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

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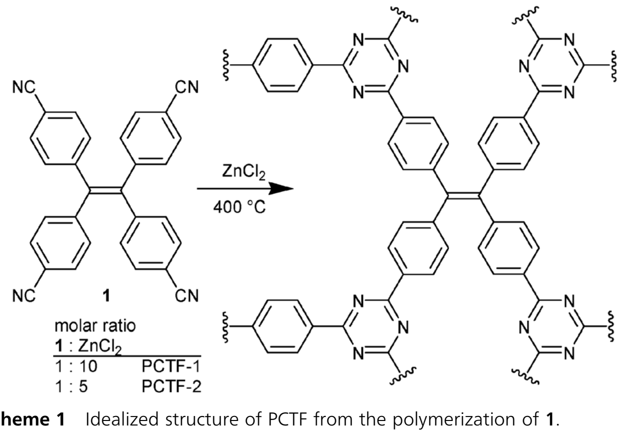
Transformation of tetra(4-cyanophenyl)ethylene under Lewis acidic ($ZnCl_2$) conditions at 400 °C leads to the formation of a porous covalent triazine-based organic framework (CTF) with a high surface area (2235 $m^2\ g^{-1}$), high CO_2 and CH_4 uptakes and the highest hydrogen uptake for a CTF material (1.86 wt% at 77 K, 1 bar).

Microporous organic polymers (MOPs) have attracted huge attention because of their potential applications in gas storage, separation, catalysis and optoelectronics.[1,2] A variety of MOPs with permanent porosity such as benzimidazole-linked polymers (BILPs),[2] hyper-cross-linked polymers (HCPs),[3] polymers of intrinsic microporosity (PIMs),[4] porous aromatic frameworks (PAFs),[5] conjugated microporous polymers (CMPs),[6] covalent organic frameworks (COFs),[7] covalent triazine-based organic frameworks (CTFs)[8] have been prepared by combinations of reversible and irreversible organic reactions[7a] and with differing gas uptake capacities.[1] MOPs have advantages, such as high stability (around 600 °C), permanent porosity with high specific surface area and light weight in contrast to metal–organic frameworks (MOFs). MOPs are mainly constructed by light elements through strong covalent bonds (*e.g.*, C–C, C–N, C–O), hence they have low densities. These features make these materials attractive for applications in which weight reduction is crucial.

Kuhn, Antonietti and Thomas *et al.* developed CTFs with permanent porosity.[8–10] In contrast to COFs or other MOPs, CTFs are interesting because of advantages such as very cheap and readily available starting materials, easy synthesis and hydrophilicity. Porous CTF materials can be synthesized by an ionothermal reaction between aromatic nitriles and $ZnCl_2$ which can be adapted to a large scale. Molten $ZnCl_2$ acts as a Lewis acid and solvent (porogen) for the polymerization. A trimerization reaction of nitrile groups can construct triazine rings. To date, CTFs from 1,4-dicyanobenzene (terephthalonitrile) have provided high surface areas (over 3000 $m^2\ g^{-1}$) only at high temperatures, *i.e.*, heating to 400 °C for 20 h and then to 600 °C for 96 h.[9] Heating to 400 °C gave a lower surface area of only 1710 $m^2\ g^{-1}$.[10] A high surface area CTF of 2390 $m^2\ g^{-1}$ could be obtained by using microwave ionothermal conditions, albeit in low yield and in a difficult-to-control reaction.[11,12] Very recently, CTFs with surface areas of up to 1152 $m^2\ g^{-1}$ were synthesized with strong Brønsted acids, such as trifluoromethanesulfonic acid, under both room temperature and microwave assisted conditions.[13]

Strong Brønsted acid conditions provide lower surface areas but they avoid decomposition and condensation reactions such as C–H bond cleavage and carbonization.[14] In contrast to strong Brønsted acids, ionothermal conditions offer the significant advantages of cheap, easy handling and yielding materials with high surface areas. Here we have employed the new tetranitrile, tetra(4-cyanophenyl)ethylene **1** (see ESI‡ for synthesis and characterization) to obtain two novel porous covalent triazine-based organic frameworks (PCTFs) identified as PCTF-1 and PCTF-2 by using different ratios of $ZnCl_2$ (Scheme 1).

The solid-state structure of the tetranitrile **1** already shows a 3D supramolecular network organized by π-stacking (Fig. 1) with potential porosity.§ The material was activated by degassing at 100 °C under high vacuum (10^{-6} Torr) for 24 h. While the pores



1 : $ZnCl_2$	
1 : 10	PCTF-1
1 : 5	PCTF-2

Scheme 1 Idealized structure of PCTF from the polymerization of **1**.

