Carboxylic acid-derived oxacalix[2]arene[2]pyrazine self-assembles into unprecedented diamondoid networks

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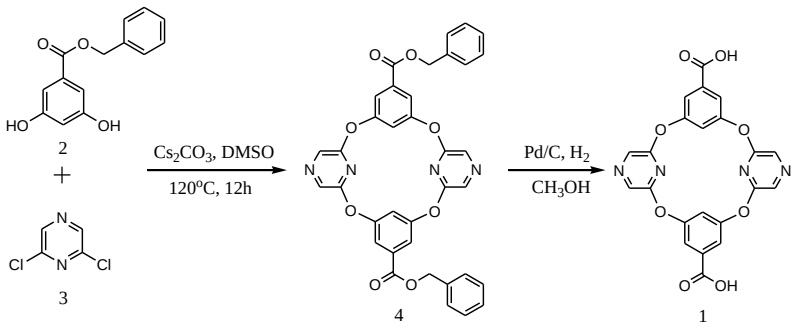
Electronic Supplementary Information

General Methods: Commercially available chemicals were used without further purification unless stated otherwise. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 500 (500 MHz) spectrometer in $CDCl_3$ or DMSO-d_6 with TMS as the reference. Crystal Structure Data Collection and Refinement. Intensity data were collected at at 173(2)K or room temperature (296K) on a diffractometer using graphite monochromated Mo Kα radiation (λ=0.71073Å). Data reduction included absorption corrections by the multi-scan method. The structures were solved by direct methods and refined by full-matrix least-squares using SHELXS-97 (sheldrick, 2008). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added at their geometrically ideal positions and refined isotropically. The supplementary crystallographic data for this paper can be obtained free of charge from the Cambridge Crystallo-graphic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif.



Scheme S1. Schematic representation of the synthesis of carboxylic acid functionalized oxacalix[2]arene[2]pyrazine **1**

Synthesis of benzyl ester functionalized oxacalix[2]arene[2]pyrazine 4: Under nitrogen atmosphere, benzyl 3,5-dihydroxybenzoate **2** (5g, 20 mmol), 2,6-dichloropyrazine **3** (3g, 20 mmol), 4 Å molecular sieves (1g) and Cs_2CO_3 (13g, 40 mmol) were mixed in 50 mL dry DMSO, and the resulting solution was stirred vigorously at 120 °C for 12h. The reaction mixture was then partitioned between EtOAc (200mL) and 0.1 M HCl (300mL), and the aqueous layer was extracted twice with EtOAc (200mL). The combined organic layer were washed with brine (300mL), dried over anhydrous Na_2SO_4. The solvent was evaporated and the crude product was purified by chromatograph on a silica gel column (petroleum ether/ethyl acetate 4:1).

Compound **4** was obtained as white powder. Yield: 5.3g (83%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (s, 4H), 7.54 (d, J = 2.2, 4H), 7.42-7.35 (m, 10H), 6.83 (t, J = 2.2, 2H), 5.31 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.61, 157.37, 152.89, 135.39, 132.91, 128.64, 128.45, 128.38, 127.68, 120.44, 120.24, 67.29; HRMS (ESI): $C_{36}H_{24}N_4O_8Na^+$ *m/z* calcd 663.1486, found 663.1499.

Synthesis of carboxylic acid functionalized oxacalix[2]arene[2]pyrazine 1: Compound **4** (2 g, 3 mmol) was dissolved in methanol (200 ml) and hydrogenated in the presence of 10% palladium on charcoal (50 mg). The product **1** was obtained by filtering the palladium on charcoal as white powder. Yield: 1.3 g (90%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.35 (s, 4H), 7.44 (s, 4H), 7.30 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 165.59, 156.44, 153.74, 133.82, 129.26, 117.72, 117.43; HRMS (ESI): $C_{22}H_{12}N_4O_8Na^+$ *m/z* calcd 483.0547, found 483.0538.

