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# Gas Storage in a Partially Fluorinated Highly Stable Three-Dimensional Porous Metal–Organic Framework

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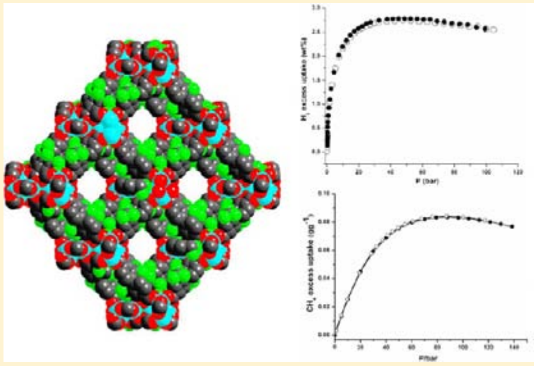
Supporting Information

**ABSTRACT:** A partially fluorinated linear rigid linker, 2,2′-bis-trifluoromethyl-biphenyl-4,4′-dicarboxylic acid ($H_2$bfbpdc), has been synthesized. This linker forms a porous three-dimensional (3D) metal–organic framework, $\{[Zn_4O(bfbpdc)_3(bpy)_{0.5}(H_2O)]\cdot(3DMF)(H_2O)\}_n$ (**1**), in the presence of the colinker 4,4′-bipyridine (bpy) and $Zn(NO_3)_2\cdot 6H_2O$ under solvothermal condition. Single crystal X-ray analysis shows that **1** contains a 3D channel structure with highly polar pore surfaces decorated with pendant trifluoromethyl groups of bfbpdc$^{2-}$ linker. Thermogravimetric analysis (TGA) and variable temperature powder X-ray diffraction (VTPXRD) exhibit high thermal stability of the framework. The solvent molecules present in the voids can be removed by heating, maintaining the integrity of the structure to afford a porous framework. Gas ($N_2$, $H_2$, $CH_4$, and $CO_2$) and water adsorption studies were performed on this framework.

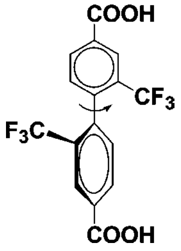


## INTRODUCTION

Design and synthesis of porous metal organic frameworks (MOFs) continue to attract considerable attention due to the ability of these materials to adsorb gas molecules such as hydrogen, methane, and others.[1] Presently, supramolecular storage of gas molecules has assumed great significance due to increasing energy demands and depleting reserves of fossil fuel.[2] Gas adsorption capacities of porous MOFs can be maximized by increasing the surface area and pore volume,[3] incorporation of coordinatively unsaturated metal centers,[4] and functionalization of organic linkers to decorate the pore surfaces.[5,6] As far as modification of the linker is concerned, replacing hydrogens by fluorines can lead to increased intermolecular forces with gas molecules. Thus, frameworks built with partially fluorinated organic linkers and metal ions (FMOFs) exhibit high gas uptake capabilities.[6] Besides, MOFs built with fluorinated organic linkers are expected to possess enhanced thermal, light, air, and chemical stability.[6,7] Linear organic linkers form highly porous MOFs especially with $\{Zn_4O^{6+}\}$ as the secondary building unit (SBU).[8] It is to be noted, however, that the design of porous MOFs with linear organic linkers to increase the pore size carries an increasing risk of interpenetration such that voids of one framework can be occupied by one or more frameworks, leading to a close packed structure without voids.[9] One way to alleviate the problem of extensive interpenetration would be the attachment of side groups such that steric hindrance comes into play against the formation of interpenetrated structures.

Bearing all of these in mind, we have designed and synthesized a linear rigid ligand, 2,2′-bis-trifluoromethyl-biphenyl-4,4′-dicarboxylic acid (bfbpdc$H_2$), which comprises a carboxylate group at each terminal while the trifluoromethyl groups in the middle decorate the pores with this group (Scheme 1).

