

Supporting Information

Microporous, Tetraarylethylene-based Polymer Networks generated in a Reductive Polyolefination Process

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Experimental details.

Unless otherwise indicated, all reagents were obtained from commercial suppliers and were used without further purification. The solvents used were of commercial p.a. quality. The reactions were carried out under argon with standard and Schlenk techniques.

Solution NMR measurments. Solution ¹H and ¹³C NMR data of the monomers were recorded on a Bruker ARX 400 or Bruker AVANCE III 600 spectrometer using the solvent proton or carbon signals as internal standard.

Elemental Analysis. Elemental analysis were obtained on a Perkin Elmer 240 B. Deviations of the elemental composition from the calculated values for such microporous polymers are due to incomplete combustion and trapped adsorbates (gases, water) [1, 2].

Mass spectrometry analysis. Mass spectrometry analysis was performed on a time-of-flight mass spectrometer (Bruker Daltonics MicrOTOF) equipped with a homemade multipurpose ion source (MPIS).

Thermogravimetric analysis. Thermogravimetric analysis were performed on a Mettler Toledo TGA Star^c System. The first decomposition step was measured under argon flow.

Nitrogen sorption measurements. The nitrogen sorption measurements were performed on a BELSORB Max (Bel Japan Inc.). The surface areas were calculated using the BET model in the pressure range p/p₀ from 0.05 – 0.25. The total pore volume was determined at a relative pressure of 0.95.

Solid-State NMR measurements. Solid-state ^{13}C CPMAS spectra were collected at 75.48 MHz using a Bruker Avance III 300 spectrometer with a contact time of 2.5 ms co-adding 4096 up to 16392 transients, depending on the required relaxation delay of 2 s up to 60 s. All experiments were carried out at room temperature using a standard Bruker 4 mm double resonance MAS probe spinning at 12 kHz, typical $\pi/2$ -pulse lengths of 4 μs and SPINAL64 proton decoupling. The spectra were referenced with respect to tetramethyl silane (TMS) using solid adamantane as secondary standard (29.46 ppm for ^{13}C).

UV-Vis. UV-Vis absorption spectra were recorded on a Shimadzu UV-2401 PC spectrophotometer at room temperature.

Photoluminescence spectroscopy. Fluorescence measurements were carried out on Fluoromax-4 equipped with Quanta-Phi integration sphere (Horiba) by using a powder sample holder at room temperature.

Gas adsorption selectivities. To evaluate the gas adsorption selectivity CO_2/CH_4 and N_2/H_2 Henry's law was used:

$$q = K * P$$

where q is the adsorbed amount per unit weight of adsorbent ($\text{cm}^3 \text{g}^{-1}$), P is the adsorbate gas pressure at equilibrium (torr), and K is the Henry's law constant ($\text{cm}^3 \text{g}^{-1} \text{torr}^{-1}$) and the related selectivities are calculated with the equation $S_{ij} = K_{(i)} / K_{(j)}$ [3].

Supercritical carbon dioxide treatment (washing). Prior to the supercritical drying process all samples were soaked with absolute ethanol (72 h). The drying procedure was performed in a supercritical point dryer from TousimisTM (Samdri – 795) with liquid CO_2 (Messer) as carbon dioxide source. The dry samples were obtained after four drying cycles:

The ethanol-containing samples were placed inside the dryer and the ethanol was exchanged by rinsing with liquid $\text{CO}_2(\text{l})$ over a period of 15 min. After that the chamber was sealed and the temperature was raised to 40 °C resulting in a chamber pressure of around 1300 psi well above the critical point of CO_2 . The chamber was held above the critical point for 1 h. This procedure was repeated for additional three times with the following modifications: second run: 5 min purging, 1 h supercritical conditions, third run: 5 min purging, 2.5 h supercritical conditions; last run 5 min purging, 14 h supercritical conditions.

PL quenching experiments. For preparation of polymer pellets 50 mg of P4 was compressed (3 tons) for 20 min. The vapor chamber was saturated with the analyte for 24 h prior to the PL quenching experiments.

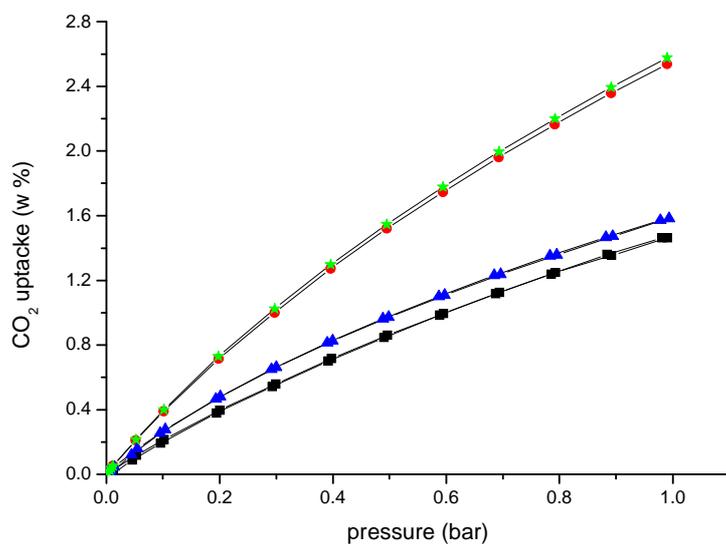


Fig. S1: Carbon dioxide adsorption isotherms at 298 K for P1 (black square), P2 (red circle), P3 (blue triangle), P4 (green star).

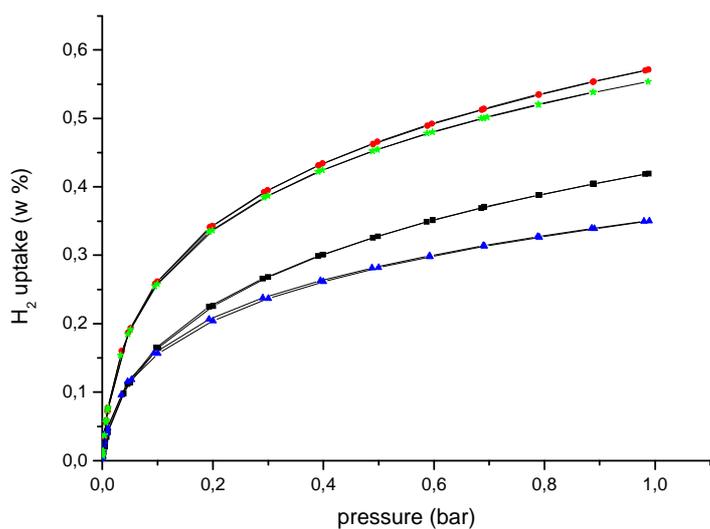


Fig. S2: Hydrogen adsorption isotherms at 77 K for P1 (black square), P2 (red circle), P3 (blue triangle), P4 (green star).

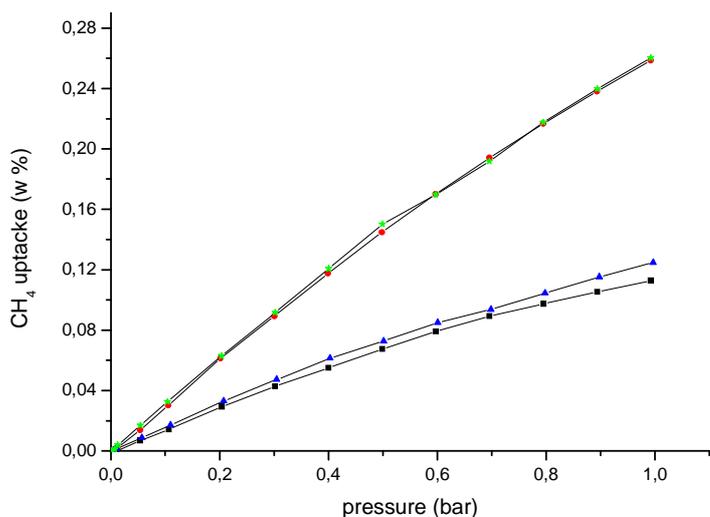


Fig S3: Methane adsorption isotherms at 77 K for P1 (black square), P2 (red circle), P3 (blue triangle), P4 (green star).

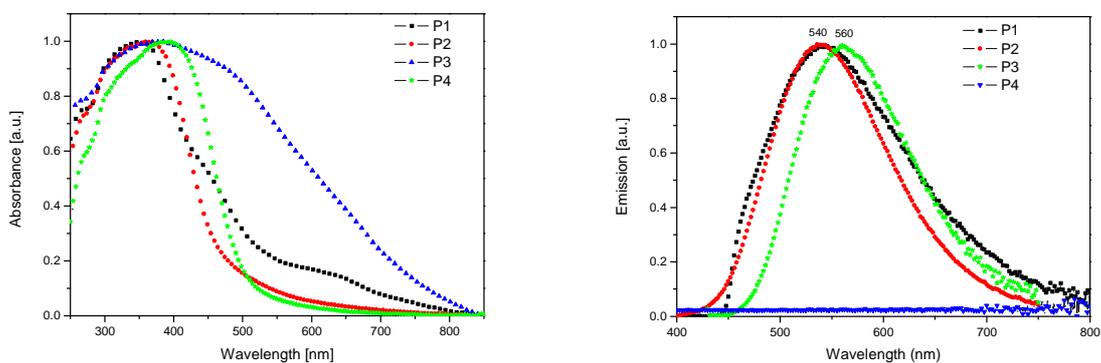
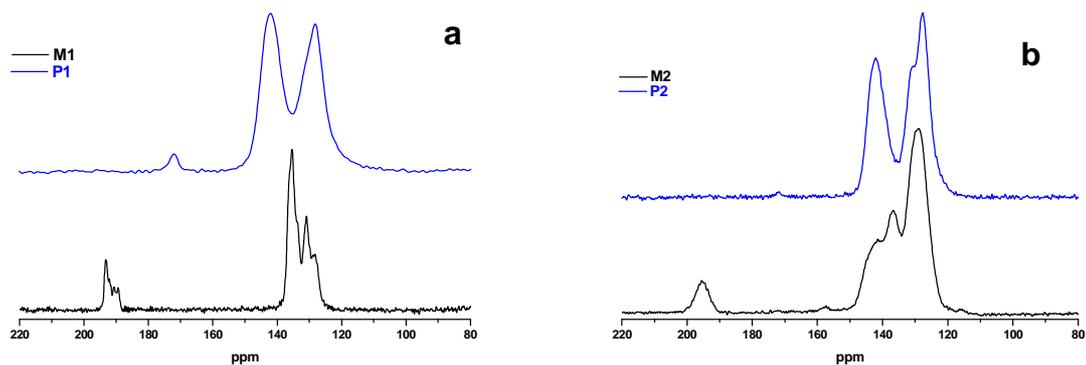


Fig. S4: Solid state UV/Vis reflection spectra measured with a 60 mm integrating sphere (left) and PL spectra measured with a Quanta-Phi integrating sphere (right) of P1 (black square), P2 (red circle), P3 (blue triangle), P4 (green star).



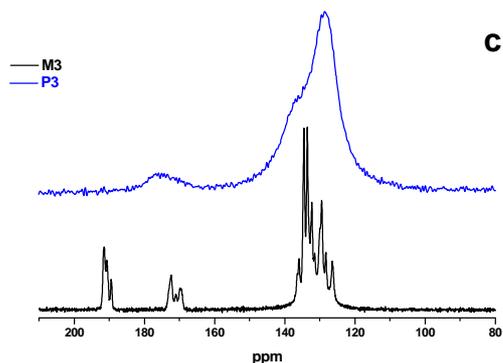


Fig. S5: Solid state ^{13}C NMR spectra of monomers M1-M3 and polymer networks P1-P3.

