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A 2D Mesoporous Imine-Linked Covalent Organic Framework for High Pressure Gas Storage Applications

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Covalent organic frameworks (COFs) are a new class of porous crystalline materials fabricated by designed synthesis to have high surface area, very low densities, and tunable pore dimensions for use in gas storage, catalysis, and optoelectronics.^[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–N^[4] bonds have been reported. The initial design of COFs was directed toward gas storage applications because of their inherent low density (i.e., made of H, C, N, B, O, Si) and high surface area, which can mitigate gravimetric and volumetric constrains for the onboard storage of hydrogen and methane.^[5] Although COFs derived from B–O bond formation have been widely investigated, their low chemical stability leads to rapid decomposition upon exposure to moisture and limits their effective use in gas storage under practical conditions. This drawback has been addressed in new COF materials constructed through the formation of C–N bonds and found to have enhanced chemical robustness. To date, C–N-linked COFs, such as triazine-, imine-, and hydrazone-linked COFs, typically possess moderate specific surface areas that can hinder their application in gas storage. Moreover, recent studies on a variety of porous materials, such as COFs, metal–organic frameworks (MOFs),^[6] porous organic polymers,^[7] etc., have correlated high surface area to enhanced gas storage capacity especially under high pressure conditions. One of the effective methods for attaining high porosity in organic materials has been the use of rigid or expanded 3D building units,^[8] however, extrapolating this approach to imine-linked COFs resulted in framework interpenetration and only moderate surface area for the 3D COF-300 ($S_{\text{BET}} = 1360 \text{ m}^2 \text{ g}^{-1}$).^[3b] Likewise, the use of π -electron rich building units has afforded low surface area for the 2D COF-66 ($S_{\text{BET}} = 360 \text{ m}^2 \text{ g}^{-1}$)^[9] and, to the best of our knowledge, the use of imine-linked COFs in gas storage has been only investigated theoretically.^[10]

In this study, we report on the synthesis of a high surface area mesoporous imine-linked COF (ILCOF-1) and demonstrate that the use of expanded pyrene cores in the construction of imine-linked COFs can significantly enhance porosity and improve performance in high pressure H_2 , CH_4 , and CO_2 storage. ILCOF-1 was synthesized by the condensation reaction between 1,3,6,8-tetrakis(*p*-formylphenyl)pyrene and *p*-phenylenediamine in 1,4-dioxane in the presence of aqueous acetic acid at 120°C over 3 days and was isolated in good yields (Figure 1). ILCOF-1 was purified by being

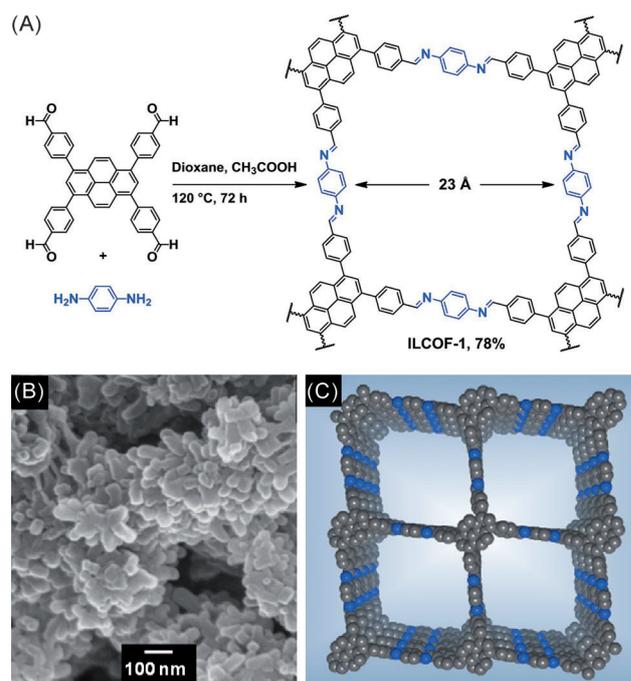


Figure 1. A) Synthesis of ILCOF-1; B) scanning electron micrograph of as-prepared materials, and C) space filling representation of the resulting 2D network; carbon (gray), nitrogen (blue), hydrogen was omitted for clarity.