**Scheme 1. 2,2′-Bis-trifluoromethyl-biphenyl-4,4′-dicarboxylic Acid ($H_2$bfbpdc)**



The presence of trifluoromethyl groups also tends to discourage extensive interpenetratation due to the steric effect. The coligand 4,4′-bipyridine having comparable length to bfbpdc$H_2$ has been used to further reinforce the structure. Since the Zn(II) ion shows a strong tendency to form the $\{Zn_4O^{6+}\}$ secondary building unit (SBU) that provides strength to the overall structure besides greater pore size,[8] it has been chosen in the present study. Herein, we report the synthesis and structural characterization of the singly interpenetrated 3D framework, $\{[Zn_4O(bfbpdc)_3(bpy)_{0.5}(H_2O)]\cdot(3DMF)(H_2O)\}_n$ (**1**) (bpy = 4,4′-bipyridine and bfbpdc = 2,2′-bis-trifluoromethyl-biphenyl-4,4′-dicarboxylate). There are a number of solvent molecules occupying the voids

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that can be removed without destroying the overall structure to afford a porous framework. Metal coordinated water molecules are also removed by heating, introducing open metal sites for the enhancement of gas uptake capacity. It possesses high thermal stability, has a highly hydrophobic surface, and exhibits permanent porosity with moderate surface area. Nitrogen, hydrogen, methane, and carbon dioxide adsorption properties of the porous framework are studied.

## ■ EXPERIMENTAL SECTION

**Materials.** The metal salt and other reagent grade chemicals were procured from Sigma-Aldrich and used as received. All the solvents were from S. D. Fine Chemicals, India. These solvents were purified following standard methods prior to use.

**Physical Measurements.** Infrared (IR) spectra (KBr disk, 400–4000 $cm^{-1}$) were recorded on a Perkin-Elmer Model 1320 spectrometer. Thermogravimetric analyses (TGA; 5 °C $min^{-1}$ heating rate under nitrogen atmosphere) were performed with a Mettler Toledo Star System. Microanalyses for the compounds were carried out using a CE-440 elemental analyzer (Exeter Analytical Inc.). Variable temperature powder X-ray diffraction (VTPXRD) studies were carried out using a Bruker D8 Advanced powder diffractometer with Cu $K\alpha$ radiation.

**Synthesis of the Ligand.** The ligand 2,2′-bis-trifluoromethylbiphenyl-4,4′-dicarboxylic acid ($bfbpdcH_2$) has been synthesized following a previously reported procedure.[10]

**Synthesis of $\{[Zn_4O(bfbpdc)_3(bpy)_{0.5}(H_2O)]\cdot(3DMF)(H_2O)\}_n$ (1).** A mixture containing $bfbpdcH_2$ (0.03 g, 0.08 mmol), 4,4′-bipyridine (0.012 g, 0.08 mmol), $Zn(NO_3)_2\cdot 6H_2O$ (0.094 g, 0.32 mmol), and 4 mL of DMF was placed in a Teflon-lined stainless steel autoclave. It was heated under autogenous pressure to 100 °C for 72 h and then allowed to cool to room temperature at a rate of 1 °C per min. Colorless block-shaped crystals of **1** were collected by filtration, washed first with DMF followed by acetone, and finally dried in the air. Yield ~47%. Anal. Calcd. for $C_{62}H_{47}F_{18}N_4O_{18}Zn_4$: C, 42.80; H, 2.72; N, 3.22%. Found: C, 42.94; H, 2.79; N, 3.15%. IR ($cm^{-1}$): 3431 (broad), 2934 (m), 1667 (s), 1624 (s), 1388 (s), 1306 (s).

**X-Ray Structural Studies.** Single crystal X-ray data on **1** were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. The data integration and reduction were performed with SAINT[11] software. An empirical absorption correction was applied to the collected reflections with SADABS[12] using XPREP.[13] The structure was solved by the direct method using SIR-97[14] and was refined on $F^2$ by the full-matrix least-squares technique using the SHELXL-97[15] program package. The non-hydrogen atoms were refined anisotropically. H atoms were placed in calculated positions using idealized geometries (riding model) and assigned fixed isotropic displacement parameters using the SHELXL default. The trifluoromethyl groups as well as the 4,4′-bipyridine were disordered. For this, several DFIX commands were used to fix the bond distances. To give an account of disordered electron densities associated with solvent molecules in **1**, the "squeeze" protocol in the PLATON package[16] was applied. The crystal and refinement data are collected in Table 1, while bond distances and bond angles are collected in Table S6 (Supporting Information).