1,3,5-Tribenzoylbenzene M1 [4]

1,3,5-Benzenetricarboxylic acid trichloride (28.0 g, 105 mmol), aluminum chloride (50.6 g, 380 mmol) and benzene (125 mL) were added to a 250 mL one-necked round-bottom flask. The reaction mixture was refluxed for 24 h. A large amount of cold water was added to quench the reaction and the reaction mixture was then extracted with DCM. The organic layer was washed with water and dried over magnesium sulfate. After filtration and solvent evaporation, the crude product was purified by silica-gel column chromatography with hexane/DCM (2:3 by volume) as eluent. The product was obtained as a white solid (38.6 g, 94 %).

^1H NMR (600 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$), δ (ppm): 8.40 (s, 3H), 7.85 (dd, $J = 5.1$ Hz, $J = 3.3$ Hz, 6H), 7.71-7.62 (m, 3H), 7.58-7.51(m, 6H).

^{13}C NMR (151 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$), δ (ppm): 195.19, 138.38, 136.51, 134.43, 133.78, 130.38, 129.05.

Anal. calc. for $\text{C}_{27}\text{H}_{18}\text{O}_3$: C, 83.06; H, 4.65; Found: C, 82.60; H, 4.66.

1,3,5-Tris(α,α -dichlorobenzyl)benzene MCl1

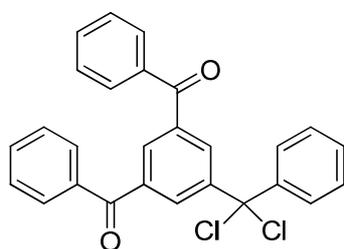
1,3,5-Tribenzoylbenzene M1 (1.0 g, 2.56 mmol), phosphorus pentachloride (3.2 g, 15.36 mmol) and 20 mL of chlorobenzene were added to a 100 mL Schlenk tube. The reaction mixture was heated at 120 °C for 4 d. The mixture was cooled down to 80 °C and chlorobenzene and POCl_3 were removed by distillation under reduced pressure. Finally,

unreacted phosphorus pentachlorid was sublimed out of the reaction tube. The yellow oil (1.42 g, 100 %) was used without further purification.

^1H NMR (600 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$), δ (ppm): 7.75 (s, 3H), 7.49-7.41 (m, 6H), 7.33-7.22 (m, 9H).
 ^{13}C NMR (151 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$), δ (ppm): 164.12, 145.57, 143.89, 130.78, 129.68, 128.37, 92.06.

In case of incomplete reaction (insufficient reaction time) both intermediates could be isolated by silica-gel column chromatography in a hexane/DCM gradient from 0 - 100 %.

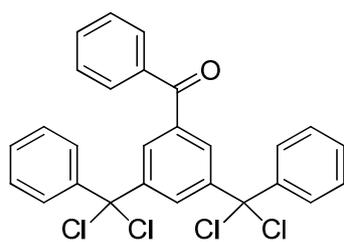
1-(α,α -Dichlorobenzyl)-3,5-dibenzoylbenzene



^1H NMR (600 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$), δ (ppm): 8.02 (t, $J = 1.9$ Hz, 1H), 7.92 (d, $J = 1.9$ Hz, 2H), 7.66 (dd, $J = 8.3$ Hz, 2H), 7.54-7.50 (m, 5H), 7.42-7.37 (m, 2 H), 7.34-7.29 (m, 6H).

^{13}C NMR (151 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$), δ (ppm): 195.12, 145.50, 142.87, 138.03, 136.51, 133.69, 132.24, 131.80, 130.38, 129.91, 128.96, 128.84, 127.49, 90.78.

1,3-Bis(α,α -dichlorobenzyl)-5-benzoylbenzene



^1H NMR (600 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$), δ (ppm): 8.18 (d, $J = 1.5$ Hz, 2 H), 8.09 (t, $J = 1.5$ Hz, 1H), 7.73 (dd, $J = 8.3$ Hz, $J = 1.2$ Hz, 4H), 7.63-7.53 (m, 4H), 7.8 (t, $J = 7.8$ Hz, 4H), 7.39-7.30 (m, 3H).

^{13}C NMR (151 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$), δ (ppm): 195.09, 145.05, 142.87, 133.60, 130.41, 130.09, 129.83, 129.61, 128.88, 128.75, 127.46, 90.90.

Polymer network P1(Co₂(CO)₈ as condensing agent)

1,3,5-Tris(α,α -dichlorobenzyl)benzene MCl1 (1.3 g, 2.27 mmol), dicobalt octacarbonyl (2.7 g, 7.83 mmol) and 20 mL of chlorobenzene were added to a 100 mL Schlenk tube. The reaction mixture was heated at 100 °C for 50 min (gas formation starts at around 80 °C). For quenching, 10 mL of 1,2-dibromoethane was added and the mixture was stirred for another 10 min. Next, the reaction mixture was purged into methanol and the solid powder collected by filtration and washed with methanol. The crude product was purified by successive Soxhlet extraction with methanol, ethyl acetate, 1,4-dioxane, and chloroform. The resulting polymer was treated (washed) with supercritical carbon dioxide. The product was obtained as a yellow powder (828 mg, quantitative yield).

¹³C-{H}-CP/MAS-NMR (75.48 MHz), δ (ppm) = 172, 142, 128.

TGA: first decomposition step 272 °C (2.50 %) (Argon).

PL: λ_{\max} (solid state)/nm: 540 (excitation: 340 nm); PLQY (solid state): 3.5 %.

UV/Vis: λ_{\max} (solid state)/nm: 352, 266sh, 440sh, 600sh.

BET: 462 m²/g, total pore volume: 1.76 cc/g.

Polymer network P1(Cr₂ac₄ as condensing agent)

1,3,5-Tris(α,α -dichlorobenzyl)benzene (1.4 g, 2.56 mmol) in 10 mL of dimethyl formamide, and chromium(II)acetate (5.3 g, 15.35 mmol) in 10 mL of chlorobenzene were introduced into a 100 mL Schlenk tube. The reaction mixture was heated at 100 °C for 50 min. For quenching, 10 mL of 1,2-dibromoethane was added and the mixture was stirred for another 10 min. Next, the reaction mixture was purged into water, the solid product collected by filtration and washed with methanol. The crude product was purified by successive Soxhlet extraction with methanol, ethyl acetate, 1,4-dioxane and chloroform. The resulting polymer was treated (washed) with supercritical carbon dioxide. The product was obtained as a yellow powder (808 mg, 92 %).

¹³C-{H}-CP/MAS-NMR (75.48 MHz) δ (ppm) = 195, 142, 128, 83.

TGA: first decomposition step 242 °C (5.69 %) (Argon).

PL: λ_{\max} (solid state)/nm: 518 (excitation: 340 nm); PLQY (solid state): 6.0 %.

UV/Vis: λ_{\max} (solid state)/nm: 334, 265sh, 600sh.

BET: 435 m²/g, total pore volume: 1.70 cc/g.

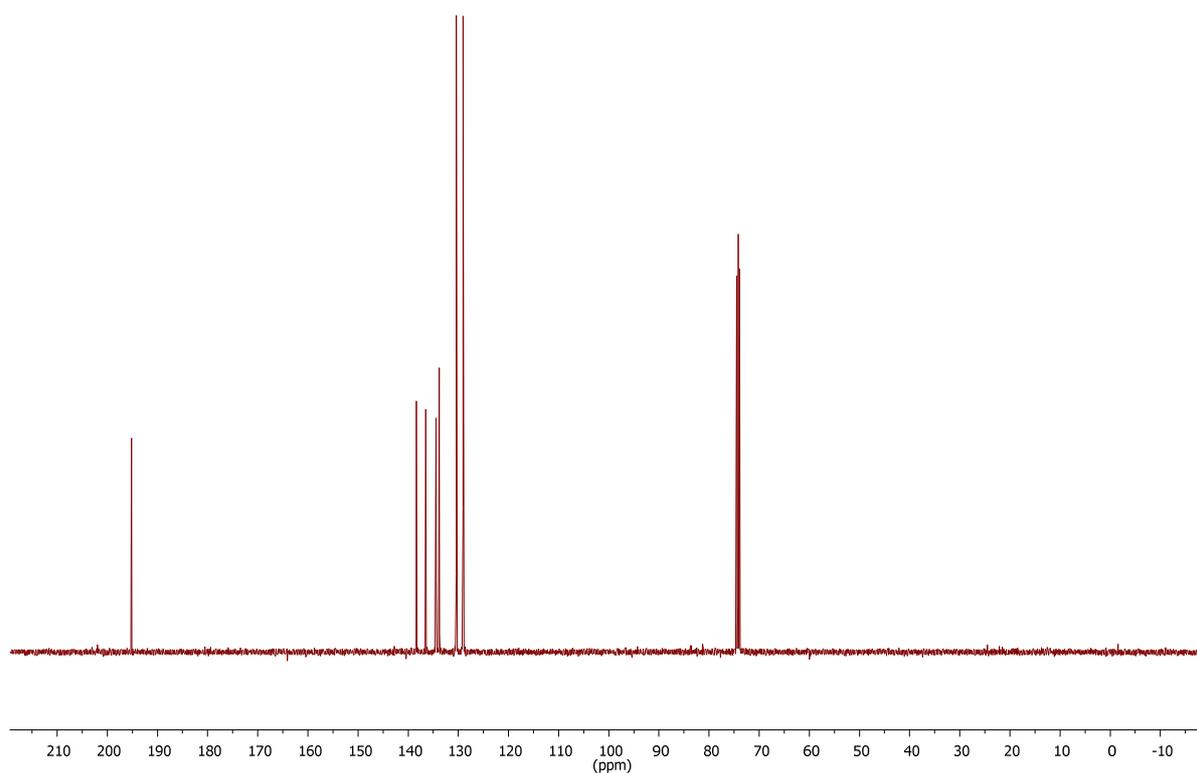


Fig. S6: ^{13}C NMR spectrum ($\text{C}_2\text{D}_2\text{Cl}_4$) of M1.

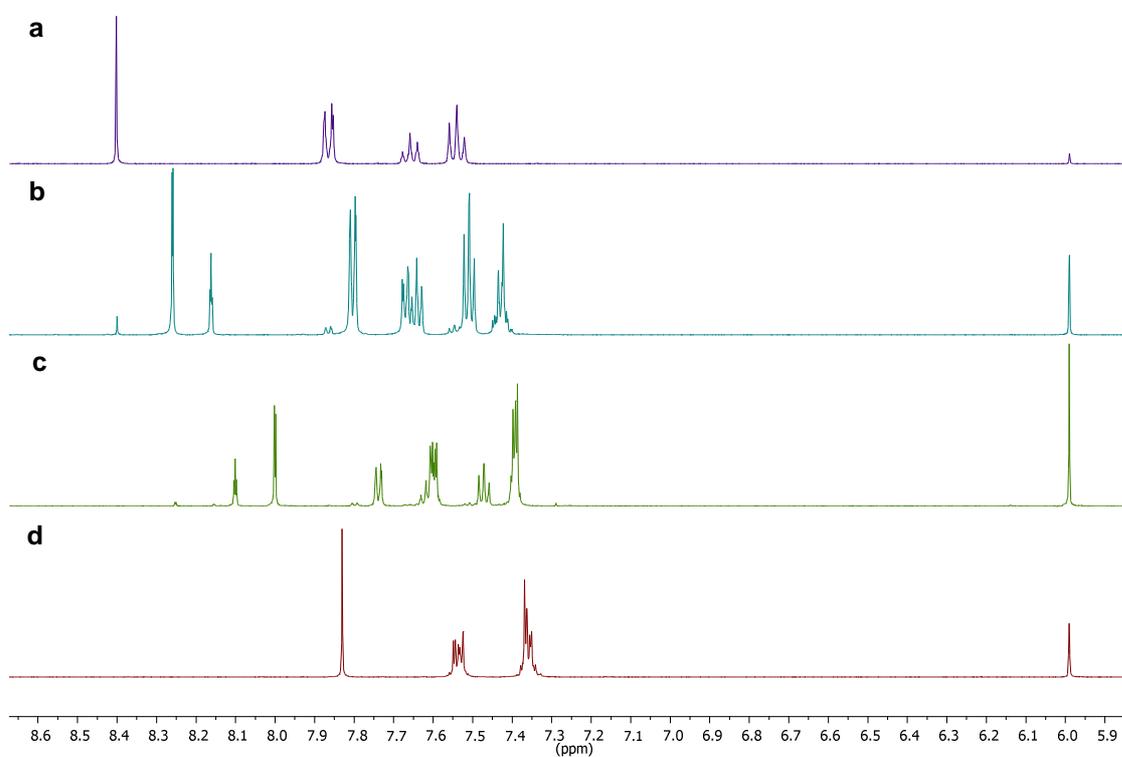


Fig. S7: ^1H NMR spectra of M1 (a), 1-(α,α -dichlorobenzyl)-3,5-dibenzoylbenzene (b), 1,3-bis(α,α -dichlorobenzyl)-5-benzoylbenzene (c), MC11 (d) in $\text{C}_2\text{D}_2\text{Cl}_4$.

