

# Covalent Triazine Frameworks Based on the First *Pseudo*-Octahedral Hexanitrile Monomer via Nitrile Trimerization: Synthesis, Porosity, and CO<sub>2</sub> Gas Sorption Properties

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## 1. General remarks

### 1.1 Analytics and Equipment

**Nuclear magnetic resonance spectroscopy (NMR):** NMR spectra were recorded on the following spectrometer: <sup>1</sup>H NMR: Bruker AC 250 (250 MHz), Bruker Avance 300 (300 MHz), Bruker Avance 400 (400 MHz); <sup>13</sup>C NMR: Bruker AC 250 (62.5 MHz), Bruker AM 400 (100 MHz); <sup>19</sup>F NMR: Bruker Avance 400 (376 MHz). All spectra were recorded at room temperature. The solvents used were Chloroform-d<sub>1</sub> from Eurisotop. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to CHCl<sub>3</sub> (δ = 7.26 ppm, s, for <sup>1</sup>H NMR and δ = 77.0 ppm, t, for <sup>13</sup>C NMR). All coupling constants (J) are absolute values, and J values are expressed in Hertz (Hz). The description of signals includes: s = singlet, AA'BB' = hydrogens on a para-substituted phenyl ring. The spectra were analyzed according to the first order. The signal structure in <sup>13</sup>C NMR was analyzed by DEPT and is described as follows: + = primary or tertiary C-atom (positive signal), − = secondary C-atom (negative signal), and C<sub>q</sub> = quaternary C-atom (no signal).

**N<sub>2</sub>-Adsorption for CTF-hex1:** The specific surface area (BET and Langmuir model), as well as the pore size volumes for CTF-hex1, were determined using a Thermo Scientific™ surfer-gas-adsorption-porosimeter from Thermo Scientific. The sample was degassed under an ultra-high vacuum at elevated temperatures. After weighing, the sample tube was then transferred to the analysis port of the sorption analyzer. N<sub>2</sub> sorption isotherms were measured at 77 K (liquid nitrogen bath). Used N<sub>2</sub> gas was of ultrahigh purity (UHP, grade 5.0, 99.999%). A blank measurement with N<sub>2</sub> was done before analysis.

**Gas adsorption:** Nitrogen sorption isotherms for CTF-hex2–5 at 77 K were obtained using a NOVA-4000e instrument within a relative pressure range of 10<sup>−6</sup>–1.0. DFT calculations for the pore size distribution curves were carried out using the native ASWin 2.03 software from Quantachrome Instruments employing the 'N<sub>2</sub> at 77 K on carbon, slit pore, nonlinear density functional theory (NLDFT) equilibrium' model as well as the 'N<sub>2</sub> at 77 K on carbon, slit pore, quenched solid density functional theory (QSDFT) adsorption branch and equilibrium model, which is favorable for disordered micro/mesoporous

carbon materials. CO<sub>2</sub> and CH<sub>4</sub> (and N<sub>2</sub> for **CTF-hex6**) sorption isotherms were measured using a Micromeritics ASAP 2020 automatic gas sorption analyzer equipped with oil-free vacuum pumps (ultimate vacuum <10<sup>−8</sup> mbar) and valves, which guaranteed contamination-free measurements. The sample was connected to the preparation port of the sorption analyzer and degassed under vacuum until the outgassing rate, i.e., the rate of pressure rise in the temporarily closed manifold with the connected sample tube, was less than 2 μTorr/min at the specified temperature of 200 °C. After weighing, the sample tube was then transferred to the analysis port of the sorption analyzer. All used gases (H<sub>2</sub>, He, N<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>) were of ultrahigh purity (UHP, grade 5.0, 99.999%), and the STP volumes are given according to the NIST standards (293.15 K, 101.325 kPa). Helium gas was used for the determination of the cold and warm free space of the sample tubes. N<sub>2</sub> sorption isotherms were measured at 77 K (liquid nitrogen bath), whereas CO<sub>2</sub> and CH<sub>4</sub> sorption isotherms were measured at 293 ± 1 K (passive thermostat) and 273.15 K (ice/deionized water bath). The DFT pore size distributions from CO<sub>2</sub> ('NLDFT slit pore' model) were calculated using the ASAP 2020 v3.05 software.

**Infrared spectroscopy:** IR spectra were recorded with an FT-IR Bruker IFS 88 spectrometer with OPUS software using the attenuated total reflection technique (ATR) or the DRIFT technique (diffused reflectance infrared Fourier transform spectroscopy) for solids. The absorption band is given in wavenumbers  $\tilde{\nu}$  in cm<sup>−1</sup>. The forms and intensities of the bands were characterized as follows: vs = very strong (0–20% T), s = strong (21–40% T), m = medium (41–60% T), w = weak (61–80% T), vw = very weak (81–100% T, transmission).

**Mass spectrometry (EI-MS, FAB-MS, HRMS):** The samples were measured either by EI-MS (Electron Ionization Mass Spectrometry) or FAB-MS (Fast Atom Bombardment Mass Spectrometry). EI- and FAB were performed by using Finnigan MAT 90 (70 eV). The molecular fragments were given as mass/charge ratio  $m/z$ ; the intensity of the signals was given as a percentage of the intensity of the base signal (100%) for the EI mass spectra. **EI-MS:** The abbreviation [M<sup>+</sup>] was used for the molecular ion. **FAB-MS:** The abbreviation [M<sup>+</sup> + H] was used for the protonated molecular ion. The following abbreviations were used for the **HRMS** (High-Resolution Mass Spectrometry): calcd. = theoretical value (calculated); found = value obtained by measurement.

**Elemental analysis (EA):** The measurements were performed on an Elementar Vario MICRO device using a Sartorius M2P precision balance. The following abbreviations were used: calcd. = calculated data, found = measured data.

**Analytical thin-layer chromatography (TLC):** TLC was carried out on Merck silica gel coated aluminum plates (silica gel 60, F<sub>254</sub>), detected under UV light at 254 nm.

**Scanning electron microscopy (SEM):** Scanning electron microscopy (SEM) images were obtained using an ESEM Quanta 400 FEG SEM equipped with a secondary electron detector.

**Analytical balance:** Weighing and yields were determined with Kern ABS.

**UV lamp:** A UV lamp from Herolab, type UV-6 S/L, was used to visualize spots on thin-layer chromatography plates.

**Ultrasonic bath:** An ultrasonic bath from Bendelin, type Sonorex Digitec, was used to dissolve solids and agglomerates better.

**Oven:** The triazine framework synthesis under ionothermal conditions was performed in a tube furnace LOBA-1200-50-400-1-OW from HTM Reetz GmbH.

**Powder X-ray diffraction (PXRD):** Diffractograms were obtained with a Bruker D2 Phaser diffractometer using a flat sample holder including a flat silicon, low background sample holder and Cu K $\alpha_1/\alpha_2$  radiation with  $\lambda = 1.5418$  Å at 30 kV. The measurement covered 2 $\theta$  angles from 5 to 80° over a time of 2 h, that is, with a scan rate of 0.01°/sec. The flat layer sample holders induced a strong broadening of the beam spot at low angle so that only a fraction of the reflected radiation reaches the detector in this angle range. Subsequently, low relative intensities were usually observed at 2 $\theta$  angles below 7°.

## 1.2. Solvents and Reagents

Solvent mixtures are understood as volume/volume. Solvents, reagents, and chemicals were purchased from *Sigma-Aldrich*, *ABCR*, *Acros Organics*, and *Fisher Scientific*. All solvents, reagents, and chemicals were used as purchased unless stated otherwise. Absolute solvents were purchased from a commercial supplier (absolute DMF (*Acros Organics*, < 50 ppm water), absolute chloroform (*Fischer Scientific*, extra dry over molecular sieves), absolute NMP (*N*-methyl-2-pyrrolidinone, *Fischer Scientific*, <50 ppm water)) 4,4'-dibromo-1,1'-biphenyl, 1,3,5-tribromobenzene und 1,4-dicyanobenzene (**2**) are commercially available.

### 1.3. Preparative Work

Before the reactions with air or moisture-sensitive reagents were carried out, the glass devices have been dried in an oven and under high. After cooling the glass, apparatuses have been sealed with rubber seals under argon counterflow. Reactions have been executed according to Schlenk-techniques using argon as an inert gas. Liquids were added via plastic syringes and V2A-needles.

Solids were added in pulverized form. Reactions at 0 °C were cooled with a mixture of ice/water.

Solvents were removed at 40 °C with a rotary evaporator. Used solvent mixtures were measured volumetrically. An ultraviolet lamp and the phosphomolybdic acid 10 wt% in ethanol were used for detection.

If not stated otherwise, solutions of inorganic salts are saturated aqueous solutions.

If not otherwise specified, the crude products were purified by flash column chromatography following the concepts of Still et al.[1] using silica gel (SIGMA ALDRICH, pore size 60 Å, particle size 40–63 µm) and sand (calcined and purified with hydrochloric acid) as stationary phase. Solvents were distilled before use or p.a. grade solvents used. Solvent mixtures were prepared individually in terms of volume ratios are given as volumetric. The use of a gradient is indicated in the experimental procedures

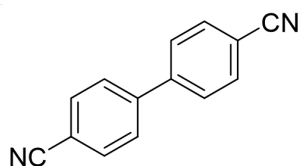
## 2. Synthetic Procedures

### 2.1. Synthesis of Non-commercially Available Nitrile Tectones

Tetraphenylmethane,[2] tetrakis(4-bromophenyl)methane,[2] 1,4-ditriylbenzene[3] and 1,4-bis(tris(4-bromophenyl)methyl)benzene[3] were synthesized according to literature processes.

4,4'-Dicyano-1,1'-biphenyl (**3**) (Scheme S1): Under an argon atmosphere, 3.00 g (9.62 mmol, 1.00 equiv.) 4,4'-dibromo-1,1'-biphenyl and 3.44 g (38.5 mmol, 4.00 equiv.) copper(I)cyanide in 60 mL DMF were refluxed in a 250 mL Schlenk-flask under vigorous stirring for 2 h. After cooling to room temperature, the solvent was removed under reduced pressure, the residue was filtered off and washed with dichloromethane. The crude product was purified via flash column chromatography (silica gel, 4 cm × 20 cm, cyclohexane/ethyl acetate 90:10 → 60:40) to give 1.11 g (5.44 mmol, 57%) of the product **3** as colorless solid.  $R_f$  = 0.71 (cyclohexane/ethyl acetate 6:4). –  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.78 (AA'BB',  $J$  = 8.3 Hz, 4 H, 3-*H*, 3'-*H*), 7.70 (AA'BB',  $J$  = 8.3 Hz, 4 H, 2-*H*, 2'-*H*) ppm. –  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 143.5 ( $\text{C}_q$ , 2 C, C-1, C-1'), 132.6 (+, 4 C, C-3, C-3'), 128.0 (+, 4 C, C-2, C-2'), 118.5 ( $\text{C}_q$ , 2 C, CN), 112.4 ( $\text{C}_q$ , 2 C, C-4, C-4') ppm. – IR (Drift):  $\tilde{\nu}$  = 2224 (w), 1602 (w), 1489 (w), 1395 (w), 1310 (vw), 1779 (w), 1224 (vw), 1005 (vw), 858 (w), 815 (s), 712 (vw), 567 (w), 543 (vw), 458 (vw)  $\text{cm}^{-1}$ . – MS (70 eV, EI),  $m/z$  (%): 204 (100) [ $\text{M}^+$ ], 177 (10) [ $\text{M}^+ - \text{HCN}$ ], 150 (3) [ $\text{M}^+ - 2 \times \text{HCN}$ ], 102 (2) [ $\text{C}_7\text{H}_4\text{N}$ ].