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washed with acetone, and then soaked in a solvent mixture of tetrahydrofuran/chloroform (v/v 1:1) for 1 day to remove trapped guest molecules, such as solvents and unreacted monomers from the pores, followed by being dried at 120°C and 1.0×10^{-3} torr prior to characterization studies.

The thermal stability of ILCOF-1 was confirmed by thermogravimetric analysis (TGA), which indicated that this COF remains stable at temperature of up to approximately 400 °C under air (Figure S1 in the Supporting Information). The formation of a uniform morphology consistent with the expected crystalline nature of the COF was evidenced by scanning electron microscopy (SEM), which indicates the formation of aggregated cubes of about 30–70 nm in size (Figure 1). The formation of imine linkage was confirmed by FT-IR and ^{13}C cross-polarization with magic angle spinning (CP-MAS) NMR spectroscopic methods. The FT-IR spectrum of ILCOF-1 (Figure S3 in the Supporting Information) contains a characteristic C=N stretch band at 1621 cm^{-1} .^[3b] The spectrum also showed a strongly attenuated C=O and N-H stretches that are present in the aldehyde- and amine-functionalized monomers used for the construction of ILCOF-1. The ^{13}C CP-NMR spectrum contains a characteristic signal for the C=N bond at 156 ppm, whereas additional signals in the aromatic range arise from the phenyl and pyrene cores of the building units (Figure S4 in the Supporting Information). To elucidate the solid-state packing of ILCOF-1 and its crystallinity, we collected powder X-ray diffraction (PXRD) patterns for multiple samples and all results supported the formation of a highly crystalline material (Figure 2E). We examined the experimental PXRD pattern of ILCOF-1 against calculated patterns of potential staggered and eclipsed conformations of the 2D sheets according to literature methods.^[2] We have constructed two plausible models in which the AA packing leads to an eclipsed arrangement with orthorhombic space group *Cmm2*, whereas the staggered AB conformation leads to a structure with orthorhombic space group *Fmm2*. These models were constructed using Materials Studio Visualizer, and their respective geometries and energies were optimized with the Forcite module.^[11]

As shown in Figure 2B, and in contrast to the calculated pattern of the staggered model (Figure 2D), the calculated diffraction pattern of the eclipsed model is consistent with the experimental PXRD pattern of ILCOF-1. The most notable difference is the reflection for the (110) plane at $2\theta = 3.32^\circ$ of the eclipsed model and experimental pattern that is absent from the PXRD pattern of the staggered model. Furthermore, the experimental powder XRD pattern of ILCOF-1 was subjected to refinement by the Rietveld method,^[12] which produced refined PXRD curves with lattice parameters of $a = 34.88$, $b = 32.41$, $c = 7.88\text{ \AA}$ that are very similar to the dimensions of the eclipsed model ($a = 34.7756$, $b = 34.1644$, $c = 6.5787\text{ \AA}$). The wRp and Rp values converged to 5.5 and 4.6%, respectively. The general broadening of the PXRD reflections is most likely due to deviation from the ideal eclipsed stacking of the 2D layers as predicted by theoretical investigation of 2D COFs that are governed by electrostatic interactions and dispersive forces of the pyrene units.^[13] Such interactions have been suggested to lead to small offsets (1.5–2.8 Å) that cannot be recognized by X-ray diffraction techniques. Furthermore, such packing can reduce pore volume and limit the uptake of

