Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information for:

Endohedrally Functionalised Porous Organic Cages

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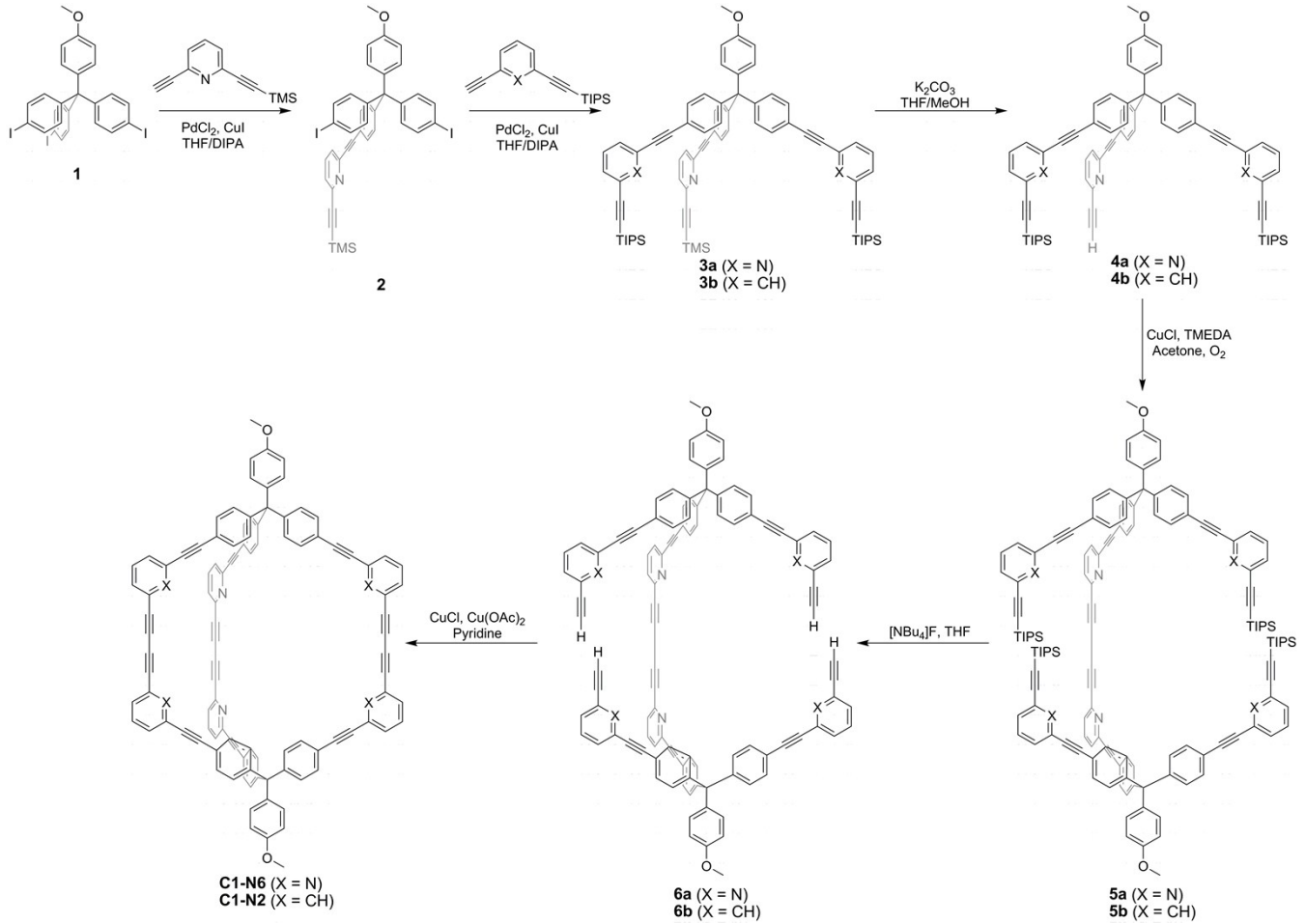
Contents

1. General Experimental

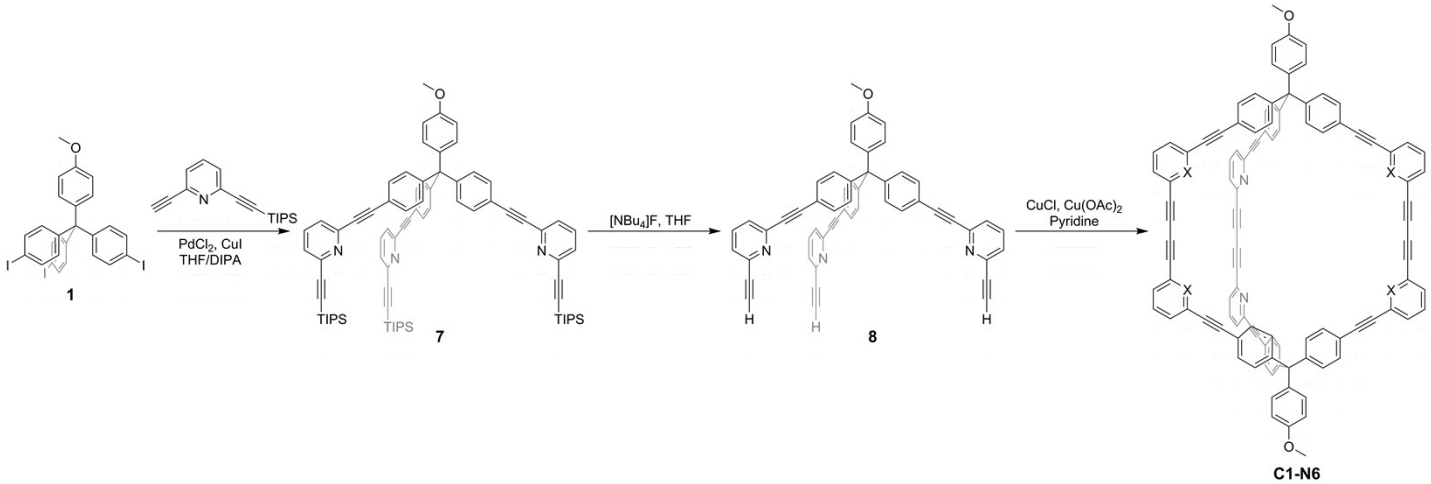
NMR spectra were recorded on Varian Gemini 500 or 600 MHz spectrometers at 23°C using a 5 mm probe. Spectra were referenced to 7.26 ppm and 77.16 ppm in $CDCl_3$, and 7.16 ppm and 128.06 ppm in C_6D_6, for ^1H and ^{13}C spectra, respectively. Infrared spectra were recorded on a Perkin-Elmer 100S Fourier-transform infrared (FT-IR) spectrometer using a universal attenuated total reflectance (UATR) accessory on a zinc-selenide crystal. Electrospray ionisation (ESI) high resolution mass spectra (HR-MS) were recorded on Q-TOF mass spectrometer (Agilent 6230). Samples were prepared by dissolution in dichloromethane and then dilution with methanol. Formic acid was added to the samples prior to measurement.

Unless otherwise stated, all compounds were obtained from commercial sources and used as received. Diisopropylamine (DIPA) and pyridine were dried over KOH before distillation under inert atmosphere.[1] Tetrahydrofuran (THF) was freshly distilled from Na/benzophenone.[1] 4-[Tris(4-iodophenyl)methyl]methoxybenzene (**1**),[2,3] 1-ethynyl-3-[2-(triisopropylsilyl)ethynyl]benzene,[4] 2-ethynyl-6-[2-(trimethylsilyl)ethynyl]pyridine,[5] and 2-ethynyl-6-[2-(triisopropylsilyl)ethynyl]pyridine[6] were prepared according to the methods described in the literature.

2. Synthetic Procedure

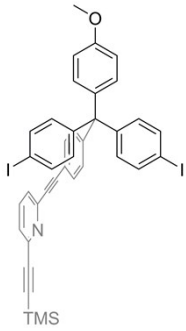


Scheme SI1. Synthesis of Cages **C1-N6** and **C1-N2** - **Method A**.



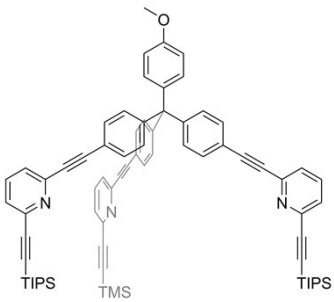
Scheme SI2. Synthesis of Cage **C1-N6** - **Method B**.

Compound 2



A 2:1 THF/DIPA mixture (54 mL) was added to a Schlenk flash containing 4-[tris(4-iodophenyl)methyl]methoxybenzene (**1**) (1.602 g, 2.200 mmol), $PdCl_2(PPh_3)_2$ (0.005 g, 0.007 mmol) and CuI (0.001 g, 0.007 mmol). The resulting solution was slowly heated to 60°C, and after all the solids have solubilised, a solution of 2-ethynyl-6-[2-(trimethylsilyl)ethynyl]pyridine (0.146 g, 0.733 mmol) in 28 mL of DIPA was added dropwise. The resulting solution was then left to stir at 60°C for 1 hour and after cooling to room temperature the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel, 1:1 dichloromethane/petroleum spirit). The excess of **1** (1.192 g, 74% recovered) was recovered from the first fraction (R_f = 0.8), and the second fraction (R_f = 0.6) afforded compound **2** (0.356 g, 61%) as a white solid. FT-IR (neat): *ν*(C≡C) 2214 cm^{-1}. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.42 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 2H), 7.38 (d, $^3J_{H\text{-}H}$ = 8.6 Hz, 4H), 7.06 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 2H), 6.99 (m, 2H), 6.95 (d, $^3J_{H\text{-}H}$ = 8.9 Hz, 2H), 6.76 (d, $^3J_{H\text{-}H}$ = 8.6 Hz, 4H), 6.69 (m, 1H), 6.64 (d, $^3J_{H\text{-}H}$ = 8.9 Hz, 2H), 3.30 (s, 3H, OCH_3), 0.19 (s, 9H, TMS). ^{13}C NMR (C_6D_6, 125 MHz): δ 158.51, 147.54, 146.35, 144.26, 144.18, 137.65, 137.26, 135.99, 133.09, 132.10, 131.85, 131.15, 126.34, 126.24, 120.86, 113.65, 92.43 ($C_{aromatic}$); 104.79, 94.88, 89.90, 89.22(C≡C); 64.20 ($C(C_6H_4)_4$); 54.81 (OCH_3); -0.29 ($Si(CH_3)_3$). HR-MS (ESI, *m/z*): calculated for $C_{38}H_{32}I_2NOSi$ 800.0343 $[M + H]^+$, found 800.0337.