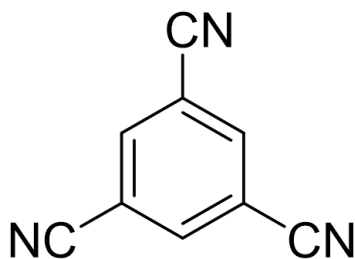
Analytical data are consistent with the literature.[4]



**Scheme S1.** 4,4'-Dicyano-1,1'-biphenyl (**3**).

1,3,5-Tricyanobenzene (**4**) (Scheme S2): In a closed 20 mL Vial, 1.00 g (3.18 mmol, 1.00 equiv.) 1,3,5-tribromobenzene, 878 mg (2.39 mmol, 0.750 equiv.) potassium hexacyanoferrate(II), 337 mg (3.18 mmol, 1.00 equiv.) sodium carbonate, 353 mg (0.636 mmol, 0.200 equiv.) 1,1'-bis(diphenylphosphino)ferrocene and 71.4 mg (0.318 mmol, 0.100 equiv.) palladium(II) acetate in 10 mL NMP were refluxed under vigorous stirring for 10 h. After cooling to room temperature, the solvent was removed under reduced pressure, and the residue was purified via flash column chromatography (silica gel, 4 cm × 20 cm, cyclohexane/ethyl acetate 100 → 50:50) to give 72.7 mg (475 μmol, 15%) of the product **4** as colorless solid.  $R_f = 0.50$  (cyclohexane/ethyl acetate 3:1). –  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.17$  (s, 3 H, 2-H, 4-H, 6-H) ppm. –  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 138.7$  (+, 3 C, CH), 116.0 ( $\text{C}_q$ , 3 C, CN), 114.6 ( $\text{C}_q$ , 3 C, C-1, C-3, C-5) ppm. – IR (Drift):  $\tilde{\nu} = 3069$  (vw), 2924 (vw), 2238 (vw), 1767 (vw), 1694 (w), 1589 (vw), 1426 (w), 1385 (vw), 1301 (vw), 1279 (vw), 1116 (vw), 942 (vw), 893 (w), 815 (vw), 711 (vw), 681 (w), 545 (vw), 503 (vw), 472 (vw), 410 (vw)  $\text{cm}^{-1}$ . – MS (70 eV, EI),  $m/z$  (%): 153 (100) [ $\text{M}^+$ ], 128 (38) [ $\text{C}_8\text{H}_3\text{N}_2 + \text{H}^+$ ].

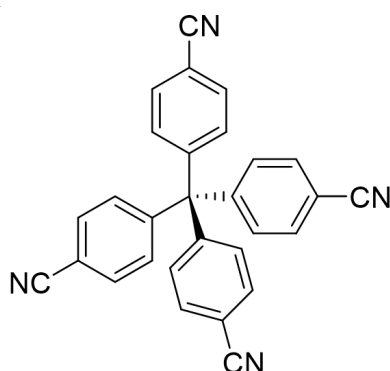
Analytical data are consistent with the literature.[5]



**Scheme S2.** 1,3,5-Tricyanobenzene (**4**)

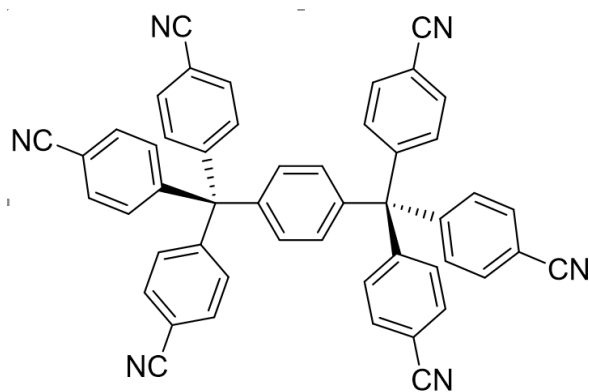
Tetrakis(4-cyanophenyl)methane (**5**) (Scheme S3): Under an argon atmosphere, 750 mg (1.18 mmol, 1.00 equiv.) tetrakis(4-bromophenyl)methane and 1.06 g (11.8 mmol, 10.0 equiv.) copper(I)cyanide in 72 mL DMF were refluxed in a 100 mL Schlenk-flask under vigorous stirring for 3 d. After cooling to room temperature, the solvent was removed under reduced pressure, and the residue was purified via flash column chromatography (silica gel, 4 cm × 20 cm, cyclohexane/ethyl acetate 3:1 → 2:1) to give 135 mg (321 μmol, 27%) of the product **5** as colorless solid.  $R_f = 0.30$  (cyclohexane/ethyl acetate 2:1). –  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.65$  (AA'BB',  $J = 8.7$  Hz, 8 H, 3-H), 7.29 (AA'BB',  $J = 8.7$  Hz, 8 H, 2-H) ppm.

The analytical data are consistent with the literature.[6]



**Scheme S3.** Tetrakis(4-cyanophenyl)methane (5)

*1,4-Bis(tris(4'-cyanophenyl)methyl)benzene* (**1**) (Scheme S4): Under argon atmosphere 3.00 g (2.90 mmol, 1.00 equiv.) 1,4-bis(tris(4-bromophenyl)methyl)benzene and 6.22 g (69.5 mmol, 24.0 equiv.) copper(I)cyanide in 100 mL DMF were refluxed in a 250 mL Schlenk-flask under vigorous stirring for 5 d. After cooling to room temperature, the solvent was removed under reduced pressure, and 150 mL of a concentrated, aqueous ammonia solution was added. After stirring overnight at room temperature, the aqueous layer was extracted with 3 × 100 mL of dichloromethane, the combined organic layers dried over sodium sulfate, and the solvent was removed under reduced pressure. The residue was purified via flash column chromatography (silica gel, 4 cm × 20 cm, cyclohexane/ ethyl acetate 100 → 60:40) to give 567 mg (795 μmol, 28%) of the product **1** as colorless solid. mp: 383 °C. –  $R_f$  = 0.42 (cyclohexane/ethyl acetate 6:4). –  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.62 (AA'BB',  $J$  = 8.4 Hz, 12 H, 3'-H), 7.25 (AA'BB',  $J$  = 8.4 Hz, 12 H, 2'-H), 7.07 (s, 4 H, 2-H, 3-H) ppm. –  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 149.2 ( $\text{C}_q$ , 6 C, C-1'), 142.8 ( $\text{C}_q$ , 2 C, C-1, C-4), 132.2 (+, 12 C, C-3'), 131.2 (+, 12 C, C-2'), 130.6 (+, 4 C, C-2, C-3), 118.0 ( $\text{C}_q$ , 6 C, CN), 111.5 ( $\text{C}_q$ , 6 C, C-4'), 65.1 ( $\text{C}_q$ , 2 C, C(Ar)<sub>4</sub>) ppm. – IR (Drift):  $\tilde{\nu}$  = 3036 (vw), 2227 (vw), 1713 (vw), 1602 (vw), 1499 (vw), 1411 (vw), 1218 (vw), 1019 (vw), 910 (vw), 823 (w), 764 (vw), 729 (w), 647 (vw), 594 (vw), 578 (w), 556 (vw)  $\text{cm}^{-1}$ . – MS (FAB, 3-NBA,  $m/z$  (%): 713 (100) [ $\text{M} + \text{H}^+$ ], 610 (84) [ $\text{M}^+ - \text{C}_7\text{H}_4\text{N}$ ].



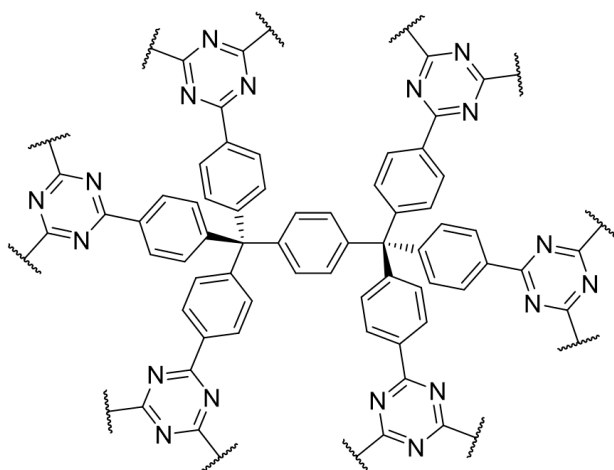
**Scheme S4.** 1,4-Bis(tris(4'-cyanophenyl)methyl)benzene (**1**)

## 2.2. Synthesis of Covalent Triazine-Based Frameworks (CTFs) via Trimerization of Aromatic Nitriles with Trifluoromethanesulfonic acid [7]

**General procedure (GP):** Under argon atmosphere in a closed 20 mL vial, abs. trifluoromethanesulfonic acid and abs. chloroform (3 mL) was cooled to 0 °C. At this temperature, HPX-nitrile **1** (1.00 eq) and the respective aryl nitrile linker (3.00 eq for di- **2** and **3**, 2.00 eq for tri-**4**, and 0.600 eq for tetratopic linker **5**) dissolved in 10 mL abs. chloroform was added over 30 min. The mixture was stirred for another 2 h at 0 °C and afterward at room temperature overnight. Then, the reaction mixture was poured on a water/ $\text{NH}_3(\text{aq})$ -

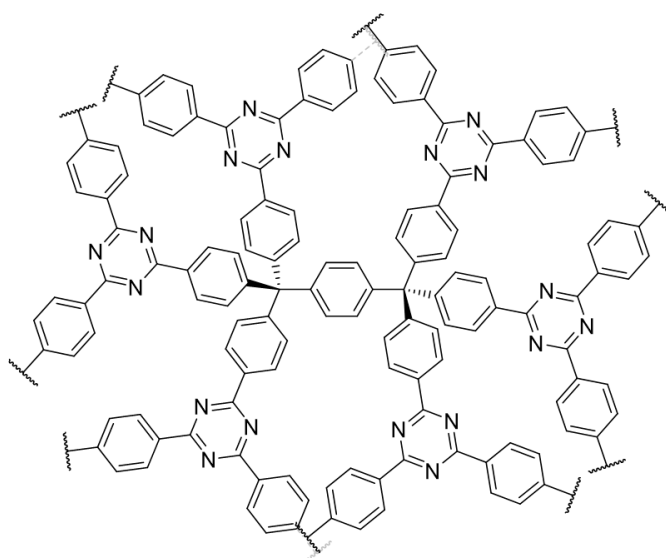
mixture (100 mL, 20:1) and stirred at room temperature for an additional 2 h. The precipitate was filtered off, washed with distilled water ( $3 \times 10$  mL), ethanol ( $3 \times 10$  mL), acetone ( $3 \times 10$  mL), and chloroform ( $3 \times 10$  mL) and dried under high vacuum at 120 °C for 2 d.

