From a supramolecular tetranitrile to a porous covalent triazine-based framework with high gas uptake capacities

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Supporting Information

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1. General methods

Infrared (IR) spectra were obtained on a Bruker FT-IR Tensor 37 Spectrometer in the 4000-550 cm⁻¹ region with 2 cm⁻¹ resolution as KBr disks. Elemental analyses were carried out with a Perkin Elmer 2400 series 2 elemental analyzer. Powder X-ray diffraction (PXRD) data was collected on a Bruker D2 phaser diffractometer using Cu K α_1/α_2 radiation with $\lambda = 1.5418$ Å. Scanning electron microscopy (SEM) images were obtained using an ESEM Quanta 400 FEG SEM equipped with a secondary electron (SE) detector. Thermogravimetric analyses (TGA) were carried out at a ramp rate of 5 °C / min in a N₂ flow with a Netzsch Thermo-Microbalance Aparatus TG 209 F3 Tarsus. ¹H and ¹³C spectra were recorded on a Bruker Avance DRX-200 and Bruker Avance DRX-500 instruments. ¹H and ¹³C NMR chemical shifts are given in ppm relative to SiMe₄ ($\delta = 0.0$ ppm) with calibration against the (residual protonated) solvent signal (CDCl₃: 7.26 (¹H) and 77.0 (¹³C)). Mass spectra were obtained on Bruker Ultraflex I TOF (MALDI), Finnigan DSQ 7000 (EI) and Bruker maXis 4G (ESI) spectrometers. Thermogravimetric-mass spectrometry coupled analysis (TG-MS) was performed on a Netzsch STA 449 C Jupiter instrument coupled with a Pfeiffer Thermostar GSD 300 mass spectrometer at 5 °C / min heating rate using corundum sample holders and N₂ as carrier gas.

Sorption isotherms were measured using a Micromeritics ASAP 2020 automatic gas sorption analyzer equipped with oil-free vacuum pumps (ultimate vacuum $<10^{-8}$ 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 200 °C. After weighing, the sample tube was then transferred to the analysis port of the sorption analyzer. All used gases (H₂, He, N₂, CO₂, CH₄) were of ultra high 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. H₂ and N₂ sorption isotherms were measured at 293±1 K (passive thermostating) and 273.15 K (ice / deionized water bath). The heat of adsorption values and the DFT calculations ('N₂ DFT slit pore' model) were done using the ASAP 2020 v3.05 software.

All chemicals were used as purchased from commercial sources without further purification.

2. General experimental procedures

Synthesis of tetra(4-bromophenyl)ethylene

This compound was synthesized according to the previously reported procedure. ¹ Tetraphenylethylene (5.0 g, 15.04 mmol) and an open vial containing bromine (6.0 mL, 117 mmol) were kept on the top and bottom of the rack in a desiccator, respectively. The desiccator was closed in such a way as to leave a small hole so that HBr which is formed during the reaction can escape from it. After five days, a greenish solid was collected. The crude solid was recrystallized from dichloromethane / methanol (2:1) to give white crystals which were dried in vacuum. Yield: 7.1 g, 73 %. ¹H NMR (200 MHz, CDCl₃, 23 °C): $\delta = 6.84$ (d, 8H), 7.26 (d, 8H) (Fig. S2). ¹³C{¹H} NMR (500 MHz, CDCl₃, 23 °C): $\delta = 121.3$ (Ar), 131.0 (Ar), 132.6 (Ar), 139.2 (Ar), 141.5 (-C=C-) (Fig. S4). IR (KBr): 3435 (br), 3048 (m), 3020 (m), 2924 (w), 2856 (w), 2362 (w), 2336 (w), 1649 (m),

1582 (m), 1449 (s), 1441 (m), 1391 (m), 1262 (w), 1070 (s), 1008 (s), 824 (w), 793 (m), 698 (s), 623 (m), 568 (m), 482 (m) cm⁻¹. EI-MS for $C_{26}H_{16}^{79}Br_4$, 644.4 g/mol: $[M]^+$ 644 with correct isotopic pattern for four ^{79/81}Br atoms.



