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Bestowing structure upon the pores of a supramolecular network

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Models of star molecules in pores of supramolecular network

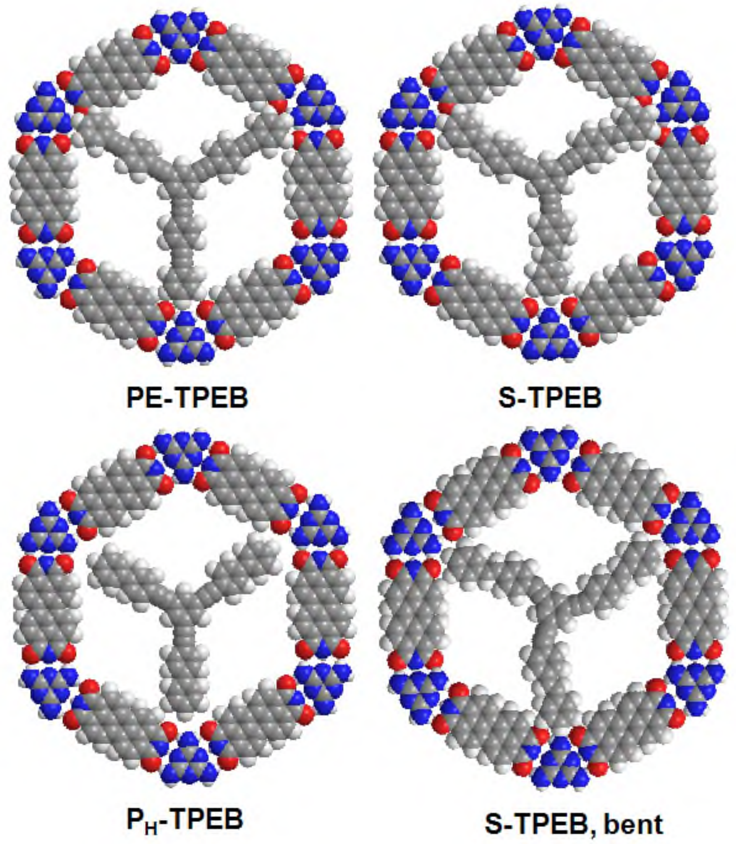

PE-TPEB
S-TPEB
P_H-TPEB
S-TPEB, bent

Fig. S1: Models of network pores modified by different star molecules. Except the bent S-TPEB molecule where the ethynyl group was distorted manually, the star molecules were optimised using MM2 as implemented in Chem3D[1]. The size of the supramolecular hexagon is set according to the 7√3×7√3 unit cell reported for the PTCDI/melamine network on Au(111)[2].

Network preparation and adsorption of star molecules

Preparation of the PTCDI/melamine network was performed as described previously.[3] Substrates of 300 nm epitaxial Au on mica (Georg Albert PVD) were flame-annealed in an oxygen rich natural gas flame before use. Stock solutions of melamine and PTCDI were prepared by sonicating i) melamine in DMF (Alfa Aesar, anhydrous, amine free) followed by filtering with grade 1 paper and ii) PTCDI powder in DMF and, after sedimentation over night, using the top part of the dispersion.

A dilute mixture of the stock solutions was used (4% vol PTCDI stock, 25% vol melamine stock, 71% vol pure DMF) for the network preparation. It is noted that, due to the low solubility of PTCDI at room temperature, it is crucial to use a dispersion in order to achieve the PTCDI concentration required for obtaining a high quality network at the temperature of the network preparation. Prior to the immersion of the substrate the mixture was heated to 100 °C for about 30 minutes. Substrates were exposed to the solution for 1 minute after which they were