'HPX-Nitril' Covalent Triazine-Based Framework (**CTF-hex1**) (Scheme S5): According to GP, 113  $\mu$ L (194 mg, 1.30 mmol, 8.10 equiv.) trifluoromethane-sulfonic acid and abs. chloroform (3 mL) was cooled to 0 °C. At this temperature, 114 mg (160  $\mu$ mol, 1.00 equiv.) HPX-nitrile **1** dissolved in abs. chloroform (10 mL) was added over 30 min. The mixture was stirred for another 2 h at 0 °C and afterward at room temperature overnight. After purification and drying under high vacuum (2 d at 120 °C and  $10^{-6}$  mbar) 95.9 mg (134  $\mu$ mol, 84%) of the product **CTF-hex1** were obtained as slightly yellow solid. IR (ATR):  $\tilde{\nu}$  = 3370 (vw), 2928 (vw), 2228 (vw), 1602 (vw), 1498 (w), 1406 (vw), 1361 (vw), 1279 (vw), 1191 (vw), 1016 (vw), 810 (vw), 759 (vw), 639 (vw), 559 (vw)  $\text{cm}^{-1}$ . – EA ( $\text{C}_{50}\text{H}_{28}\text{N}_6$ ): calcd. C 84.25, H 3.96, N 11.79, found C 71.42, H 4.19, N 9.27, S 0.91. –  $S_{\text{BET}}$  = 557  $\text{m}^2/\text{g}$ . –  $S_{\text{Langmuir}}$  = 669  $\text{m}^2/\text{g}$ . –  $V_{\text{Total, Pore}}$  = 0.246  $\text{cm}^3/\text{g}$ . (Determined surface area strongly depends on sample preparation. Measurements were performed on Thermo Scientific™ Surfer.)



**Scheme S5.** 'HPX-Nitril' Covalent Triazine-Based Framework **CTF-hex1**

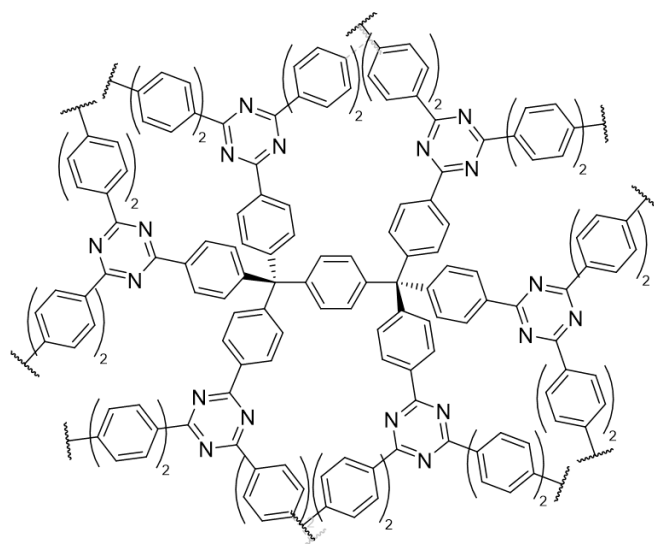
'Mono-Aryl-HPX-Nitrile' Covalent Triazine-Based Framework (**CTF-hex2**) (Scheme S6): According to GP, 66.4  $\mu$ L (114 mg, 757  $\mu$ mol, 10.8 equiv.) trifluoromethanesulfonic acid and abs. chloroform (3 mL) was cooled to 0 °C. At this temperature, 50.0 mg (70.1  $\mu$ mol, 1.00 equiv.) HPX-nitrile **1** and 26.9 mg (210  $\mu$ mol, 3.00 equiv.) 4,4'-dicyanobenzene (**2**) dissolved in abs. chloroform (10 mL) was added over 30 min. The mixture was stirred for another 2 h at 0 °C and afterward at room temperature overnight. After purification and drying under high vacuum (2 d at 120 °C and  $10^{-6}$  mbar) 35.6 mg (32.5  $\mu$ mol, 46%) of the product **CTF-hex2** were obtained as slightly yellow solid. IR (ATR):  $\tilde{\nu}$  = 3369 (vw), 2228 (vw), 1604 (vw), 1499 (w), 1407 (vw), 1360 (vw), 1017 (vw), 811 (w), 766 (vw), 549 (vw), 453 (vw)  $\text{cm}^{-1}$ . – EA ( $\text{C}_{74}\text{H}_{40}\text{N}_{12}$ ): calcd. C 81.01, H 3.67, N 15.32, found C 65.49, H 3.96, N 8.79, S 0.23. –  $S_{\text{BET}}$  = 620  $\text{m}^2/\text{g}$ . –  $S_{\text{Langmuir}}$  = 680  $\text{m}^2/\text{g}$ . –  $V_{\text{Total, Pore}}$  = 0.28  $\text{cm}^3/\text{g}$ .



**Scheme S6.** 'Mono-Aryl-HPX-Nitrile' Covalent Triazine-Based Framework **CTF-hex2**

'Bi-Aryl-HPX-Nitrile' Covalent Triazine-Based Framework (**CTF-hex3**) (Scheme S7): According to GP, 66.4  $\mu\text{L}$  (114 mg, 757  $\mu\text{mol}$ , 10.8 equiv.) trifluoromethanesulfonic acid and abs. chloroform (3 mL) was cooled to 0  $^{\circ}\text{C}$ . At this temperature, 50.0 mg (70.1  $\mu\text{mol}$ , 1.00 equiv.) HPX-nitrile **1** and 42.9 mg (210  $\mu\text{mol}$ , 3.00 equiv.) 4,4'-dicyanobiphenyl (**3**) dissolved in abs. chloroform (10 mL) was added over 30 min. The mixture was stirred for another 2 h at 0  $^{\circ}\text{C}$  and afterward at room temperature overnight. After purification and drying under high vacuum (2 d at 120  $^{\circ}\text{C}$  and  $10^{-6}$  mbar) 46.2 mg (35.1  $\mu\text{mol}$ , 50%) of the product **CTF-hex3** were obtained as slightly yellow solid.

IR (ATR):  $\tilde{\nu}$  = 3308 (vw), 2228 (vw), 1604 (vw), 1500 (w), 1360 (w), 1017 (vw), 809 (w), 766 (vw), 502 (vw)  $\text{cm}^{-1}$ . – EA ( $\text{C}_{92}\text{H}_{52}\text{N}_{12}$ ): calcd. C 83.37, H 3.95, N 12.68, found C 66.80, H 4.03, N 9.15, S 0.19. –  $S_{\text{BET}}$  = 493  $\text{m}^2/\text{g}$ . –  $S_{\text{Langmuir}}$  = 626  $\text{m}^2/\text{g}$ . –  $V_{\text{Total, Pore}}$  = 0.24  $\text{cm}^3/\text{g}$ .

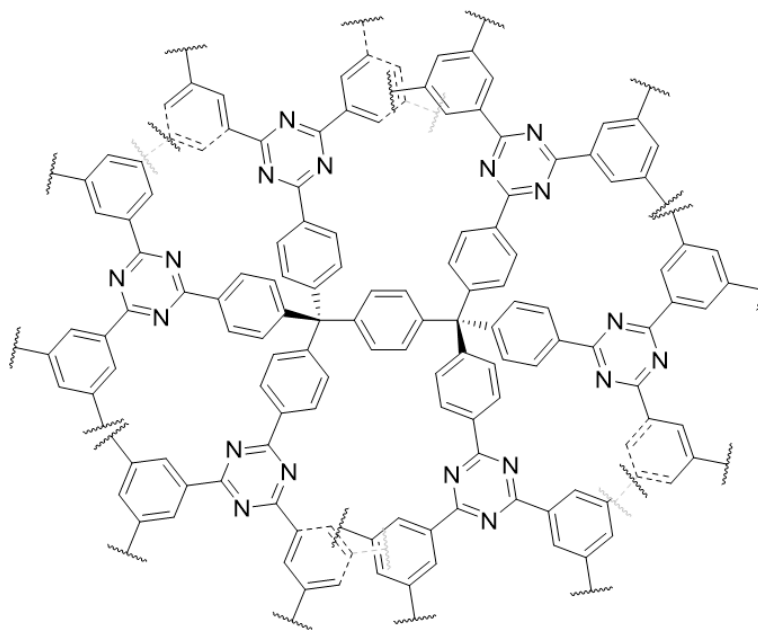


**Scheme S7.** 'Bi-Aryl-HPX-Nitrile' Covalent Triazine-Based Framework **CTF-hex3**

'Tricyanobenzol-HPX-Nitrile' Covalent Triazine-Based Framework (**CTF-hex4**) (Scheme S8): According to GP, 75.1  $\mu\text{L}$  (128 mg, 655  $\mu\text{mol}$ , 12.2 equiv.) trifluoromethanesulfonic acid and abs. chloroform (3 mL) was cooled to 0  $^{\circ}\text{C}$ . At this temperature, 50.0 mg (70.1  $\mu\text{mol}$ , 1.00 equiv.) HPX-nitrile **1** and 21.5 mg (140  $\mu\text{mol}$ , 2.00 equiv.) 1,3,5-tricyanobenzene (**4**) dissolved in abs. chloroform (10 mL) was added over 30 min. The mixture was stirred

for another 2 h at 0 °C and afterward at room temperature overnight. After purification and drying under high vacuum (2 d at 120 °C and  $10^{-6}$  mbar) 40.2 mg (39.4  $\mu$ mol, 65%) of the product **CTF-hex4** were obtained as slightly yellow solid.

IR (ATR):  $\tilde{\nu}$  = 3341 (vw), 2229 (vw), 1603 (vw), 1504 (w), 1359 (vw), 1153 (vw), 1016 (vw), 811 (vw), 767 (vw), 501 (vw)  $\text{cm}^{-1}$ . – EA ( $\text{C}_{68}\text{H}_{34}\text{N}_{12}$ ): calcd. C 80.14, H 3.36, N 16.49, found C 68.26, H 4.11, N 10.60, S 0.48. –  $S_{\text{BET}}$  = 609  $\text{m}^2/\text{g}$ . –  $S_{\text{Langmuir}}$  = 759  $\text{m}^2/\text{g}$ . –  $V_{\text{Total, Pore}}$  = 0.31  $\text{cm}^3/\text{g}$ .

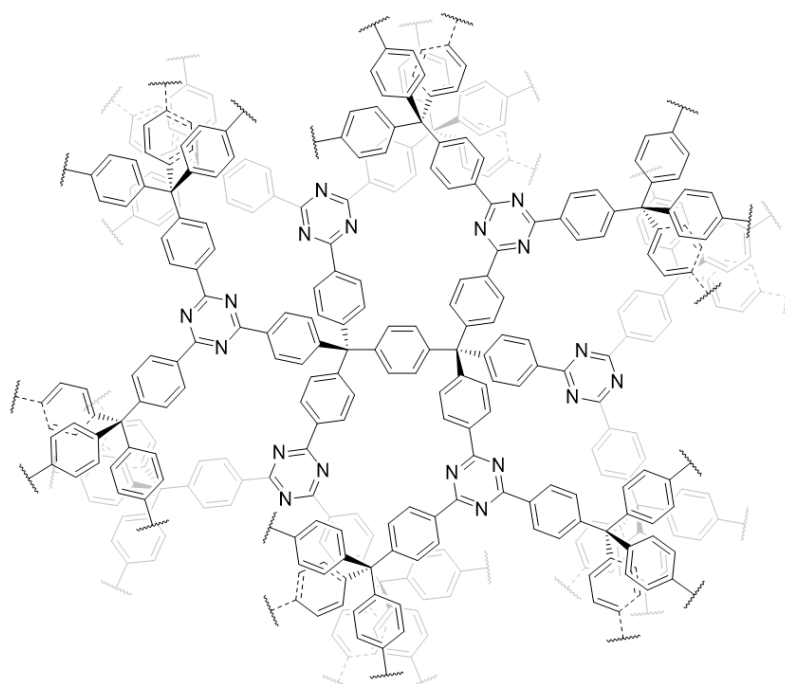


**Scheme S8.** 'Tricyanobenzol-HPX-Nitrile' Covalent Triazine-Based Framework **CTF-hex4**

'TPM-HPX-Nitril' Covalent Triazine-Based Framework (**CTF-hex5**) (Scheme S9): According to GP, 83.1  $\mu$ L (142 mg, 946  $\mu$ mol, 13.5 equiv.) trifluoromethanesulfonic acid and abs. chloroform (3 mL) was cooled to 0 °C. At this temperature, 50.0 mg (70.1  $\mu$ mol, 1.00 equiv.) HPX-nitrile **1** and 17.7 mg (42.1  $\mu$ mol, 0.600 equiv.) Tetrakis(4-cyanophenyl)methane (**5**) dissolved in abs. chloroform (10 mL) was added over 30 min. The mixture was stirred for another 2 h at 0 °C and afterward at room temperature overnight. After purification and drying under high vacuum (2 d at 120 °C and  $10^{-6}$  mbar), 35.4 mg (36.7  $\mu$ mol, 52%) of the product **CTF-hex5** were obtained as slightly yellow solid.

