VIP Porous Organic Crystals

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# Rational Construction of an Extrinsic Porous Molecular Crystal with an Extraordinary High Specific Surface Area**

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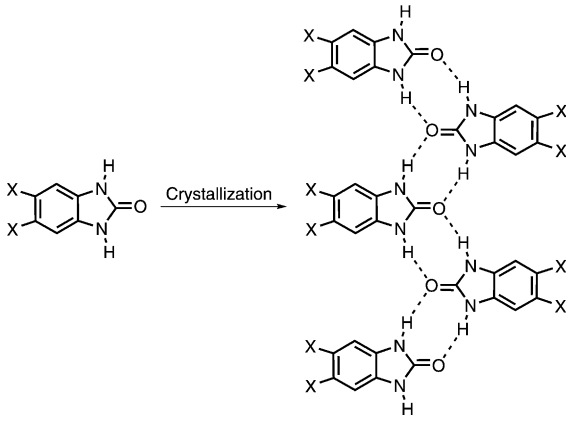
Apart from well-established porous materials, such as zeolites,[1] metal–organic frameworks (MOFs),[2] covalent organic frameworks (COFs), or amorphous polymeric organic materials,[3] porous compounds consisting exclusively of discrete organic molecules can be classified as a relatively new type of material.[4] Such materials can be subdivided mainly into two kinds: intrinsic and extrinsic porous materials.[4] Intrinsic porosity is defined as porosity that is already inherent in the molecular structure, such as shape-persistent voids, clefts, or cavities. Typical compounds that form intrinsic pores in the solid state are calixarenes,[5] cucurbiturils,[6] or shape-persistent organic cage compounds.[7] It was shown that shape-persistent cage compounds seem to be superior within this subclass of materials,[8] with Brunauer–Emmett–Teller (BET) surface areas of up to 2071 $m^2 g^{-1}$.[9]

In contrast to the high surface areas of the intrinsic porous organic materials, the values of extrinsic porous materials are significantly smaller. One of the first examples is tris(phenylenedioxy)cyclophasphazene (TPP), which was introduced in 1964 by Allcock and co-workers.[10] Sozzani et al. demonstrated first that crystals of TPP can be permanently porous, and later, Hulliger et al. reporting a Langmuir surface area of 240 $m^2 g^{-1}$.[11]

The prediction of the assembling of molecules in the solid state is still very difficult,[12] therefore it seems to be more promising to search for existing compounds that obviously exhibit pores in the crystalline state, but have not yet been proven to be permanently porous.[13] McKeown and co-workers defined some useful criteria for such a search, and revealed that there are already quite a number of potential compounds, which fulfill those criteria.[14] For 3,3′,4,4′-tetrakis(trimethylsilylethynyl)biphenyl (TTEB), they showed that this approach is successful: TTEB is permanently porous (BET surface area 278 $m^2 g^{-1}$) and adsorbs 0.8 wt% $H_2$ at 77 K and 10 bar.[14]

Re-investigations by Chen et al. demonstrated that HOF-1a, a compound introduced before,[15] is permanently porous, with a BET surface area of 359 $m^2 g^{-1}$ and selective adsorption of ethylene over ethane.[16] Other extrinsic porous materials from discrete organic molecules with relatively high surface areas are SOF-1a,[17] (BET surface area: 474 $m^2 g^{-1}$), the triptycene-derived trinuclear nickel salphens of the MacLachlan group, with BET surface areas of up to 499 $m^2 g^{-1}$,[18] or the macrocyclic bis(urea) CBDU (BET surface area 341 $m^2 g^{-1}$).[19] The highest BET surface area of an extrinsic organic compound were reported for PUNCs (phthalocyanine unsolvated nanoporous crystals), with values between 850 and 1002 $m^2 g^{-1}$.[20]