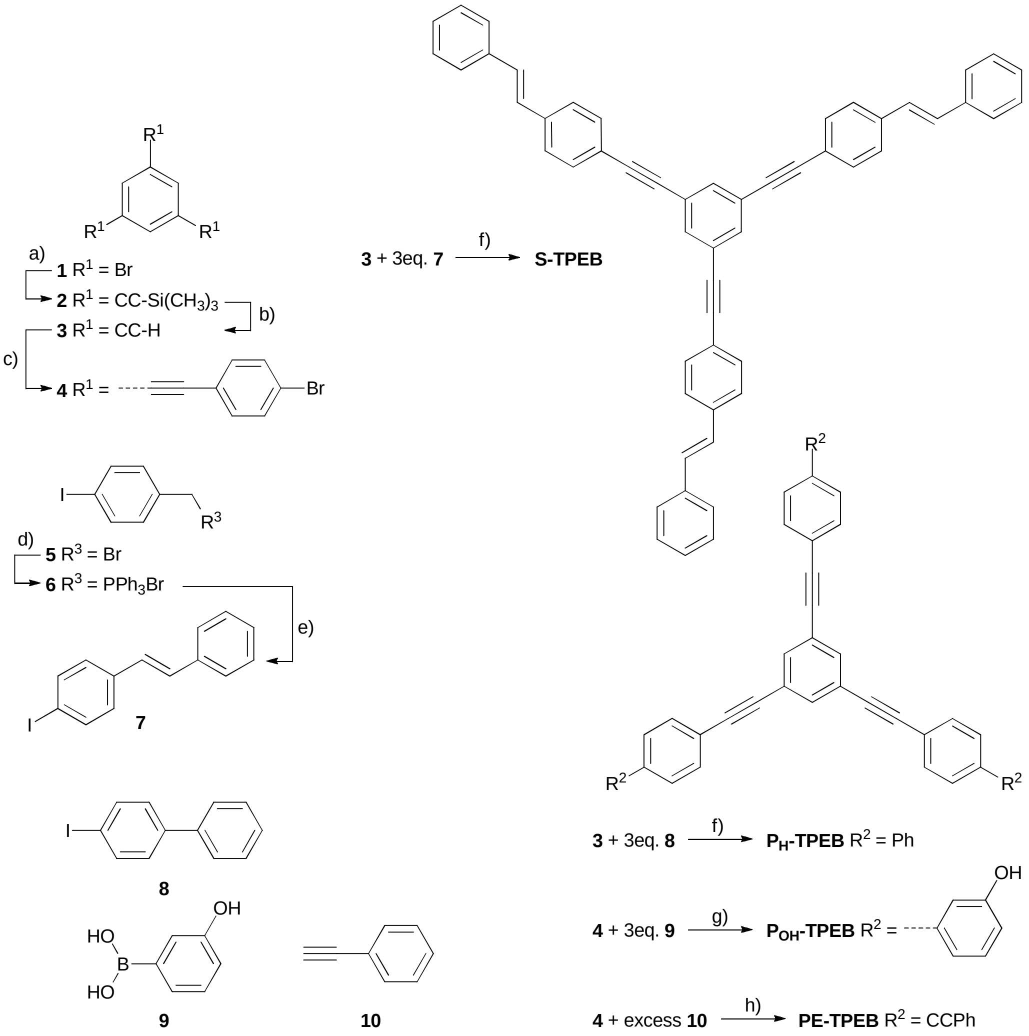
quickly rinsed with DMF at room temperature and immediately dried in a nitrogen stream.

Star molecules were adsorbed either from 1,2,4-trichlorobenzene or DMF. **PE-TPEB** and **S-TPEB** were prepared at room temperature by immersing a network modified Au/mica substrate into a solution of the respective molecules for up to 5 minutes. **P_{OH}-TPEB** and **P_H-TPEB** were adsorbed by immersion of the substrate at 60°C. During the adsorption time of about two minutes the solution was cooling down. After removal from the solution, substrates were quickly blown dry in a stream of N_2. Due to the small amounts of substances available the concentrations of the solutions of the star molecules were not exactly known and, therefore, immersion times were determined empirically by verifying that the adsorption times are sufficiently long for the formation of a full monolayer of star molecules on a clean Au substrate.

Samples were characterized in an ambient environment using a PicoPlus STM (Molecular Imaging). Tips were cut from Pt/Ir wire (80:20, 0.25 mm diameter, Advent Research Materials Ltd.). Bias and current were typically in the range of ±100-500 mV and 10-100 pA.

Synthesis of the star-type structures PE-TPEB, **S-TPEB**, **P_H-TPEB**, and **P_{OH}-TPEB**

The synthesis is displayed in **Scheme S1**. The numbering of the structures corresponds to the one used in scheme 1 of the main text. The synthesis of the four star-shaped molecules is based on Pd catalyzed cross-coupling chemistry with the 1,3,5-triethynylbenzene **3**, as common precursor. 1,3,5-Triethynylbenzene **3** was obtained from 1,3,4-tribromobenzene following a *Sonogashira* protocol followed by deprotection of the TMS masked ethynyl substituents. The benzylbromide **5** was converted into the *Wittig* salt **6** by treatment with triphenylphosphine. The *Wittig* reaction with benzaldehyde provided the iodo-functionalized trans-stilbene **7** after exposure to reversible iodine addition/elimination conditions. *Sonogashira*–type coupling between the triethynylbenzen **3** and the iodo-stilbene **7** provided the peripherally styryl functionalizes star **S-TPEB** as a white solid (49% isolated yield after column chromatography). 4-Iodo-1,1’-biphenyl **8** was obtained in a one-pot *Sandmeyer* procedure from the commercially available 4-amino-1,1’-biphenyl. A similar cross-coupling protocol as described above applied to **3** and **8** provided the peripherally phenyl functionalized star **P_H-TPEB** as a white crystalline solid (83% isolated yield after column chromatography). The hydroxyl-substituted star **P_{OH}-TPEB** was assembled in a divergent synthetic approach. Thus the 1,3,5-triethynylbenzene **3** was further functionalized by applying a *Sonogashira* protocol with 1-bromo-4-iodobenzene to provide the extended start structure **4** in 79% isolated yield. A subsequent *Suzuki* coupling with the boronic acid **9** provided the hydroxyl-substituted star **P_{OH}-TPEB** which was isolated as hardly soluble white solid (10% isolated yield after tedious purification by several columns including silica gel and recycling gel-permeation-chromatography). The extended star exposing 3 bromines **4** was also the starting point for the divergent synthesis of **PE-TPEB**. Exposing **4** together with a large excess of phenyl-acetylene to *Sonogashira* coupling conditions provided **PE-TPEB** as white solid in 80% yield.