IR (ATR):  $\tilde{\nu}$  = 3369 (vw), 2228 (vw), 1603 (vw), 1499 (w), 1363 (vw), 1193 (vw), 1016 (vw), 810 (w), 554 (vw)  $\text{cm}^{-1}$ . – EA ( $\text{C}_{67.4}\text{H}_{37.6}\text{N}_{8.4}$ ): calcd. C 84.35, H 3.91, N 11.74, found C 63.70, H 4.43, N 8.17, S 0.43. –  $S_{\text{BET}}$  = 638  $\text{m}^2/\text{g}$ . –  $S_{\text{Langmuir}}$  = 790  $\text{m}^2/\text{g}$ . –  $V_{\text{Total, Pore}}$  = 0.31  $\text{cm}^3/\text{g}$ .



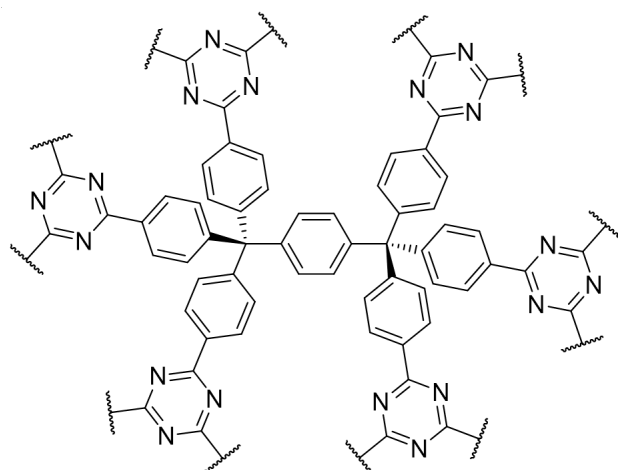


**Scheme S9.** 'TPM-HPX-Nitril' Covalent Triazine-Based Framework **CTF-hex5**

### 2.3. Synthesis of Covalent Triazine-Based Frameworks (CTFs) via Trimerization of Aromatic Nitriles using Ionothermal Conditions

'HPX-Nitrile' Covalent Triazine-Based Framework (**CTF-hex6**) (Scheme S10): A mixture of 88.0 mg (123  $\mu\text{mol}$ , 1.00 equiv.) HPX-nitrile **1** and 168 mg (1.23 mmol, 10.0 equiv.) dry zinc chloride were heated in an oven up to 400  $^{\circ}\text{C}$  in a pyrex® ampule (3  $\times$  120 mm) for 42 h. After cooling to room temperature, the ampule was opened carefully. The solid residue was washed with water (200 mL), stirred in diluted HCL (15 mL) overnight, and filtered as well as washed with water (3  $\times$  10 mL) and tetrahydrofuran (3  $\times$  10 mL). After drying under a high vacuum (150  $^{\circ}\text{C}$  and  $10^{-6}$  mbar), 59.4 mg (83.6  $\mu\text{mol}$ , 68%) of the product **CTF-hex6** were obtained as black solid.

IR (KBr):  $\tilde{\nu}$  = 3435 (vw), 2961 (vw), 2921 (vw), 2853 (vw), 2387 (vw), 2347 (vw), 2297 (vw), 1696 (vw), 1626 (vw), 1361 (vw), 1324 (vw), 1257 (vw), 1211 (vw), 1173 (vw), 1112 (vw), 1021 (vw), 877 (vw), 802 (vw), 747 (vw), 700 (vw), 591 (vw)  $\text{cm}^{-1}$ . – EA ( $\text{C}_{50}\text{H}_{28}\text{N}_6$ ): calcd. C 84.25, H 3.96, N 11.79, found C 82.19, H 3.08, N 3.58, S 0.46. –  $S_{\text{BET}}$  = 1728  $\text{m}^2/\text{g}$ . –  $S_{\text{Langmuir}}$  = 2123  $\text{m}^2/\text{g}$ . –  $V_{\text{Total, Pore}}$  = 0.87  $\text{cm}^3/\text{g}$ .

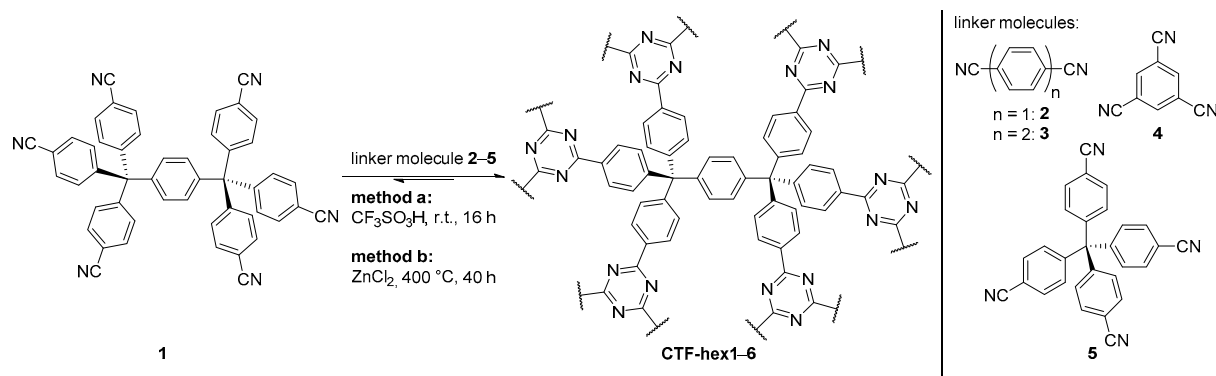


**Scheme S10.** 'HPX-Nitrile' Covalent Triazine-Based Framework **CTF-hex6**

### 3. Elemental Analysis

It is only possible to give the molecular weight of the sum formula or repeat unit for the ideal structure of each CTF, assuming 100% polymerization (Table S1).

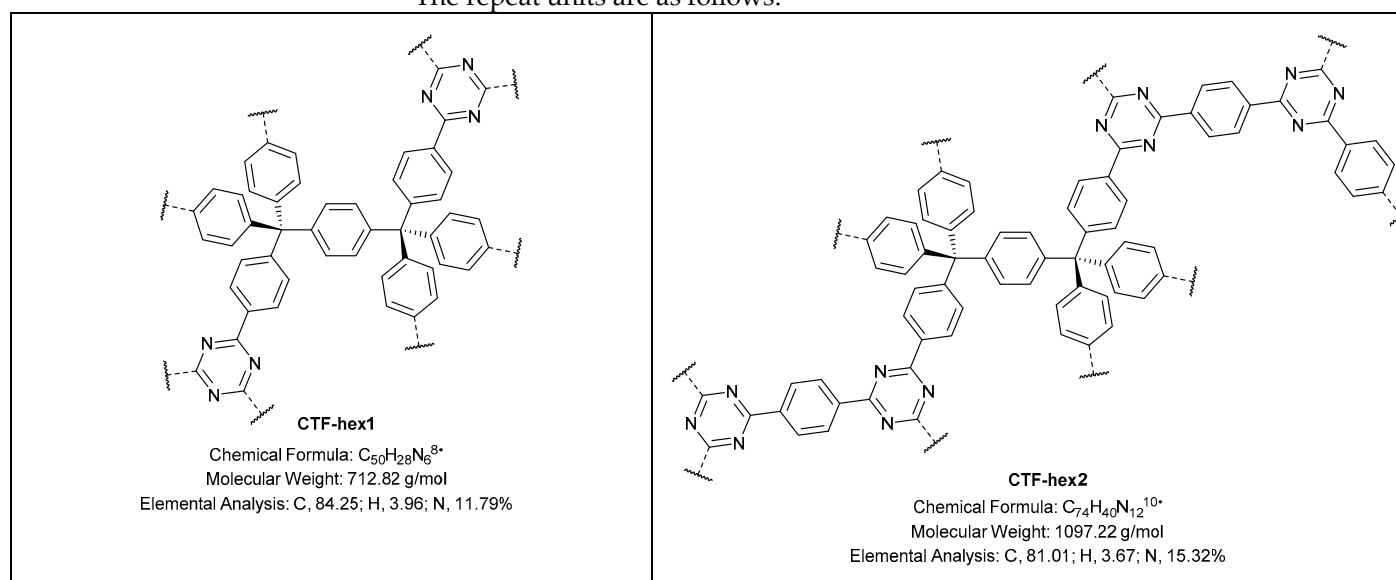
**Table S1.** Synthesized triazine-based frameworks **CTF-hex1–6** with monomers **1–5** and their sum formula and molecular weights for the idealized structures.

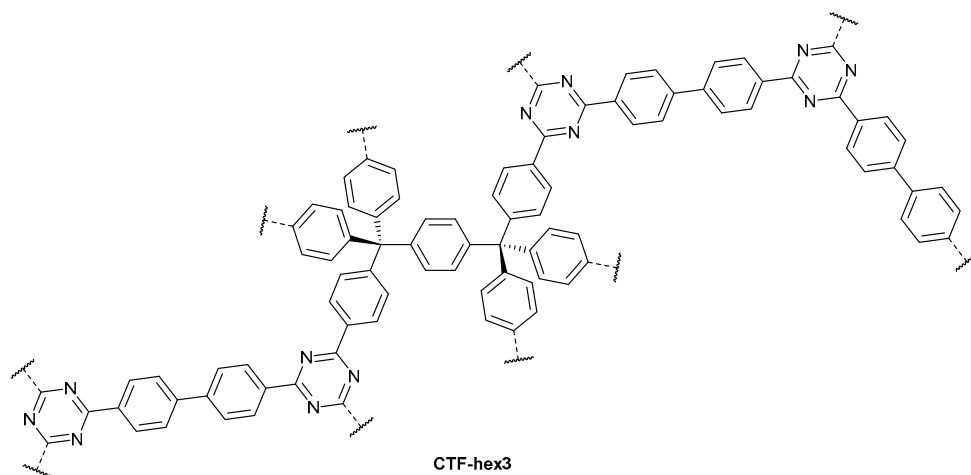


Framework <sup>a</sup>	Monomer (Molar Ratio)	Monomer Sum Formula	CTF Sum Formula <sup>b</sup>	Molecular Weight [g/mol] <sup>b</sup>
CTF-hex1	<b>1</b>	C <sub>50</sub> H <sub>28</sub> N <sub>6</sub>	C <sub>50</sub> H <sub>28</sub> N <sub>6</sub>	712.82
CTF-hex2	<b>1</b> with <b>2</b> (1:3)	C <sub>50</sub> H <sub>28</sub> N <sub>6</sub> , C <sub>8</sub> H <sub>4</sub> N <sub>2</sub> (× 3)	C <sub>74</sub> H <sub>40</sub> N <sub>12</sub>	1097.22
CTF-hex3	<b>1</b> with <b>3</b> (1:3)	C <sub>50</sub> H <sub>28</sub> N <sub>6</sub> , C <sub>14</sub> H <sub>8</sub> N <sub>2</sub> (× 3)	C <sub>92</sub> H <sub>52</sub> N <sub>12</sub>	1325.51
CTF-hex4	<b>1</b> with <b>4</b> (1:2)	C <sub>50</sub> H <sub>28</sub> N <sub>6</sub> , C <sub>9</sub> H <sub>3</sub> N <sub>3</sub> (× 2)	C <sub>68</sub> H <sub>34</sub> N <sub>12</sub>	1019.10
CTF-hex5	<b>1</b> with <b>5</b> (1:0.6)	C <sub>50</sub> H <sub>28</sub> N <sub>6</sub> , C <sub>29</sub> H <sub>16</sub> N <sub>4</sub> (× 0.6)	C <sub>67.4</sub> H <sub>37.6</sub> N <sub>8.4</sub>	965.10
CTF-hex6	<b>1</b>	C <sub>50</sub> H <sub>28</sub> N <sub>6</sub>	C <sub>50</sub> H <sub>28</sub> N <sub>6</sub>	712.82

