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

Asamanjoy Bhunia, Vera Vasylyeva and Christoph Janiak*

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Transformation of tetra(4-cyanophenyl)ethylene under Lewis acidic (ZnCl₂) conditions at 400 °C leads to the formation of a porous covalent triazine-based organic framework (CTF) with a high surface area (2235 m² g⁻¹), high CO₂ and CH₄ uptakes and the highest hydrogen uptake for a CTF material (1.86 wt% at 77 K, 1 bar).

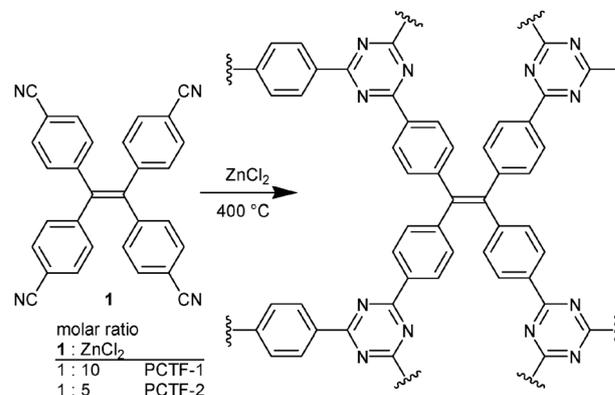
Microporous organic polymers (MOPs) have attracted huge attention because of their potential applications in gas storage, separation, catalysis and optoelectronics.^{1,2} A variety of MOPs with permanent porosity such as benzimidazole-linked polymers (BILPs),² hyper-cross-linked polymers (HCPs),³ polymers 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 ZnCl₂ which can be adapted to a large scale. Molten ZnCl₂ 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 m² 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 m² g⁻¹.¹⁰ A high surface area CTF of 2390 m² 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 m² 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 ZnCl₂ (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



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

Institut für Anorganische Chemie und Strukturchemie, Universität Düsseldorf,
40204 Düsseldorf, Germany. E-mail: janiak@uni-duesseldorf.de;

Fax: +49-211-81-12287; Tel: +49-211-81-12286

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

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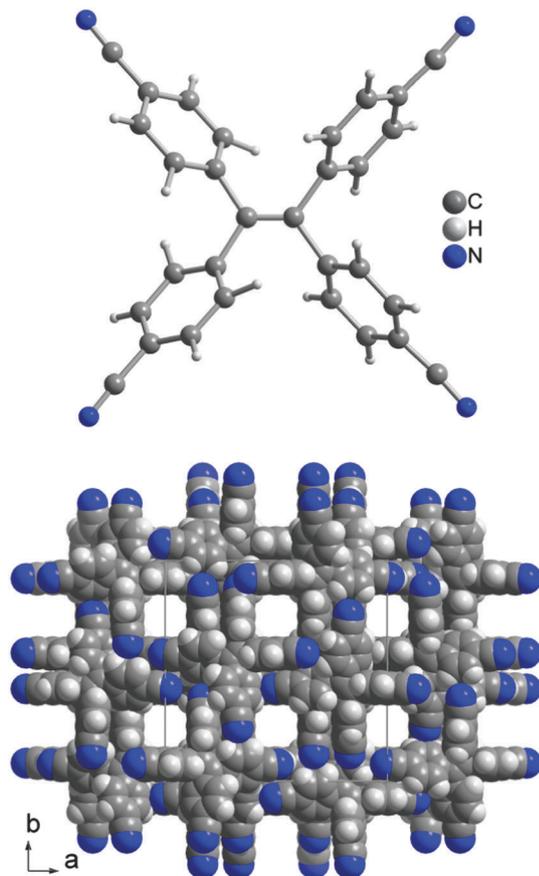


Fig. 1 Molecular unit (top) and packing diagram (bottom) of the solid-state structure of **1**. Solvent molecules in channels along the *c* direction are not shown.

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 $2235 m^2 g^{-1}$

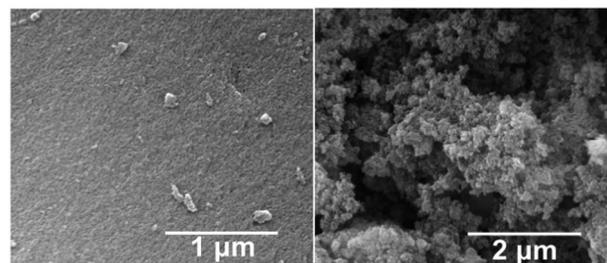


Fig. 2 Scanning electron micrographs of PCTF-1 (left) and PCTF-2 (right).

