

Targeted synthesis of a mesoporous triptycene-derived covalent organic framework†

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The synthesis and characterization of a highly porous triptycene-derived covalent organic framework (TDCOF-5) and its performance in small gas storage are reported. TDCOF-5 crystallizes into a 2D mesoporous network that contains accessible boron sites, exhibits high surface area ($SA_{Lang} = 3832 \text{ m}^2 \text{ g}^{-1}$), and high gas uptake under low pressure settings.

Covalent organic frameworks (COFs) are highly porous microcrystalline materials that have received considerable attention as a result of their potential in areas that includes gas storage, catalysis, and electronics.¹ The formation of covalent bonds involved in connecting molecular building blocks during polymerization processes can retard crystalline network formation, however, COFs based on B–O,² C–N,³ and B–N⁴ bonds have been reported. In particular, COFs based on B–O bond formation are well investigated due to the kinetically labile nature of this bond which is essential for overcoming the crystallization problem of covalent networks.^{2a} Furthermore, 2D COFs are very common and their solid-state assembly is typically driven by electron rich building blocks that exhibit favorable π – π stacking interactions that can hinder the accessibility of boron sites. These sites are very relevant to gas storage applications as demonstrated by experimental and theoretical studies.⁵ Additionally, it has been proven that enhanced porosity can be attained through exposing the latent edges of building units which act as potential interaction sites during gas storage processes.⁶ Along this line, triptycene is known to allow for a high degree of internal molecular free volume,^{7,8} and therefore, triptycene-based porous materials possess enhanced adsorptive gas uptake capacities as demonstrated for polymers of intrinsic microporosity,⁹ shape-persistent cage molecules,¹⁰ metal salphens,¹¹ and MOFs.¹²

In this study we demonstrate for the first time the use of triptycene in constructing a mesoporous 2D COF that has a high surface area, accessible boron sites, and enhanced gas storage capacity. The synthesis of TDCOF-5 was performed by the

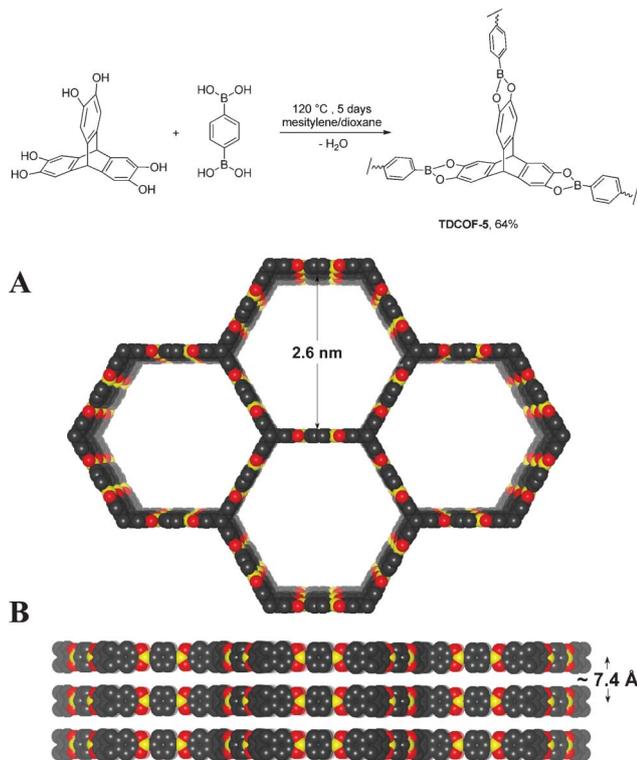
hydrothermal treatment of a mixture of 1,4-benzenediboronic acid and hexahydroxytriptycene in a solvent mixture of mesitylene–dioxane for 5 days at 120 °C (ESI†). TDCOF-5 was isolated and purified under an inert atmosphere of nitrogen and was investigated by spectral and analytical methods which included FT-IR, solid-state ¹¹B and ¹³C MAS, and elemental analysis while solid-state packing was determined by powder X-ray diffraction (PXRD) and materials modeling studies. TDCOF-5 was isolated as a white microcrystalline powder and purified by washing with anhydrous acetone then degassed at 120 °C/1.0 × 10^{−5} Torr for 16 h prior to characterization and porosity measurements (Scheme 1).