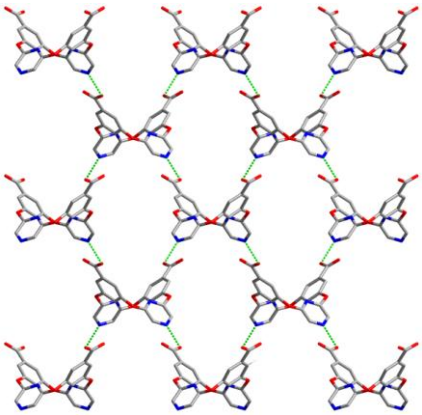


Fig. S1 Schematic presentation of the diamondoid network formed by **1**. Color code: C (gray), O (red), N (blue).

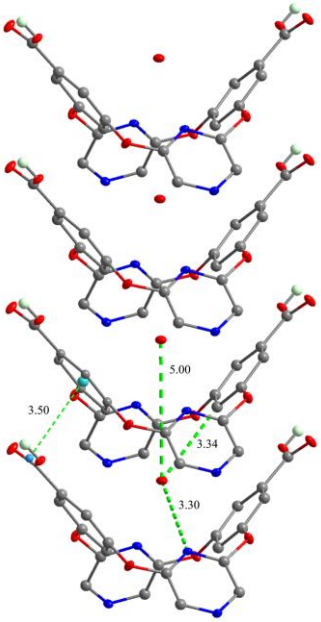


Fig. S2 Schematic view of molecular stacks of **1** in the crystal lattice, the π-π stacking interactions between the carboxylic plane and the phenyl plane of the neighbouring compound **1**, water line in the core of the molecular stacks and hydrogen bond interactions between the water molecules and compound **1**. Color code: C (gray), O (red), N (blue), H (light green)

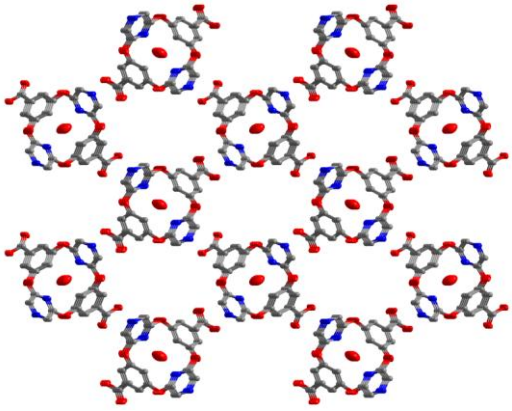


Fig. S3 The nanometer-scale hydrophobic tubular channels formed by **1** in methanol viewed along the *c*-axis, no guest molecule was filled in the channels.

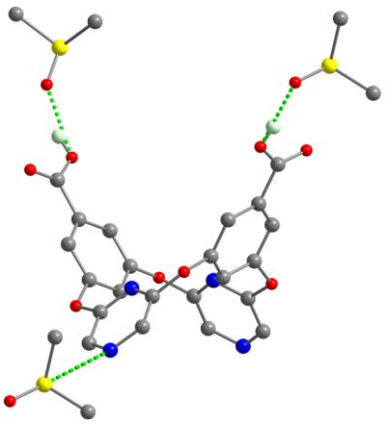


Fig. S4 Molecular structure and intermolecular interactions for **1** obtained in DMSO. Color code: C (gray), O (red), N (blue), S (yellow), H (light green).

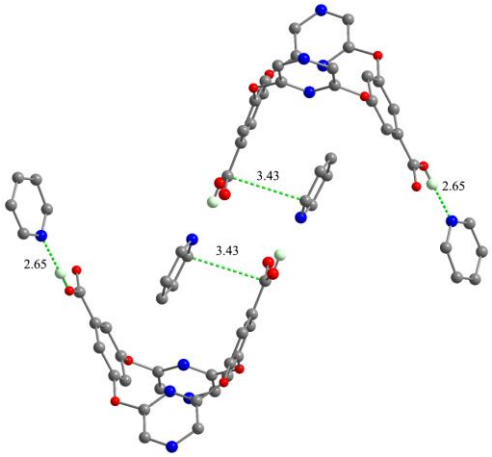


Fig. S5 Schematic presentation of the intermolecular interactions between pyridine and **1**. Color code: C (gray), O (red), N (blue), H (light green).