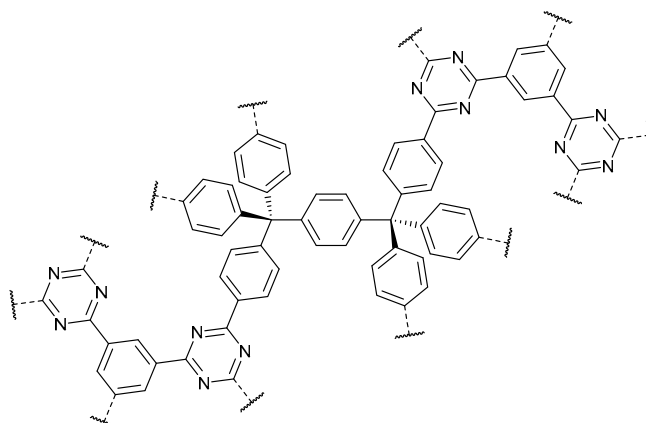
<sup>a</sup> **CTF-hex1** to **–hex5** was synthesized by using TFMS, whereas **CTF-hex6** was synthesized by using ZnCl<sub>2</sub>. <sup>b</sup> Calculation of the yield is based on hypothetical 100% polymerization.

The repeat units are as follows:

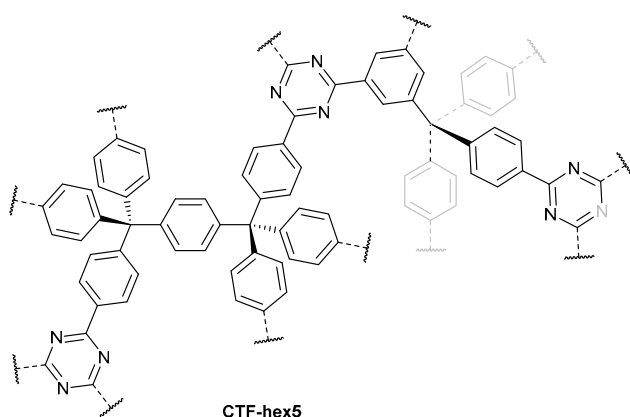


**CTF-hex3**

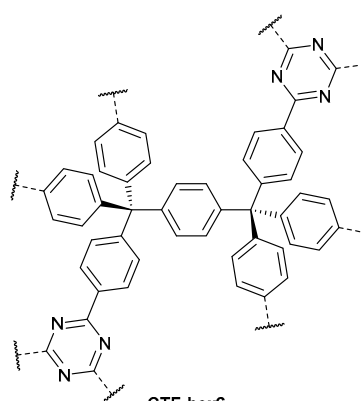
Chemical Formula:  $C_{92}H_{52}N_{12}^{10+}$   
 Molecular Weight: 1325.51 g/mol  
 Elemental Analysis: C, 83.36; H, 3.95; N, 12.68%

**CTF-hex4**

Chemical Formula:  $C_{68}H_{34}N_{12}^{12+}$   
 Molecular Weight: 1019.10 g/mol  
 Elemental Analysis: C, 80.14; H, 3.36; N, 16.49%

**CTF-hex5**

Chemical Formula:  $C_{67.4}H_{37.6}N_{8.4}^{X+}$   
 Molecular Weight: 965.10 g/mol  
 Elemental Analysis: C, 84.35; H, 3.91; N, 11.74%

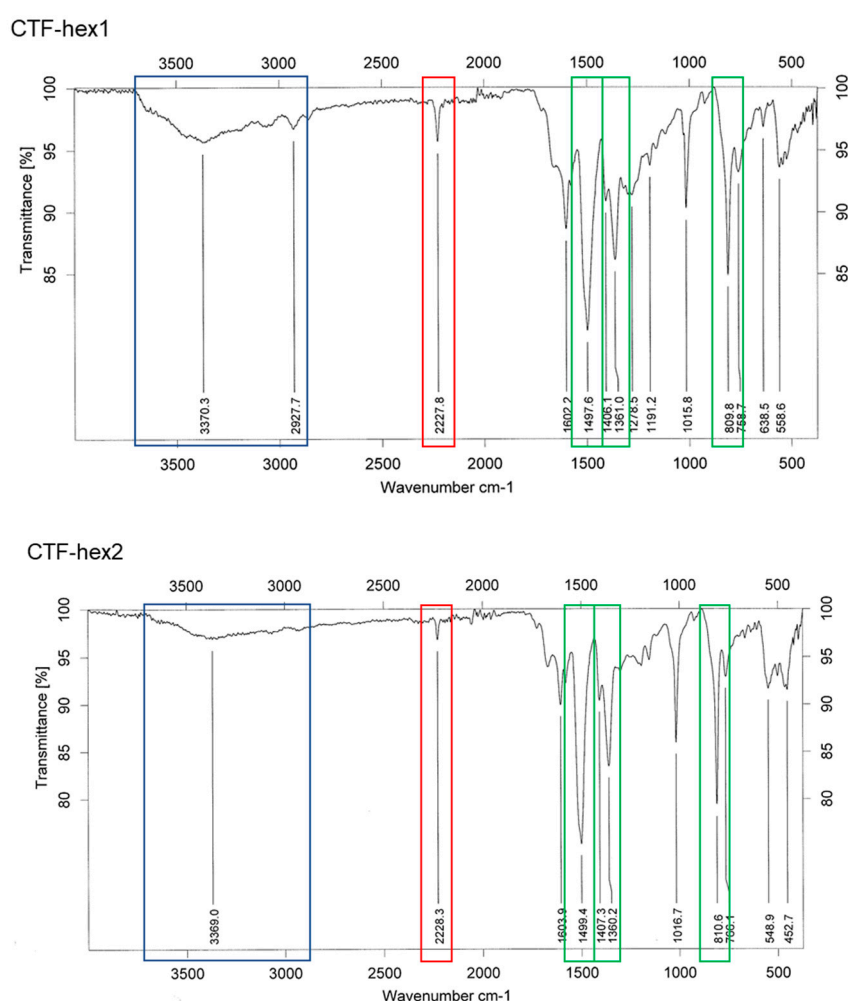
**CTF-hex6**

Chemical Formula:  $C_{50}H_{28}N_6^{8+}$   
 Molecular Weight: 712.82 g/mol  
 Elemental Analysis: C, 84.25; H, 3.96; N, 11.79%

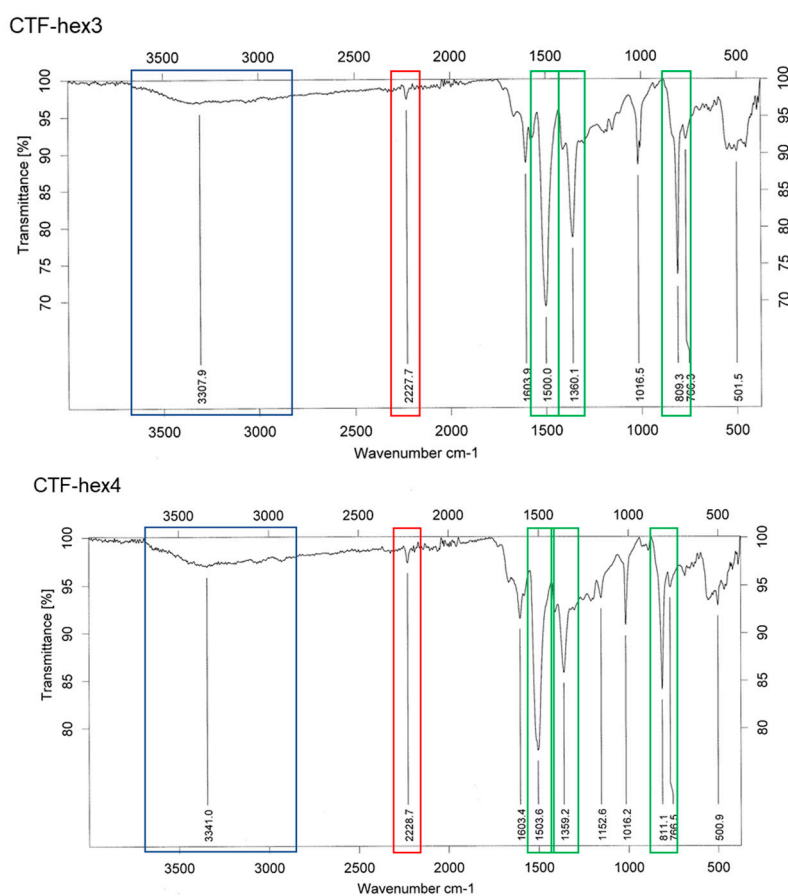
**Table S2.** Summary of the elemental analyses of the synthesized triazine-based frameworks **CTF-hex1–6** as well as the C/H- and C/N-ratios for a better comparison.

Entry	Framework	Calculated (%) <sup>a</sup>					Found (%)				
		C <sup>b</sup>	H <sup>b</sup>	N <sup>b</sup>	C/H <sup>c</sup>	C/N <sup>c</sup>	C <sup>b</sup>	H <sup>b</sup>	N <sup>b</sup>	C/H <sup>c</sup>	C/N <sup>c</sup>
1	<b>CTF-hex1</b>	84.25	3.96	11.79	1.77	8.34	71.42	4.19	9.27	1.42	8.99
2	<b>CTF-hex2</b>	81.01	3.67	15.32	1.84	6.17	65.49	3.96	8.79	1.38	8.69
3	<b>CTF-hex3</b>	83.37	3.95	12.68	1.76	7.67	66.80	4.03	9.15	1.38	8.52
4	<b>CTF-hex4</b>	80.14	3.36	16.49	1.99	5.67	68.26	4.11	10.60	1.38	7.51
5	<b>CTF-hex5</b>	84.35	3.91	11.74	1.80	8.38	63.70	4.43	8.17	1.20	9.10
6	<b>CTF-hex6</b>	84.25	3.96	11.79	1.77	8.34	82.19	3.08	3.58	2.22	26.78

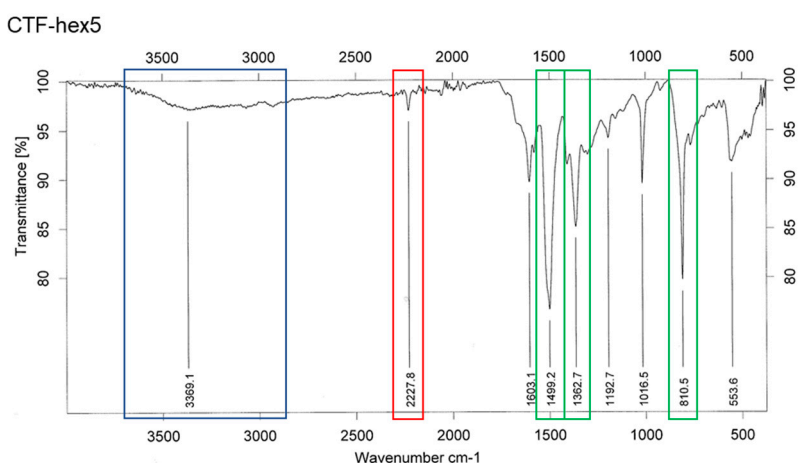
<sup>a</sup> Calculation based on the used stoichiometric ratios without considering the adsorption of moisture; <sup>b</sup> data are in wt%; <sup>c</sup> ratio of molar percentage.