The formation of the boronate ester linkage was first established by FT-IR studies (Fig. S1, ESI†) which revealed a significant depletion of the boronic acid and hydroxyl bands and the formation of characteristic bands consistent with the boronate ester bond at 1352 cm^{−1} (B–O).² The solid-state ¹¹B and ¹³C NMR further supports the formation of the C₂O₂B ring and the incorporation of an intact triptycene moiety into the framework of TDCOF-5. The signal for ¹¹B MQ-MAS (Fig. S2, ESI†) was observed as a broad signal centered about 13.4 ppm, consistent with tri-coordinate boron signals, previously reported for COFs containing boronate ester linkages.² In addition, the ¹³C CP-MAS spectrum (Fig. S3, ESI†) contains signals that arise from the triptycene and phenyl building units. The TGA trace for activated TDCOF-5 indicated thermal stability at up to 420 °C under an argon atmosphere which is in line with most COFs (Fig. S5, ESI†). The morphology and phase purity of TDCOF-5 were investigated by scanning electron microscopy (Fig. S4, ESI†) which revealed aggregated rectangular prisms of ~150 nm in size.

The structure of TDCOF-5 was investigated by a combination of powder X-ray diffraction (PXRD) and material modeling studies. The experimental PXRD pattern (Fig. 1) confirms the formation of a microcrystalline material. Given the rigid and tritopic nature of hexahydroxytriptycene, its copolymerization with 1,4-benzenediboronic acid would lead to 2D networks having hexagonal channels that can stack in either eclipsed (AA, P6/mmm) or staggered (AB, P6₃/mmc) conformations.^{2a} As such, we constructed

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Scheme 1 Synthesis of TDCOF-5 and space-filling models showing solid-state (AA) stacking; top-view (A) and side-view (B); C (gray), O (red), B (yellow), hydrogen was omitted for clarity.

two models following methods reported for 2D COFs using a Materials Studio Visualizer and optimized their geometries and energies by the Forcite module.¹³ From the data presented in Fig. 1, it is clear that TDCOF-5 crystallizes into an eclipsed arrangement similar to those of 2D COFs that employ electron rich building units such as triphenylene, pyrene, and porphyrins.¹ As shown in Fig. 1, the calculated diffraction pattern of the eclipsed model which in this case is based on $P6/mmm$ space group matches well with that of TDCOF-5 and is in sharp contrast

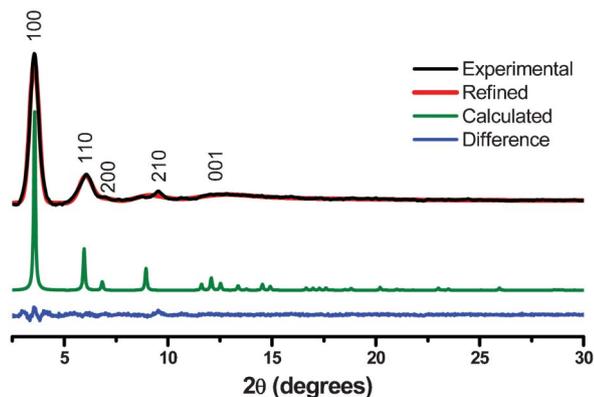


Fig. 1 PXRD pattern of TDCOF-5 with a Cu $K\alpha$ anode with the experimental pattern in black, the Rietveld refined profile in red, calculated pattern for the eclipsed model in green, and the difference plot in blue.