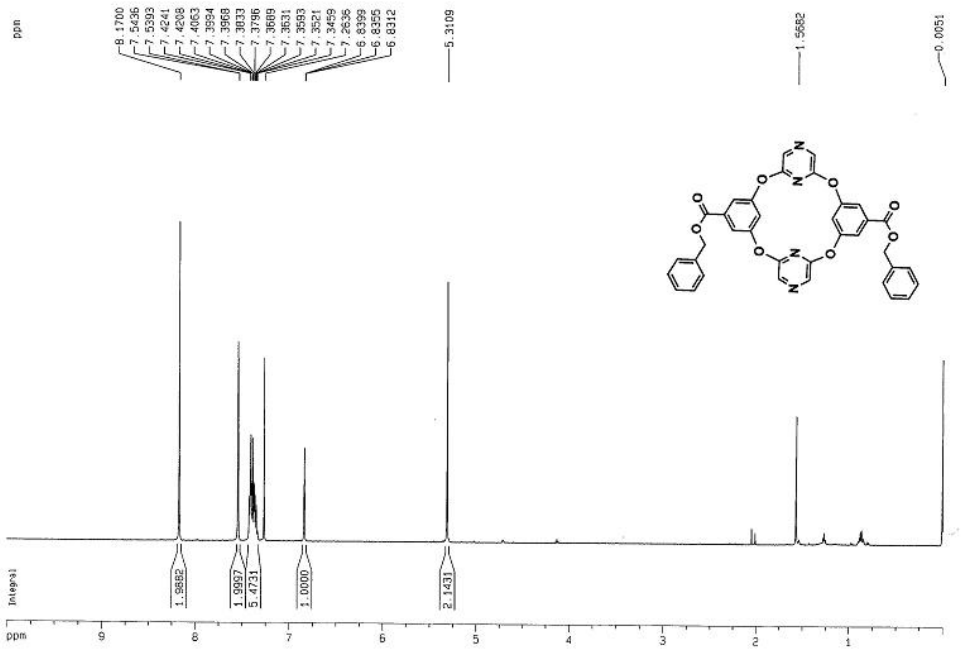


Fig.S6 ^{1}H NMR spectrum of compound **4** in $CDCl_3$

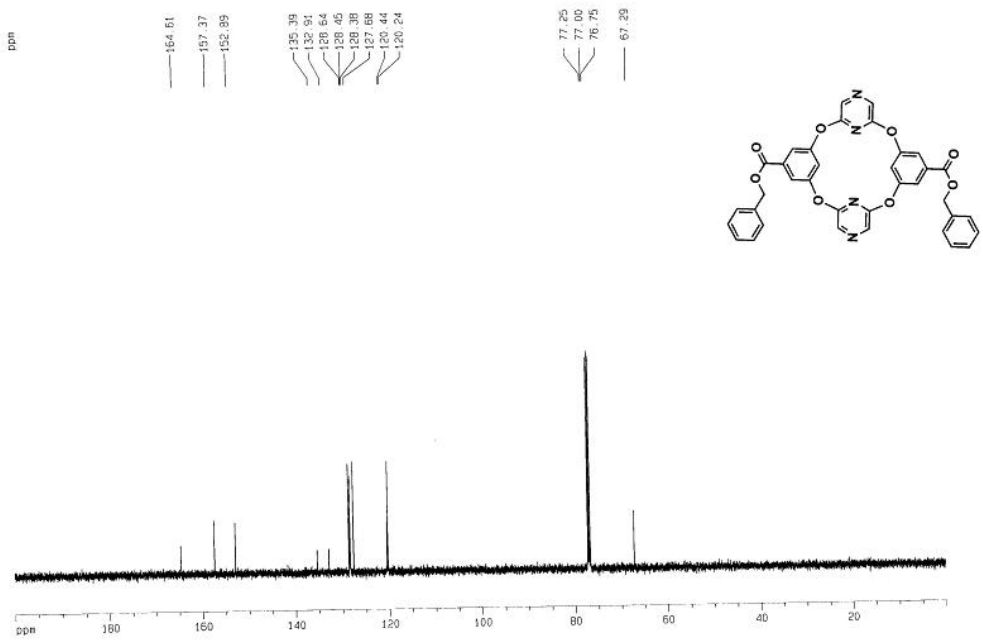


Fig.S7 ^{13}C NMR spectrum of compound **4** in $CDCl_3$