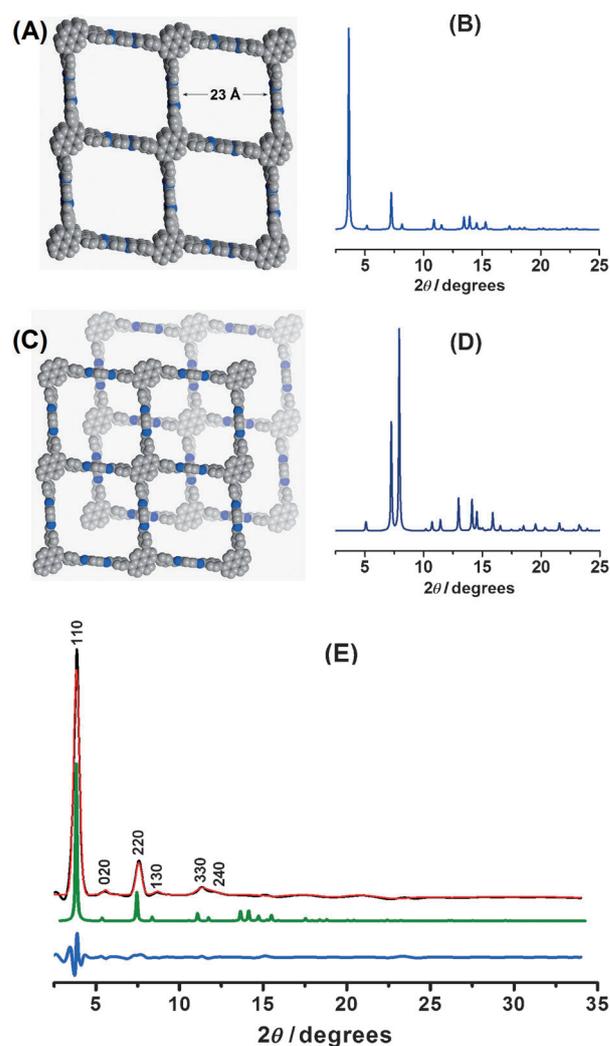


Figure 2. Space-filling models showing: A) solid-state eclipsed and C) staggered models and their corresponding PXRD patterns (B) and (D), respectively; carbon (gray), nitrogen (blue), hydrogen was omitted for clarity. E) PXRD pattern of ILCOF-1 with a $\text{Cu}_{K\alpha}$ anode with the experimental pattern in black, the Rietveld refined profile in red, calculated pattern for the eclipsed model in green, and the difference plot in blue.

large molecules like C_{60} , however, it would have a very limited impact on the admission of small gas molecules into the pores of mesoporous COFs.

Based on the modeling studies discussed above, it was anticipated that ILCOF-1 would have mesopores (pore dimensions $\sim 28.0 \times 24.3\text{ \AA}$) and high surface area (Connolly surface = $5070\text{ m}^2\text{ g}^{-1}$) that can allow for substantial gas storage capacities especially under high pressure conditions. Accordingly, the porosity of ILCOF-1 was established by argon sorption-desorption measurements. The fully reversible Type-IV isotherm (Figure 3A) exhibits a rapid uptake at low pressure followed by a sharp step in the range of $P/P_0 = 0.05\text{--}0.15$ that is typical of mesoporous COFs and in line with the predicted mesoporous nature of ILCOF-1 according to the eclipsed model. The Brunauer-Emmett-Teller and Langmuir surface areas were $\text{SA}_{\text{BET}} = 2723\text{ m}^2\text{ g}^{-1}$ and