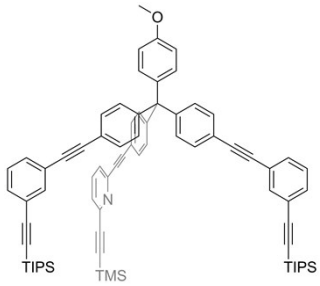
Compound 3a



A 2:1 THF/DIPA mixture (90 mL) was added to a Schlenk flash containing **2** (1.019 g, 1.274 mmol), 2-ethynyl-6-[2-(triisopropylsilyl)ethynyl]pyridine (1.084 g, 3.823 mmol), $PdCl_2(PPh_3)_2$ (0.045 g, 0.064 mmol) and CuI (0.012 g, 0.064 mmol). The reaction mixture was then heated to 60°C for 16 hours. After the reaction mixture was allowed to cool down to room temperature, the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel, 3:2 dichloromethane/petroleum spirit, R_f = 0.8) to afford compound **3a** (1.006 g, 71%) as a white powder. FT-IR (neat): *ν*(C≡C) 2201, 2217 cm^{-1}. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.41 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 2H), 7.38 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 4H), 7.12 (m, 6H), 7. 02 (m, 8H), 6.80 (m, 3H), 6.65 (d, $^3J_{H\text{-}H}$ = 8.8 Hz, 2H), 3.34 (s, 3H, OCH_3), 1.15 (s, 36H, TIPS), 0.18 (s, 9H, TMS). ^{13}C NMR (C_6D_6, 125 MHz):

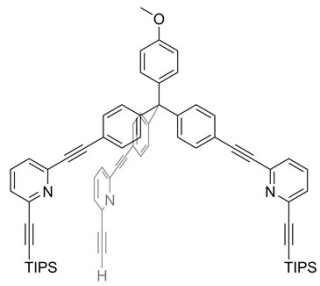
δ 158.45, 147.76, 147.72, 144.29, 144.26, 144.15, 144.07, 137.74, 136.10, 136.05, 132.18, 131.89, 131.25, 131.22, 126.54, 126.45, 126.41, 126.24, 120.69, 113.71 ($C_{aromatic}$); 106.90, 104.79, 94.77, 91.36, 89.80, 89.76, 89.46, 89.44 (C≡C); 64.81 ($C(C_6H_4)_4$); 54.87 (OCH_3); 18.91 ($CH(CH_3)_2$); 11.64 ($CH(CH_3)_2$); -0.25 ($Si(CH_3)_3$). HR-MS (ESI, *m/z*): calculated for $C_{74}H_{79}N_3ONaSi_3$ 1132.5429 $[M + Na]^+$, found 1132.5416.

Compound 3b



To a stirred solution of **2** (574 mg, 0.718 mmol), $PdCl_2(PPh_3)_2$ (25 mg, 0.036 mmol) and CuI (7 mg, 0.036 mmol) in a 2:1 THF/DIPA mixture (57 mL) was added via cannula a solution of 1-ethynyl-3-[2-(triisopropylsilyl)ethynyl]benzene (608 mg, 2.154 mmol) in DIPA (19 mL). The reaction mixture was then heated to 60°C for 16 hours. After the reaction mixture was allowed to cool down to room temperature, the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel, 1:1 dichloromethane/petroleum spirit, R_f = 0.8) to afford compound **3b** (475 mg, 60%) as a white powder. FT-IR (neat): *v*(C≡C) 2218, 2163 cm^{-1}. ^1H NMR (C_6D_6, 500 MHz): δ 7.87 (s, 2H), 7.44 (m, 6H), 7.32 (d, $^3J_{H-H}$ = 7.9 Hz, 2H), 7.28 (d, $^3J_{H-H}$ = 7.8 Hz, 2H), 7.20 (m, 6H), 7. 09 (d, $^3J_{H-H}$ = 8.9 Hz, 2H), 6.99 (d, $^3J_{H-H}$ = 7.8 Hz, 2H), 6.79 (m, 2H), 6.69 (m, 3H), 3.31 (s, 3H, OCH_3), 1.18 (s, 36H, TIPS), 0.19 (s, 9H, TMS). ^{13}C NMR (C_6D_6, 125 MHz): δ 158.51, 147.88, 147.30, 144.33, 144.15, 137.93, 135.97, 135.55, 132.27, 132.04, 131.90, 131.75, 131.54, 131.32, 128.78, 126.36, 126.20, 124.33, 124.15, 121.54, 120.79, 113.70 ($C_{aromatic}$); 107.09, 104.83, 94.80, 91.61, 90.57, 89.83, 89.48, 89.41 (C≡C); 64.82 ($C(C_6H_4)_4$); 54.81 (OCH_3); 18.95 ($CH(CH_3)_2$); 11.71 ($CH(CH_3)_2$); -0.28 ($Si(CH_3)_3$). HR-MS (ESI, *m/z*): calculated for $C_{76}H_{82}NOSi_3$ 1108.5704 $[M + H]^+$, found 1108.5699.

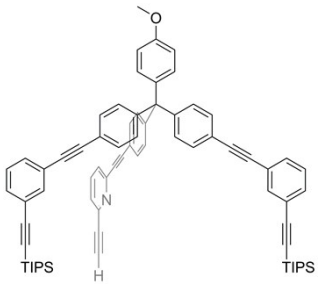
Compound 4a



To a stirred solution of **3a** (0.970 g, 0.873 mmol) in THF/methanol (60 mL, 1:1) was added K_2CO_3 (0.241 g, 1.747 mmol). After stirring at room temperature for 3 hours, the solution was concentrated to ca. 10 mL and water (50 mL) was added. The resulting precipitate was extracted with dichloromethane (3 × 25 mL), and the combined organic phases were then washed with water (2 × 25 mL) and brine (25 mL). The solvent was evaporated under reduced

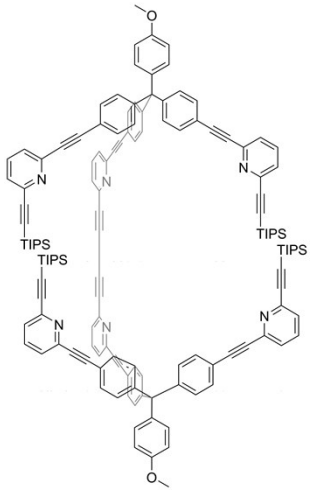
pressure to afford compound **4a** (0.904 g, 99%) as a white powder without further purification. FT-IR (neat): *v*(≡C-H) 3298, *v*(C≡C) 2213 cm^{-1}. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.40 (m, 6H), 7.12 (m, 6H), 7. 00 (m, 7H), 6.88 (d, $^{3}J_{H-H}$ = 7.8 Hz, 1H), 6.67 (m, 5H), 3.30 (s, 3H, OCH_3), 2.60 (s, 1H, ≡C-H), 1.18 (s, 36H, TIPS). ^{13}C NMR (C_6D_6, 125 MHz): δ 158.47, 147.82, 147.71, 144.40, 144.34, 144.23, 143.45, 137.82, 135.98, 135.91, 132.22, 131.90, 131.28, 131.24, 126.64, 126.47, 126.38, 126.33, 120.76, 120.66, 113.69 ($C_{aromatic}$); 106.97, 91.38, 89.84, 89.65, 89.59, 89.47, 83.09, 77.46 (C≡C); 64.83 ($C(C_6H_4)_4$); 54.79 (OCH_3); 18.90 ($CH(CH_3)_2$); 11.66 ($CH(CH_3)_2$). HR-MS (ESI, *m/z*): calculated for $C_{71}H_{71}N_3ONaSi_2$ 1060.5033 $[M + Na]^+$, found 1060.5023.