Herein, we describe a rational approach of the construction of a readily accessible molecular precursor, which forms a permanent porous crystal with a very high specific surface area of 3020 $m^2 g^{-1}$. For the design of the molecular structure, we have taken into account McKeown's criteria[14] and have also systematically searched the Cambridge Structural Database for compounds that form flat ordered sheets by self-assembling by hydrogen bonding. Interestingly, almost all 4,5-disubstituted benzimidazolones[21,22] compounds formed nearly planar ribbon-like structures by directed H-bonds of the imidazolone units (Scheme 1). Therefore, we found benzimidazolones[21,22] to be a potential subunit for designing our molecular precursor, exploiting the chance to form




***Scheme 1.*** Formation of defined ribbon-like structures in the crystalline state by H-bonding of 4,5-disubstituted benzimidazolones.[21,22] X = H, $CH_3$, F, Cl.

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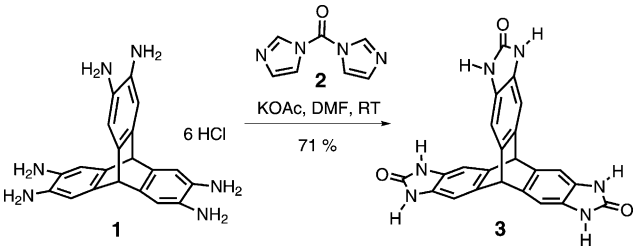
ribbon-like motifs to construct an extrinsic porous crystalline compound with one-dimensional channels.

We therefore incorporated the benzimidazolone unit into a rigid $D_{3h}$-symmetric scaffold by reacting hexaammonium triptycene hexachloride (**1**)[23] with carbonyldiimidazole (**2**) to give triptycenetrisbenzimidazolone **3** (TTBI) in 71% yield (Scheme 2). Single crystals suitable for X-ray diffraction




***Scheme 2.*** Synthesis of triptycene trisbenzimidazolone **3** (TTBI).

analysis were grown by slow vapor diffusion of acetone into a saturated DMSO solution of **3**.[24] The compound crystallizes in the tetragonal space group $P4_2/m$ with four molecules in the unit cell. These four molecules form one-dimensional cylindrical channels (Pore A in Figure 1) with an average diameter of approx. 14.5 Å (closest distances of two opposite molecules: $d(O\cdots O) = 13.8$ Å, $d$(bridgehead protons) = 16.1 Å) by a ribbon-like self-assembling of the imidazolone subunits by hydrogen bonds ($d(N\cdots O) = 2.88$ Å, $\sphericalangle(NHO) = 169°$; H-bonding pattern I). The dihedral angle of adjacent benzimidazolone subunits of the ribbon-like assemblies is with 24° larger than for the probably best comparable 4,5-dimethylbenzimidazolone (for which the dihedral angle was 15°).[21] The higher degree of tilting results in the tetragonal symmetry. Two of three benzimidazolone units are involved in forming the ribbon-like assembly, whereas one subunit forms another one-dimensional chainlike H-bonding structure with dihedral angles of two adjacent molecules of 90° ($d(N\cdots O) = 2.74$ Å, $\sphericalangle(NHO) = 139°$, H-bonding pattern II). By this pattern, additional slit-like pores (Pore B in Figure 1) are generated in between the cylindrical channels. The shortest distance is 3.8 Å for two opposite oxygen atoms, and the widest distance orthogonal to the slit elongation is 5.8 Å. Along the slit the distance is approximately 20 Å. The 1D channels (60% of the cell volume) are filled with highly disordered solvent molecules, which could not be refined satisfactorily. Therefore, the data were corrected for the influence of these solvents using the SQUEEZE routine function in PLATON,[25] resulting in an $R$ value of 0.0530. Furthermore, the calculated density of the solvent free network is 0.755 g cm$^{-3}$, which is much lower than the upper limit (0.9 g cm$^{-3}$) suggested by McKeown and co-workers for potential porous compounds.[14]