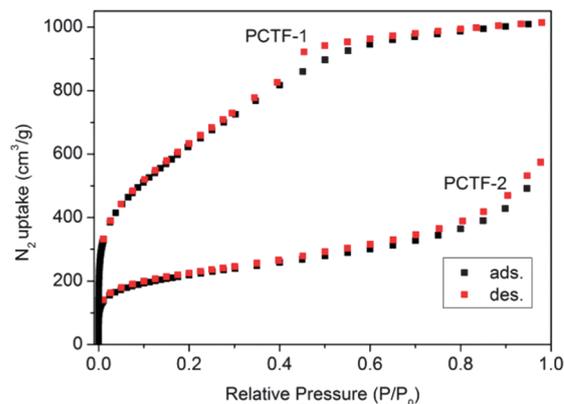


Fig. 3 N_2 sorption isotherms of PCTF-1 and PCTF-2 at 77 K.

(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.

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}^b ($m^2 g^{-1}$)	$V_{0.1}^b$ ($cm^3 g^{-1}$)	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 $P/P_0 = 0.95$.

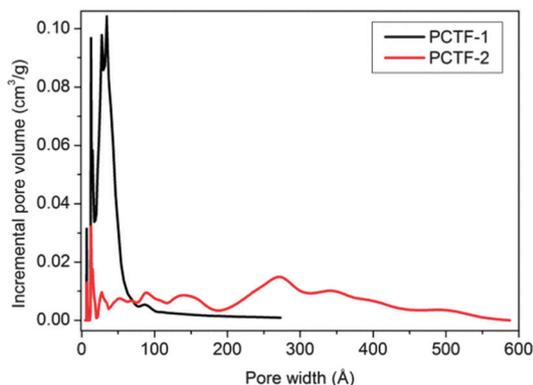


Fig. 4 NL-DFT pore size distribution curve of PCTF-1 and PCTF-2.

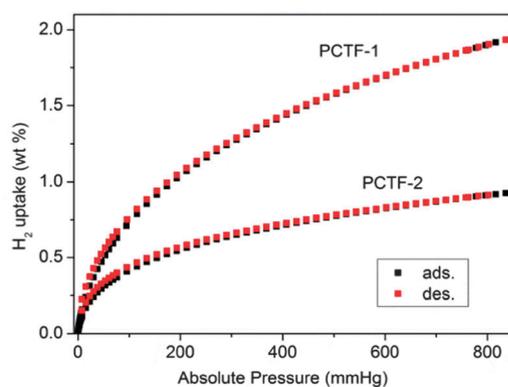


Fig. 5 H₂ sorption isotherms for PCTF-1 and PCTF-2 at 77 K.

Table 2 H₂, CO₂ and CH₄ 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 H₂ uptake at 77 K. ^b Gas uptake at 273 K. ^c Gas uptake at 293 K.

4,4'-biphenyldicarbonitrile adsorbs 1.55 wt% H₂ at 1 bar, 77 K.⁸ Microwave-obtained ionothermal CTFs showed H₂ 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% H₂ at 77 K and 1 bar. The CO₂ and CH₄ uptake capacities of the PCTFs were measured at two different temperatures at 1 bar (Table 2, Fig. S14–S17 in ESI†). The volume of CO₂ adsorbed on PCTF-1 at 273 K with 73 cm³ g⁻¹ lies towards the upper end when compared to other CTFs which showed CO₂ uptakes of 20–93 cm³ g⁻¹ at 273 K and 1 bar.¹³ The volume of CH₄ adsorbed on PCTF-1 is 23.6 cm³ g⁻¹ at 273 K. Noteworthy, for CTFs no CH₄ 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 CO₂ uptake capacity is higher than the CH₄ uptake capacity at 273 K and 293 K at 1 bar, indicating the selectivity of CO₂ sorption over CH₄ 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 CO₂ over N₂ and for CO₂ over CH₄. PCTF-1 shows selectivity ratios of 13:1 and 5:1 for CO₂:N₂ and CO₂:CH₄,

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: CO₂ 3.3 Å, N₂ 3.6 Å and CH₄ 3.8 Å) but also on the polarizability of the surface and of the gas components. Recently, Cooper *et al.* calculated CO₂:N₂ 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 H₂ 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: C₃₀H₁₆N₄, *M* = 432.47 g mol⁻¹, tetragonal, *I*₄*1*/*acd*, *a* = 22.0767(8) Å, *c* = 21.1707(10) Å, *V* = 10318.2(7) Å³, *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* > 2σ(*I*)), *wR*₂ = 0.1693 (all data), goodness of fit on *F*² = 1.105. CCDC 924716.

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