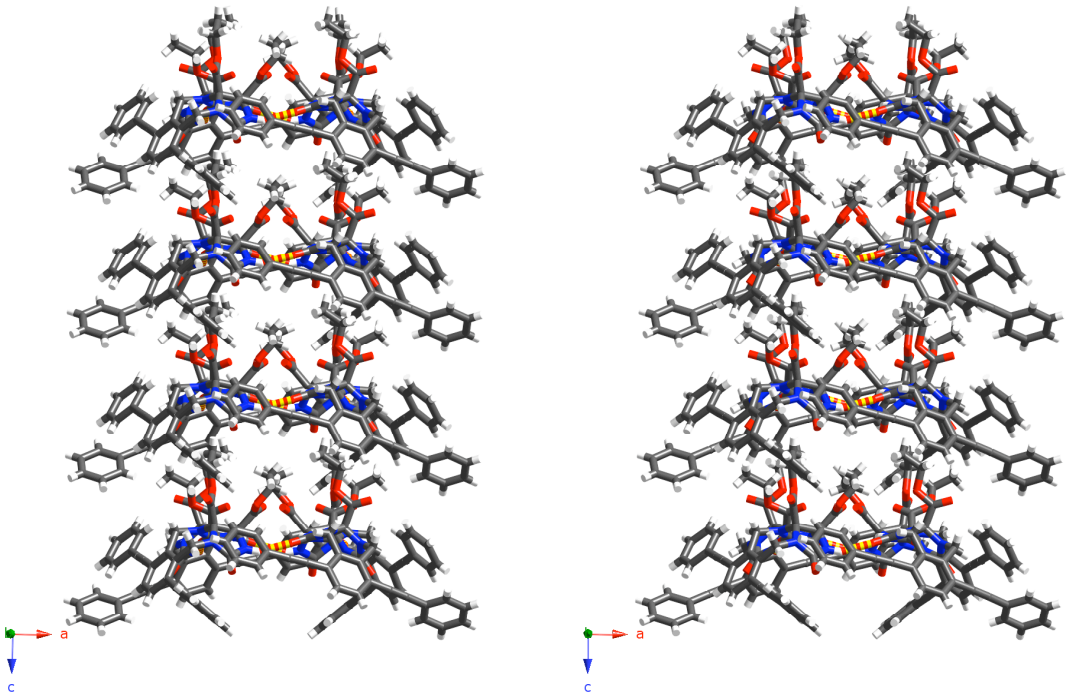


Figure 4c. Cross-eyed stereoview of the packing of $(\mathbf{1})_4$ in the crystal. Color code: C, grey; H, white; N, blue; O, red; H-bonds, red-yellow striped.