Scheme S1: Synthesis of the molecular stars **S-TPEB**, **P_H-TPEB** and **P_{OH}-TPEB**. Reagents and conditions: a) TMSA, $Pd(PPh_3)_2Cl_2$, CuI, THF, *i*Pr_2NH, 60°C, 16h, quant.; b) K_2CO_3, THF, MeOH, r.t., 6h, quant.; c) IC_6H_4Br, $Pd(PPh_3)_2Cl_2$, CuI, THF, *i*Pr_2NH, r.t., 5h, 79%; d) PPh_3, DMF, 85°C, 1h, 76%; e) 1.) toluene, 0°C, *t*BuOK, C_6H_5CHO, r.t., 16h, CC; 2.) toluene, cat. I_2, rfl., 3h, 77%; f) $Pd(PPh_3)_4$, CuI, THF, *i*Pr_2NH, r.t., 16h, 49% for **S-TPEB**, 83% for **P_H-TPEB**; g) $Pd(PPh_3)_4$, K_2CO_3, toluene, EtOH, micro wave 120°C, 45min., 10%. h) $Pd(PPh_3)_4$, CuI, DMF, *i*Pr_2NH, 60°C, 16h, 80%.

Experimental Part

General Remarks: All commercially available starting materials were of reagent grade and used as received. Analytical thin layer chromatography (TLC) was carried out on Merk silicagel 60 F254 glass TLC plates visualizing with UV light at 254 nm and 366 nm. Column chromatography was performed using silica gel 60 (230-240 mesh), except were stated otherwise. Deuterated solvents were purchased from Cambridge Isotope Laboratories. ^{1}H and ^{13}C NMR spectra were recorded with a *Bruker* DMX 400 instrument (^{1}H resonance 400 MHz, ^{13}C resonance 101 MHz) or a *Bruker* DRX 500 instrument (^{1}H resonance 500 MHz, ^{13}C resonance 125 MHz) at 298 K. Chemical shifts (δ) are quoted in parts per million (ppm) relative to the residual solvent proton peak ($CDCl_3$: 7.26 ppm) and solvent residual carbon peak ($CDCl_3$, $\delta = 77.16$.) Multiplicities are denoted; singlet (s), doublet (d), triplet (t), multiple (m) and doublet of doublets (dd). Mass spectra were obtained by GC-MS, EI (70eV, measured by Dr. H. Nadig on a Finnigan MAT 95Q), ESI (measured on a Bruker Esquire 3000) and MALDI-Tof (on an Applied Bio Systems Voyager-De). Molecular ions are denoted and only the major peak reported. Elemental analyses (EA) were measured by W. Kirsch on a Perkin-Elmer Analysator 240 and the values are given in percent.

1,3,5-tris((trimethylsilyl)ethynyl)benzene (2): Tribromobenzene (500 mg, 1.56 mmol), $PdCl_2(PPh_3)_2$ (33.1 mg, 46.7 μmol), and CuI (14.8 mg, 77.8 μmol) were placed into an oven dried 25 mL schlenk tube and placed under vacuum for 20 min. Then THF (10 mL) and $^{i}Pr_2NH$ (2 mL) were added and the mixture was degassed with inert gas. Then Ethynyltrimethylsilane (0.89 mL, 6.23 mL) was added and the solution further degassed. The mixture was then heated to 60°C overnight. The reaction was quenched with water and extracted with DCM. The organic layer was washed with 1M HCl (aq), brine and dried over $MgSO_4$. The crude was columned on SiO_2 (cyclohexane) fractions evaporated to afford **2** as off white crystals (504 mg, 88%). **mp** 76–78 °C (lit. mp 79–80 °C).[4] $\mathbf{R_{\mathit{f}}} = 0.6$ (SiO_2; cyclohexane). **^{1}H NMR** (500 MHz, $CDCl_3$): $\delta_H = 7.49$ (s, 3H), 0.24 (s, 27H). **^{13}C NMR** (126 MHz, $CDCl_3$): $\delta_C = 135.1$, 123.8, 103.3, 95.7, -0.0. **MS** (EI +, 70 eV) *m*/*z* = 366.2 [M^+], 351.2 $[M–CH_3]^{\cdot+}$. **MS** (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{21}H_{30}Si_3$, 366.2; found 366.16. **EA** Calcd for $C_{21}H_{30}Si_3$: C, 68.78; H, 8.25. Found: C, 68.79; H, 8.23.