**Physisorption Measurements.** The $N_2$ physisorption isotherm was measured at 77 K up to 1 bar pressure using a Quantachrome Autosorb1C apparatus. High-pressure $H_2$ physisorption measurements at 77 K up to the pressure of 104 bar were performed using a volumetric BELSORP-HP apparatus. High pressure $CH_4$ and $CO_2$ adsorption were studied using a magnetic suspension balance (Rubotherm Co.). The buoyancy corrections were performed as described earlier.[17] The total gas uptake was calculated by $N_{total} = N_{excess} + \rho_{bulk}V_{pore}$, where $\rho_{bulk}$ equals the density of compressed gases at the measured temperature and pressure, and $V_{pore}$ was obtained from the $N_2$ sorption isotherm at 77 K.

**Table 1. Crystal and Structure Refinement Data for 1**

| | compound **1** |
|---|---|
| formula | $C_{62}H_{47}F_{18}N_4O_{18}Zn_4$ |
| fw | 1739.5 |
| temp | 100 K |
| radiation | Mo $K\alpha$ |
| wavelength | 0.71073 Å |
| cryst syst | monoclinic |
| space group | $C2/c$ |
| $a$, Å | 22.530(5) |
| $b$, Å | 25.597(5) |
| $c$, Å | 34.009(5) |
| $\alpha$ (deg) | 90 |
| $\beta$ (deg) | 107.439(5) |
| $\gamma$ (deg) | 90 |
| $V$, Å$^3$ | 18712(6) |
| $Z$ | 8 |
| $\rho_{calc}$ g/cm$^3$ | 1.065 |
| $\mu$, mm$^{-1}$ | 1.089 |
| $F(000)$ | 5928 |
| reflns collected | 47086 |
| $R_{int}$ | 0.1367 |
| independent reflns | 8653 |
| refinement method | full-matrix least-squares on $F^2$ |
| GOF | 0.937 |
| final $R$ indices $[I > 2\sigma(I)]$ | $R_1 = 0.0889$ |
| | $wR_2 = 0.2130$ |
| $R$ indices (all data) | $R_1 = 0.1408$ |
| | $wR_2 = 0.2352$ |

High purity gases were used for the adsorption measurements (nitrogen, 99.999%; hydrogen, 99.999%; methane, 99.995%; carbon dioxide, 99.95). Water vapor physisorption was investigated at 298 K using a Hydrosorb 1000 apparatus (Quantachrome Co.) with an equilibration time of 300 s. Prior to all physisorption measurements, the sample was dried *via* supercritical $CO_2$ (SCD) and additionally activated at 120 °C for 16 h.

## ■ RESULTS AND DISCUSSION

The compound, $\{[Zn_4O(bfbpdc)_3(bpy)_{0.5}(H_2O)]\cdot(3DMF)(H_2O)\}_n$ (**1**), was easily synthesized adopting the solvothermal technique in moderate yields by reacting $bfbpdcH_2$, 4,4′-bipyridine, and $Zn(NO_3)_2\cdot 6H_2O$ in DMF at 100 °C for 72 h. Once isolated, **1** was found to be air-stable and insoluble in common organic solvents and water. In the IR spectra of **1**, broad bands around 3431 $cm^{-1}$ suggest the existence of coordinated as well as lattice water molecules, whereas sharp peaks in the range 1667–1624 $cm^{-1}$ are attributable to C=O stretching vibrations of DMF molecules present in the channel as well as metal coordinated carboxylate groups (Supporting Information, Figure S1).[18]

**Thermal Stability.** Thermogravimetric analyses (TGA) and variable temperature powder X-ray diffraction (VTPXRD) measurements were carried out to examine the thermal stability of this framework. The TGA curve of **1** shows that all solvent molecules in the voids as well as coordinated water molecule can be removed by heating up to 160 °C. The TGA curve (Figure 1) of **1** reveals a weight loss of 13.8% in the temperature range of 95–140 °C, corresponding to a loss of $H_2O$ and DMF molecules present in the lattice (calcd 13.6%). Another weight loss of ~1% in the temperature range 140–160 °C is attributable to the release of coordinated $H_2O$ molecules (calcd. 1%). No further