Compound 4b



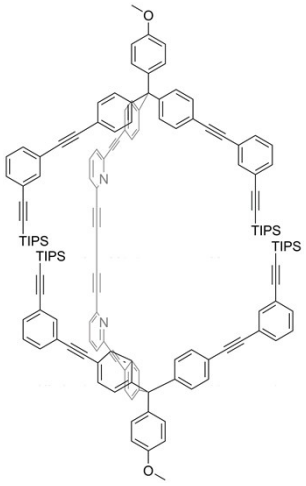
Compound **4b** was synthesised following the same procedure as for compound **4a**. Starting from **3b** (475 mg, 0.428 mmol) and K_2CO_3 (118 mg, 0.857 mmol) in THF/MeOH (1:1, 30 mL), compound **4b** was obtained as a white powder (438 mg, 99%). FT-IR (neat): *v*(≡C-H) 3293, *v*(C≡C) 2213, 2165 cm^{-1}. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.88 (s, 2H), 7.43 (m, 6H), 7.32 (d, $^{3}J_{H-H}$ = 7.8 Hz, 2H), 7.28 (d, $^{3}J_{H-H}$ = 7.8 Hz, 2H), 7.20 (m, 6H), 7. 09 (d, $^{3}J_{H-H}$ = 8.9 Hz, 2H), 6.99 (d, $^{3}J_{H-H}$ = 7.8 Hz, 1H), 6.89 (d, $^{3}J_{H-H}$ = 7.8 Hz, 1H), 6.79 (m, 2H), 6.67 (m, 3H), 3.31 (s, 3H, OCH_3), 2.61 (s, 1H, ≡C-H), 1.18 (s, 36H, TIPS). ^{13}C NMR (C_6D_6, 125 MHz): δ 158.51, 147.93, 147.29, 144.36, 143.45, 137.93, 136.00, 135.55, 132.27, 132.05, 131.91, 131.76, 131.55, 131.32, 128.78, 126.64, 126.42, 124.33, 124.15, 121.55, 120.72, 113.71 ($C_{aromatic}$); 107.09, 91.62, 90.57, 89.69, 89.54, 89.50, 83.08, 77.50 (C≡C); 64.82 ($C(C_6H_4)_4$); 54.81 (OCH_3); 18.95 ($CH(CH_3)_2$); 11.71 ($CH(CH_3)_2$). HR-MS (ESI, *m/z*): calculated for $C_{73}H_{74}NOSi_2$ 1036.5309 $[M + H]^+$, found 1036.5300.

Compound 5a



A 140 mL acetone solution of CuCl-TMEDA catalyst (712 mg of CuCl, 8.5 mL of TMEDA) prepared previously under inert atmosphere[7] was transferred by syringe in 10 mL aliquots, over a period of 2 hours, to a stirred solution of **4a** (854 mg, 0.822 mmol) in acetone (140 mL) with oxygen bubbling through the solution. After the last aliquot was added, the reaction was left stirring at room temperature with the oxygen bubbling for one hour, and then the solvent was evaporated under reduced pressure. The resulting residue was dissolved in dichloromethane (50 mL) and washed with a 14% ammonia solution (2 × 25 mL) to remove any copper residue. The organic phase was further washed with H_2O (2 × 25 mL) and brine (25 mL), and the solvent was evaporated. The residue was purified by column chromatography (silica gel, 1:1 ethyl acetate/petroleum spirit, R_f = 0.8) to afford compound **5a** (677 mg, 79%) as a light yellow powder. FT-IR (neat): *ν*(C≡C) 2213 cm^{-1}. ^1H NMR (C_6D_6, 500 MHz): δ 7.42 (d, $^3J_{H\text{-}H}$ = 8.4 Hz, 4H), 7.39 (d, $^3J_{H\text{-}H}$ = 8.4 Hz, 8H), 7.14 (m, 12H), 7. 02 (m, 14H), 6.86 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 2H), 6.76 (m, 6H), 6.66 (d, $^3J_{H\text{-}H}$ = 8.8 Hz, 4H), 3.34 (s, 6H, OCH_3), 1.16 (s, 72H, TIPS). ^{13}C NMR (C_6D_6, 125 MHz): δ 158.45, 147.89, 147.73, 144.56, 144.27, 144.15, 142.61, 137.76, 136.18, 136.04, 132.19, 131.95, 131.91, 131.28, 131.23, 127.46, 127.20, 126.54, 126.41, 120.69, 120.54, 113.72 ($C_{aromatic}$); 106.90, 91.39, 89.87, 89.79, 89.51 (2 × C), 81.70, 73.67 (C≡C); 64.83 ($C(C_6H_4)_4$); 54.86 (OCH_3); 18.91 ($CH(CH_3)_2$); 11.65 ($CH(CH_3)_2$). HR-MS (ESI, *m/z*): calculated for $C_{142}H_{140}N_6O_2NaSi_4$ 2096.0013 $[M + Na]^+$, found 2095.9985.

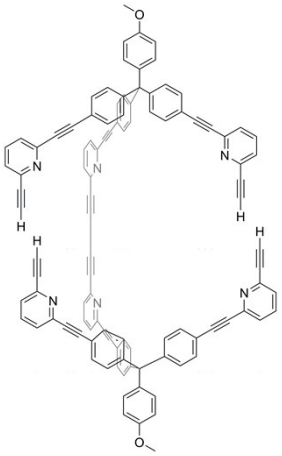
Compound 5b



Compound **5b** was synthesised following the same procedure as for compound **5a**. Starting from **4b** (462 mg, 0.446 mmol) in acetone (76 mL), and an acetone solution (76 mL) of CuCl-TMEDA catalyst (386 mg of CuCl, 4.6 mL of TMEDA), compound **5b** was obtained as a white powder (349 mg, 76%) after purification by column chromatography (silica gel, 7:3 dichloromethane/petroleum spirit, R_f = 0.8). FT-IR (neat): *ν*(C≡C) 2214, 2165 cm^{-1}. ^1H NMR (C_6D_6, 500 MHz): δ 7.86 (s, 4H), 7.44 (m, 12H), 7.32 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 4H), 7.27 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 4H), 7.21 (m, 12H), 7. 09 (d, $^3J_{H\text{-}H}$ = 8.8 Hz, 4H), 6.97 (d, $^3J_{H\text{-}H}$ = 7.7 Hz, 2H),

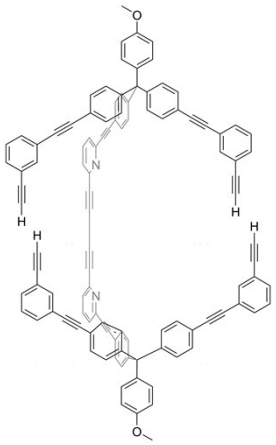
6.80 (m, 6H), 6.66 (m, 6H), 3.32 (s, 6H, OCH_3), 1.18 (s, 72H, TIPS). ^{13}C NMR (C_6D_6, 125 MHz): δ 158.50, 148.03, 147.28, 144.57, 142.66, 137.90, 136.05, 135.54, 132.26, 132.05, 131.95, 131.76, 131.55, 131.35, 131.31, 128.78, 127.39, 127.10, 124.32, 124.14, 121.53, 120.61, 113.71 ($C_{aromatic}$); 107.07, 91.61, 90.56, 89.85, 89.54, 89.48, 81.69, 73.70 (C≡C); 64.83 ($C(C_6H_4)_4$); 54.82 (OCH_3); 18.95 ($CH(CH_3)_2$); 11.71 ($CH(CH_3)_2$). HR-MS (ESI, *m/z*): calculated for $C_{146}H_{144}N_2O_2NaSi_4$ 2092.0203 $[M + Na]^+$, found 2092.0210.

Compound 6a



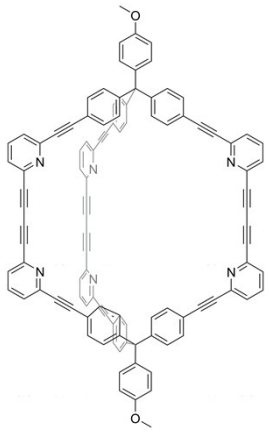
To a stirred solution of **5a** (659 mg, 0.318 mmol) in THF (100 mL) was added dropwise 1.91 mL of a tetra-n-butylammonium fluoride (TBAF) solution in THF (1M). After the solution was left stirring at room temperature for 90 mins, water (100 mL) was added to quench the reaction. The THF was then removed under reduce pressure and the resulting precipitate was extracted with dichloromethane (3 × 40 mL). The combined organic phases were washed with H_2O (2 × 50 mL), brine (50 mL), dried over $MgSO_4$ and the solvent was evaporated. The residue was purified by column chromatography (silica gel, 4:1 dichloromethane/acetone, R_f = 0.9) to afford compound **6a** (328 mg, 71%) as a light yellow powder. FT-IR (neat): *v*(≡C-H) 3289, *v*(C≡C) 2212 cm^{-1}. ^1H NMR (C_6D_6, 500 MHz): δ 7.42 (m, 12H), 7.14 (m, 16H), 7. 04 (d, $^3J_{H-H}$ = 8.9 Hz, 4H), 6.99 (d, $^3J_{H-H}$ = 7.5 Hz, 4H), 6.97 (d, $^3J_{H-H}$ = 7.9 Hz, 2H), 6.89 (d, $^3J_{H-H}$ = 7.5 Hz, 4H), 6.77 (d, $^3J_{H-H}$ = 7.7 Hz, 2H), 6.64 (m, 10H), 3.30 (s, 6H, OCH_3), 2.61 (s, 4H, ≡C-H). ^{13}C NMR (C_6D_6, 125 MHz): δ 158.50, 147.87, 147.78, 144.60, 144.38, 143.45, 142.70, 137.78, 136.01, 132.23, 131.95, 131.92, 131.31, 131.29, 127.35, 127.06, 126.66, 126.41, 120.70, 120.62, 113.72 ($C_{aromatic}$); 89.83, 89.68, 89.57 (2 × C), 83.08, 81.73, 77.50, 73.70 (C≡C); 64.85 ($C(C_6H_4)_4$); 54.81 (OCH_3). HR-MS (ESI, *m/z*): calculated for $C_{106}H_{60}N_6O_2Na$ 1471.4675 $[M + Na]^+$, found 1471.4730.