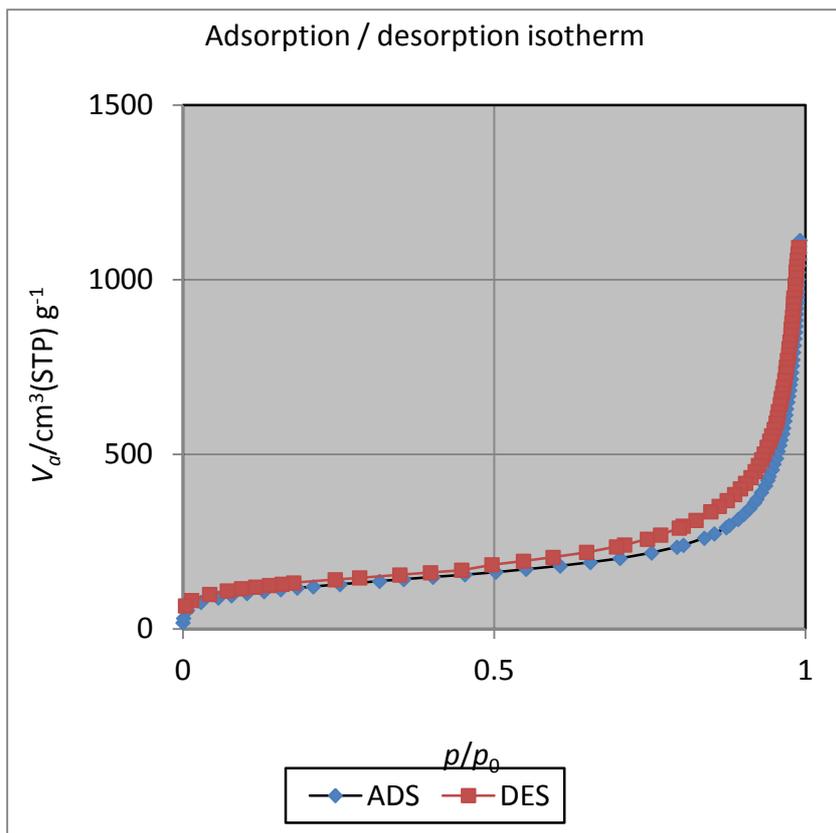


Fig. S8: Nitrogen adsorption isotherm of P1 [$\text{Co}_2(\text{CO})_8$].

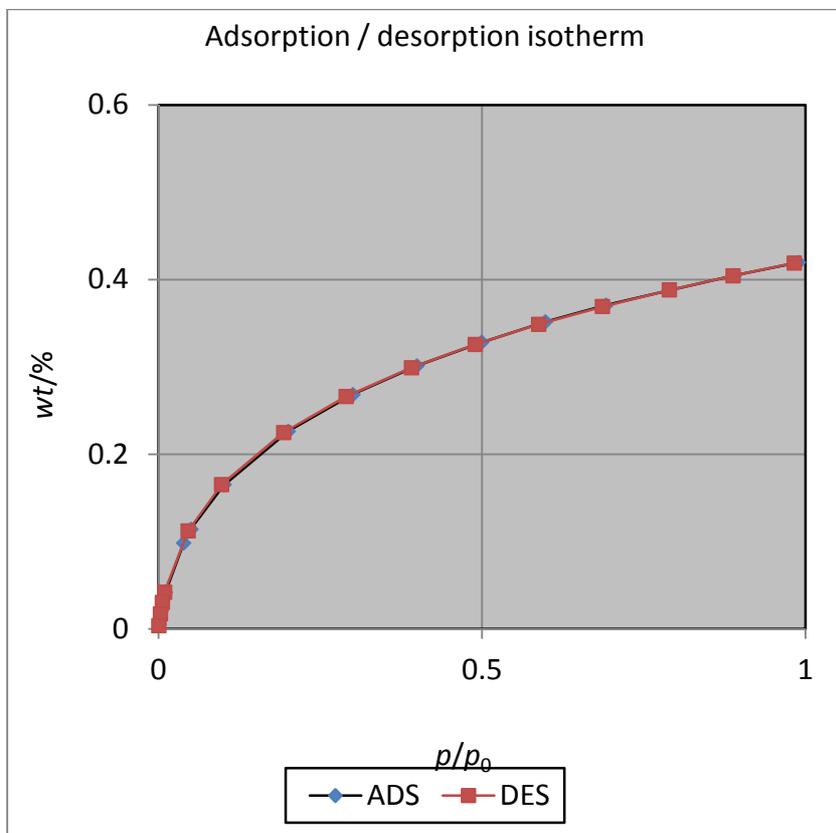


Fig. S9: Hydrogen adsorption isotherm of P1 [$\text{Co}_2(\text{CO})_8$] at 77 K.

1,3,5-Tris(4-bromophenyl)benzene [5]

4-Bromoacetophenone (3.5 g, 17.42 mmol) was dissolved in ethanol (55 mL) at 0 °C. Tetrachlorosilane (22.2 g, 131 mmol) was added slowly to the reaction mixture at 0 °C and stirred over night at ambient condition. The reaction mixture was poured into an ice/water mixture and was extracted with DCM. The crude product was purified by silica-gel column chromatography in a hexane/DCM gradient from 2 to 50 % of DCM, followed by a recrystallization from a mixture of ethanol and chloroform. The product was obtained as a white solid (2.0 g, 63 %).

¹H NMR (400 MHz, C₂D₂Cl₄), δ (ppm): 7.71 (s, 3H), 7.63 (d, J = 8.6 Hz, 6H), 7.57 (d, J = 8.6 Hz, 6H).

¹³C NMR (101 MHz, C₂D₂Cl₄), δ(ppm): 141.61, 139.80, 132.37, 129.24, 125.27, 122.37.

Anal. calc. for C₂₅H₁₅Br₃: C, 53.08; H, 2.78; Found: C, 53.30; H, 2.36.

APLI (m/z): 543.8443 (calc. 543.8686).

1,3,5-Tris(4-cyanophenyl)benzene

1,3,5-Tris(4-bromophenyl)benzene (4.7 g, 8.65 mmol) and copper(I)cyanide (7.8 g, 87.0 mmol) were added to 100 mL of dimethyl formamide and stirred under argon overnight at 140 °C. After cooling to 90 °C 200 mL of ethanol were added and the mixture stirred for another 1 h. The resulting brown residue was filtered off and extracted three times with hot toluene, hot chloroform and hot tetrahydrofuran each. The organic solvents were evaporated under reduced pressure. The crude product was purified by silica-gel column chromatography with DCM yield (0.7 g, 21 %) of a white solid.

¹H NMR (400 MHz, C₂D₂Cl₄), δ (ppm): 7.82 (s, 3H), 7.81 (s, 12H).

¹³C NMR (101 MHz, C₂D₂Cl₄), δ (ppm): 144.82, 141.36, 133.14, 128.33, 126.67, 119.23, 111.84.

APLI (m/z): 381.1039 (calc. 381.1266).

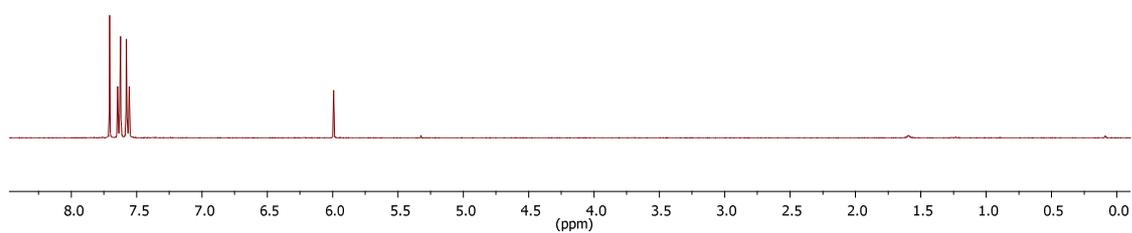
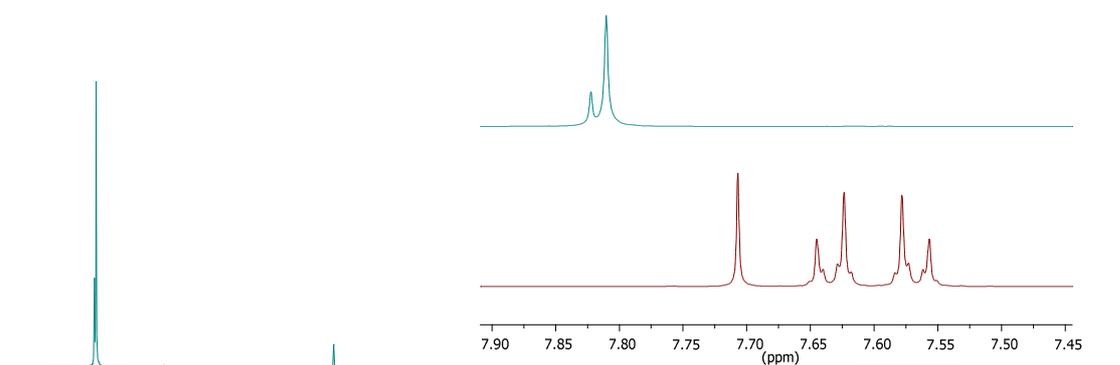


Fig. S10: ^1H NMR spectra of 1,3,5-tris(4-cyanophenyl)benzene (top) and 1,3,5-tris(4-bromophenyl)benzene (down) in $\text{C}_2\text{D}_2\text{Cl}_4$.

