Enhancing the rigidity of a network polymer of intrinsic microporosity by the combined use of phthalocyanine and triptycene components.

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Materials and Methods.

1. General. Infra-red spectra were recorded in the range 4000-600 cm⁻¹ using a Perkin-Elmer 1600 series FTIR instrument. Elemental analysis was carried out with a Carlo Erba EA1101 elemental analyser. UV/vis absorption spectra were recorded in the range 200-800 nm using a Jasco V-570 UV/vis/NIR spectrophotometer. ¹H NMR spectra were recorded in CDCl₃ using an Avance Bruker DPX 400 instrument (400 MHz) with ¹³C NMR spectra recorded at 100 MHz respectively. MALDI-TOF mass spectroscopic analysis was performed with a Waters MALDI Micro MX spectrometer. Volumetric N₂ sorption studies were undertaken at 77 K using a Beckman Coulter 3100 Surface Area Analyzer (Fullerton, California, USA). Apparent surface areas were calculated from N₂ adsorption data by multipoint BET analysis. ¹³C Solid State NMR was provided by the EPSRC National Solid-state Research Service using a Varian VNMRS spectrometer operating at 100.56 MHz and with a 4 mm magic-angle spinning probe. The precursor 9,10-diethyl-2,3,6,7-tetramethoxyanthracene was prepared as reported previously [ref. 16] from propanaldehyde and veratrole.



2. 14,15-Dibromo-9,10-diethyl-2,3,6,7-tetramethoxy-9,10-triptycene (1). To a stirred solution of 9,10-diethyl-2,3,6,7-tetramethoxyanthracene (2g, 5.65 mmol) and 1,2,4,5-tetrabromobenzene (2.22 g, 5.65 mmol) in dry toluene (20 mL) at room temperature under nitrogen was added *n*-butyllithium (6 mmol) in hexane (30 mL) dropwise over 0.5 h. The reaction mixture was stirred for an additional 3 h, then methanol (10 mL) was added. The solvents were removed under reduced pressure and the resulting yellow oily solid was purified by column chromatography using hexane:DCM (1:1) as an eluent to give an off-white powder. Yield: 0.485 g, 0.83 mmol (14.6%); Mp: 170-174 °C (decomposition); ¹H NMR (400 MHz; CDCl₃) δ (ppm): 1.63 (t, 6H, *J* = 7.0 Hz), 2.84 (q, 4H, *J* = 7.0 Hz), 3.77 (s, 12H), 6.91 (s, 4H), 7.43 (b, 2H); ¹³C NMR (100 MHz; CDCl₃) δ (ppm): 11.27, 20.24, 53.12, 56.73, 108.81, 120.45, 146.2; HRMS, *m/z*, (EI): 586.0355 [M⁺], calculated for C₂₈H₂₈O₄⁷⁹Br₂: 586.0354.



3. 14,15-Dicyano-9,10-diethyl-2,3,6,7-tetramethoxy-9,10-triptycene (2). A mixture of 14,15dibromo-9,10-diethyl-2,3,6,7-tetramethoxytriptycene (1; 1.2 g, 2.04 mmol) and copper cyanide (3.73 g, 41.6 mmol) in dry DMF (40 mL) was refluxed for 6 h. After cooling to room temperature, the reaction mixture was poured into concentrated ammonia (300 mL) and stirred for 2 h. The resulting precipitate was collected by filtration and dissolved in chloroform (15 mL) and eluted through a column of silica gel using DCM as eluent to give a pale yellow powder. Yield: 0.67 g, 1.35 mmol (69 %); Mp: 128-132 °C (decomposition); ¹H NMR (400 MHz; CDCl₃) δ (ppm): 1.53 (t, 6H, J= 7.0 Hz), 2.79 (q, 4H, J= 7.0 Hz), 3.66 (s, 12H), 6.81 (s, 4H), 7.46 (b, 2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 11.29, 20.05, 53.91, 56.73, 108.21, 112.48, 116.41, 146.62, 150.02; HRMS, *m/z*, (EI): 480.2052 [M]⁺, calculated for C₃₀H₂₈N₂O₄: 480.2049.

4. Phthalocyanine precursor (3)



A mixture of 14,15-dicyano-9,10-diethyl-2,3,6,7-tetramethoxytriptycene (**2**; 0.98g, 2.04 mmol) and zinc(II) acetate (0.52g, 2.84mmol) were refluxed in DMAc (30 mL) for 48 h. On cooling, water (50 mL) was added and the mixture extracted with chloroform. The organic solvent was removed under reduced pressure and the green solid was purified by passing through a short column of silica using chloroform as an eluent to give **3** as a green powder. Yield: 0.82 g, 0.41 mmol (81%); Mp >300 °C; ¹H NMR (400 MHz; CDCl₃) δ (ppm): 1.67 (t, 24H, J= 7.0 Hz), 2.95 (q, 16H, J= 7.0 Hz), 3.77 (s, 48H), 6.94 (br s, 16H), 7.67 (br s, 8H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 12.03, 21.23, 54.52, 56.8, 135.98, 146.2, 154.1; UV/vis (DCM): λ_{max} 685, 615, 348, 296, 229 nm; MS(*MALDI-TOF*): cluster centred at *m/z* 1987, calc.: 1987 g mol⁻¹.