Compound 6b



Compound **6b** was synthesised following the same procedure as for compound **6a**. Starting from **5b** (339 mg, 0.164 mmol) and TBAF (1 mL, 1M in THF) in THF (50 mL), compound **6b** was obtained as a white powder (184 mg, 78%) after purification by column chromatography (silica gel, 4:1 dichloromethane/petroleum spirit, R_f = 0.6). FT-IR (neat): *v*(≡C-H) 3289, *v*(C≡C) 2215 cm^{-1}. ^1H NMR (C_6D_6, 500 MHz): δ 7.77 (s, 4H), 7.46 (d, $^3J_{H-H}$ = 8.3 Hz, 4H), 7.43 (d, $^3J_{H-H}$ = 8.2 Hz, 8H), 7.31 (d, $^3J_{H-H}$ = 7.8 Hz, 4H), 7.21 (m, 16H), 7. 10 (d, $^3J_{H-H}$ = 8.6 Hz, 4H), 6.96 (d, $^3J_{H-H}$ = 7.9 Hz, 2H), 6.76 (m, 6H), 6.68 (d, $^3J_{H-H}$ = 8.6 Hz, 4H), 6.61 (m, 2H), 3.30 (s, 6H, OCH_3), 2.67 (s, 4H, ≡C-H). ^{13}C NMR (C_6D_6, 125 MHz): δ 158.49, 148.02, 147.31, 144.54, 142.62, 137.89, 136.10, 135.53, 132.26, 132.07, 132.05, 131.96, 131.55, 131.34, 131.32, 128.80, 127.41, 127.14, 124.18, 123.21, 121.47, 120.60, 113.73 ($C_{aromatic}$); 90.59, 89.87, 89.54, 89.34, 82.99, 81.70, 78.60, 73.71 (C≡C); 64.83 ($C(C_6H_4)_4$); 54.84 (OCH_3). HR-MS (ESI, *m/z*): calculated for $C_{110}H_{65}N_2O_2$ 1445.5046 $[M + H]^+$, found 1445.5018.

Cage C1-N6

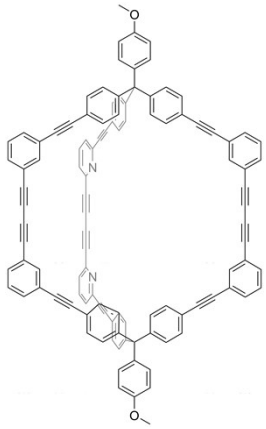


Method A. Copper(II) acetate monohydrate (448 mg, 2.242 mmol) and copper(I) chloride (154 mg, 1.552 mmol) were combined in a Schlenk flask and dried under vacuum at 70°C during 2 hours. After having backfilled the Schlenk flask with argon, 32 mL of pyridine was added. The resulting suspension was stirred at 70°C until all the solids dissolved, and then a solution of **6a** (50 mg, 0.034 mmol) in pyridine (16 mL) was slowly added dropwise via cannula over a period of 6 hours. After the addition has finished, the reaction mixture was stirred at 70°C for 1 more hour. Then the solvent was removed under reduced pressure and the resulting residue was dissolved in dichloromethane (30 mL). The organic phase was washed with a 14% ammonia solution (20 mL) to remove any copper residues, then washed with H_2O (2 × 20 mL), brine (20 mL), dried over $MgSO_4$ and the solvent evaporated. The residue was redissolved in a 9:1 mixture of dichloromethane/triethylamine and passed through a small basic alumina column. The yellow band was collected and the solvent evaporated. The residue was dissolved in

toluene and crystallisation by vapour diffusion of hexane over a period of 3 days afforded **C1-N6** as yellow crystals (26 mg, 52%).

Method B. Starting from copper(II) acetate monohydrate (1.538 g, 7.701 mmol) and copper(I) chloride (528 mg, 5.332 mmol) in pyridine (60 mL), compound **8** (86 mg, 0.118 mmol) in pyridine (20 mL), and following the same procedure as for **Method A**, cage **C1-N6** was obtained as a yellow crystalline powder (3 mg, 4%). FT-IR (neat): *ν*(C≡C) 2220, 2212 cm^{-1}. ^{1}H NMR (C_6D_6, 600 MHz): δ 7.48 (d, $^{3}J_{H-H}$ = 8.6 Hz, 12H), 7.14 (m, 16H), 6. 92 (d, $^{3}J_{H-H}$ = 7.9 Hz, 6H), 6.75 (d, $^{3}J_{H-H}$ = 7.7 Hz, 6H), 6.66 (d, $^{3}J_{H-H}$ = 8.9 Hz, 4H), 6.58 (m, 6H), 3.30 (s, 6H, OCH_3). ^{13}C NMR (C_6D_6, 150 MHz): δ 158.45, 147.93, 144.71, 142.70, 137.64, 135.95, 132.28, 132.01, 131.30, 126.44, 126.38, 120.65, 113.68 ($C_{aromatic}$); 89.74, 89.56, 81.76, 73.61 (C≡C); 64.82 ($C(C_6H_4)_4$); 54.78 (OCH_3). HR-MS (ESI, *m/z*): calculated for $C_{106}H_{57}N_6O_2$ 1445.4543 $[M + H]^+$, found 1445.4531.

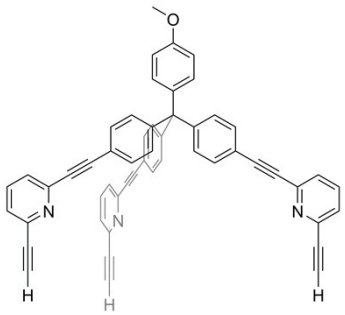
Cage C1-N2



Copper(II) acetate monohydrate (269 mg, 1.349 mmol) and copper(I) chloride (92 mg, 0.934 mmol) were combined in a Schlenk flask and dried under vacuum at 70°C during 2 hours. After having backfilled the Schlenk flask with argon, 20 mL of pyridine was added. The resulting suspension was stirred at 70°C until all the solids dissolved, and then a solution of **6b** (30 mg, 0.021 mmol) in pyridine (10 mL) was slowly added dropwise via cannula over a period of 4 hours. After the addition has finished, the reaction mixture was stirred at 70°C for 1 more hour. Then the solvent was removed under reduced pressure and the resulting residue was dissolved in dichloromethane (30 mL). The organic phase was successively washed with a 1 M HCl solution (2 × 20 mL), a saturated $NaHCO_3$ solution (2 × 20 mL), H_2O (2 × 20 mL), brine (20 mL), then dried over $MgSO_4$ and the solvent evaporated. The residue was purified by column chromatography (silica gel, 4:1 dichloromethane/petroleum spirit, R_f = 0.7) to afford cage **C1-N2** (16 mg, 53%) as a white powder. FT-IR (neat): *ν*(C≡C) 2217, 2206 cm^{-1}. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.83 (s, 4H), 7.50 (d, $^{3}J_{H-H}$ = 8.5 Hz, 4H), 7.46 (d, $^{3}J_{H-H}$ = 8.4 Hz, 8H), 7.21 (m, 20H), 7. 11 (d, $^{3}J_{H-H}$ = 7.7 Hz, 4H), 6.92 (d, $^{3}J_{H-H}$ = 7.8 Hz, 2H), 6.76 (d, $^{3}J_{H-H}$ = 7.7 Hz, 2H), 6.70 (m, 8H), 6.59 (m, 2H), 3.32 (s, 6H, OCH_3). ^{13}C NMR (C_6D_6, 125 MHz): δ 158.57, 148.10, 147.52, 144.64, 142.68, 137.47, 137.37, 136.01, 132.41, 131.99, 131.83, 131.57, 131.44, 131.40, 131.38, 128.88, 126.59, 126.53,

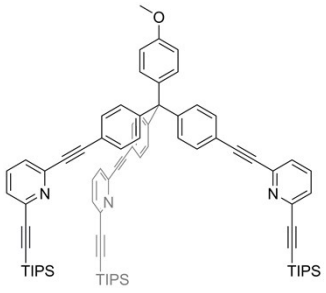
124.42, 122.65, 121.48, 120.73, 113.73 ($C_{aromatic}$); 90.83, 89.67, 89.65, 89.13, 81.81, 81.68, 75.60, 73.57 (C≡C); 64.80 ($C(C_6H_4)_4$); 54.82 (OCH_3). HR-MS (ESI, *m/z*): calculated for $C_{110}H_{61}N_2O_2$ 1441.4733 $[M + H]^+$, found 1441.4707.

Compound 7



A 1:1 THF/DIPA mixture (50 mL) was added to a Schlenk flask containing **1** (350 mg, 0.481 mmol), 2-ethynyl-6-[2-(triisopropylsilyl)ethynyl]pyridine (681 mg, 2.403 mmol), $PdCl_2(PPh_3)_2$ (25 mg, 0.036 mmol) and CuI (7 mg, 0.036 mmol). The reaction mixture was then heated to 70°C for 16 hours. After the reaction mixture was allowed to cool down to room temperature, the solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, 1:1 dichloromethane/petroleum spirit, R_f = 0.6) to afford compound **7** (512 mg, 89%) as a white powder. FT-IR (neat): *v*(C≡C) 2214 cm^{-1}. ^1H NMR (C_6D_6, 500 MHz): δ 7.39 (d, $^3J_{H-H}$ = 8.4 Hz, 6H), 7.12 (d, $^3J_{H-H}$ = 8.4 Hz, 6H), 7.00 (m, 8H), 6.71 (m, 3H), 6.65 (d, $^3J_{H-H}$ = 8.9 Hz, 2H), 3.30 (s, 3H, OCH_3), 1.17 (s, 54H, TIPS). ^{13}C NMR (C_6D_6, 125 MHz): δ 158.46, 147.72, 144.33, 144.21, 137.82, 135.93, 132.21, 131.89, 131.23, 126.48, 126.35, 120.73, 113.69 ($C_{aromatic}$); 106.97, 91.36, 89.83, 89.48 (C≡C); 64.82 ($C(C_6H_4)_4$); 54.80 (OCH_3); 18.90 ($CH(CH_3)_2$); 11.66 ($CH(CH_3)_2$). HR-MS (ESI, *m/z*): calculated for $C_{80}H_{91}N_3ONaSi_3$ 1216.6368 $[M + Na]^+$, found 1216.6381.