Because the pore dimensions exceed those of other reported crystalline extrinsic porous organic compounds (such is TPP, TTEB, SOF-1a), we investigated the material in terms of permanent porosity. TGA measurement of fresh prepared crystals showed a steady loose of roughly 20% mass upon heating until 440 °C, before decomposing (Supporting Information, Figure S5). Powder X-ray diffraction at different temperatures revealed a phase change already at ambient temperatures (Supporting Information, Figure S6). For the removal of solvent, we decided to not treat the porous assembling thermally to avoid any stress for the hydrogen bonding pattern. Instead, we exchanged the solvent inside the voids, first by immersing the sample in acetone (5 × 24 h) and second in $n$-pentane (3 × 24 h). The crystals were collected and the sample was degassed for 96 h at 30 °C and 0.01 mbar prior to measurements of nitrogen sorption at 77 K. The isotherm shows a steep slope at low $P/P_0$ values and a type I form that is typical for microporous materials (Figure 2).[26] Adsorption and desorption data points show no hysteresis and are nearly congruent, which is a hint for the stability of the three-dimensional network. The overall uptake of nitrogen is 754 cm$^3$ g$^{-1}$ at $P/P_0 = 0.95$. The measured BET surface area is 2796 m$^2$ g$^{-1}$ and the Langmuir surface area is 3020 m$^2$ g$^{-1}$.[27] The measurement of a second sample confirmed the reproducibility of the results (see values in parentheses in Table 1). To the best of our knowledge, these high surface areas exceed all reported values for microporous

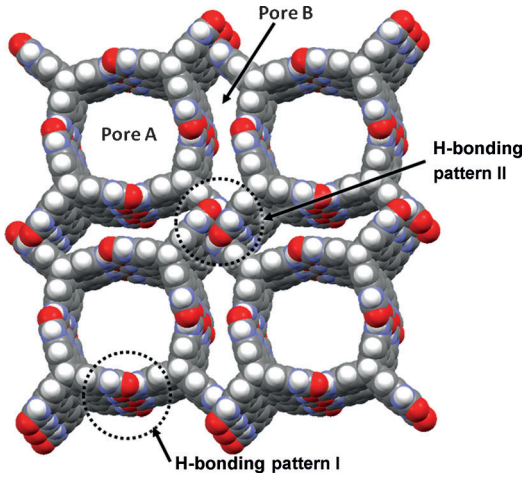



***Figure 1.*** Single-crystal X-ray structure of **3**. View along the crystallographic $c$ axis of a 2 × 2 × 2 unit cell. C gray, H white, O red, N blue.

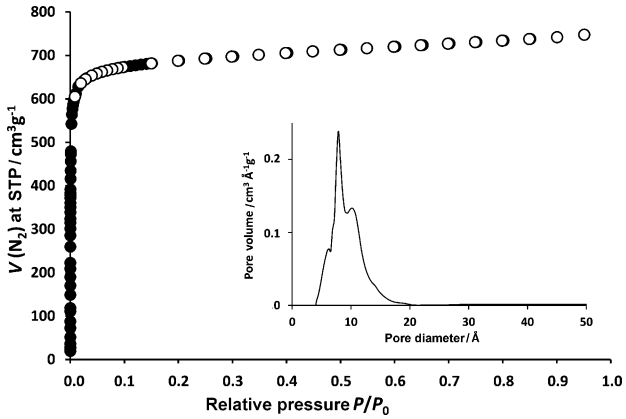



***Figure 2.*** Nitrogen sorption isotherm of activated **3** at 77 K: ● adsorption, ○ desorption. The inset shows the NLDFT pore-size distribution.