1,3,5-triethynylbenzene (3): A round bottom flask was charged with **2** (500 mg, 1.36 mmol) dissolved in a 1:1 mixture of THF:MeOH to make up a 10 mL solution, this solution was bubble purged with argon for 20 min before K_2CO_3 (952 mg, 6.82 mmol) was added and the mixture stirred at RT for 3 hr, after which time it was passed through a short-plug of SiO_2 (DCM), solvent removed to afford **3** as a white, low vapor pressure solid (184 mg, 90%). **^{1}H NMR** (400 MHz, $CDCl_3$): $\delta_H = 7.57$ (s, 3H), 3.10 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$): $\delta_C = 135.8$, 123.1, 81.7, 78.8. **MS** (EI +, 70 eV) *m*/*z* (%) = 150.0 (100) [M^+].

1,3,5-tris((4-bromophenyl)ethynyl)benzene (4): A two necked flask under argon was charged with 1-bromo-4-iodobenzene (3.7 g, 13.3 mmol), dry THF (80 mL) and *i*Pr_2NH (4 mL). The reaction mixture was bubbled with argon for 10 min before the triethynylbenzene **3** was added. The reaction mixture was bubbled with argon for another 5 min before $Pd(PPh_3)_2Cl_2$ (120 mg, 0.166 mmol), and CuI (30 mg, 0.166 mmol) were added. The reaction mixture was stirred at room temperature for 5h, poured into ice cold 1 M HCl and extracted with CH_2Cl_2(3x). The combined organic layers were washed with water, dried over Na_2SO_4, and were evaporated to dryness. Column chromatography (silica gel, CH_2Cl_2/cyclohexane 5:95) of the crude provided **4** as oil (1.61 g, 2.62 mmol, 79%). TLC (SiO_2, hexane): $\mathbf{R_{\mathit{f}}} = 0.18$. **^{1}H NMR** ($CDCl_3$, 400 MHz) $\delta_H = 7.63$ (s, 3H, CH), 7.49 (dt, $^{3}J_{HH} = 8.6$ Hz, $^{4}J_{HH} = 2.0$ Hz, 6H, CH), 7.38 (dt, $^{3}J_{HH} = 8.6$ Hz, $^{4}J_{HH} = 2.0$ Hz, 6H, CH). **^{13}C NMR** ($CDCl_3$, 100 MHz) $\delta_C = 134.2$ (CH, 3C), 133.1 (CH, 6C), 131.8 (CH, 6C), 123.9 (Cq, 3C), 123.0 (Cq, 3C), 121.7 (Cq, 3C), 89.7 (CH, 3C), 88.7 (CH, 3C).

(4-iodobenzyl)triphenylphosphonium bromide (6): A two necked flask charged with 4-iodobenzylbromide (1.024 g, 3.45 mmol) in dry DMF (30 mL) was heated at 85°C. Triphenylphosphine (905 mg, 3.45 mmol) was added and the reaction mixture was stirred at this temperature for 1h and then allowed to cool down to room temperature. Toluene (20 mL) was added and the reaction mixture was cooled in an ice bath. The desired product **6** was isolated as white precipitate which was twice washed with toluene and centrifuged (1.46 g, 2.61 mmol, 76 %). The crude compound was immediately used without further purification. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H = 7.75 (m, 9H, CH), 7.60 (m, 6H, CH), 7.37 (d, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 2.5 Hz, 2H, CH), 6.91 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{PH}$ = 2.5 Hz, 2H, CH), 5.52 (d, $^2J_{PH}$ = 14.8 Hz, 2H, CH).