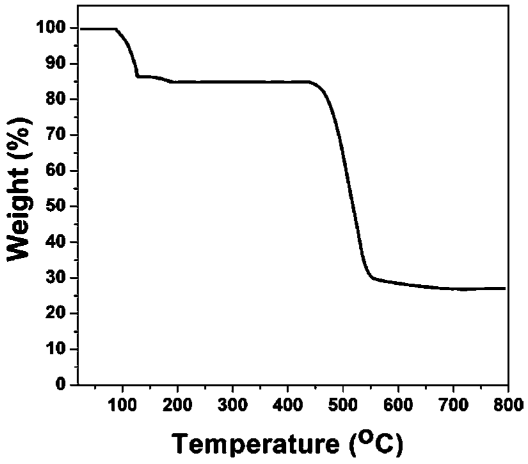

**Figure 1.** Thermogravimetric analysis of complex **1**.

weight loss is observed until 450 °C, and complete decomposition is achieved beyond this temperature.

The thermal stability and phase purity of **1** were also confirmed by variable temperature PXRD (Figure 2). It clearly indicates the overall framework structure to be intact at least up to 350 °C.

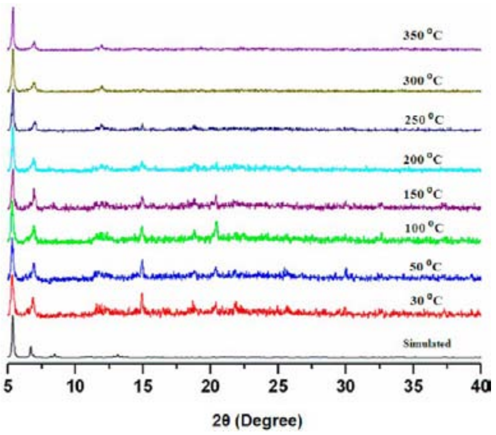

**Figure 2.** Variable temperature PXRD pattern of complex **1**.

**Stability in the Presence of Water Vapor.** The stability of the compound in the presence of water vapor was checked. The desolvated sample was taken in a glass vial and kept in a slightly bigger screw cap bottle containing water. The PXRD of the sample was recorded after different time intervals. The framework stability was confirmed from the PXRD pattern (Figure 3). However, most MOFs, in particular zinc-based MOFs, are moisture-sensitive because the weak metal−oxygen coordination allows for attack by water molecules, resulting in the phase transformation and decomposition of the framework.[19] Here, the water stability of this framework might be due to introducing hydrophobic functional groups like $-CF_3$ into the framework structures, which make the framework water resistant.[20]

Single crystal X-ray analysis reveals that the structure crystallizes in the monoclinic space group *C*2/*c*. The asymmetric unit consists of four Zn(II), three bfbpdc$^{2-}$, a half of 4,4′-bipyridine, and one $H_2O$ molecule bound to metal (Figure 4). It contains a $\{Zn_4O^{6+}\}$ secondary building unit (SBU) connected