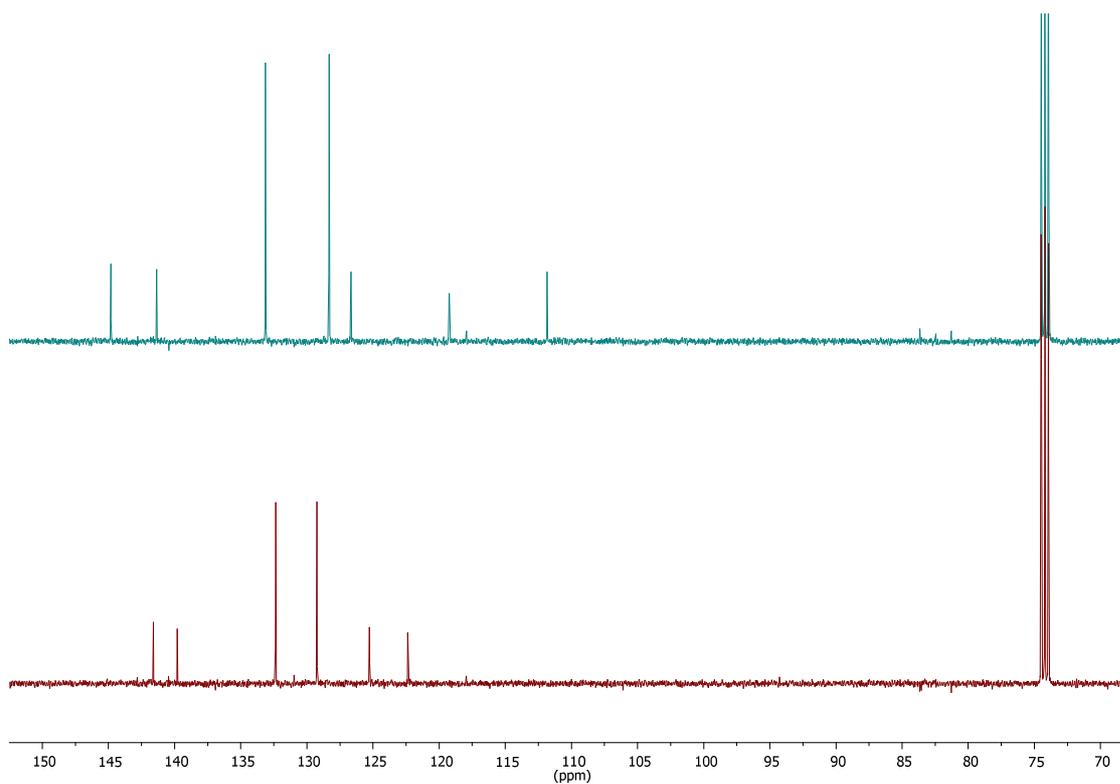


Fig. S11: ^{13}C NMR spectra of 1,3,5-tris(4-cyanophenyl)benzene (top) and 1,3,5-tris(4-bromophenyl)benzene (down) in $\text{C}_2\text{D}_2\text{Cl}_4$.

1,3,5-Tris(4-benzoylphenyl)benzene M2

1,3,5-Tris(4-cyanophenyl)benzene (0.7 g, 1.83 mmol) and phenyl magnesium bromide (3 mL, 3 mol/L in THF) was refluxed in THF (25 mL) over night. After addition of 4N hydrochloride solution the reaction mixture was refluxed for an addition 1 h. The resulting mixture was extracted three times with diethylether and dried over magnesium sulfate. Collected organic phase was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography using chloroform/hexane (7:3) yielded (0.5 g, 44 %) as off white solid.

^1H NMR (600 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$), δ (ppm): 7.93 (d, $J = 6.7$ Hz, 9H), 7.84 (t, $J = 7.6$ Hz, 12H), 7.62 (t, $J = 7.4$ Hz, 3H), 7.52 (t, $J = 7.7$ Hz, 6H).

^{13}C NMR (151 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$), δ (ppm): 196.58, 144.76, 141.82, 137.71, 136.95, 133.02, 131.15, 130.34, 128.78, 127.60, 126.47.

APLI (m/z): 618.2180 (calc. 618.2189).

1,3,5-Tris[4-(α,α -dichlorobenzyl)phenyl]benzene MC12

1,3,5-Tris(4-benzoylphenyl)benzene M2 (0.2 g, 0.32 mmol), phosphorus pentachloride (0.4 g, 1.94 mmol) and 20 mL of chlorobenzene were placed in a 100 mL Schlenk tube. The reaction mixture was heated at 120 °C for 4 d. The mixture was cooled to 80 °C and chlorobenzene and POCl_3 were distilled off under reduced pressure. Finally, unreacted phosphorus pentachloride was sublimed out of the tube. The resulting yellow oil (0.25 g, 100 %) was used without further purification.

^1H NMR (400 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$), δ (ppm): 7.88 (s, 3H), 7.79 (d, $J = 8.4$ Hz, 6H), 7.74 (d, $J = 8.7$ Hz, 14H), 7.50-7.40 (m, 9H).

^{13}C NMR (101 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$), δ (ppm): 143.98, 143.56, 141.48, 141.46, 129.52, 128.55, 128.32, 127.65, 127.25, 125.82, 92.22.

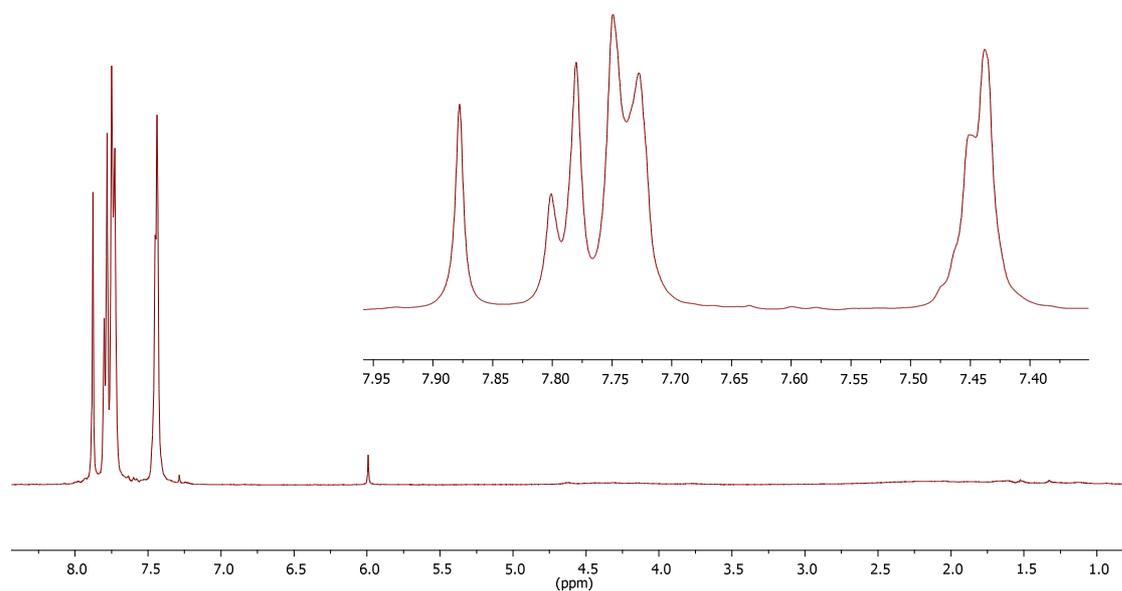


Fig. S12: ^1H NMR spectrum of 1,3,5-tris[4-(α,α -dichlorobenzyl)phenyl]benzene MCl₂ in $\text{C}_2\text{D}_2\text{Cl}_4$.

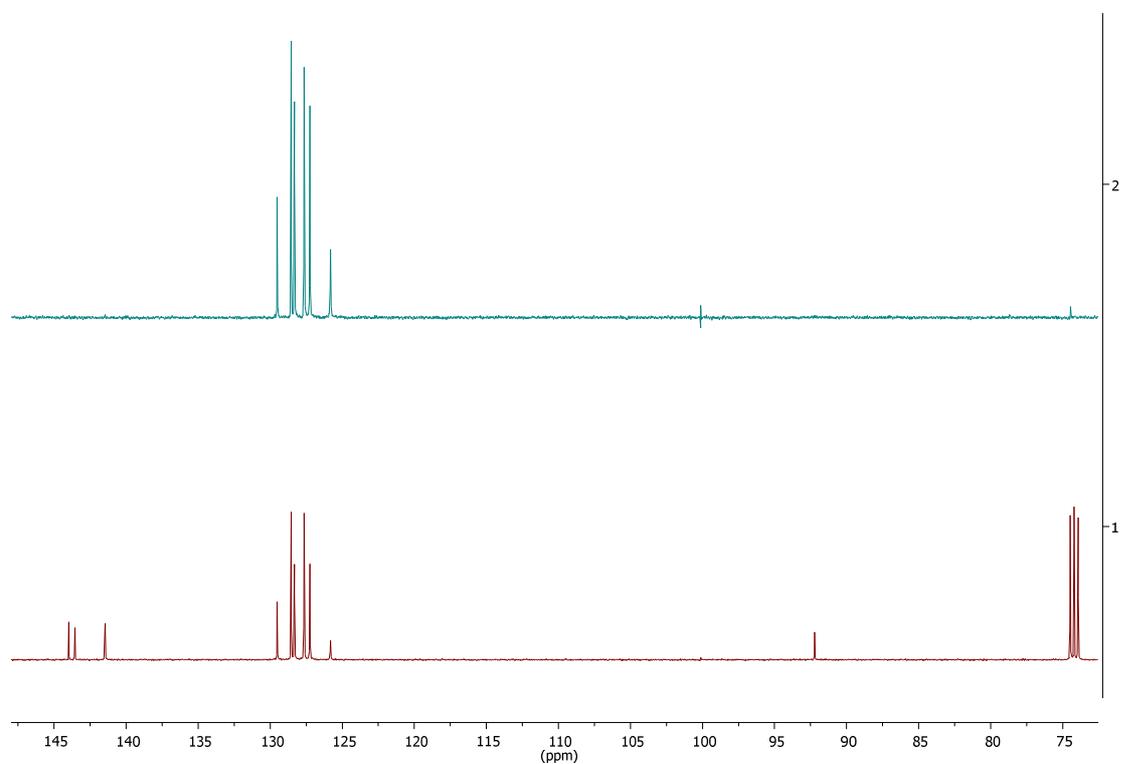


Fig. S13: ^{13}C NMR DEPT (top) and ^{13}C NMR (down) spectra of 1,3,5-tris[4-(α,α -dichlorobenzyl)phenyl]benzene MCl₂ in $\text{C}_2\text{D}_2\text{Cl}_4$.

Polymer network P2

1,3,5-Tris[4-(α,α -dichlorobenzyl)phenyl]benzene MCl_2 (0.25 g, 0.39 mmol) in 10 mL dimethyl formamide and dicobalt octacarbonyl (0.4 g, 1.10 mmol) in 10 mL of chlorobenzene were placed in a 100 mL Schlenk tube. The reaction mixture was heated at 100 °C for 50 min. For quenching, 10 mL of 1,2-dibromoethane was added and the mixture stirred for another 10 min. Next, the reaction mixture was purged into water, the solid product collected by filtration and washed with methanol. The crude product was purified by successive Soxhlet extraction with methanol, ethyl acetate, 1,4-dioxane and chloroform. The resulting polymer was treated (washed) with supercritical carbon dioxide. The product was obtained as a yellow powder (170 mg, 87 %).

^{13}C -{H}-CP/MAS-NMR (75.48 MHz) δ (ppm) = 170, 130, 127.

TGA: first decomposition step 386 °C (2.64 %) (Argon).

PL: λ_{max} (solid state)/nm: 540 (excitation: 340 nm); PLQY (solid state): 6.5 %.

UV/Vis: λ_{max} (solid state)/nm: 363, 270sh.

BET: 502 m^2/g , total pore volume: 1.87 cc/g .