Synthesis of Tetra(4-cyanophenyl)ethylene (1)

Tetra(4-bromophenyl)ethylene (1.34 g, 2.07 mmol) and CuCN (1.07 g, 11.95 mmol) were dissolved in DMF (20 mL) under N₂. Then the reaction mixture was refluxed for 24 h.² After cooling to room temperature, the reaction mixture was diluted with water (50 mL), filtered and the gray colored solid collected. The solid product was dissolved in water (75 mL) at room temperature, treated with ethylenediamine (4 mL, 59.83 mmol) and the solution stirred at 25 °C for 1 h. The light gray colored solid which formed was collected by filtration and extracted with CH₃CN (50 mL). From the acetonitrile extracts the solvent was evaporated, the residue dried in vacuum and then recrystallized from CH₂Cl₂. The recrystallized product was collected by filtration and dried in vacuum. Yield: 0.68 g, 76 %. Crystals suitable for X-ray diffraction analysis (see Fig. S1) were grown from a dichloromethane / ethanol (2:1) solution of the mixture at room temperature. ¹H NMR (200 MHz, CDCl₃, 23 °C): δ = 7.07 (d, 8H), 7.49 (d, 8H) (Fig. S3). ¹³C{¹H} NMR (500 MHz, $CDCl_3$, 23 °C): $\delta = 112.0$ (Ar), 118.2 (-CN), 131.4 (Ar), 132.4 (Ar), 141.6 (-C=C-), 145.6 (Ar) (Fig. S5). IR (KBr): 3432 (br), 2921 (w), 2853 (w), 2358 (w), 2226 (w), 1675 (m), 1603 (s), 1559 (w), 1501 (m), 1403 (m), 1374 (m), 1301 (w), 1262 (w), 1176 (w), 1112 (m), 1018 (s), 875 (w), 840 (s), 816 (w), 754 (m), 695 (w), 626 (w), 569 (m), 482 (m) cm⁻¹. ESI-MS for $C_{30}H_{16}N_4$, 432.5 g/mol: $[M+H_2O+H]^+$ 451.2.





Fig. S1: Photograph of compound 1 which is formed during the crystallization process.

3. General synthesis procedure for porous covalent triazine-based organic frameworks (PCTFs)

This compound was synthesized according to a literature procedure.³ A mixture of tetra(4cyanophenyl)ethylene (1) (0.087 g, 0.2 mmol) and anhydrous $ZnCl_2$ (0.272 g, 2.0 mmol) was placed into a Pyrex ampule under inert conditions. The ampule was evacuated, sealed and heated to 400 °C for 48 h followed by cooling to room temperature. The black solid was collected and stirred in water for 72 h to extract $ZnCl_2$. Then the product was isolated by filtration and again stirred with 200 mL of 2 mol/L HCl for 24 h. The resulting black powder was finally washed with water, THF and dried in vacuum. PCTF-1 (82 mg, 94 % yield) was collected as a black powder.

Similarly, for PCTF-2 from tetra(4-cyanophenyl)ethylene (1) (0.087 g , 0.2 mmol) and anhydrous $ZnCl_2$ (0.136 g, 1.0 mmol) was collected as a black powder. Yield 79 mg, 91 %.

A rationale to the conditions is stated in the reference by P. Kuhn, A. Thomas and M. Antonietti, *Macromolecules*, 2009, **42**, 319-326:

"From the trimerization of aromatic nitriles through Lewis acid catalysis at temperatures of about 300-400 °C, triazines can be conveniently prepared. This reaction is moreover reversible as the retro-trimerization is also occurring at these temperatures, thus opening the opportunities of dynamic self-optimization of the as formed network structure."

"To develop and preserve porosity in a material, a porogen is required, being often simply the solvent itself. For performing reactions at the targeted temperatures, a high-temperature stable solvent has to be chosen. At these temperatures, inorganic salts can be reasonably envisaged, and zinc chloride turned out to be a good choice for several reasons."

"It is a smooth Lewis acid and therefore a catalyst for the trimerization, it is liquid in the desired temperature range for the reaction (280-730 $^{\circ}$ C), and finally it is miscible in all proportions with all the nitriles ..."

 $ZnCl_2$ acts also as a porogen. At a ratio of only 1:5 not enough porogen is present and the surface area as well as pore volume remain small.



Scheme S1: Ideal structure of PCTF from the polymerization of 1.