Compound 8



To a stirred solution of **7** (158 mg, 0.132 mmol) in THF (15 mL) was added dropwise 0.66 mL of a TBAF solution in THF (1M). After the solution was left stirring at room temperature for 90 mins, water (40 mL) was added to quench the reaction. The THF was then removed under reduce pressure and the resulting precipitate was extracted with dichloromethane (3 × 20 mL). The combined organic phases were washed with H_2O (2 × 25 mL), brine (25 mL), dried over $MgSO_4$ and the solvent was evaporated. The residue was purified by column chromatography (silica gel, 1:1 ethyl acetate/petroleum spirit, R_f = 0.5) to afford compound **8** (86 mg, 90%) as a white powder. FT-IR (neat): *v*(≡C-H) 3286, *v*(C≡C) 2210, 2111 cm^{-1}. ^1H NMR (C_6D_6, 500 MHz): δ 7.42 (d, $^3J_{H-H}$ = 8.5 Hz, 6H), 7.14 (d, $^3J_{H-H}$ = 8.5 Hz, 6H), 7.03 (d, $^3J_{H-H}$ = 8.9 Hz, 2H), 6.99 (d, $^3J_{H-H}$ = 7.8 Hz, 3H), 6.89 (d, $^3J_{H-H}$ = 7.8 Hz, 3H), 6.66 (m,

5H), 3.30 (s, 3H, OCH_3), 2.61 (s, 3H, ≡C-H). ^{13}C NMR (C_6D_6, 125 MHz): δ 158.49, 147.78, 144.37, 143.45, 137.78, 136.01, 132.23, 131.91, 131.28, 126.65, 126.41, 120.69, 113.71 ($C_{aromatic}$); 89.67, 89.56, 83.08, 77.70 (C≡C); 64.83 ($C(C_6H_4)_4$); 54.80 (OCH_3). HR-MS (ESI, *m/z*): calculated for $C_{53}H_{32}N_3O$ 726.2545 $[M + H]^+$, found 726.2534.

3. NMR spectra of cages C1-N2 and C1-N6

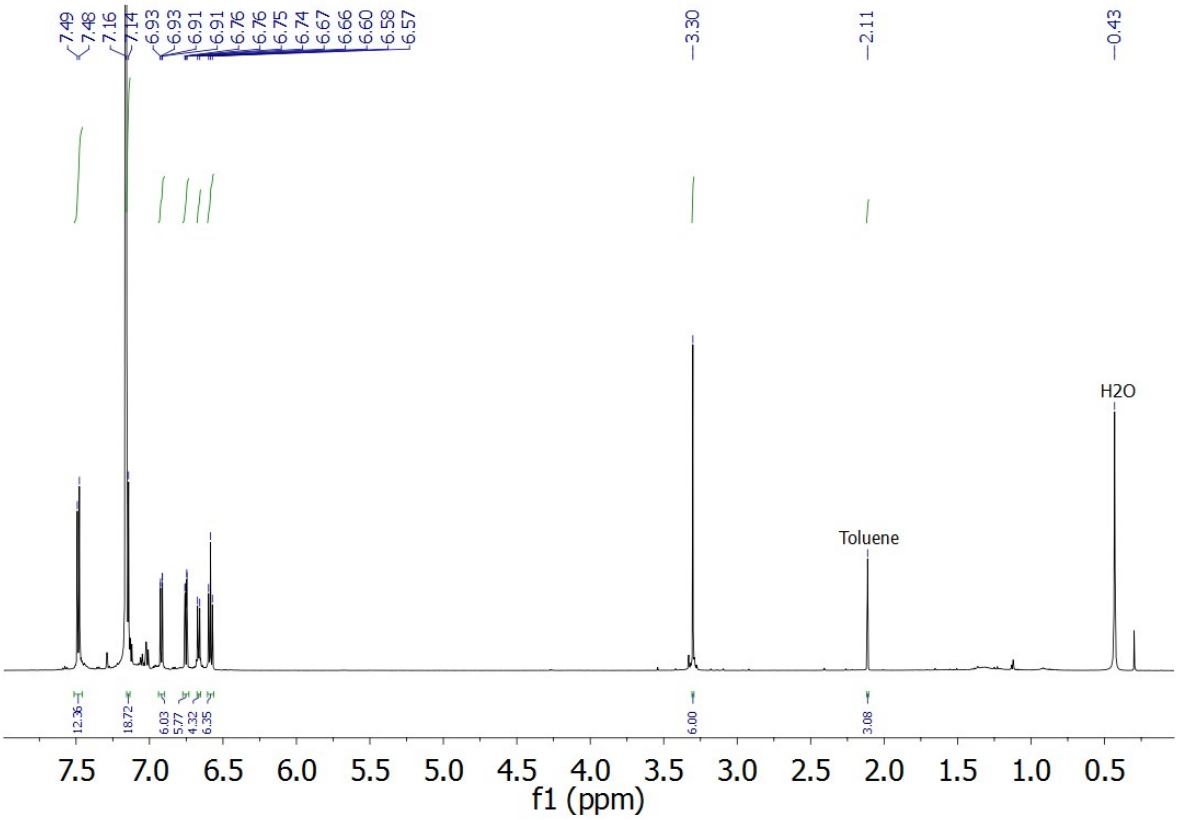


Figure SI1. ^{1}H NMR spectrum of **C1-N6** (crystals)[8] in C_6D_6.

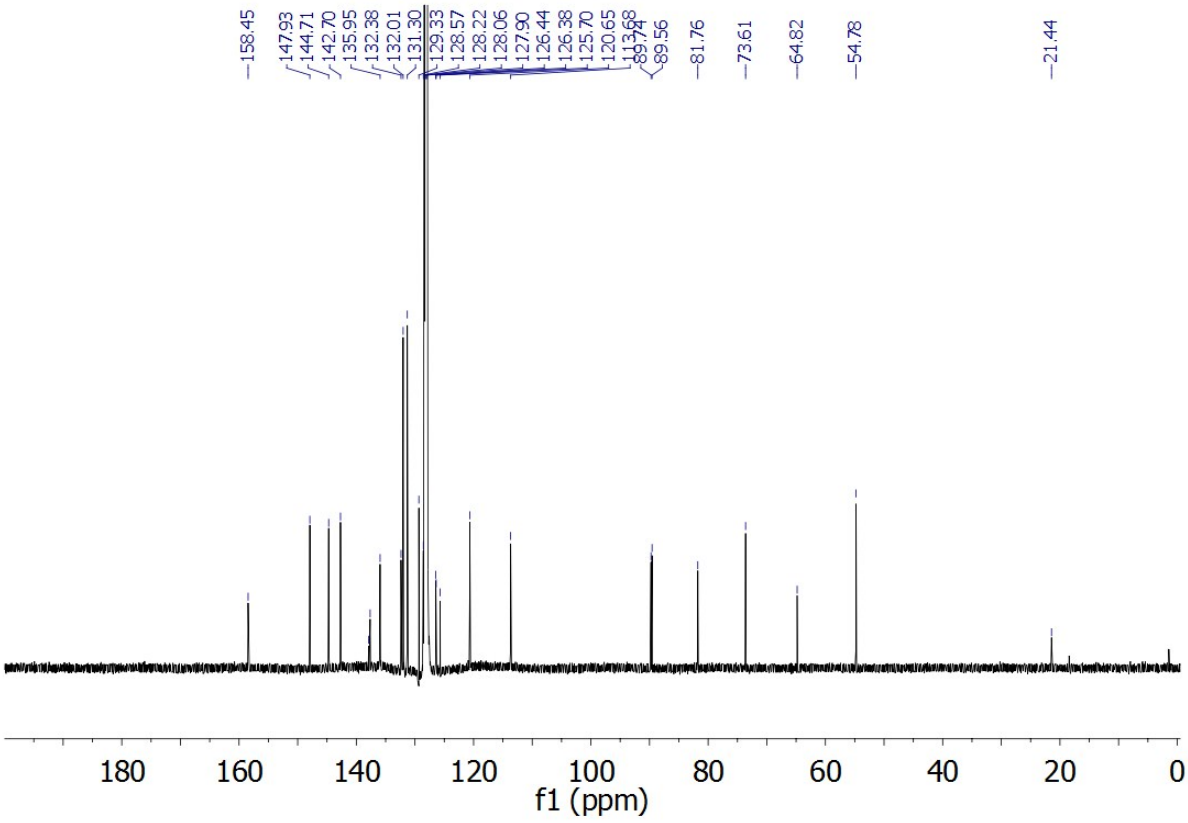


Figure SI2. ^{13}C NMR spectrum of **C1-N6** (crystals)[8] in C_6D_6.