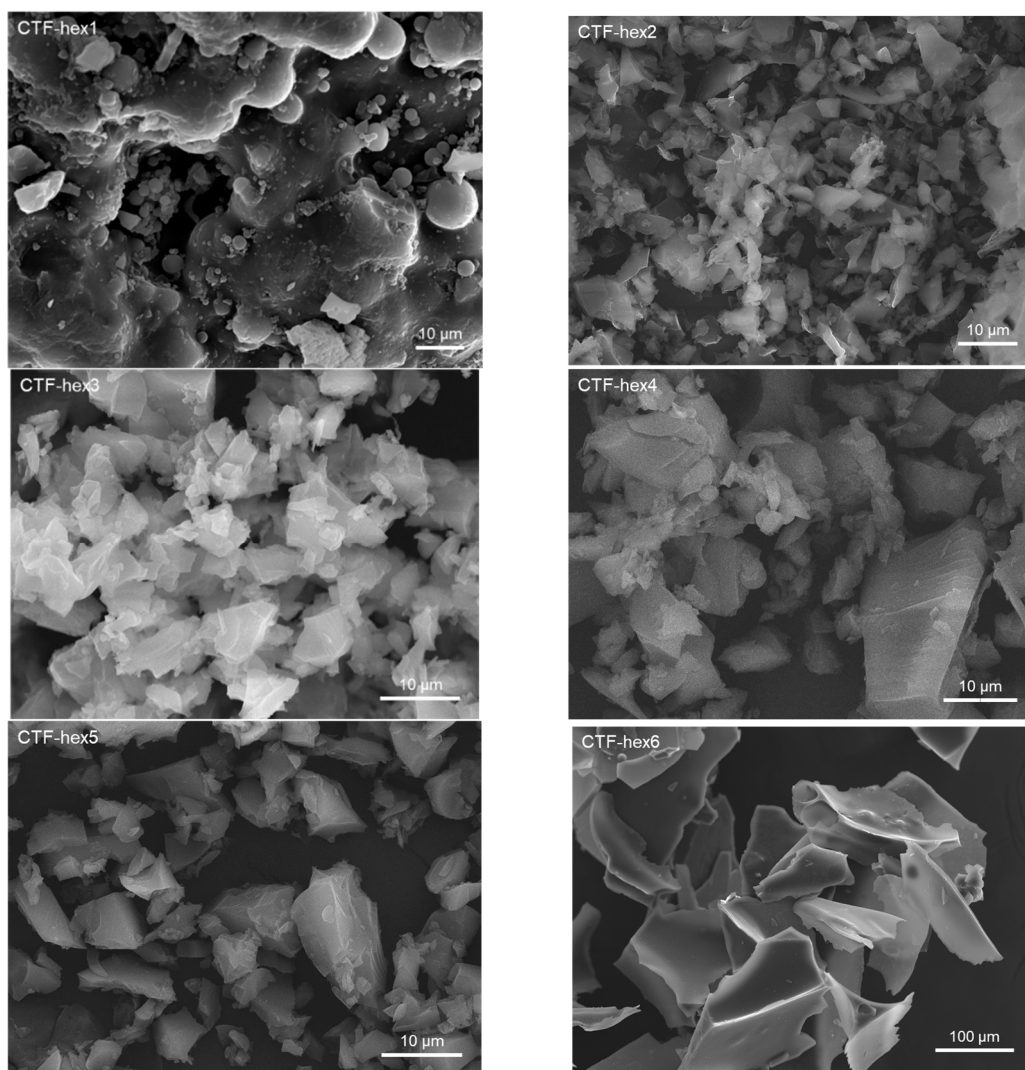
**Figure S1.** IR spectra of the triazine-based framework structures **CTF-hex1** and **CTF-hex2**. In green at around 1500, 1360, and 810  $\text{cm}^{-1}$ , the IR bands for triazine units are shown; in red at around 2230  $\text{cm}^{-1}$  is a small IR band for the nitrile moiety in all spectra and between 2900 and 3600  $\text{cm}^{-1}$  a significant signal for water is observed (blue).



**Figure S2.** IR spectra of the triazine-based framework structures **CTF-hex3** and **CTF-hex4**. In green at around 1500, 1360, and 810  $\text{cm}^{-1}$ , the IR bands for triazine units are shown; in red at around 2230  $\text{cm}^{-1}$  is a small IR band for the nitrile moiety in all spectra and between 2900 and 3600  $\text{cm}^{-1}$  a significant signal for water is observed (blue).



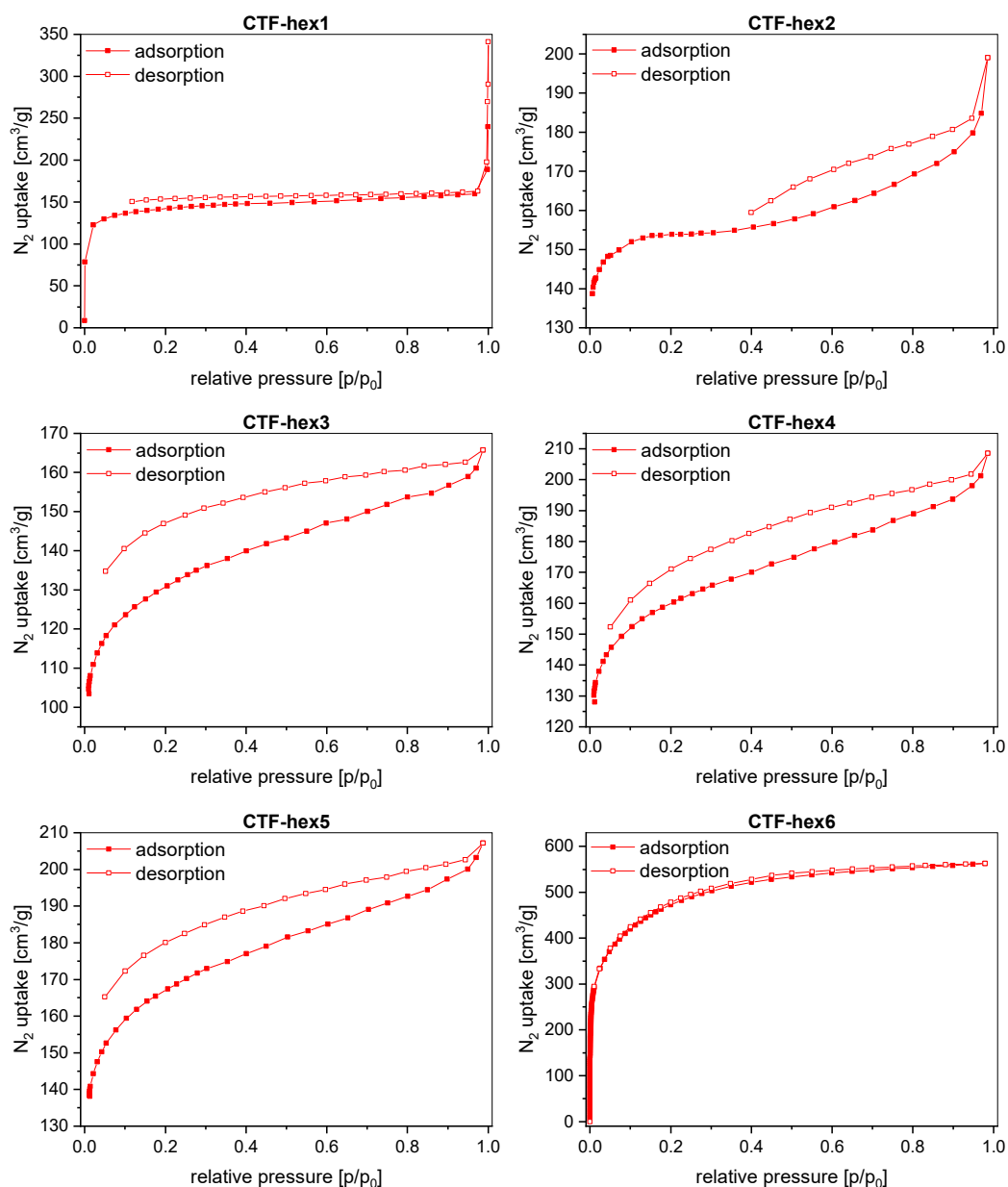
**Figure S3.** IR spectrum of the triazine-based framework structure **CTF-hex5**. In green at around 1500, 1360, and 810  $\text{cm}^{-1}$ , the IR bands for triazine units are shown; in red at around 2230  $\text{cm}^{-1}$  is a small IR band for the nitrile moiety in all spectra and between 2900 and 3600  $\text{cm}^{-1}$  a significant signal for water is observed (blue).



**Figure S4.** SEM images of the covalent triazine-based frameworks **CTF-hex1–6** (labels are given in the upper left corner of each image).

#### 4. Gas sorption Measurements

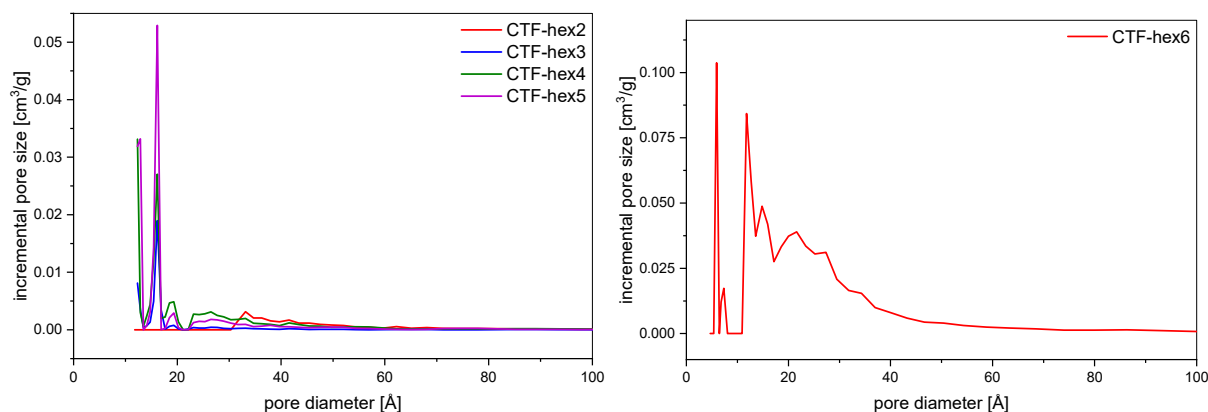
##### 4.1. Nitrogen Adsorption-desorption Isotherms



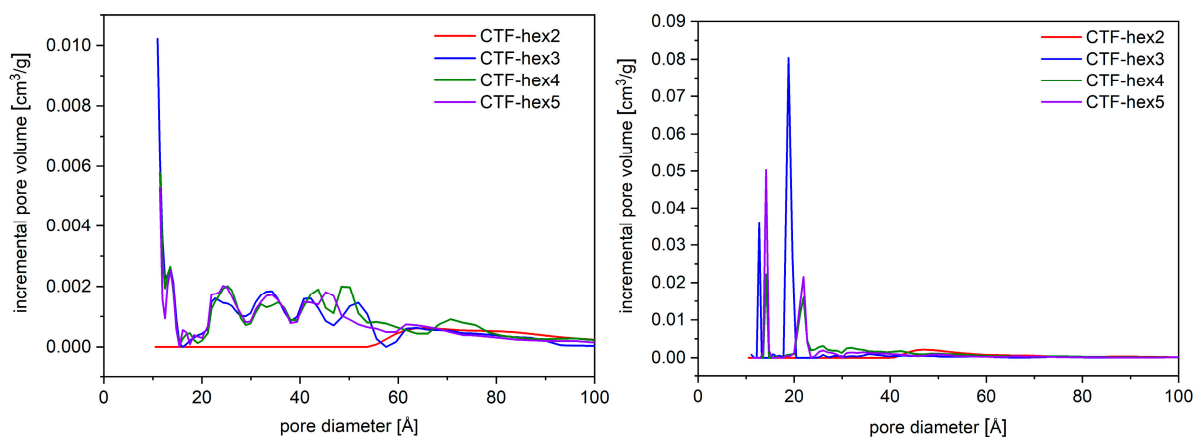
**Figure S5.** Nitrogen adsorption-desorption isotherms at 77 K (closed symbols for adsorption and open symbols for desorption) for CTF-hex1–6. CTF-hex2–5 were measured on a NOVA-4000e instrument. CTF-hex1 was measured on a Thermo Scientific™ adsorption porosimeter, and the surface depends strongly on the preparation conditions. CTF-hex6 was measured using a Micromeritics ASAP 2020.