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† Dedicated to Prof. Dr Werner Uhl for his 60th birthday.

‡ Electronic supplementary information (ESI) available: Experimental part, NMR, IR, TG-MS, XRD, gas uptake and selectivity. CCDC 924716. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc41382a

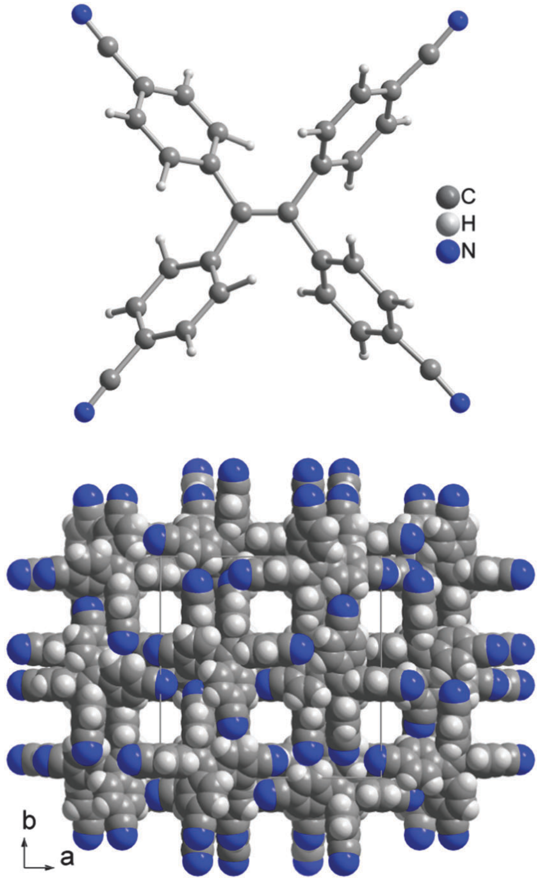

Fig. 1 Molecular unit (top) and packing diagram (bottom) of the solid-state structure of **1**. Solvent molecules in channels along the *c* direction are not shown.

were too narrow for N_2 adsorption at 77 K (kinetic hindrance), H_2 and CO_2 (77 K and 273 K, respectively) were adsorbed up to 8.9 and 7.6 $cm^3\ g^{-1}$ (as found for other organic frameworks),[15] corresponding to 0.08 and 1.49 wt%, respectively at $P/P_0 = 0.95$ bar.

The aim of the synthesis of CTFs is to obtain high surface areas at lower temperatures (400 °C) instead of 500–700 °C to reduce energy and avoid unnecessary decomposition. Here, a mixture of **1** and $ZnCl_2$ in quartz ampoules was heated at 400 °C for 48 h. The crude product was stirred in water and diluted HCl for 24–48 h (see ESI‡). The yield of the frameworks (PCTF-1 and PCTF-2) is around 90%. In FT-IR the intense CN band around 2226 cm^{-1} disappeared for both materials, indicating complete reaction of the nitrile groups (Fig. S6, ESI‡).[9] From TGA it was observed that the PCTFs start to decompose with significant weight loss only above 450 °C (Fig. S8, ESI‡). Elemental analysis (Table S1, ESI‡) of these frameworks indicate nitrogen elimination during the polymerization reaction. In TG-MS the formation of CN and HCN was observed (Fig. S9, ESI‡). Powder X-ray diffraction of the frameworks confirmed their expected amorphous nature. Scanning electron microscopy images illustrate macro- and mesoporosity with the porosity of PCTF-1 being more homogeneous than that of PCTF-2 (Fig. 2).

Nitrogen sorption studies of PCTF-1 and PCTF-2 at 77 K (Fig. 3) showed a first step at $P/P_0 < 0.05$ corresponding to gas sorption in micropores. The nitrogen uptake at low pressures increases from PCTF-1 to PCTF-2 concomitantly with a gain in the overall surface area. PCTF-1 provided a remarkable surface area of 2235 $m^2\ g^{-1}$ (Table 1) with the type IV isotherm and an associated H2 type hysteresis, typical for a microporous material with additional mesoporosity,[7,9] possibly formed by close-packed nanoparticles (Fig. 3). PCTF-2 exhibited a surface area of 784 $m^2\ g^{-1}$. Only a small degree of hysteresis was observed upon desorption. The isotherm is of type II with some type IV character, indicating a material with relatively large pores (Fig. 3). The surface area and pore volume depend on the amount of $ZnCl_2$ porogen.