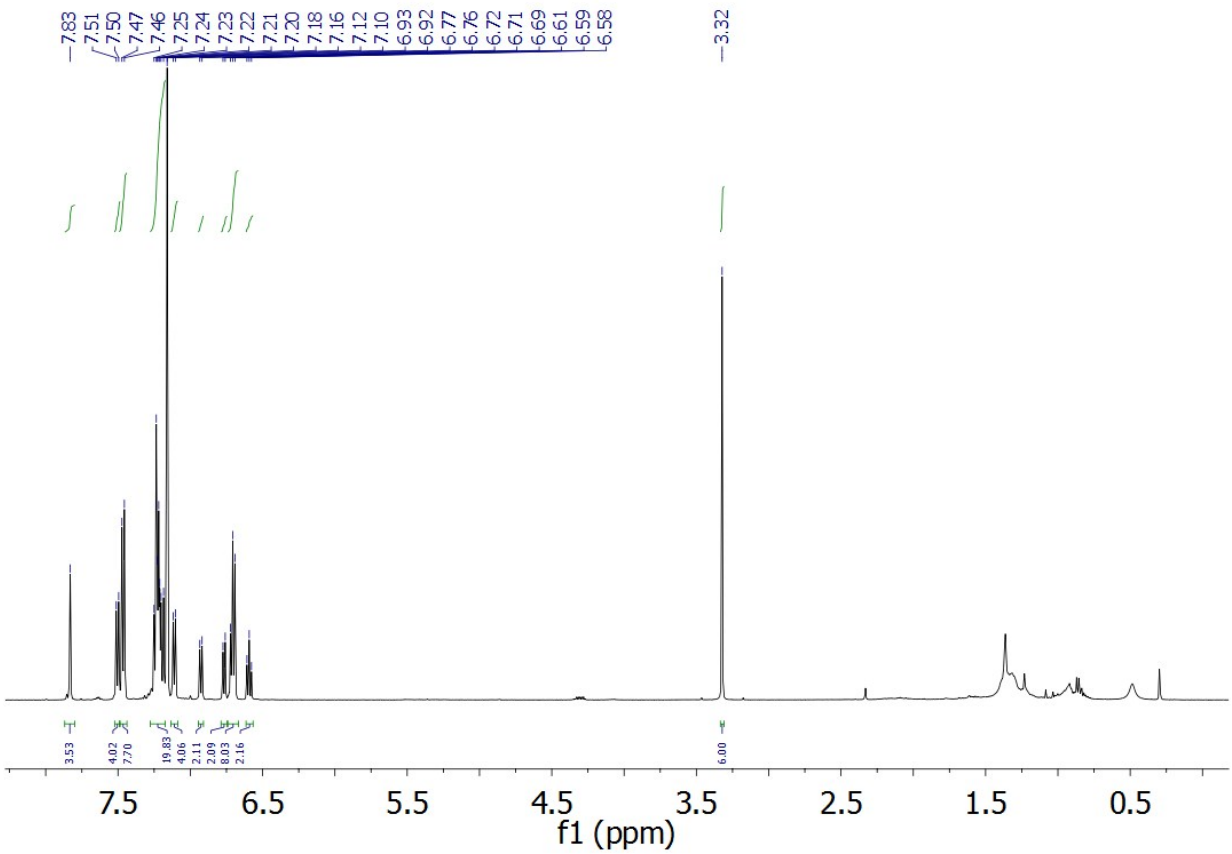


Figure SI3. ^{1}H NMR spectrum of **C1-N2** in C_6D_6.

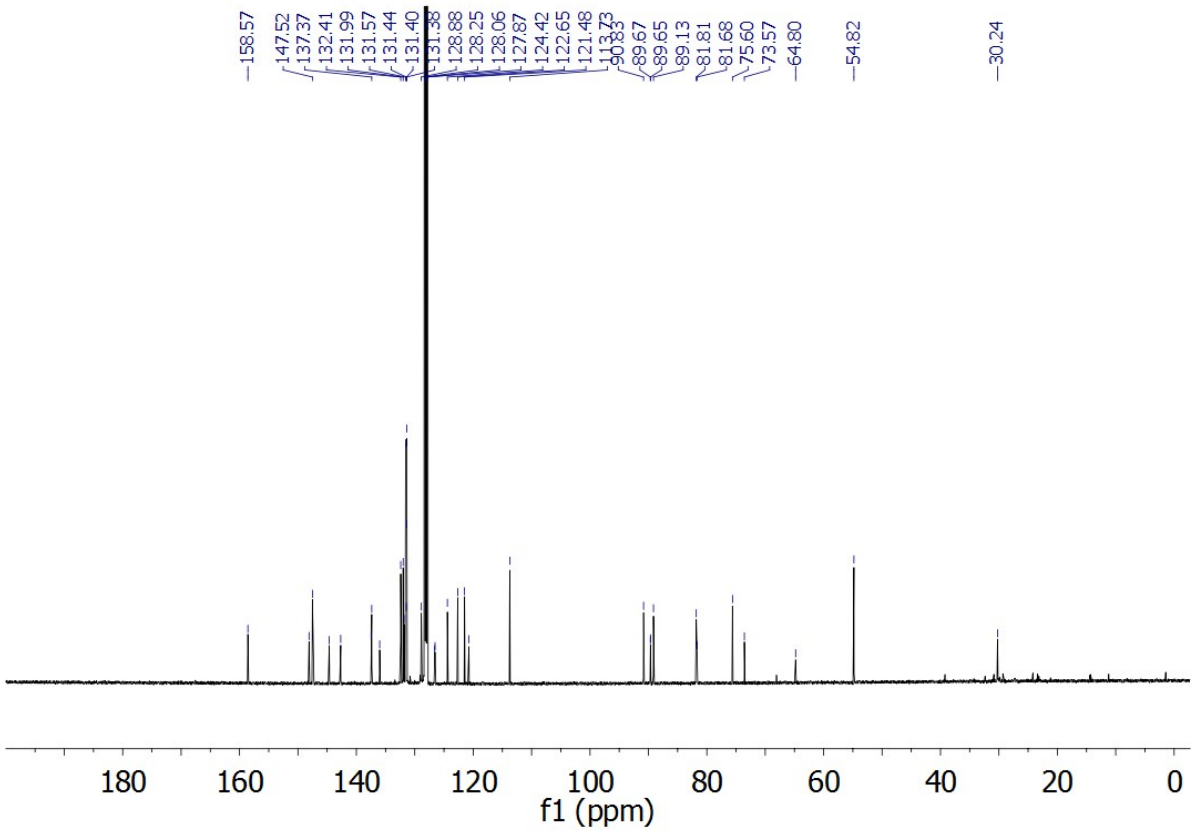


Figure SI4. ^{13}C NMR spectrum of **C1-N2** in C_6D_6.

4. Powder X-ray Diffraction

Powder X-ray diffraction data were collected on a Bruker Advance D8 diffractometer (capillary stage) using Cu Kα radiation (λ = 1.5418 Å, 40 kW/40mA, 2θ = 2 – 55°) or on a Rigaku Hi-Flux Homelab system using Cu-Kα radiation (λ = 1.54056 Å) with an R-Axis IV++ image plate. Samples were mounted in glass capillaries (0.5 or 0.8 mm outer diameter, D8 diffractometer) or on nylon loop (Hi-Flux Homelab).

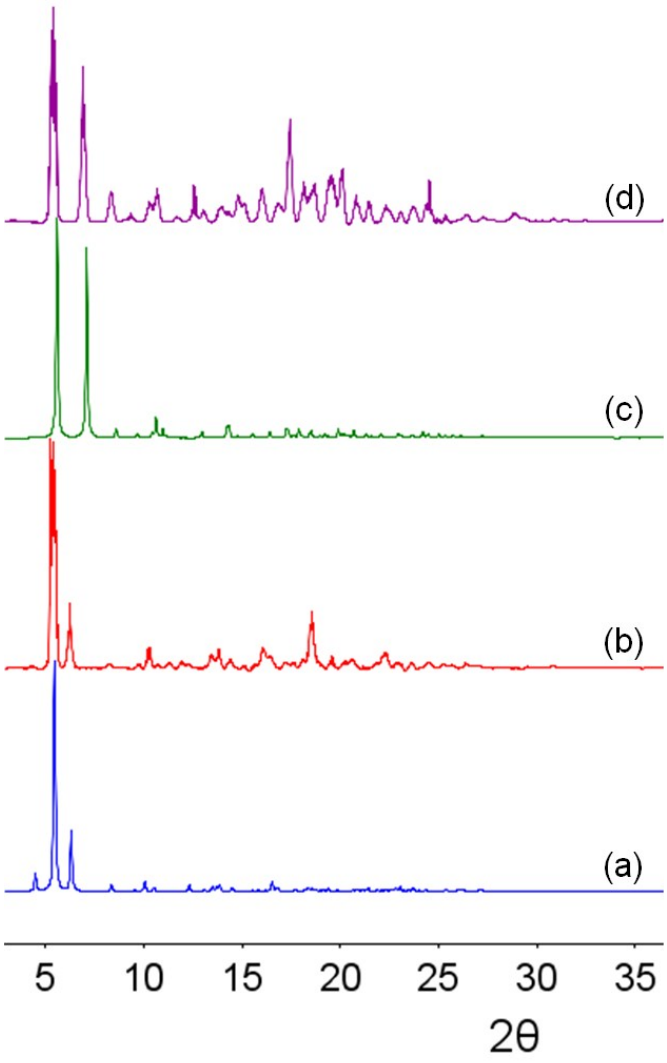


Figure SI5. PXRD patterns for **C1-N2α** and **C1-N2β**. (a) **C1-N2α** simulated. (b) **C1-N2α** experimental. (c) **C1-N2 β** simulated. (d) **C1-N2 β** experimental.