*Table 1:* Comparison of characteristic sorption data of selected extrinsic porous crystalline organic compounds.

| | $SA_{BET}$[a] $[m^2 g^{-1}]$ | $SA_{Langmuir}$[a] $[m^2 g^{-1}]$ | $V_{MP}$[b] $[cm^3 g^{-1}]$ | $V(N_2)$[c] $[cm^3 g^{-1}]$ | $V(CO_2)$[d] $[cm^3 g^{-1}]$ | $V(CH_4)$[d] $[cm^3 g^{-1}]$ | $V(H_2)$[e] $[cm^3 g^{-1}]$ |
|---|---|---|---|---|---|---|---|
| **3 (TTBI)** | **2796 (2783)** | **3020 (2974)** | **1.02** | **754 (748)** | **81** | **21** | **10.8** |
| PUNCs[20] | 850–1000 | –[f] | 0.40–0.46 | 291 | –[f] | –[f] | –[f] |
| SOF-1 a[17] | 474[g] | 639[g] | 0.23[g] | 143[g] | 16[h] | 32[i] | –[f] |
| HOF-1 a[16] | 359[j,k,l] | 609[j] | –[f] | –[f] | 225[m] | –[f] | –[f] |
| CBDU[19] | 341[j] | –[f] | –[f] | –[f] | 72[n] | –[f] | –[f] |
| TTEB[14] | 278 | –[f] | 0.16 | –[f] | –[f] | –[f] | 3.9[o] |
| TTP[11b,c] | –[f] | 240 | 0.09 | –[f] | 22[h] | 8.4[h] | |

[a] Determined by $N_2$ sorption at 77 K with data points in the range for $P/P_0$ between 0.01 and 0.04 for determining BET surface area and between 0.01 and 0.15 for the Langmuir surface area. [b] Calculated with the NL-DFT method. [c] Measured at 77 K and $P/P_0 \approx 0.95$. [d] Measured at 273 K and 1 bar. [e] Measured at 77 K and 1 bar. [f] Not reported. [g] Calculated from $N_2$ adsorption at 125 K and 1 bar. [h] Measured at 298 K and 1 bar. [i] Measured at 298 K and 16 bar. [j] Determined by $CO_2$ adsorption at 196 K. [k] Data points $P/P_0$ between 0.1 and 0.3. [l] BET C-constant is negative. [m] At 196 K and 1 bar. [n] 196 K, 1 bar at $P/P_0 = 0.5$. [o] At 77 K and 10 bar.

materials derived from discrete organic molecules, especially those that contain exclusively extrinsic pores (see Table 1).[20] The exceptional high surface area of the material can best be attributed to the fact that there is no lost of accessible surface of overlapping molecular π planes by π–π stacking. The molecules self-assemble by H-bonds exclusively, which can ideally be seen as point contacts, thus only a few molecular surface is sacrificed by the formation of the H-bonding ribbons.

By NL-DFT methods, a micropore volume of $V_{mp} = 1.02\ cm^3 g^{-1}$ was calculated. The pore-size distribution is quite narrow, with a maximum at 7.8 Å (NL-DFT method; see inset in Figure 2). The peak clearly shows a shoulder at approximately 10 Å. Re-examination of the sample by PXRD methods shows very sharp reflexes, confirming that the sample stays highly crystalline after gas sorption measurements (Supporting Information, Figure S12).[7d]

We investigated the adsorption of other gases, such as $CO_2$, $CH_4$, and $H_2$. The material adsorbed $80.7\ cm^3 g^{-1}$ (15.9 wt %) $CO_2$ at 273 K and 1 bar. To the best of our knowledge, this is the highest value reported for any porous material derived from discrete molecules and is even comparable to some of the best performing MOFs (for example $Co_4(OH)_2$(p-CDC) adsorbs 16.4 wt %).[28] A reasonable explanation for the relatively high amount of adsorbed $CO_2$ is probably an attractive interaction of the polar surface containing the benzimidazolone subunits with the quadrupolar $CO_2$. In contrast, only $21\ cm^3 g^{-1}$ of the nonpolar $CH_4$ was adsorbed at 1 bar and 273 K. This corresponds to $0.95\ mmol g^{-1}$ or 1.5 wt %.