(*E*)-1-iodo-4-styrylbenzene (7): A two necked flask under argon was charged with **6** (517 mg, 0.924 mmol) in dry toluene (15 mL). This suspension was cooled to 0°C and potassium tert. butoxide (120 mg, 0.924 mmol) was added. The orange reaction mixture was stirred at this temperature for 1h30 min. and then benzaldehyde (120 mg, 1.13 mmol) was injected all at once. The reaction mixture was stirred at room temperature overnight and then evaporated. The obtained oil was dissolved in CH_2Cl_2 and washed with water. The organic layer was dried over Na_2SO_4, and evaporated to dryness providing a yellow solid. Column chromatography (silica gel, CH_2Cl_2/cyclohexane 2:1) provided the crude reaction product as a mixture of *E*/*Z* isomers. The crude was refluxed for 6 hours in toluene (10 mL) with traces of iodine to provide the *E* isomer as yellow solid (217 mg, 0.709 mmol, 77%) after filtration of the reaction mixture through a SiO_2 short plug and subsequent evaporation. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ_H = 7.66 (d, $^3J_{HH}$ = 8.3 Hz, 2H, CH), 7.49 (d, $^3J_{HH}$ = 7.7 Hz, 2H, CH), 7.35 (dd, $^3J_{HH}$ = 7.6 Hz, 2H, CH), 7.26 (t, $^3J_{HH}$ = 7.3 Hz, 1H, CH), 7.22 (d, $^3J_{HH}$ = 8.3 Hz, 2H, CH), 7.09 (d, $^3J_{HH}$ = 16.3 Hz, 1H, CH), 6.99 (d, $^3J_{HH}$ = 16.3 Hz, 1H, CH). **^{13}C NMR** ($CDCl_3$, 126 MHz) δ_C = 137.8 (CH, 2C), 137.0 (Cq, 1C), 136.9 (Cq, 1C), 129.6 (CH, 1C), 128.8 (CH, 2C), 128.3 (CH, 2C), 128.0 (CH, 1C), 127.6 (CH, 1C), 126.7 (CH, 2C), 92.9 (Cq, 1C). **EI-MS** m/z (%int.): found: 306 ([$M^{+\cdot}$], 100%), 178.1 (57%), 152 (8%), 89 (10%); calc. for $C_{23}H_{27}NO_2$: 305.99 **EA** (%) for $C_{23}H_{27}NO_2$: found: C = 54.82, H = 3.76; calc.: C = 54.93, H = 3.62.

1,3,5-Tris((4-((E)-styryl)phenyl)ethynyl)benzene (S-TPEB): A 50 mL three neck round bottom flask was charged with (*E*)-1-iodo-4-styrylbenzene **7** (212 mg, 693 µmol), CuI (1.65 mg, 8.66 µmol) $Pd(PPh_3)_4$ (10.1 mg, 8.66 µmol) and **3** (26 mg, 173 µmol) dissolved in THF (10 mL) and *i*Pr_2NH (4.5 mL). The solution was bubble purged with argon for 20 min, and then stirred at RT overnight. Water was added and extracted with CH_2Cl_2. The organic phase was washed with H_2O, 2M HCl (aq), brine and dried over $MgSO_4$. The crude was passed through a column of SiO_2 (3:1 cyclohexane:CH_2Cl_2). The mixed fractions recovered were passed though a second column of SiO_2 (2:1 cyclohex:CH_2Cl_2), fractions combined and solvent removed to afford **S-TPEB** as a white solid (58.1 mg, 49%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H = 7.56 – 7.50 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.13 (q, *J* = 16.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ_C = 137.8, 137.2, 134.1, 132.2, 130.0, 128.9, 128.1, 128.0, 126.8, 126.6, 124.2, 121.9, 90.9, 88.9. **MS** (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{54}H_{36}$, 684.28; found 684.52.

1,3,5-Tris([1,1'-biphenyl]-4-ylethynyl)benzene (P_H-TPEB): A round bottom flask was charged with 4-iodobiphenyl **8** (463 mg, 1.65 mmol) and catalytic system of CuI (3.93 mg, 20.6 µmol) and Pd(PPh$_3$)$_4$ (47.7 mg, 42.3 µmol) dissolved in *i*Pr$_2$NH and THF. Finally **3** (62 mg, 413 µmol) dissolved in THF was added dropwsie and the reaction stirred overnight giving a yellow solution. Extraction with CH$_2$Cl$_2$, the organic layer washed with 2M HCl (aq), brine and dried over MgSO$_4$. After two sequential columns were made on SiO$_2$ (10:1 cyclohexane:CH$_2$Cl$_2$), fractions combined and solvent removed to afford **P$_H$-TPEB** as a white crystalline solid (208 mg, 83%). **^{1}H NMR** (400 MHz, CDCl$_3$): δ_H = 7.69 (s, 3H), 7.64 – 7.59 (m, *J* = 5.7 Hz, 18H), 7.46 (t, *J* = 7.6 Hz, 6H), 7.37 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl$_3$): δ_C = 141.5, 140.4, 134.2, 132.3, 129.0, 127.9, 127.2, 127.2, 124.2, 121.8, 90.6, 88.7. **MS** (MALDI-TOF) *m*/*z*: [M–H]$^-$ calcd for $C_{48}H_{29}$, 605.23; found 605.00. Also See the X-ray data below.