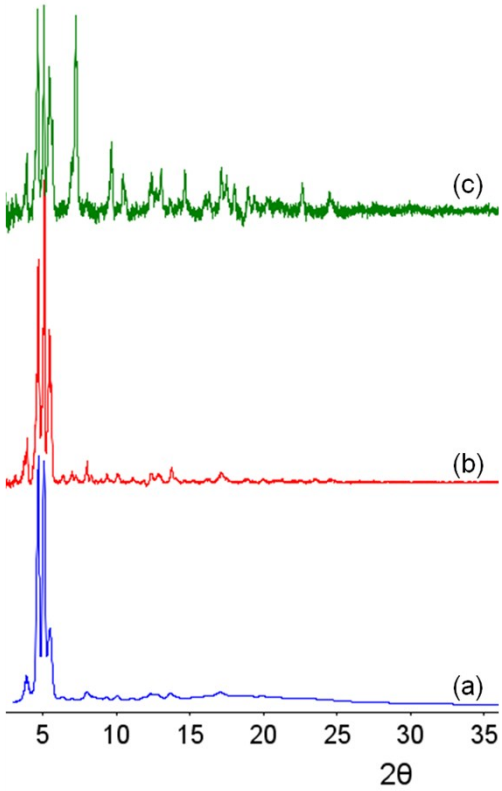


Figure SI6. PXRD patterns for **C1-OMe** and **C1-N2γ**. (a) **C1-OMe** rapidly precipitated from dichloromethane/methanol. (b) **C1-N2γ** rapidly precipitated from dichloromethane/methanol. (c) **C1-N2γ** activated.

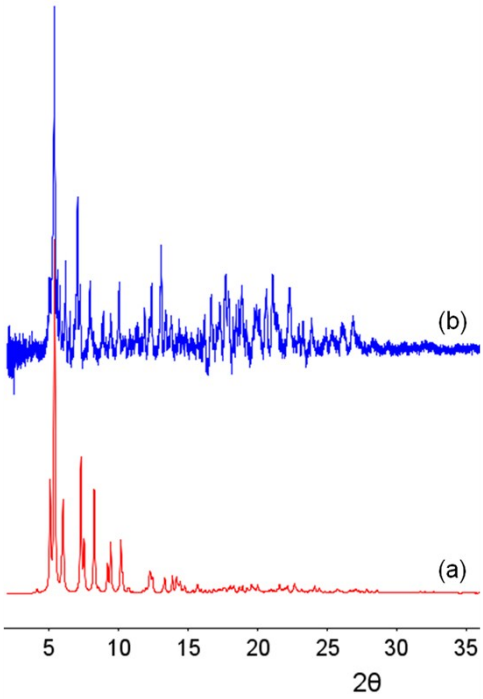


Figure SI7. PXRD patterns for **C1-N6**. (a) Simulated from the crystal structure. (b) Crystals loaded in the crystallisation solvent mixture.[9]

5. Gas adsorption

Gas adsorption isotherms were measured using a Micromeritics 3-Flex analyzer (Micromeritics Instrument Corporation, Norcross, GA, USA) at 77 K (utilizing a cryo-cooler circulator). Brunauer–Emmett–Teller (BET) surface areas and pore size distributions were calculated using software on the Micromeritics 3-Flex analyser. UHP grade (99.999%) N_2 and (99.999%) H_2 was used for all measurements.

Activation conditions for C1-N2γ: The **C1-N2γ** precipitate formed by rapid precipitation from dichloromethane/methanol was filtered, washed with fresh methanol and dried under high vacuum during 2 hours at 60°C prior to the adsorption measurement.

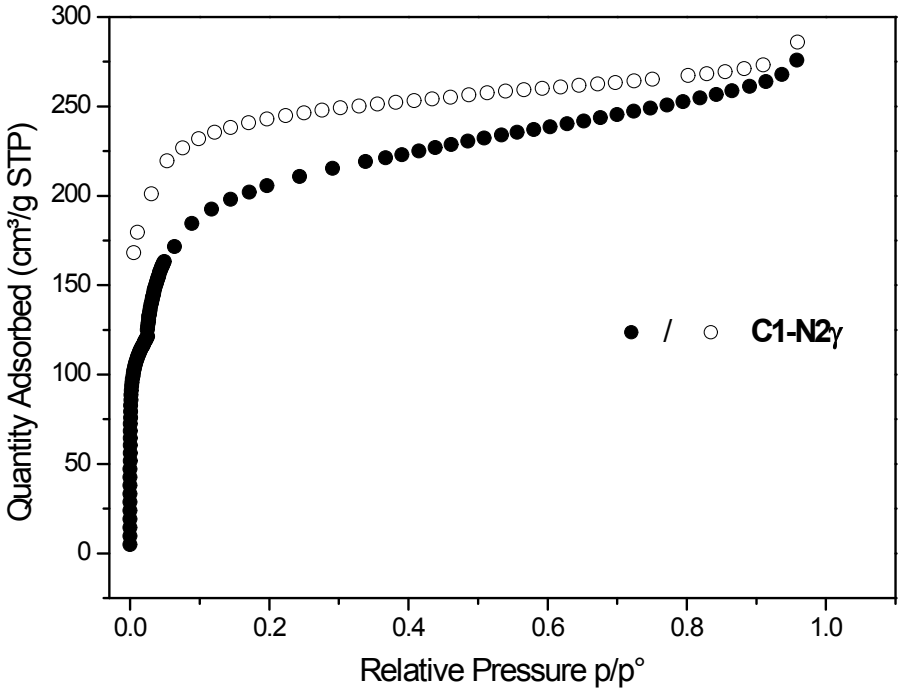


Figure SI8. N_2 adsorption isotherm collected at 77K for polymorph **C1-N2γ**. Closed and open symbols represent adsorption and desorption data, respectively.

Table SI1. BET parameters from for the N_2 adsorption isotherm at 77 K for **C1-N2γ**.

BET Surface Area:	844.9047 ± 21.7664 m^2/g
Slope:	0.005085 ± 0.000133 g/cm^3 STP
Y-Intercept:	0.000066 ± 0.000006 g/cm^3 STP
C:	77.624902
Qm:	194.1159 cm^3/g STP
Correlation Coefficient:	0.9986435
Molecular Cross-Sectional Area:	0.1620 nm^2

6. SEM imaging of C1-N2γ

Scanning Electron Microscopy images were obtained on a Philips XL30 field emission Scanning Electron Microscope at Adelaide Microscopy, The University of Adelaide.

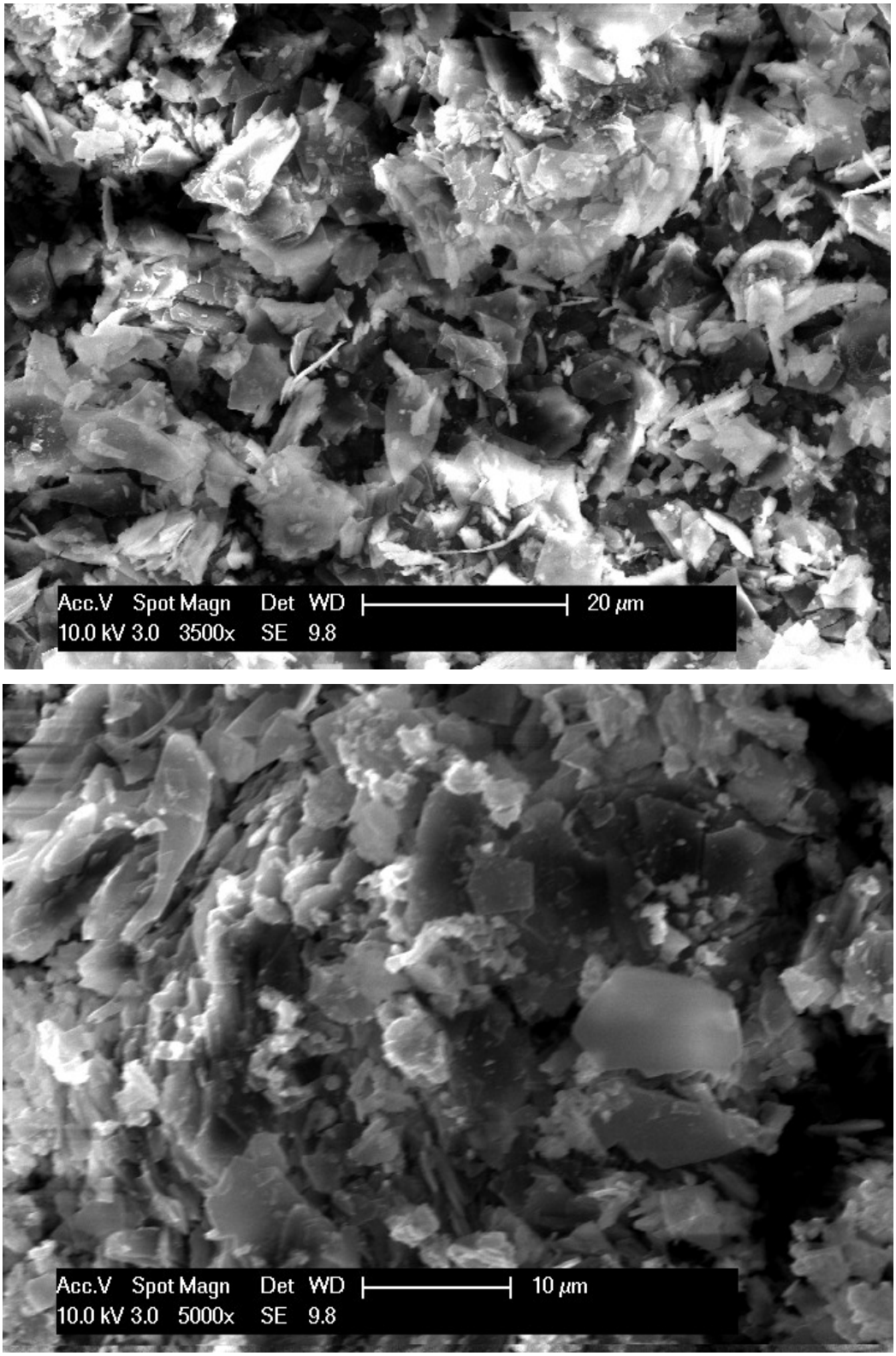


Figure SI9. SEM images of **C1-N2γ** (activated).