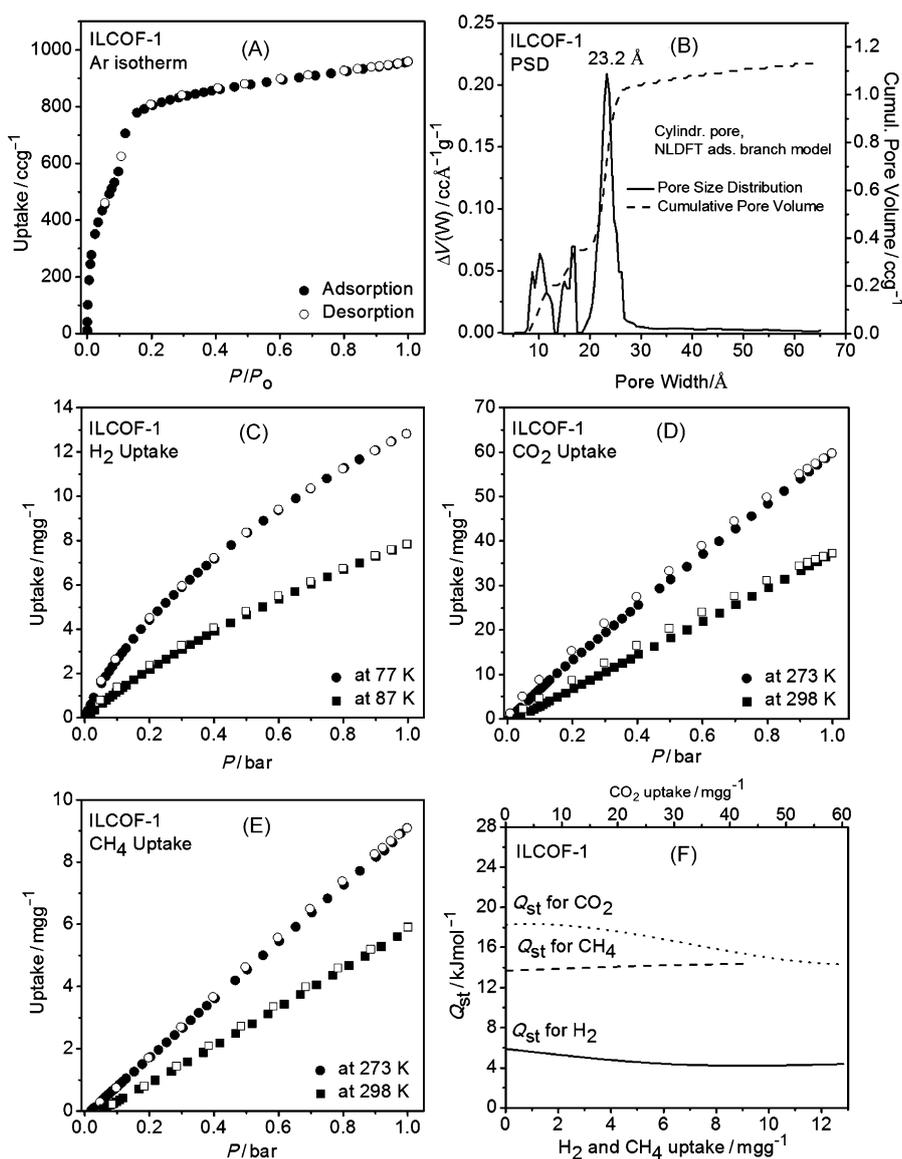


Figure 3. Gas sorption measurements for ILCOF-1: A) argon, B) pore-size distribution from nonlocal density functional theory, C) hydrogen, D) carbon dioxide, E) methane, and F) their respective isosteric heats of adsorption. Adsorption (filled symbols) and desorption (empty symbols).

$SA_{Lang} = 3453 \text{ m}^2 \text{ g}^{-1}$, respectively. Pore-size distribution was estimated from the argon uptake isotherm by nonlocal density functional theory (NLDFT, Figure 3B) and revealed two minor ranges that peak at 10 and 17 Å, and a major one centered at around 23 Å that is very similar to the calculated pore width of the model (24.3 Å) defined by the distance between the phenyl linkers. The total pore volume was calculated from a single point measurement at $P/P_0 = 0.96$ and was found to be $1.21 \text{ cm}^3 \text{ g}^{-1}$. The calculated surface area (SA_{BET}) and major pore-size distribution are considerably higher than those reported for crystalline imine-linked COFs: COF-300 ($1360 \text{ m}^2 \text{ g}^{-1}$, 7.2 Å),^[3b] COF-366 ($735 \text{ m}^2 \text{ g}^{-1}$, 17.6 Å),^[9] and COF-LZU1 ($410 \text{ m}^2 \text{ g}^{-1}$, 12 Å),^[14] imine-linked porous organic frameworks (POFs, 466–1521 $\text{m}^2 \text{ g}^{-1}$),^[15] and the closely related hydrazone-linked

COF-42 ($620 \text{ m}^2 \text{ g}^{-1}$, 23 Å) and COF-42 ($610 \text{ m}^2 \text{ g}^{-1}$, 38 Å).^[3a] The physicochemical stability and high porosity of ILCOF-1 intrigued us to investigate its performance in gas storage under both high and low pressure conditions. The onboard storage of H_2 and CH_4 fuels in automotive applications remains a considerable challenge and has to meet volumetric and gravimetric targets to be effective. On the other hand, CO_2 capture from flue gas and sequestration (CCS) is vital for mitigating global warming. As such, developing new adsorbents that have enhanced storage capacities remains one of the central themes of current research activities directed toward developing a clean and sustainable energy future. At 1.0 bar, ILCOF-1 stores moderate amounts of hydrogen (1.3 wt. %, 77 K), CH_4 (0.9 wt. %, 273 K), and CO_2 (6.0 wt. %, 273 K), as shown in Figure 3C–E. The hydrogen uptake is in line with many of the reported porous organic materials,^[7] but considerably lower than those of the best performing benzimidazole-linked polymer (BILP-4, 2.3)^[16] or the microporous polycarbazole CPOP-1 (2.8 wt. %).^[17] Table S4 in the Supporting Information). The moderate gas uptake capacity of ILCOF-1 is consistent with its mesoporous

nature that does not facilitate small gas storage under low pressure.