Crystals of phthalocyanine **3** were prepared by the slow diffusion of MeOH into a CHCl₃ solution. Single-crystal XRD data were collected at 150 K using graphite monochromated MoK α radiation on a Bruker-Nonius Kappa CCD diffractometer with an Oxford Cryosystems cooling apparatus. The structure was solved from these data by direct methods and refined using SHELX-97. Crystal size 0.3 x 0.2 x 0.2 mm, triclinic, space group *P-1*, a = 13.0853, b = 18.0594, c = 18.6508 Å, a = 79.027, $\beta = 75.275$, $\gamma = 72.973$, V = 4043.7 Å³, Z = 1, $\mu = 0.740$ µm⁻¹, 22912 reflections measured, 15100 unique reflections ($R_{int} = 0.0553$), 9528 reflections with $I > 2\sigma(I)$, R = 0.1629 and $\omega R2 = 0.4436$ (observed data), R = 0.2130 and $\omega R2 = 0.4765$ (all data). The asymmetric unit contains one phthalocyanine complex molecule. The unit cell contains one molecule of the phthalocyanine and various CHCl₃ molecules at partial occupancy. A methanol molecule is present axially bonded to the central Zn atom and disordered over 4 sites.



Figure SI 1. Packing of phthalocyanine **3** viewed along the axis *b* and *c* axis. For the latter the solvent molecules are removed for clarity. Looking at the view along the *c* axis it is possible to see that the phthalocyanine cores are disposed along parallel planes which are 11.28 Å apart, and the minimum distance between the central metals is equal to 13.08 Å

5. Phthalocyanine monomer (4)



In a 100 ml two-necked round bottom flask, precursor **3** (0.7 g, 0.35 mmol, 1.00 eq.) was dissolved in dry dichloromethane (40 mL). Upon cooling in an ice bath, boron tribromide (1.41 mL, 5.64 mmol, 16 eq.) was added dropwise and the reaction mixture was stirred for 24 h at room temperature. The mixture was poured into water (50 mL) and stirred for 0.5 h. After filtration, the precipitate was washed with water then recrystallised from a mixture of methanol/chloroform to give **4** as a green powder. Yield: 0.53 g, 2.95 mmol (86 %); Mp >300 °C (decomposition); ¹H NMR (400 MHz; DMSO-d₆) δ (ppm): 1.68 (t, 24H, *J* = 7.0 Hz), 2.91 (q, 16H, *J* = 7.0 Hz), 6.93 (b s, 16H), 7.68 (br s, 8H); UV/vis (MeOH): λ_{max} 684, 617, 359, 313, 225 nm; MS(*MALDI-TOF*): cluster cantered at *m/z*: 1764, calculated: 1763 g mol⁻¹.

6. Phthalocyanine-based network polymer



Figure SI 2. The ¹³C solid state NMR of Trip-Pc-PIM network polymer (EPSRC National Solid-state NMR Research Service).

To a stirred mixture of compound (47) (0.4341 g, 0.246 mmol) and 2,3,5,6-tetrafluoroterephthalonitrile (0.1970 g, 0.984 mmol) in anhydrous DMF (50 mL) was added a fine powder of anhydrous potassium carbonate (0.68 g, 4.92 mmol) in one portion. The reaction mixture was then heated at 80 °C under nitrogen for 48 hours. On cooling, the reaction mixture was poured into 100 mL of stirred acidified water; the deep green precipitate was collected by suction filtration then washed with water and methanol. Purification was achieved by refluxing the product in DMAc, THF, acetone, and methanol respectively. The product was ground into a fine green powder and dried in a vacuum oven at 120 °C for 24 h, yield: 0.514 g (93%); elemental analysis calc (%) for $C_{136}H_{64}N_{16}O_{16}Zn$: C, 72.81; H, 2.90; N, 9.98; Found: C, 71.08; H, 2.83; N, 8.95; IR (KBr, cm⁻¹): 2883, 2240, 1768, 1725, 1601, 1441, 1355, 1268, 1156, 1010, 868, 744; surface area (BET): 806 m² g⁻¹, total pore volume 0.403 mL g⁻¹ at (*p/p^o* = 0.98, adsorption); TGA (Nitrogen): Degradation commences at 450 °C.