Note that the desorption branch has not closed for CTF-hex2–5 due to the set time constraints during the measurement. The used instrument NOVA 4000e was set for short measurements due to high demand.

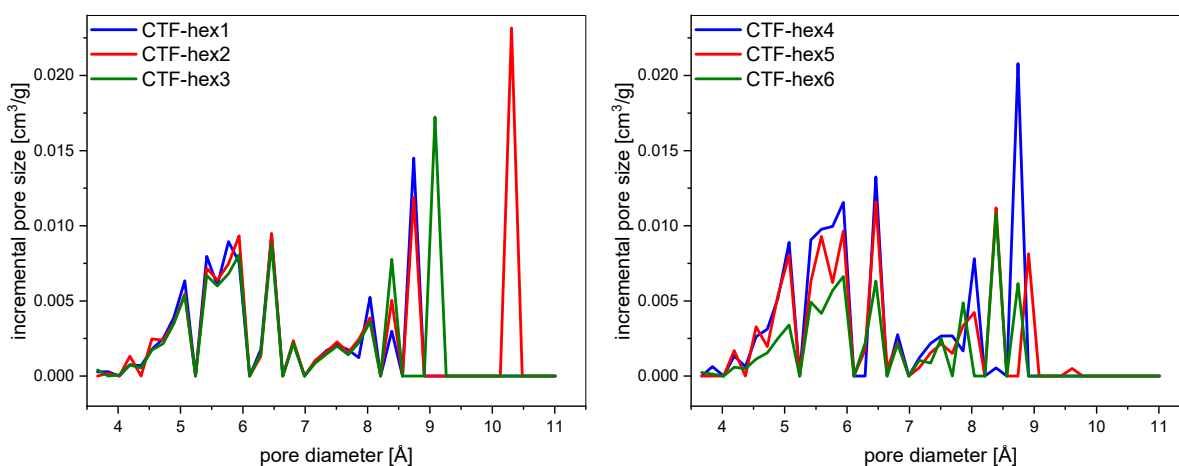
#### 4.2. Pore size distributions



(a) from N<sub>2</sub> sorption, NLDFT



(b) from N<sub>2</sub> sorption, QSDFT, adsorption branch only      ads. and des. (equilibrium model)



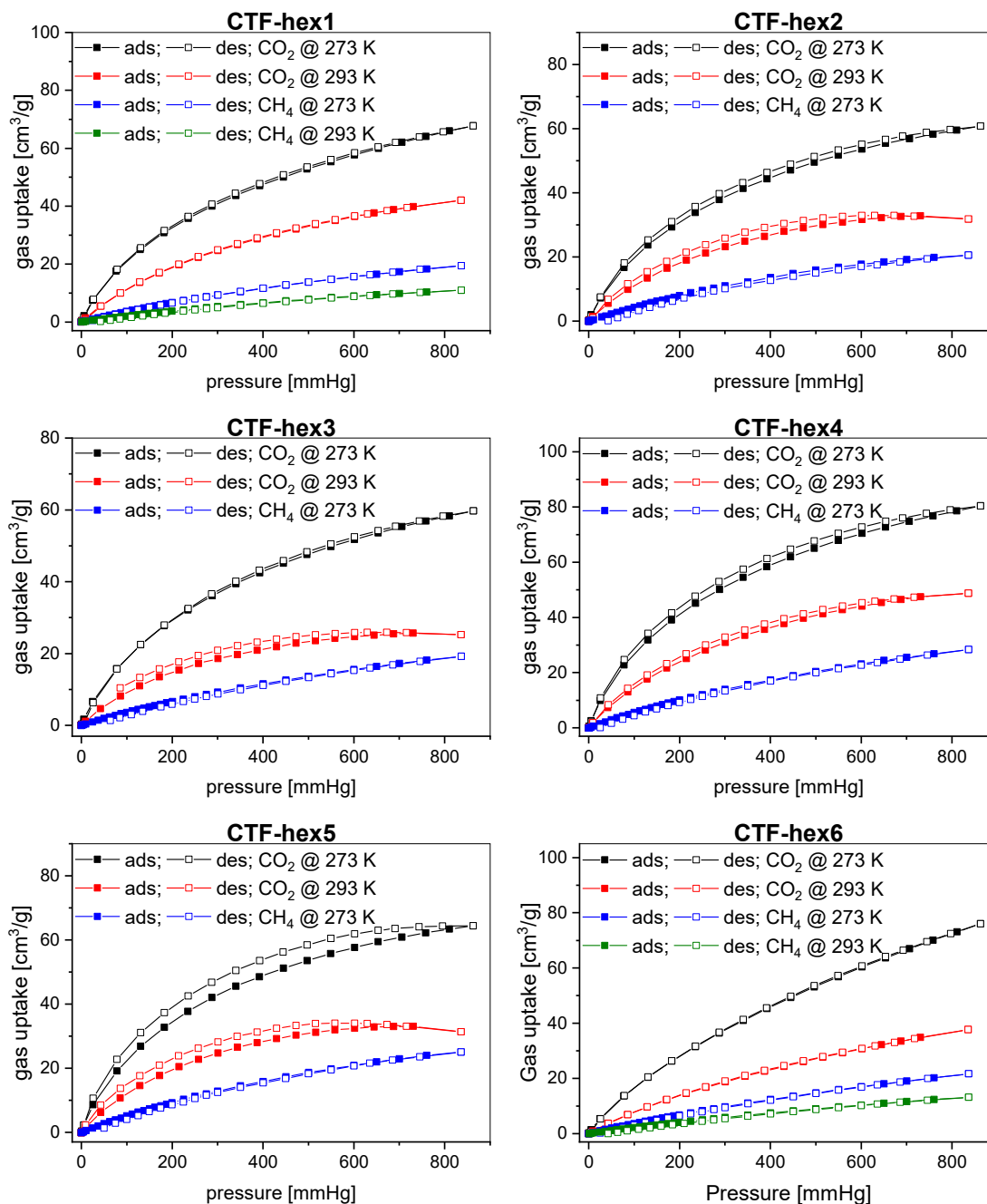
(c) from CO<sub>2</sub> adsorption

**Figure S6.** (a) NLDFT pore size distributions for **CTF-hex2–5** and **CTF-hex6** from N<sub>2</sub> ad- and desorption isotherms at 77 K. (b) QSDFT pore size distributions for **CTF-hex2–5** from N<sub>2</sub> adsorption isotherms at 77 K (left) and from adsorption and desorption isotherms (equilibrium model, right); note the different scale for the left and right graph. (c) Pore size distributions from CO<sub>2</sub> adsorption isotherms at 273 K. Micropores have diameters of less than 20 Å (2 nm), mesopores range from 20–500 Å (2–50 nm). The jagged lines for the micropore distribution graphs in c) must not be overinterpreted as the number of data points in the relevant low-pressure range for the CO<sub>2</sub> measurement was relatively low (Figure S7).



Note: for NLDFT, only an equilibrium model using the ad- and desorption branch was available, while for QSDFT besides the equilibrium model also the adsorption branch could be used only, in view of the not closed desorption isotherms (Figure S5).

#### 4.3. CO<sub>2</sub> and CH<sub>4</sub> Adsorption-desorption Isotherms up to 1 bar



**Figure S7.** CO<sub>2</sub> and CH<sub>4</sub> sorption isotherms for CTF-hex1–6 (closed symbols for adsorption and open symbols for desorption). A slightly negative slope for CTF-hex3 and –hex5 at 293 K is sometimes seen for materials where the gas uptake induces a phase transition.

#### 4.4. Literature Values for CO<sub>2</sub> Uptake for Comparison

For comparison of the CO<sub>2</sub> uptake capacity, values of CO<sub>2</sub> adsorption properties of other CTFs are collected in Table S3.

**Table S3.** Surface area and CO<sub>2</sub> adsorption properties of triazine-based polymers.

Compound	BET [m <sup>2</sup> /g]	CO <sub>2</sub> uptake [mmol/g] at 1 bar		Q <sub>st</sub> <sup>a</sup>	Ref.
		273 K	298 K or 293 K		
CTF-0	2011	4.22	-	-	[8]
CTF-1	746	2.47	1.41	27.5	[9]
CTF-1-600	1533	3.82	2.25	30.0	[9]
FCTF-1	662	4.67	3.21	35.0	[9]
FCTF-1-600	1535	5.53	3.41	32	[9]
CTF-P2	776	1.84	-	-	[7]
CTF-P3	571	2.22	-	-	[7]
CTF-P4	867	3.05	-	-	[7]
CTF-P5	960	2.94	-	-	[7]
CTF-P6	1152	3.32	-	-	[7]
CTF-P1M	4	0.92	-	-	[7]
CTF-P2M	464	1.87	-	-	[7]
CTF-P3M	523	2.21	-	-	[7]
CTF-P4M	542	1.83	-	-	[7]
CTF-P5M	542	2.03	-	-	[7]
CTF-P6M	947	4.12	-	-	[7]
MCTP-1	1452	4.61	2.65		[10]
MCTP-2	859	3.65	2.42		[10]
Polymer 2	-	-	1.56		[11]
Polymer 3	646	-	1.68		[11]
Polymer 4	1266	-	2.09		[11]
Polymer 2C	427	-	2.99		[11]
Polymer 3C	1173	-	3.08		[11]
Polymer 4C	1316	-	3.61		[11]
NOP-1	978	1.83	1.06	32.8	[12]
NOP-2	1055	2.37	1.40	34.1	[12]
NOP-3	1198	2.51	1.39	33.8	[12]
NOP-4	635	1.71	0.83	31.9	[12]
NOP-5	913	1.45	0.72	30.5	[12]
NOP-6	1130	1.31	0.49	29.2	[12]
MCTF-300	640	2.25	1.39	24.6	[13]
MCTF-400	1060	2.36	1.55	25.4	[13]
MCTF-500	1510	3.16	2.22	26.3	[13]
fl-CTF300	15	1.27	0.71	43.1	[14]
fl-CTF350	1235	4.28	2.29	32.7	[14]
fl-CTF400	2862	4.13	1.97	30.7	[14]
fl-CTF500	2322	3.26	1.65	31.7	[14]
fl-CTF600	2113	3.48	1.80	32.4	[14]
COP-1	168	-	1.33	-	[15]
COP-2	158	-	0.91	-	[15]
PCTF-1	2235	3.21	1.84	30	[16,17]
PCTF-2	784	1.83	0.992	26	[16,17]
PCTF-3	641	2.14	1.32	27	[16,17]
PCTF-4	1090	2.27	1.49	28	[16,17]

PCTF-5	1183	2.55	1.48	27	[16,17]
PCTF-6	79	-	-	-	[16,17]
PCTF-7	613	2.15	1.32	25	[16,17]
HPF-1	576	-	2.8	43	[18]
CTF-TPC	1668	4.19	2.47	32	[19]
CTF-FL	773	3.22	2.00	35	[19]
CTF-FUM-350	230	3.44	2.31	-	[20]
CTF-DCN-500	735	2.66	1.55	-	[20]
pym-CTF500	208	2.75	1.77	40.5	[21]
pym-CTF600	689	3.34	2.15	37.4	[21]
bipy-CTF300-600	360-2479	1.87-5.58	0.98-2.95	33.3-35.2	[21]
lut-CTF300-600	486-2815	3.63-4.99	2.14-2.52	33.3-38.2	[21]
Ad4L1	1617	3.36	1.97	34.3	[22]
Ad4L2	1885	2.47	1.94	32.6	[22]
Ad4L3	1341	3.28	1.42	37.1	[22]

<sup>a</sup> heat of adsorption (negative adsorption enthalpy).