We also determined the isosteric heats of adsorption (Q_{st}) using the virial method, and compared the resulting values to Q_{st} values calculated with the Clausius–Clapeyron method.^[18] The H_2 isotherms were collected at 77 and 87 K, whereas the CO_2 and CH_4 isotherms were measured at 273, 288, and 298 K (Figure S13–S18 in the Supporting Information). The Q_{st} values obtained from the virial and Clausius–Clapeyron methods resulted in very similar values. At zero-coverage, the Q_{st} values for H_2 , CH_4 and CO_2 were found to be 5.9, 13.7, and 18.3 kJ mol^{-1} , respectively (Figure 3F). Noteworthy is that the low-pressure gas adsorption isotherms described above (Figure 3C–E) are far from saturation, and suggest that ILCOF-1 can store additional

amounts at higher pressure conditions, for which high surface area and pore volume parameters are known to improve the gas storage capacities of porous adsorbents.

As stated above, the onboard storage of methane and hydrogen remains a considerable technological challenge to the widespread commercialization of these fuels. In order to meet gravimetric and volumetric targets, both gases need to be stored under high pressure conditions.^[5] The US Department of Energy (DOE) has set a target for onboard methane storage at 180 v/v at room temperature and 35 bar,^[5a] whereas the gravimetric and volumetric density targets for hydrogen are 5.5 wt.% and 40 gL⁻¹, respectively, for 2015.^[5b] The use of porous materials, such as porous organic polymers, MOFs, and porous carbon, etc., remains very attractive because of their ability to fuel-defuel at acceptable rates and due to their tailored high surface areas that can enable high storage capacities. In spite of these promising properties the low binding affinity for H₂ necessitates the use of low temperature and high pressure conditions in order to achieve tangible storage levels. Likewise, meeting the volumetric constrain for onboard methane storage has proven to be very difficult and still needs to be addressed for proper assessment of new adsorbents. Additionally, carbon dioxide is usually separated at ambient pressure and then sequestered at a much higher pressure. With these considerations in mind, we set out to evaluate the gravimetric and volumetric performance of ILCOF-1 in gas storage at high pressure. Accordingly, high pressure (up to 40 bar) gas sorption measurements for H₂, CH₄ and CO₂ were performed and the resulting isotherms are presented in Figure 4.

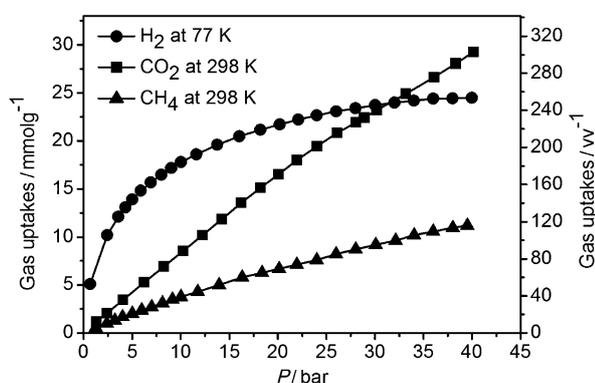


Figure 4. High pressure excess gas sorption measurements for hydrogen, carbon dioxide, and methane.

The hydrogen uptake shows a gradual increase with pressure and reaches saturation at approximately 35 bar; the gravimetric surface excess uptake (4.7 wt.%, 77 K and 40 bar) is higher than most of the organic polymers of similar surface area^[7] but lower than those of high surface area, 3D COFs (~7.0 wt.%),^[19] porous aromatic frameworks (PAFs; 4.2–7.0 wt.%),^[8c] and porous polymer networks, PPN-4 (8.34 wt.%)^[8b] collected at a higher pressure (60 bar).