7. Single Crystal X-ray Diffraction

Crystals of cages **C1-N2** and **C1-N6** suitable for X-ray crystallographic studies were grown by slow diffusion of petroleum spirit into a benzene solution of **C1-N2**, and hexane into a **C1-N6** toluene solution. **C1-N2** invariably crystallised as a mixture of two distinct crystal forms, specifically as colorless rod-shaped crystals (**C1-N2**α) and colorless plate-like crystals (**C1-N2**β). Single crystals were selected and mounted on a nylon loop in paratone-N cryo-protectant. Single-crystal X-ray diffraction was performed at 100(2) K on the MX-1 or MX-2 beamlines of the Australian Synchrotron (λ = 0.7107 Å).[10] Data sets were corrected for absorption using a multi-scan method, and structures were solved by direct methods using SHELXS-2013 and refined by full-matrix least squares on F_2 by SHELXL-2014,[11] interfaced through the program X-Seed.[12] In general, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as invariants at geometrically estimated positions, unless specified otherwise. Highly disordered pore solvent electron density was removed after analysis using the SQUEEZE routine in PLATON.[13] Further details of the data collection and structure refinement are provided below, see Table SI2.

CIF data have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference numbers 1475472**,** 1475473 and 1476345 (where **C1-N2**α = 1476345; **C1-N2**β = 1475473 and **C1-N6** = 1475472).

Special refinement details

Cage **C1-N2**α. The position of the pyridine nitrogen atoms within the α-form of **C1-N2** could not be determined and thus the structure was modelled with CH:N 2:1 ratio at all six chemically relevant sites. EXYZ and EADP restraints were used to allow a stable refinement to proceed. A 50% occupied benzene solvate molecule was identified in the difference map.

Cage **C1-N2**β. The position of the pyridine nitrogen atoms within the β-form of **C1-N2** could not be determined and thus the structure was modelled with CH:N 2:1 ratio at all six chemically relevant sites. EXYZ and EADP restraints were used to allow a stable refinement to proceed.

Cage **C1-N6**. There was appreciable thermal displacement for several atoms within one 'arm' of the cage and a series of AFIX 66 commands were used to maintain chemically sensible bond lengths for aromatic rings.

Table SI2. X-Ray experimental and refinement data for **C1-N2α**, **C1-N2β** and **C1-N6**.

Compound	**C1-N2α·C_6H_6**	**C1-N2β**	**C1-N6**
Empirical formula	$C_{116}H_{66}N_2O_2$	$C_{110}H_{60}N_2O_2$	$C_{106}H_{56}N_6O_2$
Formula weight	1519.70	1441.60	1445.56
Crystal system	tetragonal	orthorhombic	triclinic
Space group	$I4_1/acd$	*Pbcn*	*P*-1
a (Å)	39.280(6)	31.580(6)	16.792(3)
b (Å)		18.296(4)	19.978(4)
c (Å)	39.780(8)	20.075(4)	23.171(5)
α (°)			102.93(3)
β (°)			101.11(3)
γ (°)			112.55(3)
Volume ($Å^3$)	61377(21)	11599(4)	6654(3)
Z	16	4	2
Density (calc.) g/m^3	0.658	0.826	0.722
Absorption coefficient (mm^{-1})	0.039	0.049	0.043
F(000)	12672	3000	1500
Crystal size (mm^3)	1.00 x 0.10 x 0.10	0.20 x 0.20 x 0.02	0.60 x 0.06 x 0.05
θ range for collection (°)	1.037 to 28.279	1.286 to 22.758	1.168 to 19.905
Reflections collected	712819	106587	44726
Observed reflections [R(int)]	18597 [0.0266]	6642 [0.0343]	7096 [0.0435]
Goodness-of-fit on F_2	1.141	1.084	1.328
R_1 [I>2σ(I)]	0.0910	0.0942	0.1241
wR_2 (all data)	0.2806	0.2764	0.3559
Largest diff. peak and hole ($e.Å^{-3}$)	0.488, -0.208	0.218, -0.211	0.427, -0.289

8. Computational Methods

As required, C1-OMe, C1-N2 and C1-N6 were geometry optimized with default convergence criteria employing M06-2X/6-31G(d) theory[14] using Gaussian 09 (Revision D.01) software package.[15] Structures were calculated *in vacuo* and in an implicit pyridine solvent (dielectric constant ε = 12.978) using the SMD continuum solvation model.[16] The electron density from the DFT calculations was used to calculate molecular dipole moments, electron density isosurfaces, and electrostatic potential maps. For all of the molecules studied, several conformers exist with energies within 1 kJ/mol, but the electron density distributions of all conformers are similar; thus the results for a single conformer of each molecule can be generalised to all conformers. Assuming point dipoles in a continuum medium, the dipole moments of the C1-N6 half-cages translate to a maximum electrostatic interaction energy (for aligned dipoles at the approximate separation (16 Å) of the half-cage centres-of-charge) in the full-cage molecule of only 0.53 kJ/mol in vacuo and 0.08 kJ/mol in pyridine – substantially less than the thermal energy – for the C1-N6 half-cages, with considerably smaller energies for the C1-OMe half-cages. To verify that this result was not an artefact of the point-dipole approximation, we also carried out scans of the energy to bring together two rigid half-cage molecules in pyridine from a large separation and found the energy to change by less than ±1 kJ/mol until the molecules were essentially overlapping.

N_2 accessible surface areas (probe radius = 1.82 Å) and pore metrics of crystal structures C1-N2α, C1-N2β and C1-N6 were generated using Zeo++(0.2.1).[17]

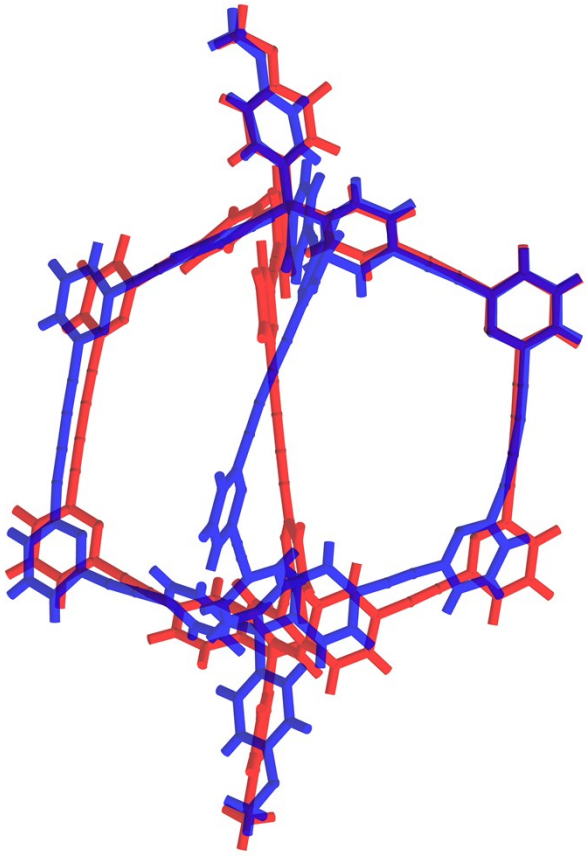


Figure SI10. Comparison of *in vacuo* optimized **C1-N6** structure (red) and **C1-N6** geometry extracted from crystal structure (blue).

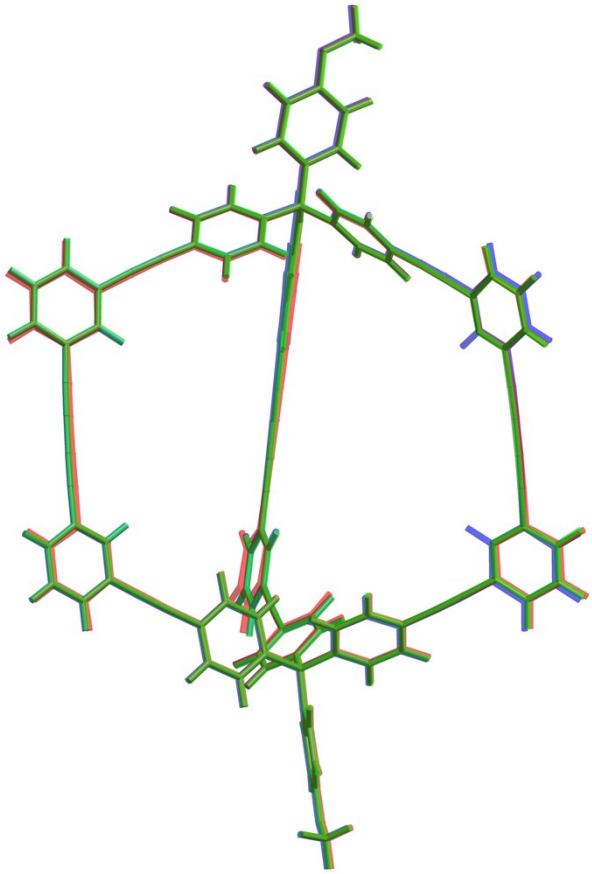


Figure SI11. Comparison of *in vacuo* optimized **C1-OMe**, **C1-N2** and **C1-N6** structures (blue, red and green, respectively).

9. References

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(9) Filtration/desolvation of the **C1-N6** crystals resulted into the formation of an amorphous solid.

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