### 5. Calculation of Isostatic Heat of Adsorption ( $Q_{st}$ ) using Virial Fitting Method

The isosteric heat of adsorption ( $Q_{st}$ ) for the CO<sub>2</sub> adsorption of CTF-hex1–6 were calculated from isotherms at different temperatures (273 K and 293 K), applying the virial fitting method (Equation (1)).

$$\ln P = \ln N + \frac{1}{T} \sum_{i=0}^m a_i N^i + \sum_{i=0}^n b_i N^i \quad (1)$$

In Equation (1),  $P$  is the pressure expressed in Torr,  $N$  is the amount adsorbed in mmol/g,  $T$  is the temperature in K,  $a_i$  and  $b_i$  are virial coefficients, and  $m$ ,  $n$  represents the number of coefficients required to describe the isotherms adequately. Then values of the virial coefficients  $a_0$  through  $a_m$  were employed to calculate the  $Q_{st}$  using the following expression (Equation (2)).

$$Q_{st} = -R \sum_{i=0}^m a_i N^i \quad (2)$$

$R$  is the universal gas constant with  $R = 8.314 \text{ J/(K mol)}$ .

The  $Q_{st}$  at zero coverage ( $Q_{st}^0$ ) is calculated according to (Equation (3)).

$$Q_{st} = -R \sum_{i=0}^m a_0 \quad (3)$$

**Table S3.** List of  $a_0$  and  $Q_{st}^0$  values of the CO<sub>2</sub> adsorption isotherms for CTF-hex1-6 obtained from the virial fitting method.

Entry	CTF-hex	$a_0$	$Q_{st}^0$ (CO <sub>2</sub> ) [kJ/mol]
1	CTF-hex1	−3964.67286	33
2	CTF-hex2	−2770.73334	23
3	CTF-hex3	−3857.17197	32
4	CTF-hex4	−3475.35261	29
5	CTF-hex5	−3534.26034	29
6	CTF-hex6	−4450.11578	37

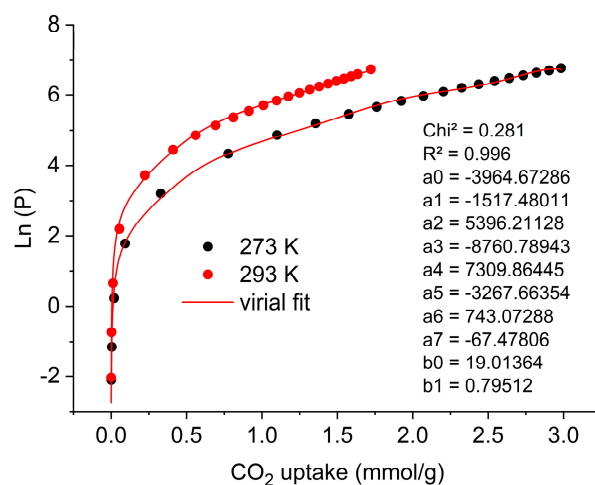


Figure S8. CO<sub>2</sub> adsorption isotherms for **CTF-hex1** fitted by the virial method.

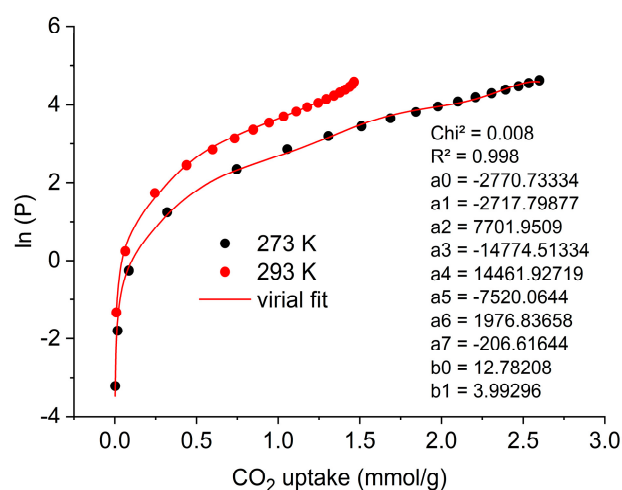


Figure S9. CO<sub>2</sub> adsorption isotherms for **CTF-hex2** fitted by the virial method.

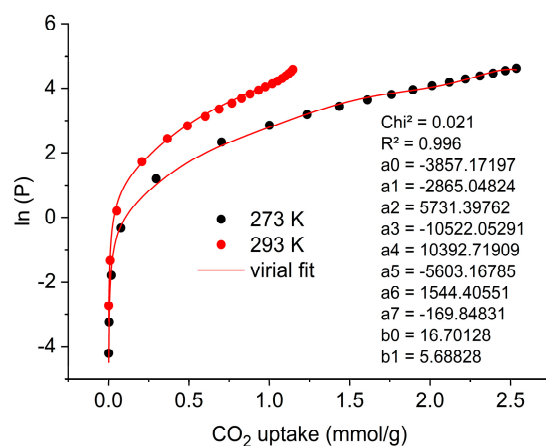


Figure S10. CO<sub>2</sub> adsorption isotherms for **CTF-hex3** fitted by the virial method.

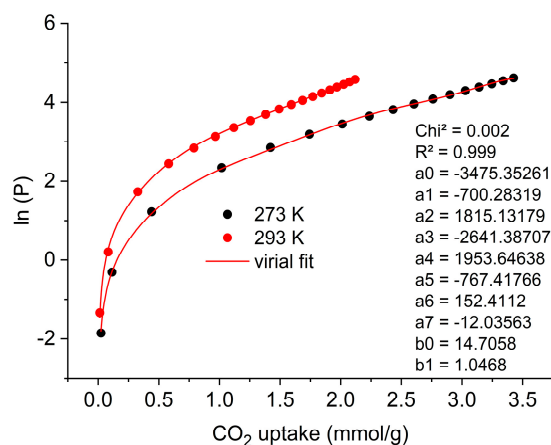


Figure S11. CO<sub>2</sub> adsorption isotherms for CTF-hex4 fitted by the virial method.

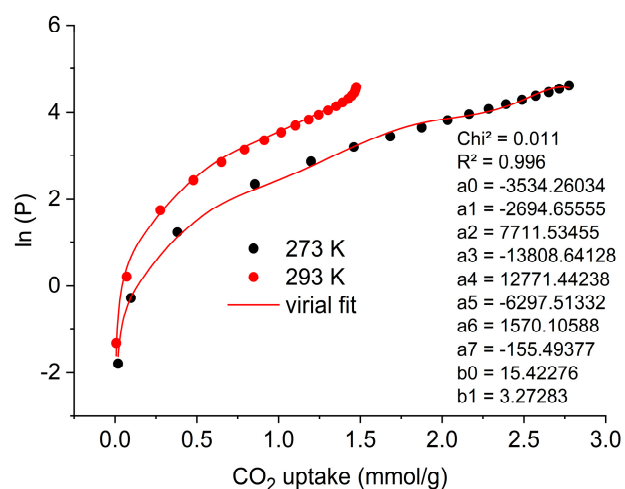


Figure S12. CO<sub>2</sub> adsorption isotherms for CTF-hex5 fitted by the virial method.

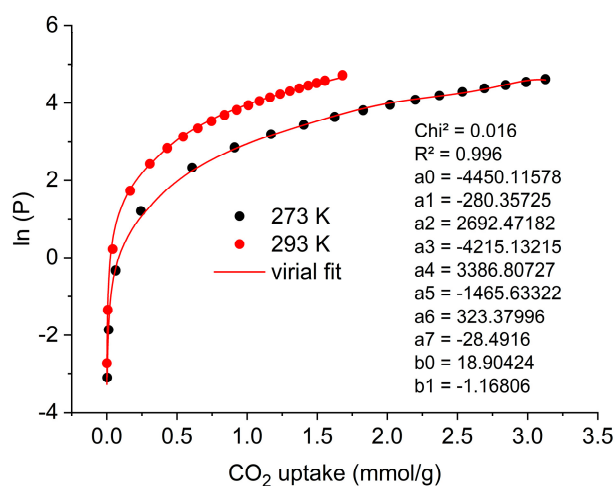
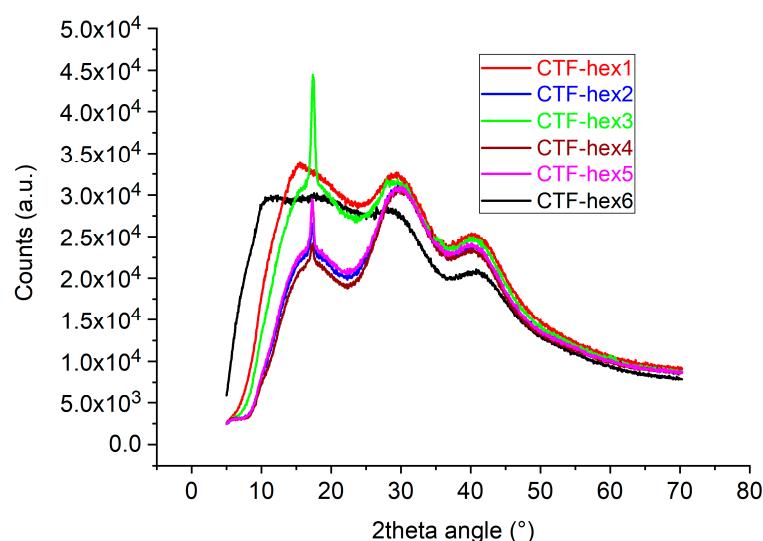


Figure S13. CO<sub>2</sub> adsorption isotherms for CTF-hex6 fitted by the virial method.



**Figure S14.** Powder X-ray diffractograms of CTF-hex1–6. In other work on mixed-linker CTFs which were prepared by ionothermal synthesis with  $\text{ZnCl}_2$ , [22][23] the comparatively sharp peak at  $2\theta = 17^\circ$  was assigned to the (111) plane reflection from  $\text{ZnCl}_2$ . This assignment was not correct, however, in view of the synthesis of mixed-linker CTF-hex2–5 with the Brønsted acid trifluoromethanesulfonic acid. At present, the origin of this sharp reflection at  $2\theta = 17^\circ$  remains unclear.

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