The CO₂ uptake was significant (29.3 mmol g⁻¹ at 298 K and 40 bar) and exceeds those of 2D and 3D COFs (5.2–27.3 mmol g⁻¹ at 298 K and 55 bar) and those of hyperbranched conjugated polymers (HCPs; 10.6–13.3 mmol g⁻¹ at 298 K and 35 bar)^[20] and it rivals the performance of PAF-1 (29.6 mmol g⁻¹ at 298 K and 40 bar)^[8a] but falls short of PPN-4 (~39 mmol g⁻¹ at 295 K and 50 bar).^[8b] In contrast to the nitrogen-free frameworks of COFs, PAFs, and HCP, the nitrogen-functionalized pore walls of ILCOF-1 can enhance CO₂ binding through N...CO₂ interactions, which can be one of the reasons behind the observed high CO₂ uptake. The gravimetric surface excess methane uptake was 11.2 mmol g⁻¹ at 298 K and 40 bar, which is higher than the reported methane uptakes for 2D COFs and in line with those of 3D COFs (~11 mmol g⁻¹).^[19] The performance of ILCOF-1 in volumetric (v/v) gas storage at high pressure was also assessed (Figure 4). The volumetric storage capacity of an adsorbent determines how densely the gas molecules are stored within the pores and is very relevant to express the efficiency of low density adsorbents like COFs. Under high pressure conditions, the void space of the pores can hold a significant amount of compressed gas, and therefore, the absolute amounts adsorbed (total) were calculated from experimentally determined surface excess adsorptions (Figures S19–S21 in the Supporting Information).^[21] The absolute gravimetric and volumetric (v/v) uptakes for hydrogen at 77 K and 40 bar is 6.1 wt.% and 30 gL⁻¹ (335 LL⁻¹), respectively. Similarly the absolute adsorbed amount for CH₄ in volumetric units was estimated to be 129 LL⁻¹ (92 gL⁻¹) at 298 K and 35 bar, which is comparable to that of COF-102 (136 LL⁻¹)^[19] but still lower than the DOE target for 2015 (180 v/v). The volumetric CO₂ adsorption capacity at 298 K and 35 bar is 587 gL⁻¹ (299 LL⁻¹), which is approximately eight times the density of carbon dioxide at the same temperature and pressure.^[22]

We have demonstrated that the use of expanded pyrene building units can be very effective in the preparation of highly crystalline mesoporous imine-linked COFs. The strong π - π stacking interactions of the pyrene moieties not only direct the 2D solid-state packing, but also prevent network interpenetration and thereby enhance the porosity and performance of COFs in gas storage. In addition to the promising gas storage properties of ILCOF-1, this COF is expected to have other potential applications in gas separation or as a catalyst support for heterogeneous catalysis in which the nitrogen functionalized pore walls can facilitate selective gas adsorption and catalyst immobilization, respectively.

Experimental Section

Synthesis of ILCOF-1: Tetrakis(*p*-formylphenyl)pyrene (20 mg, 32 μ mol) and 1,4-*p*-phenylenediamine (7.0 mg, 64 μ mol) were suspended in anhydrous 1,4-dioxane (3.0 mL) in the presence of aqueous acetic acid (0.6 mL, 3.0 M) in a Pyrex tube. The mixture was then degassed by freeze-pump-thaw technique twice using liquid nitrogen bath. Finally the tube was frozen by using liquid nitrogen then flame-sealed under reduced

pressure (150 mtorr). The sealed tube was heated at 120°C for 3 days to yield a yellow solid, which was filtered and washed with THF. The resulting powder was soaked in a THF/chloroform mixture (1:1) for 1 day during which the solvents were replenished twice then filtered over a medium glass frit and dried at 120°C and 150 mtorr to give ILCOF-1 as a yellow powder (19 mg, 78% based on TFPPy). Solid state ¹³C NMR: δ = 156 (C=N), 148, 141, 135, 133, 129, 125, 121, 118, 113 ppm; FTIR (KBr): $\tilde{\nu}$ = 3410, 3027, 2920, 2860, 1700, 1621 (C=N), 1602, 1558, 1491, 1460, 1409, 1305, 1194, 1173, 1105, 1005, 980, 880, 838, 814 cm⁻¹; elemental analysis calcd (%) for C₅₆H₃₄N₄·4H₂O: C 80.55, H 5.07, N 6.71; found: C 80.45, H 6.40, N 4.23.

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Keywords: adsorption • carbon dioxide • covalent organic frameworks • hydrogen storage • microporous materials

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