4',4'',4'''-(Benzene-1,3,5-triyltris(ethyne-2,1-diyl))tris(([1,1'-biphenyl]-3-ol)) (P$_{OH}$-TPEB): A microwave vial was charged with **4** (102 mg,166 µmol), Pd(PPh$_3$)$_4$ (9.58 mg, 8.29 µmol), K$_2$CO$_3$ (76.4 mg, 547 µmol) and 3-Hydroxyphenylboronic acid **9** (91.5 mg, 663 µmol) dissolved in a degassed mixture of toluene (10 mL) and EtOH (5 mL). The MW vial was sealed and irradiated in the MW (5 min pre-stirring, normal absorbance, 45 min at 120°C). Then the mixture was poured into water, and extracted with *tert*.butylmethylether. The organic layer was washed with 2M HCl (aq), brine and dried over MgSO$_4$. The crude was passed through a column of SiO$_2$ (1:1 cyclohexane:CH$_2$Cl$_2$), fractions combined and the crude passed through recycling GPC (loaded in CHCl$_3$, crude was not very soluble and thus, only the fraction dissolved in 2 mL was purified) and solvent removed to afford **P$_{OH}$-TPEB** as a white solid (10.2 mg, 10%). **^{1}H NMR** (400 MHz, CDCl$_3$): δ_H = 7.64 (s, 3H), 7.61 (s, 12H), 7.25 (t, *J* = 7.9 Hz, 3H), 7.09 (d, *J* = 7.8 Hz, 3H), 7.06 (d, *J* = 1.8 Hz, 3H), 6.80 (dd, *J* = 8.1, 1.7 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ_C = 159.1, 142.9, 142.8, 134.8, 133.2, 131.0, 128.1, 125.7, 122.8, 119.2, 115.8, 114.7, 91.6, 89.1. **MS** (MALDI-TOF) *m*/*z*: [M]$^+$ calcd for $C_8H_{30}O_3$, 654.22; found 654.26.

1,3,5-Tris((4-(phenylethynyl)phenyl)ethynyl)benzene (PE-TPEB): A round bottom flask was charged with **4** (152 mg, 0.247 mmol), CuI (2.35 mg, 12.4 µmol) and Pd(PPh$_3$)$_4$ (14.3 mg, 12.4 µmol) and dried under vacuum for 30 min. Then dry DMF (10 mL) and *i*Pr$_2$NH (5 mL) were added and bubble purged with argon for 20 min. Finally a large excess of phenyl-acetylene (0.5 ml) was added and the reaction mixture was stirred under argon at 60°C for 16 hr. After work-up and purification by column chromatography (SiO$_2$, cyclohexane/CH$_2$Cl$_2$) **PE-TPEB** was isolated as white solid (134 mg, 80%). **^{1}H NMR** (400 MHz, CDCl$_3$): δ_H = 7.67 (s, 3H), 7.53 (m, 18H), 7.36 (m, 9H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ_C = 134.2, 131.7, 131.7, 131.6, 128.6, 128.4, 124.0, 123.6, 123.0, 122.6, 91.5, 90.4, 89.5, 89.0. **MS** (MALDI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{54}H_{31}$, 679.23; found 679.31.

X-ray structure of P$_H$-TPEB

The identity of **P$_H$-TPEB** was corroborated by analysis of its solid-state structure. Single crystals suitable for x-ray analysis were obtained by slow evaporation of the solvent from a concentrated sample of **P$_H$-TPEB** dissolved in chloroform. The solid state structure is displayed in Fig. S2. In the x-ray structure the phenyl rings of the branches are considerably twisted out of the molecule’s plane, probably to optimize the intermolecular packing in the solid state. Apart from this obvious difference between the arrangement on the Au(111) sample and the solid state, the observed angles and distances match the values common for such structures.