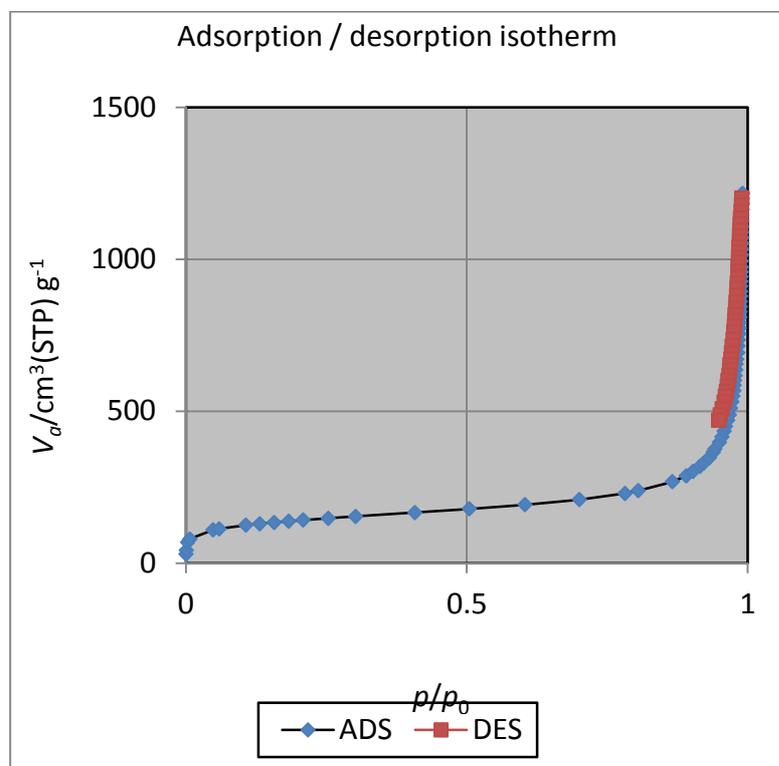


Fig. S14: Nitrogen adsorption isotherm of P2.

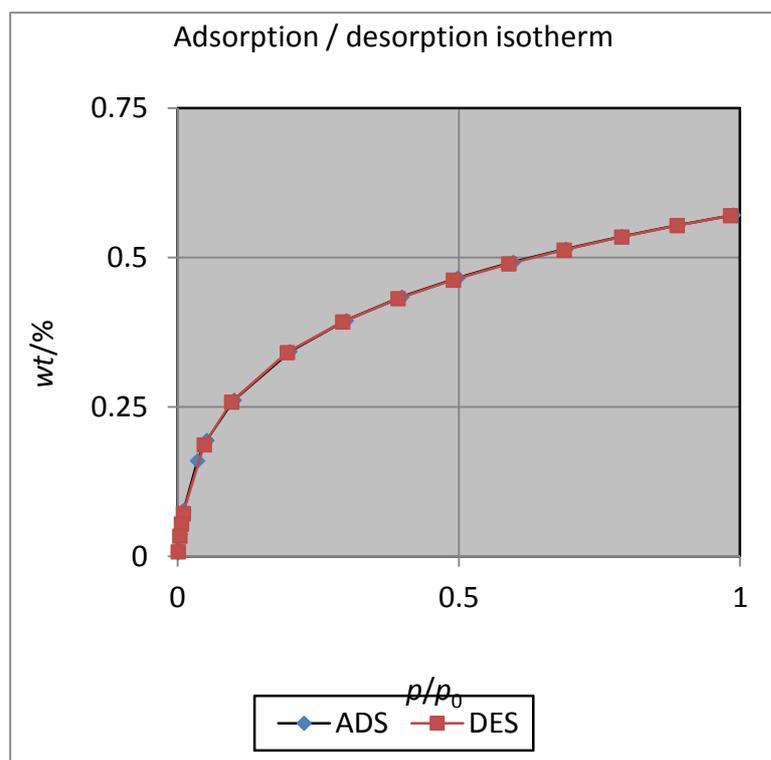


Fig. S15: Hydrogen adsorption isotherm of P2 at 77 K.

Tris(2,4,6-benzoyl)-1,3,5-triazine M3

Carefully dried potassium 1,3,5-triazine-2,4,6-tricarboxylate [6-8] (5.0 g, 15.27 mmol) was suspended in POCl_3 (50 mL, freshly distilled) and the mixture was stirred for 12 h at room temperature and for additional 12 h at 80°C . The color of the suspension gradually turned to yellow-brownish and a solid residue is formed. Excess of POCl_3 is distilled off under reduced pressure. The solid residue was suspended with dry benzene (80 mL) and aluminum chloride (7.3 g, 55.00 mmol) was added under external cooling with ice. The dark red suspension was stirred for 4 h at room temperature and then poured into a mixture of 100 g of ice and 100 mL of concentrated hydrochloric acid. Next, the organic products were extracted with toluene. After drying the organic phase over calcium chloride the solvent was removed under reduced pressure. The product was recrystallized from toluene to yield (3.5 g, 58 %) of white needles.

^1H NMR (400 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$), δ (ppm): 8.08 (dd, $J = 8.3$ Hz, $J = 1.2$ Hz, 6H), 7.72 (tt, $J = 7.5$ Hz, $J = 1.2$ Hz, 3H), 7.56 (t, $J = 7.8$ Hz, 6H).

^{13}C NMR (101 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$), δ (ppm): 188.64, 171.44, 135.54, 133.35, 131.15, 129.34.

APLI (m/z): 394.1231 (calc. 394.1186).

Anal. calc. for $\text{C}_{24}\text{H}_{15}\text{N}_3\text{O}_3$: C, 73.27; H, 3.84; N, 10.68; Found: C, 73.36; H, 3.79; N, 10.47.

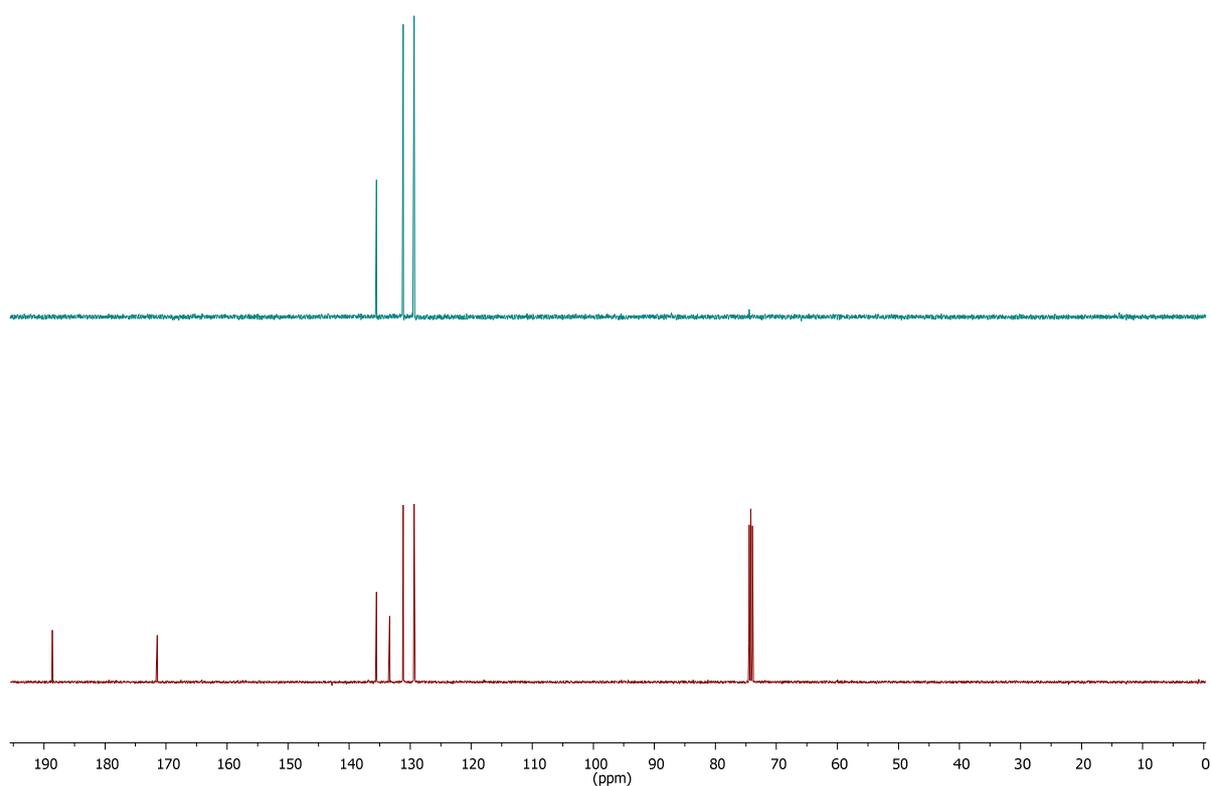


Fig. S16: ^{13}C NMR DEPT (top) and ^{13}C NMR (down) spectra of tris(2,4,6-benzoyl)-1,3,5-triazine M3 in $\text{C}_2\text{D}_2\text{Cl}_4$.

2,4,6-Tris(α,α -dichlorobenzyl)-1,3,5-triazine MCl3

Tris(2,4,6-benzoyl)-1,3,5-triazine (0.4 g, 1.07 mmol), phosphorus pentachloride (3.0 g, 14.41 mmol) and 20 mL of chlorobenzene were added to a 100 mL Schlenk tube. The reaction mixture was heated at 120 °C for 4 d. After cooling to 80 °C chlorobenzene and POCl_3 were distilled off under reduced pressure. Finally, unreacted phosphorus pentachloride was sublimed out of the reaction tube. The resulting yellow oil (0.6 g, 99 %) was used without further purification.

^1H NMR (600 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$), δ (ppm): 7.62 (dd, $J = 7.1$ Hz, $J = 1.6$ Hz, 6H), 7.36-7.30 (m, 9H).

^{13}C NMR (151 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$), δ (ppm): 178.12, 139.50, 129.95, 129.80, 128.55, 127.71, 88.61.

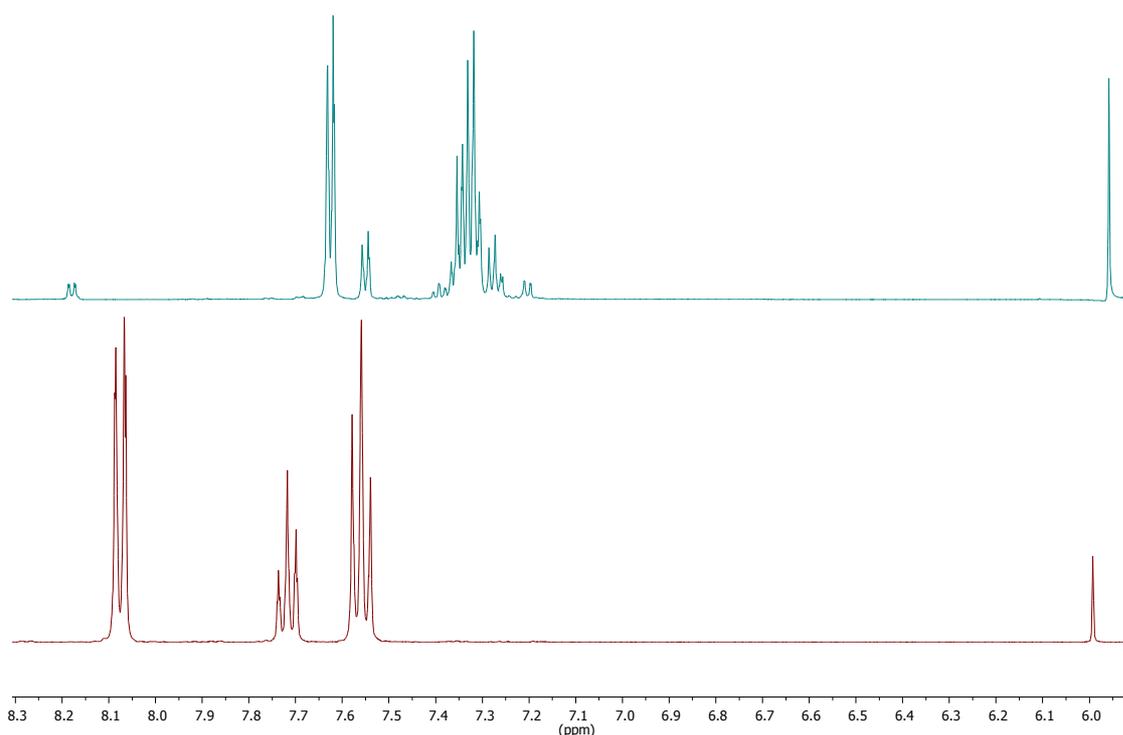


Fig. S17: ^1H NMR spectra of 2,4,6-tris(α,α -dichlorobenzyl)-1,3,5-triazine MCl3 (top) and tris(2,4,6-benzoyl)-1,3,5-triazine M3 (down).