4. **Elemental analysis of PCTF-1 and PCTF-2**

a	ble S1: Ele	mental analy	sis of l	CTF-	I and P	CTF-2						
	рсте	molar ratio	Calculated (%) ^a					Found (%)				
	ICIF	of 1 : ZnCl ₂	С	Н	N	C/H	C/N	C	Н	Ν	C/H	C/N
	PCTF-1	1:10	83.32	3.73	12.95	22.34	6.43	82.45	3.33	2.81	24.76	29.34

12.95

Τa

83.32

1:5

3.73

PCTF-2

^a Assuming the idealized structure as depicted in Scheme S1 with formation of a triazine ring from three nitrile groups and no decomposition.

22.34

6.43

75.02

3.87

3.36

The elemental analysis gives a much lower nitrogen content and concomitantly a much higher than calculated C/N ratio. This indicates that most of the nitrogen is lost to decomposition (Scheme S2, see also section 7, thermogravimetric analysis).



Scheme S2: General schematic representation for the decomposition of a triazine ring.

19.38 22.33

5. NMR spectroscopy



Fig. S2: ¹H NMR (200 MHz, CDCl₃, 23 °C) spectrum of tetra(4-bromophenyl)ethylene.



Fig. S3: 1 H NMR (200 MHz, CDCl₃, 23 $^{\circ}$ C) spectrum of compound 1.

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Fig. S4: ¹³C NMR (500 MHz, CDCl₃, 23 °C) spectrum of tetrakis(4-bromophenyl)ethylene.



Fig. S5: ¹³C NMR (500 MHz, CDCl₃, 23 °C) spectrum of compound 1.

We have tried to collect a solid state MAS ¹³C NMR spectrum. However, similar to graphene-like or other carboneous materials the black samples of PCTF-1 and PCTF-2 are most likely conductive.

Rapid rotation of a conductive sample in a magnetic field will lead to strong heating of the sample and rotor.

The MAS NMR operator already had an accident where a graphene-like sample had exploded in the rotor, destroying the rotor and parts of the probe head and causing about 7000 EUR of damage inside the NMR instrument.

It was still tried to measure our PCTF samples by rotating them slowly at about 2-3 kHz instead of the normal 20-30 kHz with 13C- onepuls-experiments with decoupling and waiting times of 10 and 40 sec. Consequently only a broad hump was seen from 100-160 ppm. Such a broad hump from 100 to 160 ppm without fine-structure resolution was also seen in the solid state NMR of, e.g., graphite oxide (L. B. Casabianca, M. A. Shaibat, W. W. Cai, S. Park, R. Piner, R. S. Ruoff, and Y. Ishii, *J. Am. Chem. Soc.*, 2010, **132**, 5672-5676.), graphene nanosheets (X. Wang. Y. Hu, L. Song, H. Yang, W. Xing, H. Lu, *J. Mater. Chem.*, 2011, **21**, 4222-4227.), hydrothermally (from graphite oxide) reduced graphene sheets (D. Long, W. Li, L. Ling, J. Miyawaki, I. Mochida, S.-H. Yoon, *Langmuir*, 2010, **26**, 16096-16102.) or multi-walled carbon nanotubes (E. Abou-Hamad, M.-R. Babaa, M. Bouhrara, Y. Kim, Y. Saih, S. Dennler, F. Mauri, J.-M. Basset, C. Goze-Bac, and T. Wågberg, *Phys. Rev. B*, 2011, **84**, 165417.)

Hence, similar to graphene no fine structure could be seen in the solid-state MAS ¹³C NMR spectra of the PCTF samples.

6. FT-IR Spectrum of compound 1, PCTF-1 and PCTF-2



Fig. S6: FT-IR spectrum of tetra(4-cyanophenyl)ethylene compound **1**.



Fig. S7a: FT-IR spectrum of PCTF-1.



Fig. S7b: FT-IR spectrum of PCTF-2.



7. Thermogravimetric analysis (TGA)

Fig. S8: Thermogravimetric analysis (TGA) data for PCTF-1 (red) and -2 (black).