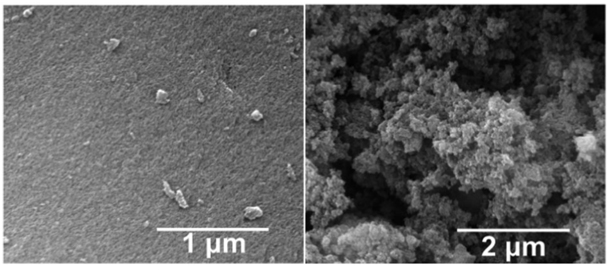

Fig. 2 Scanning electron micrographs of PCTF-1 (left) and PCTF-2 (right).

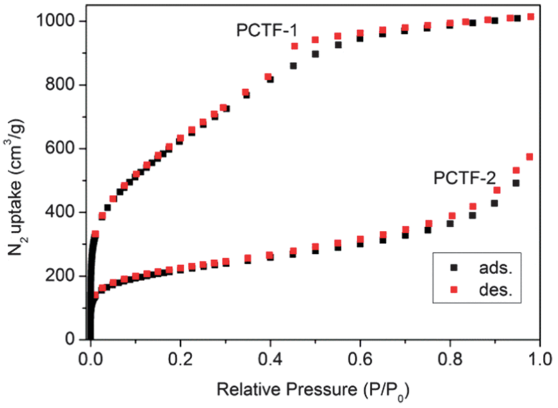

Fig. 3 N_2 sorption isotherms of PCTF-1 and PCTF-2 at 77 K.

Non-local density functional theory (NLDFT) pore size distributions using a slit pore model for PCTF-1 and PCTF-2 indicate that a significant fraction of the pores surface still originates from micropores with a diameter less than 2 Å (Fig. 4, $V_{0.1}$ in Table 1). Supermicropores are expected for CTFs between 10 and 20 Å due to the triazine system and pore opening of the hexamer.[9] However, this fraction is much smaller for PCTF-2 than PCTF-1. For PCTF-1 the additional mesopores are broadly distributed between 20 and 60 Å. For PCTF-2 the pore size distribution extends from 20 Å to well over 100 Å. The level of microporosity was compared by the ratio of micropore to total pore volume ($V_{0.1}/V_{tot}$, Table 1). $V_{0.1}/V_{tot} \sim 0.5$ and less indicates the presence and increasing dominance of mesopores.[16]

Most interestingly, PCTF-1 adsorbs 1.86 wt% H_2 at 77 K and 1 bar (Fig. 5). To the best of our knowledge, this is the highest value reported for any type of CTFs. The polymer from

Table 1 Porosity data for PCTFs from N_2 isotherms at 77 K

Comp	S_{BET} ^{a} ($m^2\ g^{-1}$)	S_{Lang} ($m^2\ g^{-1}$)	$V_{0.1}$ ^{b} ($cm^3\ g^{-1}$)	V_{tot} ^{c} ($cm^3\ g^{-1}$)	$V_{0.1}/V_{tot}$
PCTF-1	2235	2777	0.79	1.56	0.51
PCTF-2	784	1313	0.29	0.76	0.38

[a] Calculated BET surface area over the pressure range 0.01–0.05 P/P_0. [b] Pore volume at $P/P_0 = 0.1$. [c] Total pore volume at $P/P_0 = 0.95$.

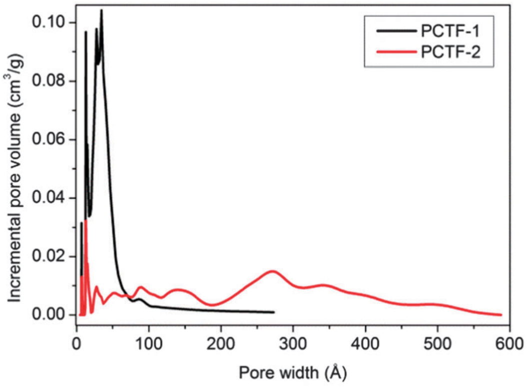

Fig. 4 NL-DFT pore size distribution curve of PCTF-1 and PCTF-2.