Polymer network P3

2,4,6-Tris(α,α -dichlorobenzyl)-1,3,5-triazine MCl3 (0.6 g, 1.06 mmol) in 10 mL of chlorobenzene and dicobalt octacarbonyl (1.0 g, 3.81 mmol) in 10 mL of chlorobenzene were placed into a 100 mL Schlenk tube. The mixture was reacted at 100 °C for 50 min. For quenching, 10 mL of 1,2-dibromoethane was added and the mixture was stirred for another 10 min. Next, the reaction mixture was purged into water, the solid product collected by filtration and washed with methanol. The crude product was purified by successive Soxhlet extraction with methanol, ethyl acetate, 1,4-dioxane, tetrahydrofuran and chloroform. The resulting polymer was treated (washed) with supercritical carbon dioxide. The product was obtained as a brown powder (275 mg, 67 %).

^{13}C -{ ^1H }-CP/MAS-NMR (75.48 MHz), δ (ppm) = 175, 136, 128.

TGA: first decomposition step 296 °C (7.95 %) (Argon).

PL: λ_{max} (solid state)/nm: no PL detected.

UV/Vis: λ_{max} (solid state)/nm: 367, 267sh, 450sh.

BET: 200 m²/g, total pore volume: 1.05 cc/g.

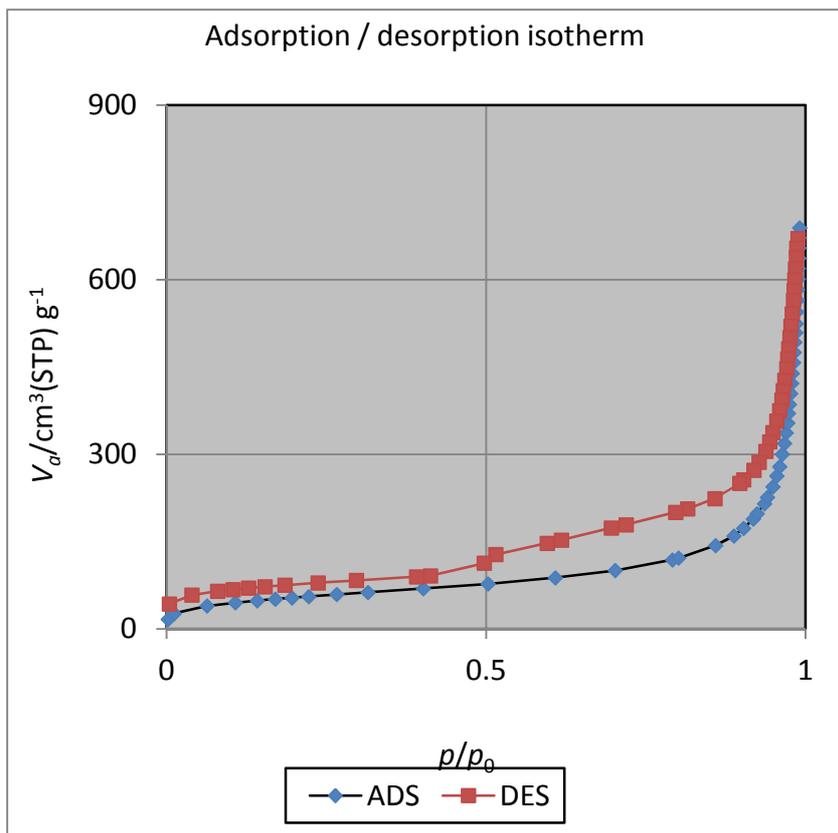


Fig. S18: Nitrogen adsorption isotherm of P3.

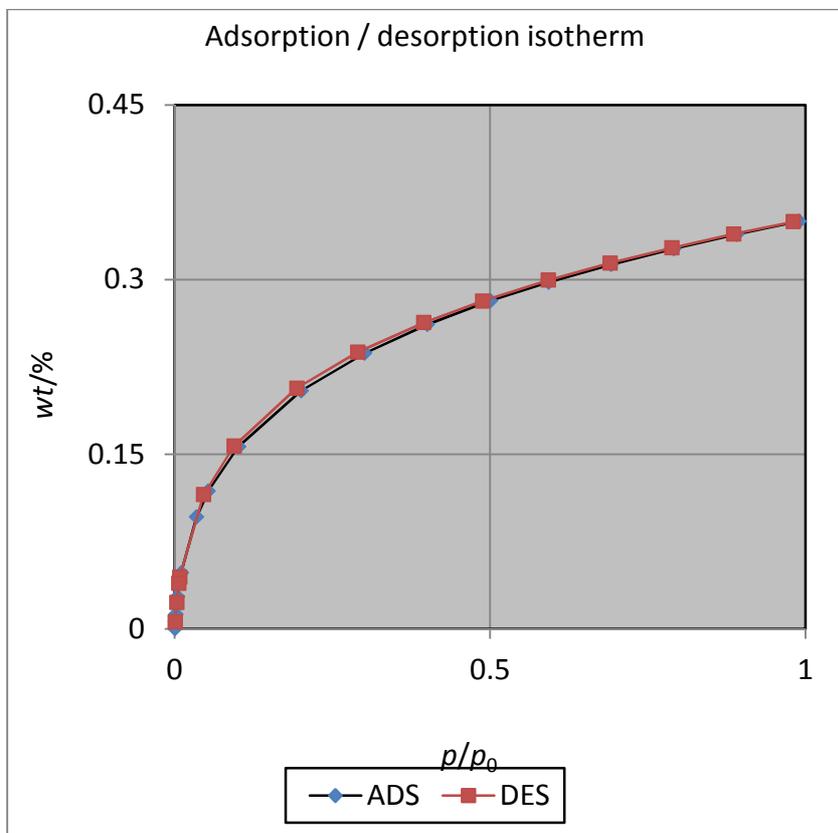


Fig S19: Hydrogen adsorption isotherm of P3 at 77 K.

2,4,6-Tris(4-methylphenyl)-1,3,5-triazine [9]

4-Methylbenzotrile (29.4 g, 251 mmol) was added to trifluoromethane sulfonic acid (30 mL, 338 mmol) at 0 °C under inert atmosphere. The mixture solidifies and after 3 d at room temperature the mixture was heated up to 65 °C for additional 4 h. The product was purged into 2 L of an ice/water mixture and extracted three times with diethylether. The organic phase was dried over magnesium sulfate and concentrated under reduced pressure. The crude solid product was recrystallized from toluene (24.0 g, 82 %) white crystals.

^1H NMR (400 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$), δ (ppm): 8.65 (d, $J = 8.0$ Hz, 6H), 7.40 (d, $J = 8.0$ Hz, 6H), 2.50 (s, 9H).

^{13}C NMR (101 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$), δ (ppm): 171.67, 143.52, 133.88, 129.80, 22.12.

IR (KBr) ν/cm^{-1} : 3067, 3035, 2918, 2881, 1608, 1585, 1517, 1406, 1369, 799.

APLI (m/z): 352.1771 (calc. 352.1814).

Anal. calc. for $\text{C}_{24}\text{H}_{21}\text{N}_3$: C, 82.02; H, 6.02; N, 11.96; found C, 81.90; H 5.97; N, 11.76.

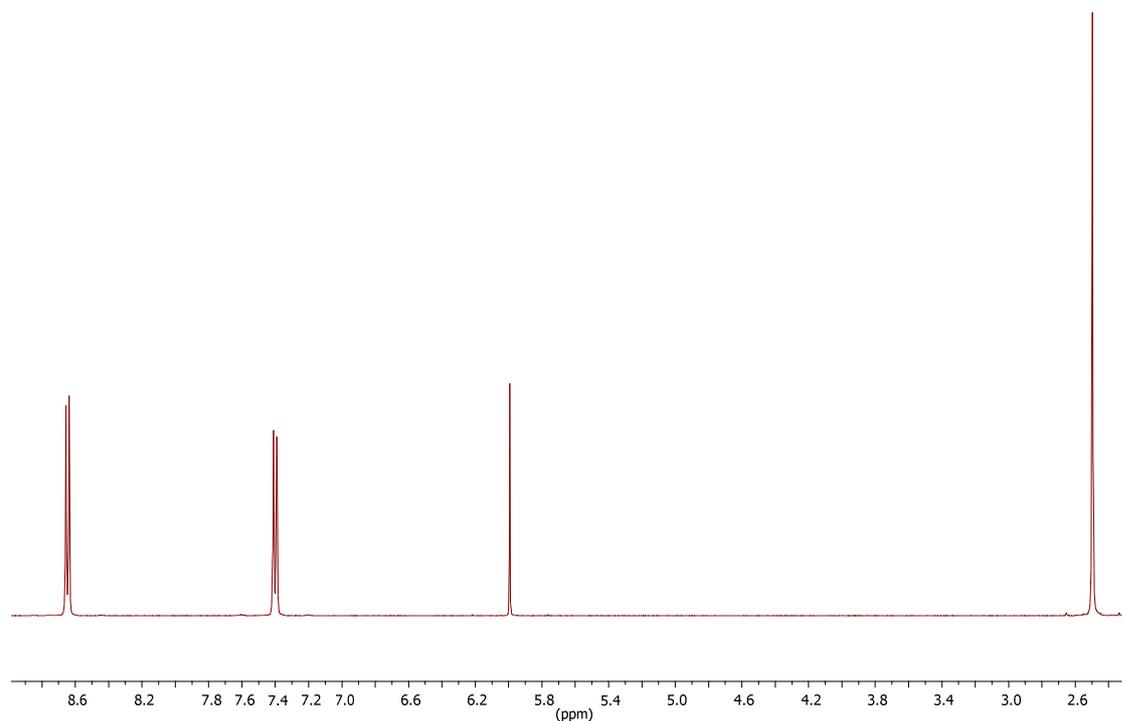


Fig. S20: ^1H NMR spectrum of 2,4,6-tris(4-methylphenyl)-1,3,5-triazine in $\text{C}_2\text{D}_2\text{Cl}_4$.