Thermogravimetric-mass spectrometry coupled analysis (TG-MS)

In order to identify the gaseous decomposition products formed during the tetra-nitrile polymerization at 400 °C, we performed the reaction in a TG-MS instrument. Unfortunately, we did not detect very strong mass peak intesities probably because of low amount (8.3 mg, 0.019 mmol and 13 mg, 0.030 mmol) of starting material of compound **1** with $ZnCl_2$ (26 mg, 0.19 mmol and 20 mg, 0.15 mmol) in a 1:10 and 1:5 molar ratio respectively. Dinitrogen, N₂ was used as carrier gas in the TGA instrument. In this experiment, we observed the elimination of CN (m = 26) and HCN (m = 27) (Fig. S9b and 9c, respectively).



Fig. S9a: Thermogravimetric (TG) and differential thermal analysis (DTA) curves during the formation of PCTF-1 (red) and -2 (blue).



Fig. S9b: TGA / DTA / MS curves during the formation of PCTF-2 at a heating rate of 5 °C / min. The MS curve shows the ion current (in 10^{-13} A) at m/z = 26, corresponding to CN⁺.



Fig. S9c: TGA / DTA / MS curves during the formation of PCTF-2 at a heating rate of 5 °C / min. The MS curve shows the ion current (in 10^{-12} A) at m/z = 27, corresponding to HCN⁺.

8. Powder X-ray diffraction patterns of PCTF-1 and PCTF-2



Fig. S10a: Powder X-ray diffraction pattern of PCTF-1.



Fig. S10b: Powder X-ray diffraction pattern of PCTF-2. 2 θ values from the peak maxima were computed into a lattice spacing by the Bragg equation $n\lambda = 2d \sin\theta$.



Fig. S11a: Top: Schematic drawing of a larger section of an idealized triazine network built from the tetranitrile **1**. It is evident that there will be not small repeat unit. In addition, the idealized network cannot be planar but has to extent above and below the plane, e.g. as indicated at the nitrile rings with truncated wedged and dashed bonds.

Bottom: Possible lattice plane spacings indicated by red and green lines. For clarity only two of the frequent spacings between the nitrile aryl rings are indicated.

The diffractogram of PCTF-1 shows one broad peak centered around $2\theta = 10.2^{\circ}$.

The diffractogram of PCTF-2 exhibit two broad peaks centered around $2\theta = 10.2^{\circ}$ and $2\theta = 24.9^{\circ}$, respectively. In addition there is a sharper reflection at $2\theta = 17.8^{\circ}$.

From the Bragg equation $n\lambda = 2d \sin\theta$ the 2 θ values of 10.2°, 17.8° and 24.9° were computed into lattice spacings d = 8.7 Å, 5.0 Å and 3.6 Å, respectively.

The experimentally determined lattice spacing of ~8.7 Å in both PCTF-1 and -2 may correspond to the distance between lattice planes originating from the triazine rings.

The experimentally determined lattice spacing of ~5.0 Å in PCTF-2 may be assigned to the distance between lattice planes from the aryl rings of the tetra-aryl-ethylene building unit.

Finally, the experimentally determined lattice spacing of ~3.6 Å in PCTF-2 can be due to the stacking distances of layer motifs which would be in the π - π stacking range of 3.5–3.7 Å.

The less-porous material PCTF-2 which was synthesized with less $ZnCl_2$ can be assumed to contain a larger portion of ordered aryl rings of the tetra-aryl-ethylene building unit and π - π stacking of layer motifs.

It was not feasible to assume for PCTF-1 and PCTF-2 a 2D hexagonal model as in S. Ren, M. J. Bojdys, R. Dawson, A. Laybourn, Y. Z. Khimyak, D. J. Adams and A. I. Cooper, *Adv. Mater.*, 2012, **24**, 2357-2361. In this literature source the 2D models were based on CTFs from di- or trinitriles.

9. Gas uptake

Table S2: N₂ (BET surface area), H₂, CO₂ and CH₄ adsorption of PCTF-1 and -2.

Compounds	$\frac{S_{BET}}{(m^2/g)^{a)}}$	S_{Lang} (m ² /g)	CH ₄ (cm ³ /g) at 273 K, 1 bar	CO ₂ (cm ³ /g) at 273 K, 1 bar	H ₂ (wt %) at 77 K, 1 bar
PCTF-1 sample from batch 1	2235	2778	23.6	73.0	1.86
PCTF-1 sample from batch 2	2125	2641	b)	b)	b)
PCTF-2	783	1013	15.1	41.5	0.9

^{a)}Calculated BET surface area over the pressure range $0.01-0.05 P/P_0$; ^{b)} not measured.