to the calculated pattern of the staggered model ($P6_3/mmc$). The latter conformation results in an intense reflex at $2\theta = 7.06^\circ$ that corresponds to the (101) plane (Fig. S11, ESI†) which is absent from the experimental PXRD pattern of TDCOF-5. The powder-XRD pattern was subjected to refinement by the Rietveld¹⁴ method and produced lattice parameters of $a = b = 29.7042 \text{ \AA}$ and $c = 7.4121 \text{ \AA}$; these numbers agree well with the values of the theoretical eclipsed conformation ($a = b = 31.3283 \text{ \AA}$ and $c = 7.5183 \text{ \AA}$). The wRp and Rp values converged to 2.80% and 2.04%, respectively. The d -spacing (7.4121 \AA) between the 2D layers is considerably larger than those reported for eclipsed 2D COF structures derived from the hexahydroxytriphenylene unit as a result of the non-coplanar conformation of the triptycene core. From the modeling studies, we anticipated TDCOF-5 to be highly porous and therefore, we set out to investigate its porosity and gas uptake at low pressure.

Prior to porosity and gas uptake measurements, a sample of TDCOF-5 ($\sim 75 \text{ mg}$) was activated by degassing at $120 \text{ }^\circ\text{C}$ and $1 \times 10^{-5} \text{ Torr}$ for 16 h to remove residual solvent and gas molecules from the pores. The Type IV argon isotherm (Fig. 2A) is consistent with a mesoporous material that is characterized by a sharp uptake at $P/P_0 = 10^{-5}$ to 10^{-2} followed by a second step starting around $P/P_0 = 10^{-1}$ due to pore filling. The calculated Brunauer–Emmett–Teller (BET) surface area was found to be $2497 \text{ m}^2 \text{ g}^{-1}$ while the Langmuir model gave a surface area of $3832 \text{ m}^2 \text{ g}^{-1}$ that is similar to the calculated Connolly surface ($4973 \text{ m}^2 \text{ g}^{-1}$). The

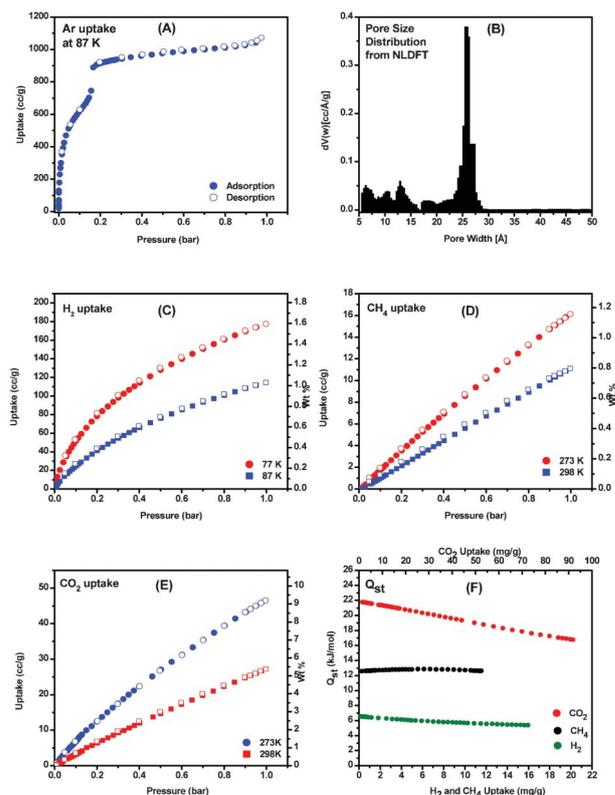


Fig. 2 Gas uptake measurements, Ar (A); PSD from NLDFT (B); H_2 (C); CH_4 (D); CO_2 (E); and respective isosteric heats of adsorption (F). Adsorption (filled) and desorption (empty).