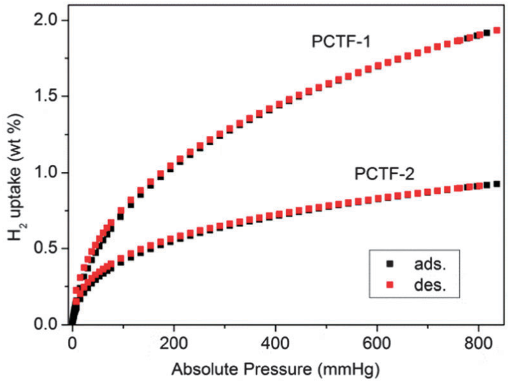

Fig. 5 H_2 sorption isotherms for PCTF-1 and PCTF-2 at 77 K.

Table 2 H_2, CO_2 and CH_4 uptakes of PCTF-1 and PCTF-2 at 1 bar

Comp	H_2 [a] (wt%)	CO_2 [b] ($cm^3\ g^{-1}$)	CO_2 [c] ($cm^3\ g^{-1}$)	CH_4 [b] ($cm^3\ g^{-1}$)	CH_4 [c] ($cm^3\ g^{-1}$)
PCTF-1	1.86	73.0	44.9	23.6	15.2
PCTF-2	0.9	41.5	24.2	15.1	8.0

[a] H_2 uptake at 77 K. [b] Gas uptake at 273 K. [c] Gas uptake at 293 K.

4,4′-biphenyldicarbonitrile adsorbs 1.55 wt% H_2 at 1 bar, 77 K.[8] Microwave-obtained ionothermal CTFs showed H_2 uptake capacities ranging from 0.7 to 1.78 wt% at 1 bar and 77 K.[11] At the same time, PCTF-2 adsorbed 0.9 wt% H_2 at 77 K and 1 bar. The CO_2 and CH_4 uptake capacities of the PCTFs were measured at two different temperatures at 1 bar (Table 2, Fig. S14–S17 in ESI‡). The volume of CO_2 adsorbed on PCTF-1 at 273 K with 73 $cm^3\ g^{-1}$ lies towards the upper end when compared to other CTFs which showed CO_2 uptakes of 20–93 $cm^3\ g^{-1}$ at 273 K and 1 bar.[13] The volume of CH_4 adsorbed on PCTF-1 is 23.6 $cm^3\ g^{-1}$ at 273 K. Noteworthily, for CTFs no CH_4 sorption data have been recorded yet. In line with the smaller surface area and pore volume the gas uptake capacity of PCTF-2 is roughly half that of PCTF-1.

Moreover, the CO_2 uptake capacity is higher than the CH_4 uptake capacity at 273 K and 293 K at 1 bar, indicating the selectivity of CO_2 sorption over CH_4 sorption. The ratio of the initial slopes in the Henry region of the adsorption isotherms (Fig. S20–S24 in ESI‡)[17,18] determines the selectivities exhibited by PCTF-1 and PCTF-2 for adsorption of CO_2 over N_2 and for CO_2 over CH_4. PCTF-1 shows selectivity ratios of 13 : 1 and 5 : 1 for $CO_2 : N_2$ and $CO_2 : CH_4$, respectively, at 273 K. The selectivity of PCTF-1 or PCTF-2 does not depend only on the size of the gas components (kinetic diameter: CO_2 3.3 Å, N_2 3.6 Å and CH_4 3.8 Å) but also on the polarizability of the surface and of the gas components. Recently, Cooper *et al.* calculated $CO_2 : N_2$ selectivities for various CTFs between 16 and 31 at 273 K using the Ideal Adsorbed Solution Theory (IAST).[13]

In summary, tetranitrile tetra(4-cyanophenyl)ethylene not only gives a porous supramolecular network but also yields a porous CTF with a high surface area already at 400 °C under ionothermal conditions. PCTF-1 shows the highest H_2 uptake capacity (1.86 wt%) for a CTF material. Such a tetranitrile provides a novel strategy for the development of functional CTF materials with a high surface area and gas storage capacity.

Notes and references

§ Crystal data for **1**: $C_{30}H_{16}N_4$, M = 432.47 g mol^{-1}, tetragonal, $I4_1/acd$, a = 22.0767(8) Å, c = 21.1707(10) Å, V = 10318.2(7) Å^3, Z = 16, μ(Cu-Kα) = 0.543 mm^{-1}, T = 173(2) K, 10 909 reflections measured, 753 independent (R_{int} = 0.0295), final R_1 0.0592 ($I > 2\sigma(I)$), wR_2 = 0.1693 (all data), goodness of fit on F^2 = 1.105. CCDC 924716.