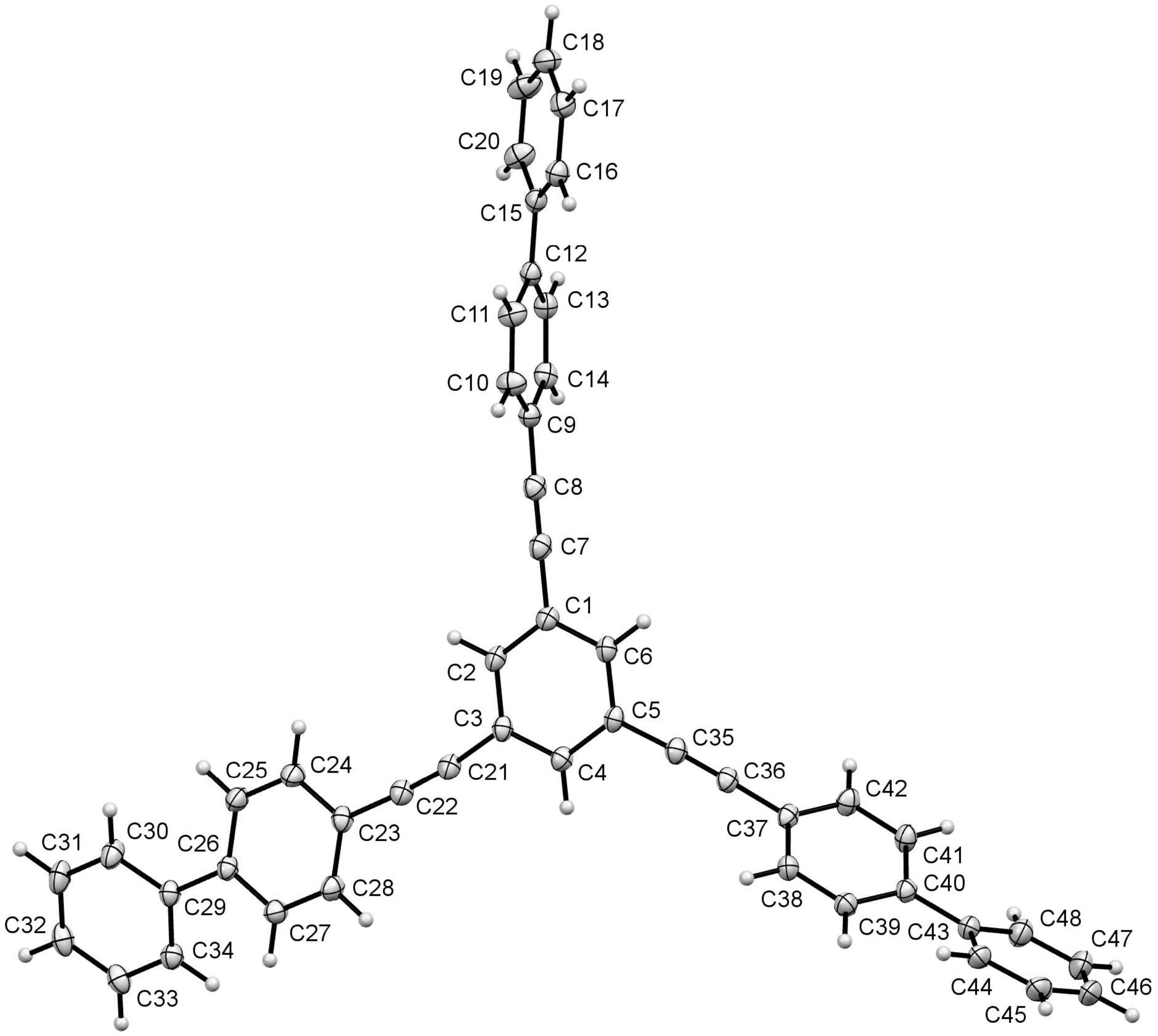


Fig. S2: Solid-state structure of **P_H-TPEB**.

Crystal data for **P_H-TPEB**: formula $C_{48}H_{30}$, M = 606.77, F(000) = 1272, colourless block, size 0.090 · 0.140 · 0.210 mm^3, monoclinic, space group P $2_1/c$, Z = 4, a = 9.6393(13) Å, b = 10.6477(14) Å, c = 32.761(4) Å, $\alpha = 90°$, $\beta = 96.789(3)°$, $\gamma = 90°$, V = 3338.9(8) $Å^3$, $D_{calc.}$ = 1.207 Mg · m^{-3}. The crystal was measured on a Bruker Kappa Apex2 diffractometer at 123K using graphite-monochromated Mo K_α-radiation with λ = 0.71073 Å, Θ_{max} = 32.629°. Minimal/maximal transmission 0.99/0.99, μ = 0.068 mm^{-1}. The Apex2 suite[5] has been used for datacollection and integration. From a total of 59189 reflections, 12147 were independent (merging r = 0.045). From these, 7487 were considered as observed ($I>2.0\sigma(I)$) and were used to refine 433 parameters. The structure was solved by direct methods using the program SIR92.[6] Least-squares refinement against F was carried out on all non-hydrogen atoms using the program CRYSTALS.[7] R = 0.0524 (observed data), wR = 0.0976 (all data), GOF =

1.1097. Minimal/maximal residual electron density = -0.20/0.32 e Å^{-3}. Chebychev polynomial weights[8] were used to complete the refinement. Plots were produced using MERCURY.[9] Bond distances and angles are unexceptional in this structure. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Center, the deposition number is 1000630. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