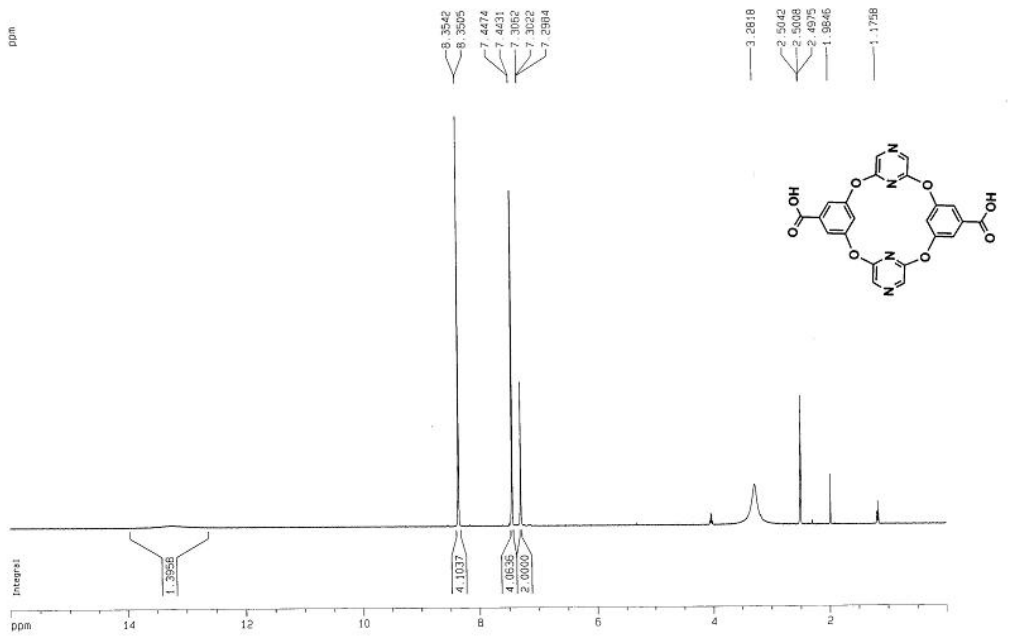


Fig.S8 ^{1}H NMR spectrum of compound **1** in DMSO-d_6

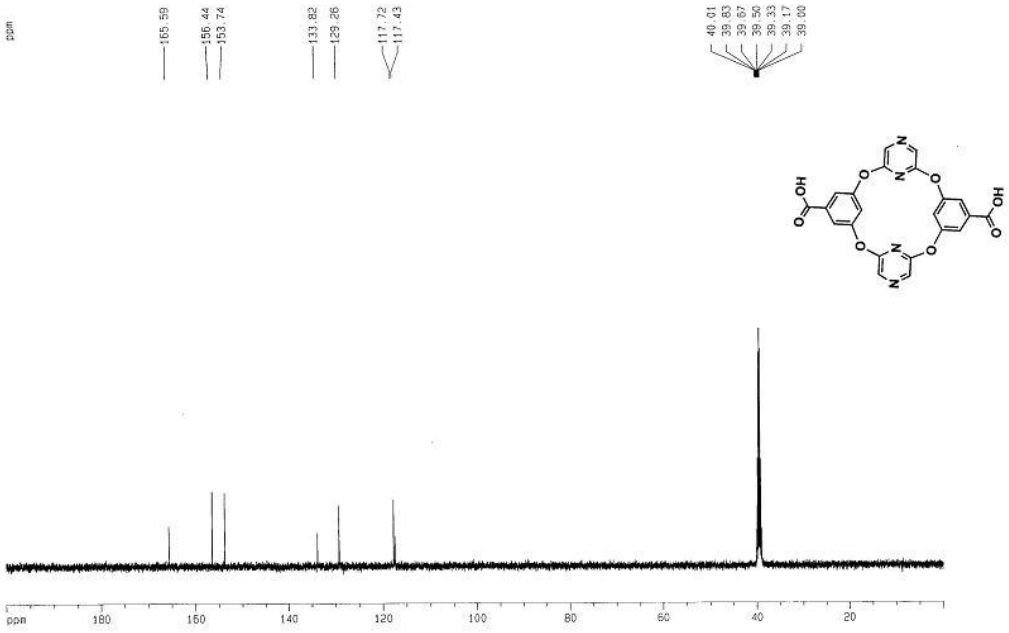


Fig.S9 ^{13}C NMR spectrum of compound **1** in DMSO-d_6