Most interestingly, the material adsorbs $243\ cm^3 g^{-1}$ ($10.8\ mmol g^{-1}$; 2.2 wt %) of $H_2$ at 77 K and 1 bar. This is, again, the highest value reported for a material consisting only of one distinct compound. It is worthwhile to mention that for hydrogen adsorption at such conditions, the material can compete with the best performing MOFs that do not have any open metal sites, and is even comparable to the values reported for Mg-MOF-74 (2.2 wt % at 1 bar and 77 K),[29,30] which is a framework that does contain accessible metal sites.

To summarize, we demonstrated by a rational approach that an extrinsic porous material can be generated from readily accessible small organic molecules, which self-assemble by cooperative hydrogen bonding. The resulting microporous crystalline material is stable upon desolvation, and has an exceptional high surface area of $2796\ m^2 g^{-1}$ (BET model) or $3020\ m^2 g^{-1}$ (Langmuir model). This is the highest reported surface area of any porous material consisting of discrete molecules. Furthermore, the material adsorbs $CO_2$ (15.9 wt %) preferably to $CH_4$ (1.5 wt %) and also adsorbs a relatively high amount of $H_2$ (2.2 wt %).

Currently, we are designing more molecular structures that are potentially good candidates for the formation of highly porous organic crystals by directed H-bonding.

## Experimental Section

**3**: Hexaammoniumtriptycene hexachloride **1**[23] (140 mg), carbonyldiimidazole (160 mg), and potassium acetate (160 mg) were suspended in dry DMF (3 mL) and stirred four days at room temperature. The resulting yellow solid was collected by suction filtration, washed with water (3 × 10 mL) and diethyl ether (10 mL), and dried in vacuum, giving compound **3** as an off-white solid (150 mg, 71 %). Crystalline material was generated as follows: The trisbenzimidazolone **3** was dissolved in DMSO (5 mL) and diluted by acetone by vapor diffusion to give colorless needles after several days. $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta = 10.37$ ppm (s, 6 H), 6.95 (s, 6 H), 5.44 ppm (s, 3 H). $^{13}$C NMR (125 MHz, [D$_6$]DMSO): $\delta = 155.6$, 139.4, 125.7, 104.8, 52.2 ppm. IR (KBr-pellet): $\tilde{\nu} = 3415$ (s, br), 3239 (s, br), 1686 (vs, br), 1472 (s), 1370 (w), 1324 (m), 1204 (w), 1012 (w), 866 (w), 709 (m), 571 cm$^{-1}$ (s). ESI-HRMS (MeOH/DMSO/TFA): *m/z* calculated for $C_{23}H_{14}N_6O_3 \cdot C_2H_6SO$: 501.13395; found: 501.13310.

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[24] Data were collected on an Xcalibur/SuperNova from Oxford Diffraction with a copper microfocus source and focusing multilayer mirror optics. The structure was solved by direct methods and refined by full-matrix least squares on $F^2$ using SHELXTL-97.[31] All non-hydrogen atoms were refined using anisotropic thermal parameters. CCDC 866091 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.). Crystal Data for **3**: $T = 193(2)$ K, $C_{23}H_{14}N_6O_3$, $M = 422.40\ g\,mol^{-1}$, tetragonal space group $P4_2/m$, $a = b = 22.5124(2)$ Å, $c = 7.3367(1)$ Å, $V = 3718.30(7)$ Å$^3$, $Z = 4$, $D_C = 0.755\ g\,cm^{-3}$, $\mu = 0.433\ mm^{-1}$, $3.93° < \Theta < 72.97°$, reflections collected/unique 8363/3936, [$R$(int) = 0.0223], data(observed)/restrains/parameters 3110/0/154, GOF 1.197, final $R$[x$I$>2$\sigma$($I$)] $R1 = 0.0530$, $wR2$ (all data) = 0.1697, residual density 0.211 and $-0.260\ e\,A^{-3}$.

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