Additional STM images

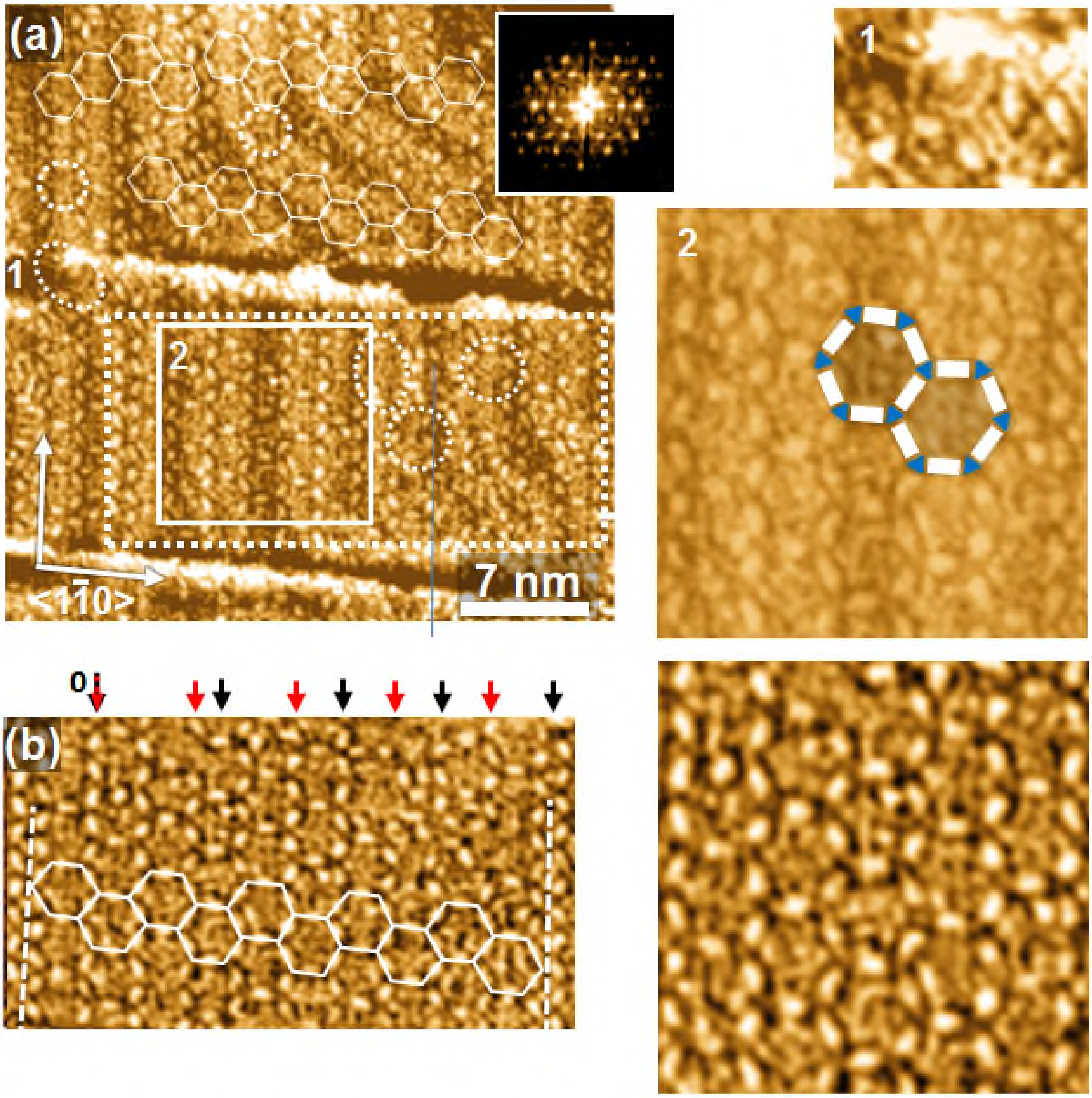


Fig. S3: STM images of PTCDI-melamine on Au(111)/mica after exposure to a solution of S-TPEB. (a) Image as acquired (unfiltered and not drift corrected). To guide the eye some cells are marked by white hexagons. Encircled areas mark defects in network where S-TPEB molecules are adsorbed. Inset at top right of image shows Fourier transform. Numbered images on the right show selected regions of left image at higher magnification.

(b) Left: Image of the area marked by dashed rectangle in (a) but Au reconstruction removed by Fourier filtering. Black arrows mark the middle of the dark fcc regions of the substrate seen in (a). Red arrows denote the 60.6 Å periodicity of the network along the <1$\bar{1}$0>

direction (√3 times the network lattice constant of 35 Å). The changing distance between black and red arrows indicate a mismatch in periodicities between the Au reconstruction and the network. Dashed lines indicate stacking faults in the network structure running along the $<1\bar{1}0>$ direction. Right: enlarged view of the filtered images from the same region as shown in (a).

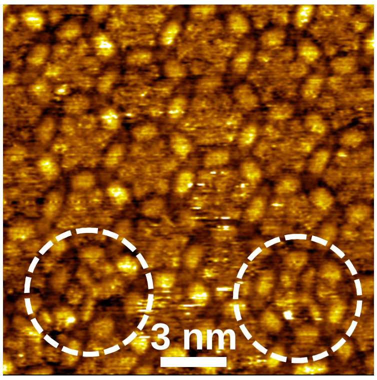


Fig. S4: STM image of P_H-TPEB adsorbed in pores of PTCDI/melamine network on Au(111)/mica. Circles mark pores where star molecules are seen.

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