experimental surface area values are considerably higher than those reported for the analogous COF-5: $S_{\text{BET}} = 2050 \text{ m}^2 \text{ g}^{-1}$ and $S_{\text{Lang}} = 3300 \text{ m}^2 \text{ g}^{-1}$.^{15a} Pore size distribution (PSD) was estimated from non-local density functional theory (NLDFT) calculations (Fig. 2B) and found to be centered at about 26 Å and somewhat smaller than the predicted pore aperture of the eclipsed model (31 Å), while the pore volume at $P/P_0 = 0.95$ was $1.3 \text{ cm}^3 \text{ g}^{-1}$. This discrepancy may arise from imperfect solid-state stacking of the eclipsed 2D sheets that cannot be identified by PXRD studies as reported for many 2D COFs and predicated by theoretical studies.¹⁶ In contrast to 2D COFs that employ electron-rich building units and assemble into eclipsed structures driven by the strong π - π interactions, the use of the triptycene core in TDCOF-5 leads to more accessible boron sites that can facilitate interaction with gas molecules. For example, COF-10 exhibits a remarkably high NH_3 uptake driven by the interactions between NH_3 and the boron sites.^{5b} Furthermore, reducing the number of latent edges of molecular building units in porous architectures can provide additional gas interaction sites and is believed to enhance adsorptive gas storage.⁶ Since both features were tailored into the structure of TDCOF-5, we tested its performance in gas storage. We collected hydrogen isotherms at 77 K and 87 K (Fig. 2C) and calculated the hydrogen isosteric heat of adsorption (Q_{st}) by using the virial method.¹⁷ The H_2 uptake at 77 K/1.0 bar (1.6 wt%) is the highest among all known 2D and 3D COFs derived from B-O bond formation and almost double the uptake of COF-5 (0.9 wt%),¹⁵ it is also comparable to those of porous organic polymers and other COFs (0.38–2.07).¹⁸ The Q_{st} value for hydrogen at low coverage was found to be 6.6 kJ mol^{-1} which is within the range of 2D COFs (6.0 – 7.0 kJ mol^{-1})^{15a} and other organic polymers. We collected CH_4 and CO_2 isotherms at 273 K and 298 K (Fig. 2D and E) to mainly investigate the binding affinity for these gases. Methane is abundant and has a low carbon footprint, whereas CO_2 capture from flue gas is highly desirable because of the greenhouse effect of CO_2 . At 273 K and 1.0 bar, TDCOF-5 can store up to 9.2 wt% (2.1 mmol g^{-1}) of CO_2 and $11.5 \text{ cm}^3 \text{ g}^{-1}$ of CH_4 with respective Q_{st} values of 21.8 and 12.6 kJ mol^{-1} . Again, it is worth mentioning that the CO_2 uptake is higher than those of reported COFs and only exceeded by the uptake of COF-6 which has much narrower channels (9 Å), but is lower than the uptakes and binding affinities of functionalized porous organic polymers such as BILPs,¹⁹ POFs,²⁰ and PPNs.²¹ TDCOF-5 also shows somewhat lower gas uptakes than those reported recently for the triptycene trisbenzimidazolone (TTBI) which consists of discrete molecules and has a very high surface area ($2796 \text{ m}^2 \text{ g}^{-1}$).²² The methane uptake at 273 K/1.0 bar ($11.5 \text{ cm}^3 \text{ g}^{-1}$) was compared to data available for COFs; COF-10 ($8.0 \text{ cm}^3 \text{ g}^{-1}$) and COF-102 ($14 \text{ cm}^3 \text{ g}^{-1}$).^{15a} Interestingly, the uptake by TDCOF-5 is considerably higher than that of COF-10 and exceeds the uptake of COF-102 even though the latter has a higher surface area and much narrower channels ($\sim 12 \text{ Å}$) which typically favor methane storage at low pressure. The calculated Q_{st} for methane at low coverage was found to be 12.6 kJ mol^{-1} which is only exceeded by the affinities of COF-6 and COF-1 (pore width $\sim 9 \text{ Å}$); this enhanced binding affinity can be one of the reasons behind the high methane uptake observed for TDCOF-5. The above discussed

adsorptive gas properties of TDCOF-5 are consistent with our recent DFT calculations which revealed that H_2 , CH_4 , and CO_2 molecules favor interaction with boron-containing heterocyclic building units over phenyl moieties in organic polymers.^{5a}

To conclude, we have demonstrated that integrating triptycene into the backbone of COFs can significantly enhance their porosity and performance in small gas storage at low pressure settings. These attributes are most likely driven by the ability of triptycene to reduce π - π interactions between the building units and thereby render the boron sites more accessible for interaction with gas molecules.

Acknowledgements

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