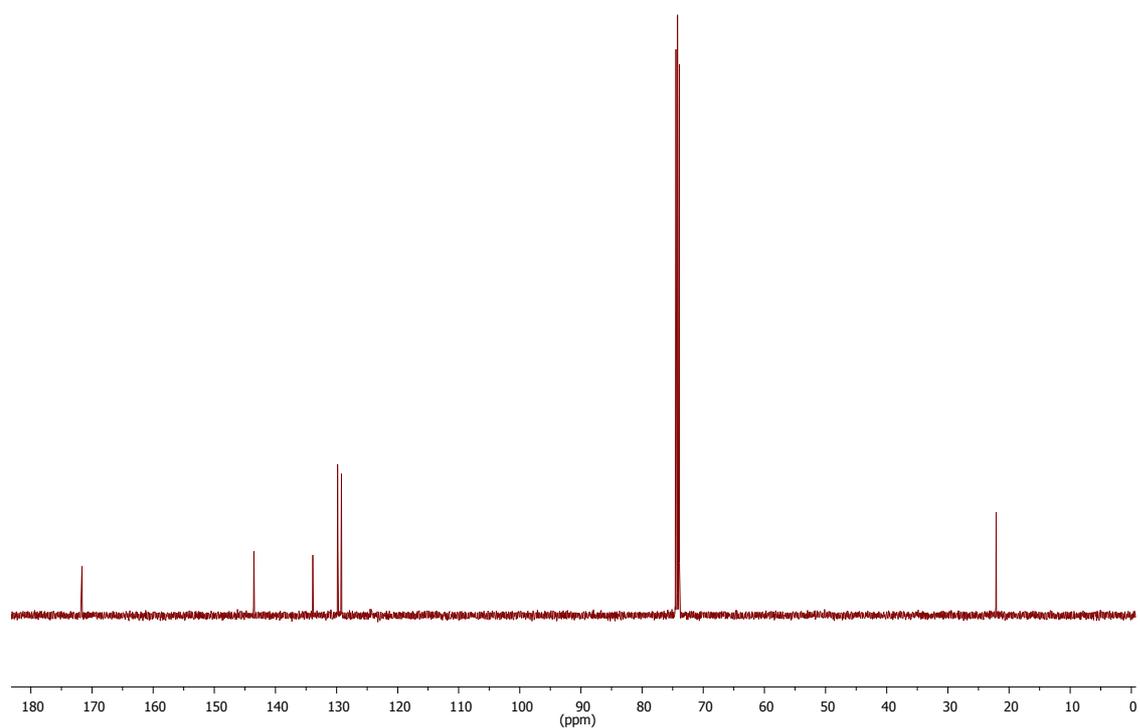


Fig. S21: ^{13}C NMR spectrum ($\text{C}_2\text{D}_2\text{Cl}_4$) of 2,4,6-tris(4-methylphenyl)-1,3,5-triazine.

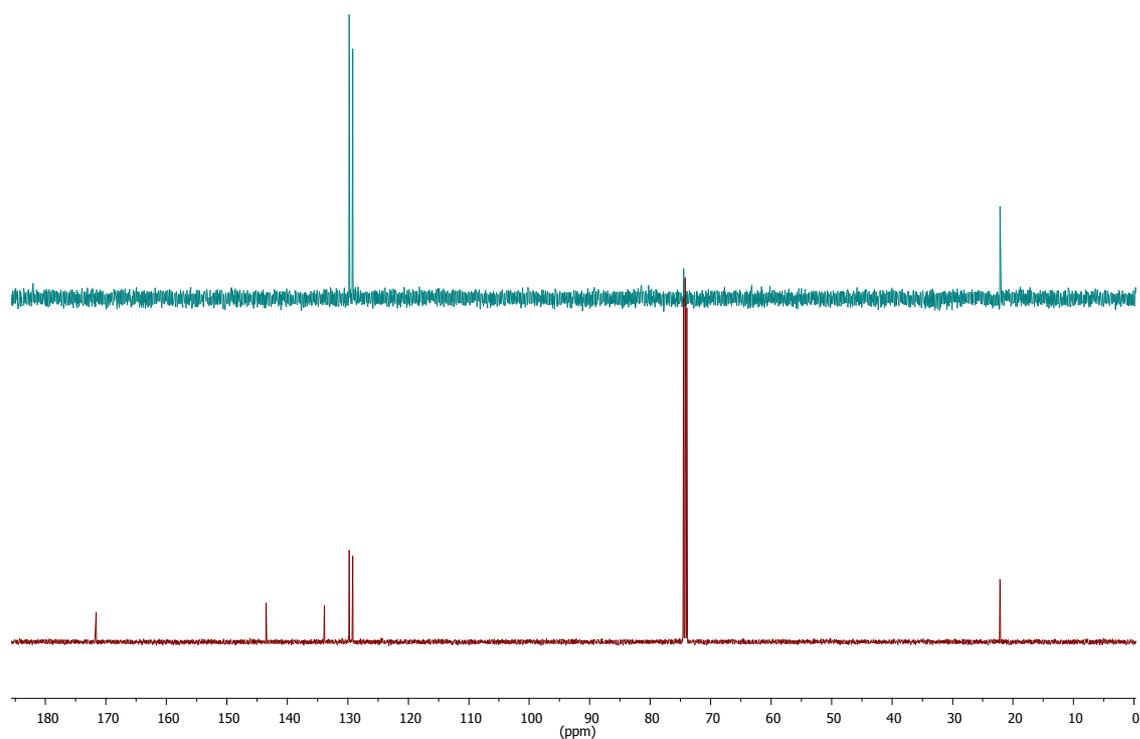


Fig. S22: ^{13}C NMR DEPT (top) and ^{13}C NMR (down) spectra of 2,4,6-tris(4-methylphenyl)-1,3,5-triazine in $\text{C}_2\text{D}_2\text{Cl}_4$.

2,4,6-Tris(4-carboxyphenyl)-1,3,5-triazine

Chromium trioxide (14.2 g, 142 mmol) dissolved in acetic acid (100 mL) was slowly added (ice-cooling; attention: strong exothermic reaction!!!!) to a suspension of 2,4,6-tris(4-methylphenyl)-1,3,5-triazine (5.0 g, 14.23 mmol) in concentrated sulfuric acid (10 mL) / acetic acid (50 mL). The reaction temperature should not exceed 50 °C. The reaction mixture was finally stirred over night at room temperature. Excess of chromium trioxide was quenched with ethanol (100 mL) by stirring for one 1 h at room temperature. The mixture was purged into 2 L of ice/water and the resulting solid was collected by filtration. Recrystallization of the crude product from N,N-dimethylformamide yielded (5.2 g, 83 %) a white powder.

^1H NMR (400 MHz, DMSO), δ (ppm): 13.28 (bs, 3H), 8.70 (d, $J = 8.6$ Hz, 6H), 8.12 (d, $J = 8.6$ Hz, 6H).

^{13}C NMR (101 MHz, DMSO), δ (ppm): 170.41, 166.73, 138.63, 134.60, 129.68, 128.72.

Anal. calc. for $\text{C}_{24}\text{H}_{15}\text{N}_3\text{O}_6$: C, 65.31; H, 3.43; N, 9.52; Found: C, 63.32; H, 3.81; N, 9.22.

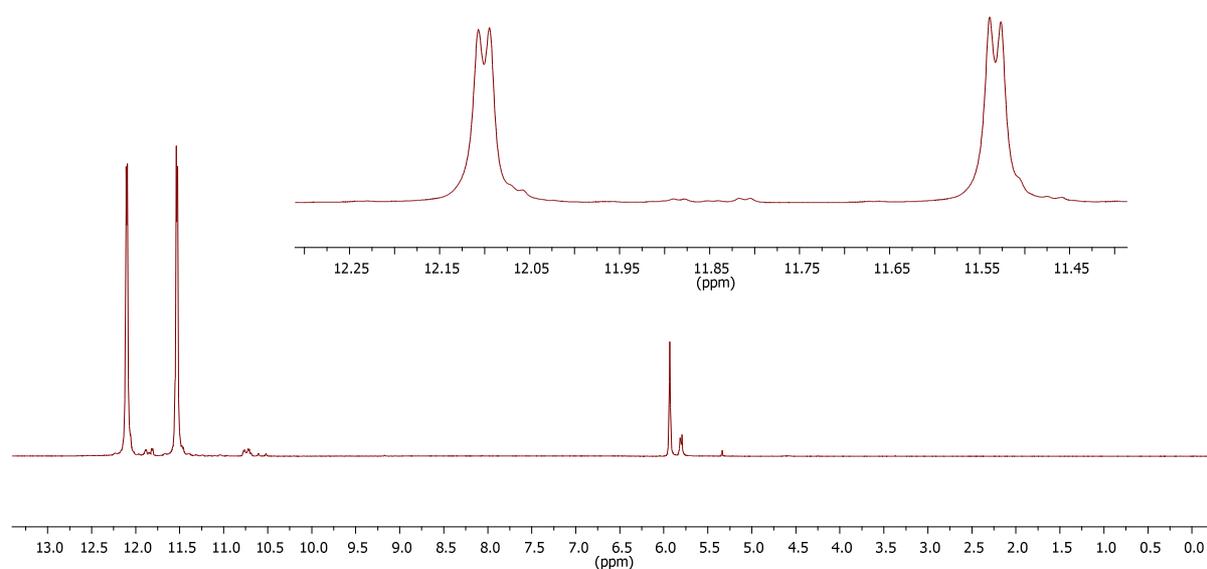


Fig. S23: ^1H NMR spectrum of 2,4,6-tris(4-carboxyphenyl)-1,3,5-triazine in $\text{C}_2\text{D}_2\text{Cl}_4$.

2,4,6-Tris(4-benzoylphenyl)-1,3,5-triazine

2,4,6-Tris(4-carboxyphenyl)-1,3,5-triazine (5.0 g, 11.33 mmol) was suspended in benzene (50 mL). Then, N,N-dimethylformamide (1 drop) and thionyl chloride (5.4 g, 45.3 mmol) were added and the mixture was refluxed for 2 h till a clear solution is formed. Excess of thionyl chloride and benzene were removed under reduced pressure. The solid residue was re-dissolved in benzene (100 mL). This solution and aluminum chloride (6.0 g, 45.3 mmol) were added to a 250 mL one-necked round-bottom flask. The reaction mixture was stirred at room temperature for 24 h. The mixture was purged into cold water and then extracted with DCM. The organic phase was isolated, washed with water and finally dried over magnesium sulfate. After removing the solvent the crude product was purified by silica-gel column chromatography with hexane/DCM (2:3 by volume) as eluent. The product was obtained as white solid (1.5 g, 23 %).

^1H NMR (400 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$) δ (ppm): 8.93 (d, $J = 8.5$ Hz, 6H), 8.03 (d, $J = 8.5$ Hz, 6H), 7.95-7.84 (m, 6H), 7.74-7.64 (m, 3H), 7.56 (t, $J = 7.6$ Hz, 6H).

^{13}C NMR (101 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$) δ (ppm): 196.57, 171.55, 141.36, 139.33, 137.26, 133.40, 130.58, 130.45, 129.32, 128.87.

MS EI (m/z): 622.20 ($+\text{H}^+$) (calc. 621.20).

2,4,6-Tris(4-dichlorobenzylphenyl)-1,3,5-triazine

2,4,6-Tris[4-benzoylphenyl]-1,3,5-triazine (1.0 g, 1.61 mmol), phosphorus pentachloride (2.0 g, 9.65 mmol) and 20 mL of chlorobenzene were placed into to a 100 mL Schlenk tube. The reaction mixture was stirred at 120 °C for 4 d. The resulting mixture was cooled to 80 °C. Chlorobenzene and POCl_3 were distilled off under reduced pressure. Finally, unreacted phosphorus pentachloride was sublimed out of the reaction mixture under reduced pressure. The resulting yellow oil (1.26 g, 99 %) was used without further purification.

^1H NMR (400 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$), δ (ppm): 8.74 (d, $J = 8.6$ Hz, 6H), 7.85 (d, $J = 8.6$ Hz, 6H), 7.75-7.64 (m, 6H), 7.49-7.35 (m, 9H).

^{13}C NMR (101 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$), δ (ppm): 171.27, 148.34, 143.63, 136.59, 129.66, 129.15, 128.65, 128.15, 127.60, 91.69.