1 S.-Y. Ding and W. Wang, *Chem. Soc. Rev.*, 2013, **42**, 548–568; Y. Jin, Y. Zhu and W. Zhang, *CrystEngComm*, 2013, **15**, 1484–1499; Z. Xiang and D. Cao, *J. Mater. Chem. A*, 2013, **1**, 2691–2718; N. B. McKeown and P. M. Budd, *Macromolecules*, 2010, **43**, 5163–5176; R. Dawson, A. I. Cooper and D. J. Adams, *Prog. Polym. Sci.*, 2012, **37**, 530–563; J. Germain, J. M. J. Fréchet and F. Svec, *Small*, 2009, **5**, 1098–1111; P. Kaur, J. T. Hupp and S. T. Nguyen, *ACS Catal.*, 2011, **1**, 819–835; U. H. F. Bunz, *Chem. Rev.*, 2000, **100**, 1605–1644.
2 M. G. Rabbani and H. M. El-Kaderi, *Chem. Mater.*, 2012, **24**, 1511–1517.
3 J. Germain, J. Hradil, J. M. J. Fréchet and F. Svec, *Chem. Mater.*, 2006, **18**, 4430–4435.
4 B. S. Ghanem, K. J. Msayib, N. B. McKeown, K. D. M. Harris, Z. Pan, P. M. Budd, A. Butler, J. Selbie, D. Book and A. Walton, *Chem. Commun.*, 2007, 67–69.
5 T. Ben, H. Ren, S. Ma, D. Cao, J. Lan, X. Jing, W. Wang, J. Xu, F. Deng, J. M. Simmons, S. Qiu and G. Zhu, *Angew. Chem., Int. Ed.*, 2009, **48**, 9457–9460.
6 J.-X. Jiang, F. Su, A. Trewin, C. D. Wood, N. L. Campbell, H. Niu, C. Dickinson, A. Y. Ganin, M. J. Rosseinsky, Y. Z. Khimyak and A. I. Cooper, *Angew. Chem., Int. Ed.*, 2007, **46**, 8574–8578.
7 (*a*) S. Kandambeth, A. Mallick, B. Lukose, M. V. Mane, T. Heine and R. Banerjee, *J. Am. Chem. Soc.*, 2012, **134**, 19524–19527; (*b*) A. I. Cooper, *CrystEngComm*, 2013, **15**, 1483; (*c*) K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol and T. Siemieniewska, *Pure Appl. Chem.*, 1985, **57**, 603–619.
8 P. Kuhn, M. Antonietti and A. Thomas, *Angew. Chem., Int. Ed.*, 2008, **47**, 3450–3453.
9 P. Kuhn, A. l. Forget, D. Su, A. Thomas and M. Antonietti, *J. Am. Chem. Soc.*, 2008, **130**, 13333–13337.
10 P. Kuhn, A. Thomas and M. Antonietti, *Macromolecules*, 2009, **42**, 319–326.
11 W. Zhang, C. Li, Y.-P. Yuan, L.-G. Qiu, A.-J. Xie, Y.-H. Shen and J.-F. Zhu, *J. Mater. Chem.*, 2010, **20**, 6413–6415.
12 Several attempts to synthesize CTFs under microwave irradiation at high temperature were unsuccessful in our hands and led only to damages of the microwave as well as the crucible in the solid-state reaction. Under these reaction conditions we also observed only low yield of the product from 1,4-dicyanobenzene.
13 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.
14 I. B. Johns, E. A. McElhill and J. O. Smith, *Ind. Eng. Chem. Prod. Res. Dev.*, 1962, **1**, 277–281.
15 Y. Jin, B. A. Voss, R. McCaffrey, C. T. Baggett, R. D. Noble and W. Zhang, *Chem. Sci.*, 2012, **3**, 874–877.
16 R. Dawson, A. Laybourn, R. Clowes, Y. Z. Khimyak, D. J. Adams and A. I. Cooper, *Macromolecules*, 2009, **42**, 8809–8816.
17 V. Abetz, T. Brinkmann, M. Dijkstra, K. Ebert, D. Fritsch, K. Ohlrogge, D. Paul, K. V. Peinemann, S. Pereira-Nunes, N. Scharnagl and M. Schossig, *AIChE J.*, 2006, **8**, 328–358.
18 Y.-S. Bae, O. K. Farha, A. M. Spokoyny, C. A. Mirkin, J. T. Hupp and R. Q. Snurr, *Chem. Commun.*, 2008, 4135–4137.