Fig. S12: NL-DFT pore size distribution curve of PCTF-1.



Fig. S13: NL-DFT pore size distribution curve of PCTF-2.



Fig. S14: CO₂ sorption isotherms at 273 K and 293 K for PCTF-1.



Fig. S15: CH₄ sorption isotherms at 273 K and 293 K for PCTF-1.



Fig. S16: CO₂ sorption isotherms at 273 K and 293 K for PCTF-2.



Fig. S17: CH₄ sorption isotherms at 273 K and 293 K for PCTF-2.



Fig. S18: H₂ adsorption of tetra(4-cyanophenyl)ethylene, compound 1 at 77 K.



Fig. S19: CO₂ adsorption of tetra(4-cyanophenyl)ethylene, compound 1 at 273 K.

10. Selectivity

Selectivities were estimated from the ratio of the initial slopes in the Henry region of the adsorption isotherms.

Table	S3:	Initial	slopes	of adsor	rption i	isotherms	and	selectivities	for	$CO_2:N_2$	and	CO ₂ :CI	\mathbf{H}_4 at	273
	and	l 293 K	PCTF-	-1 and -2	2.									

	1 4114 21								
	initial slopes for gas adsorption isotherms								
	C	O ₂	N_2	CH ₄					
Compounds	s at 273 K at 293 K		at 273 K	at 273 K	at 293 K				
PCTF-1	120	64	9	25	20				
PCTF-2 80.5		42	9	22	13				
	gas selectivities								
	CO ₂ :N ₂ se	lectivity at	CO ₂ :CH ₄ selectivity	CO ₂ :CH ₄ selectivity					
	273	3 K	at 273 K	at 293 K					
PCTF-1	13:1		5:1	3:1					
PCTF-2	9	:1	4:1	3:1					



Fig. S20: The initial slope in the Henry region of the adsorption isotherms of CO₂ (red) and CH₄ (blue) of PCTF-1 at 273 K.



Fig. S21: The initial slope in the Henry region of the sorption isotherms of CO_2 (red) and CH_4 (blue) of PCTF-1 at 293 K.



Fig. S22: The initial slope in the Henry region of the adsorption isotherms of CO₂ (red) and CH₄ (blue) of PCTF-2 at 273 K.



Fig. S23: The initial slope in the Henry region of the adsorption isotherms of CO₂ (red) and CH₄ (blue) of PCTF-2 at 293 K.



Fig. S24: The initial slope in the Henry region of the sorption isotherms of N₂ at 273 K of PCTF-1 (red) and PCTF-2 (blue).

11. X-ray crystallography

Suitable single crystals were carefully selected under a polarizing microscope. *Data collection*: Compound 1: Bruker Kappa APEX2 CCD diffractometer (with microfocus tube), Cu–K α radiation ($\lambda = 1.54178$ Å), multilayer mirror monochromator, ω - and φ -scan at 173 ± 2 K; data collection with Apex2,⁴ cell refinement and data reduction with SAINT,⁴ experimental absorption correction with SADABS.⁵ *Structure analysis and refinement*: The structure of **1** was solved by direct methods using SHELXS-97; refinement was done by full-matrix least squares on F^2 using the SHELXL-97 program suite.⁶ All non-hydrogen positions were refined with anisotropic displacement parameters. Hydrogen atoms were partly determined during the refinement, the remaining ones were positioned geometrically and refined using riding models with U_{iso}(H) = 1.2 U_{eq}(CH, CH₂).

The solvent ethanol molecule in the channels of compound **1** was found highly disordered and could not be properly defined. Hence, the option SQUEEZE in PLATON for Windows⁷ was used to refine the framework structure without the disordered electron density in the voids. Four ethanol molecules per unit cell were squeezed. Several crystals of **1** were measured both at room and low temperature. Because of the high symmetry not only small crystals but also larger crystals of the size up to 0.3 x 0.3 x 0.2 mm³ do not diffract over $2\theta \approx 77^{\circ}$. For this reason the 2 θ angle was decided to be limited to 79° for the given measurement, which causes Alerts level A: "ratio of reflections to parameters < 6", "value of sine(theta_max) / wavelength is less than 0.550" and "poor data / parameter ratio". Graphics were drawn with DIAMOND.⁸

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