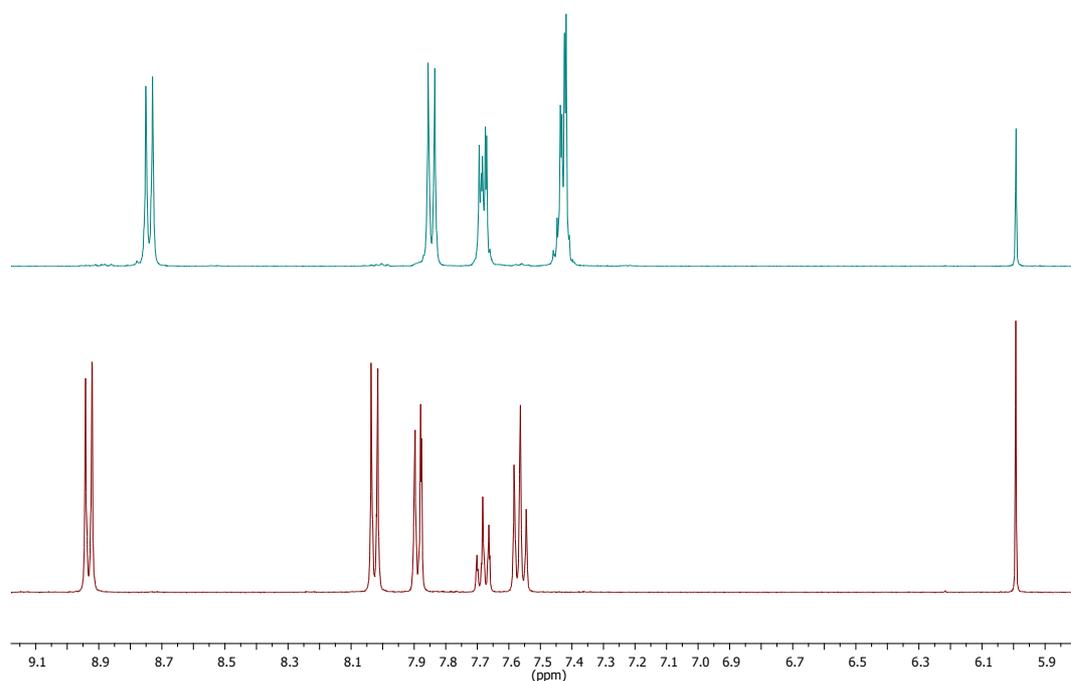


Fig. S24: ^1H NMR spectrum of 2,4,6-tris(4-benzoylphenyl)-1,3,5-triazine (top) and 2,4,6-tris(4-dichlorobenzoylphenyl)-1,3,5-triazine (down).

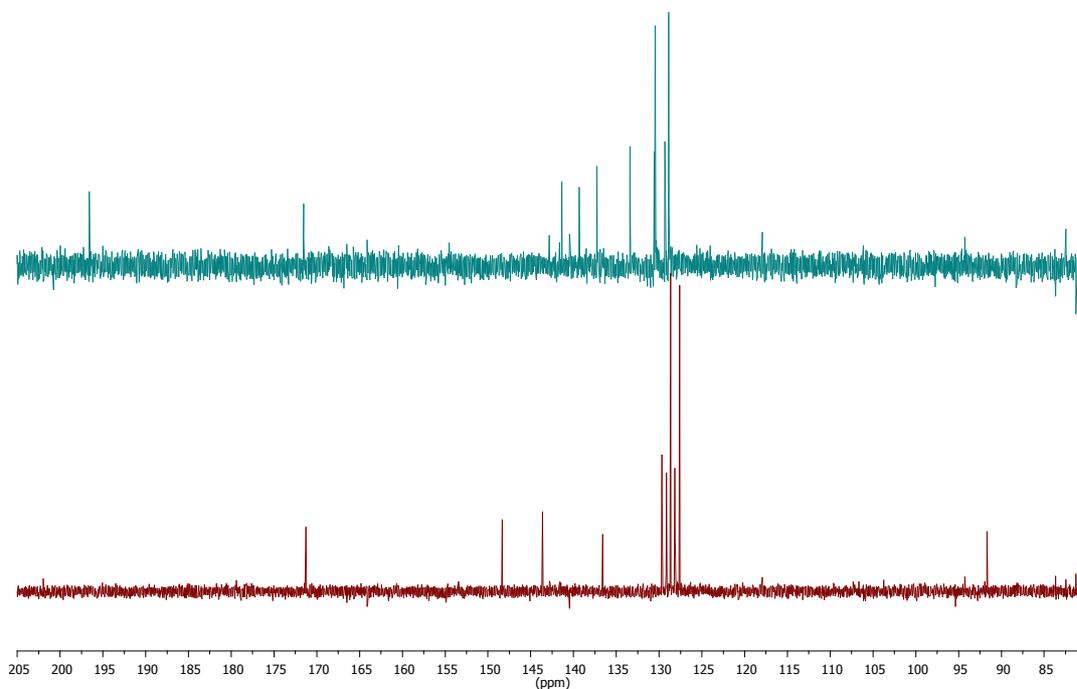


Fig S25: ^{13}C NMR spectra of 2,4,6-tris(4-benzoylphenyl)-1,3,5-triazine (top) and 2,4,6-tris(4-dichlorobenzoylphenyl)-1,3,5-triazine (down).

Polymer network P4

2,4,6-Tris(4-dichlorobenzylphenyl)-1,3,5-triazine MCl_4 (1.2 g, 1,61 mmol), dicobalt octacarbonyl (2.7 g, 7.83 mmol) and 20 mL chlorobenzene were added to a 100 mL Schlenk tube. The mixture was reacted at 100 °C for 50 min (gas formation starts at around 80 °C). For quenching, 10 mL of 1,2-dibromoethane was added and the mixture was stirred for another 10 min. Next, the reaction mixture was purged into methanol, the solid product collected by filtration and washed with methanol. The crude product was purified by successive Soxhlet extraction with methanol, ethyl acetate, 1,4-dioxane and chloroform. The resulting polymer was treated (washed) with supercritical carbon dioxide. The product was obtained as a yellow powder (960 mg, quantitative yield).

^{13}C -{H}-CP/MAS-NMR (75.48 MHz): δ (ppm) = 171, 147, 142, 134, 128.

TGA: first decomposition step 408 °C (1.46 %) (Argon).

PL: λ_{max} (solid state)/nm: 560 nm (excitation 400 nm); PLQY: 25.3 %.

UV/Vis: λ_{max} (solid state)/nm: 392, 273sh.

BET: 475 m^2/g , total pore volume: 1.16 cc/g .

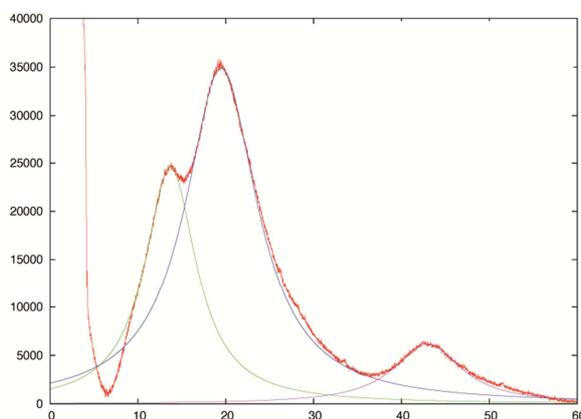


Fig. S26: Powder XRD pattern of polymer network P4 including a numerical peak deconvolution.

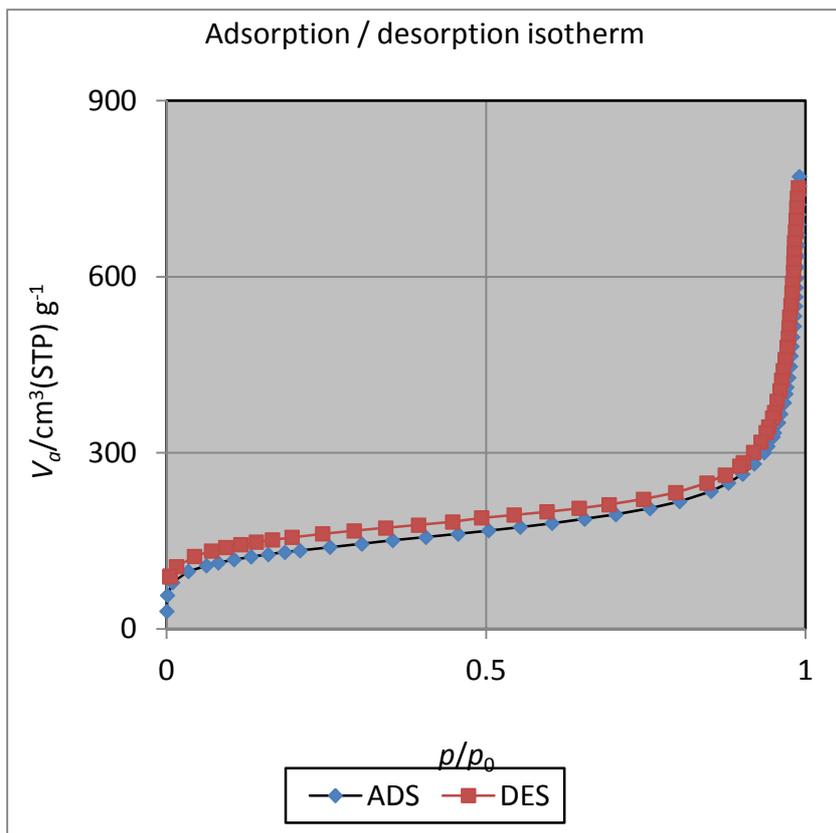


Fig. S27: Nitrogen adsorption isotherm of P4.

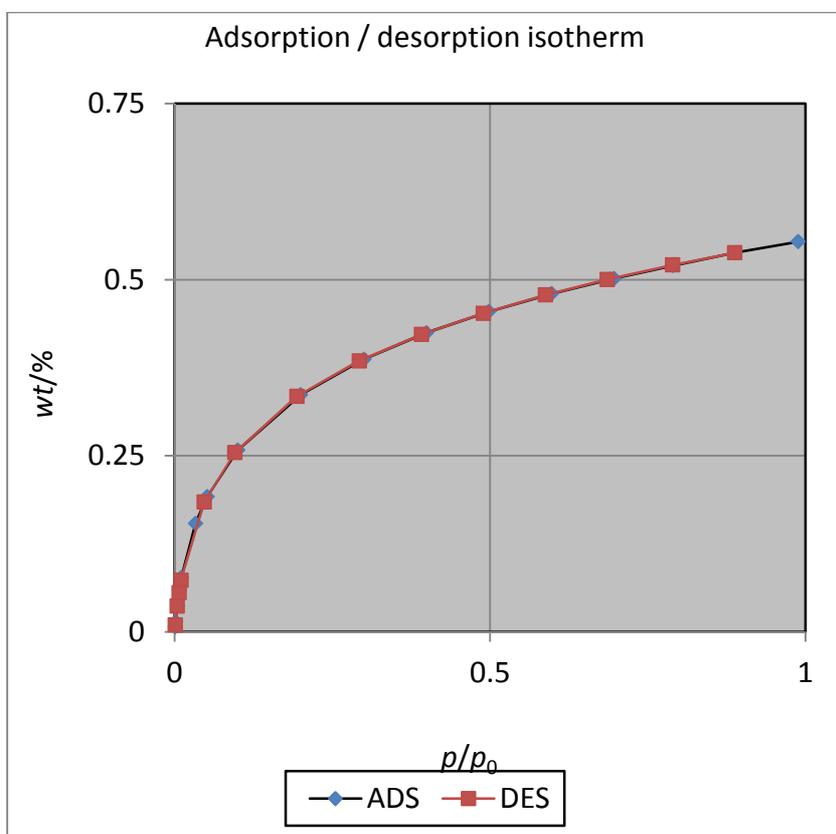


Fig. S28: Hydrogen adsorption isotherm of P4 at 77 K.

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