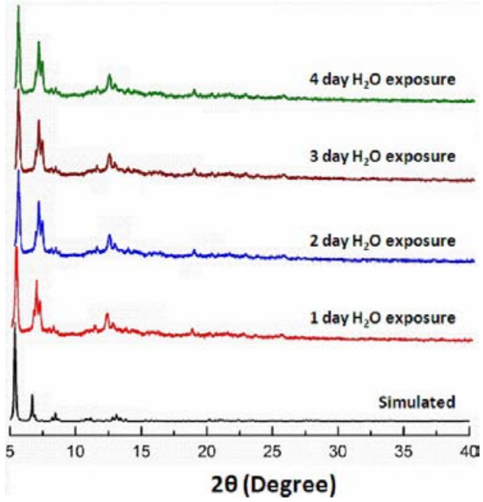

**Figure 3.** PXRD patterns for complex **1** after exposure to water vapor for 1 day, 2 days, 3 days, and 4 days.

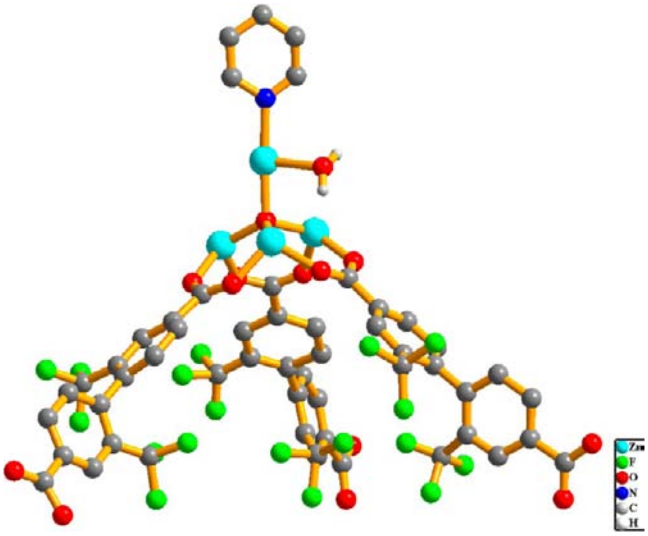

**Figure 4.** The perspective view of the asymmetric unit of **1** (hydrogen atoms are omitted for clarity.).

to six carboxylates from six different bfbpdc$^{2-}$ ligand units and one N from a 4,4′-bipyridine and one $H_2O$ (Figure 5). As shown in Figure 2, the Zn(1), Zn(2), and Zn(3) ions show tetra-coordination where each metal ion is bonded in bridging mode to three carboxylate O atoms from three different bfbpdc$^{2-}$ units and the $\mu_4$-O atom at the center of the cluster. The Zn(4) ion, on the other hand, shows hexa-coordination with additional ligation from one N atom of 4,4′-bipyridine and one water molecule. Upon removal of the coordinated water molecule from Zn(4), it will be coordinately unsaturated, and the open metal site can play an important role in gas adsorption and other applications. All Zn−O bond distances lie in the range 1.901(12)−2.200(16) Å, while the Zn−N bond distance is 2.107(17) Å. Every bfbpdc$^{2-}$ ligand is connected to one SBU at either end to describe a cubane-like framework. Two such cubane frameworks interpenetrate one another. Each 4,4′-bipyridine coligand connects the two cubane frameworks via coordination to the Zn(4) ion (Figure 6) to further reinforce the structure.

Rectangular channels along the crystallographic *c* axis can be observed with the approximate dimensions, 10.76 × 8.94 Å$^2$

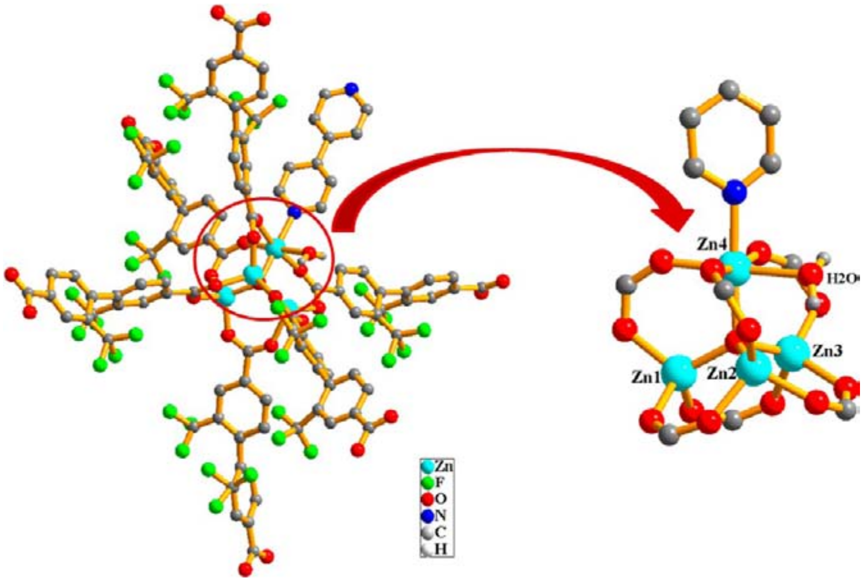

**Figure 5.** The perspective view of the coordination environment of Zn(II) ions and the $Zn_4O$ cluster as its SBU in compound **1** (hydrogen atoms are omitted for clarity).

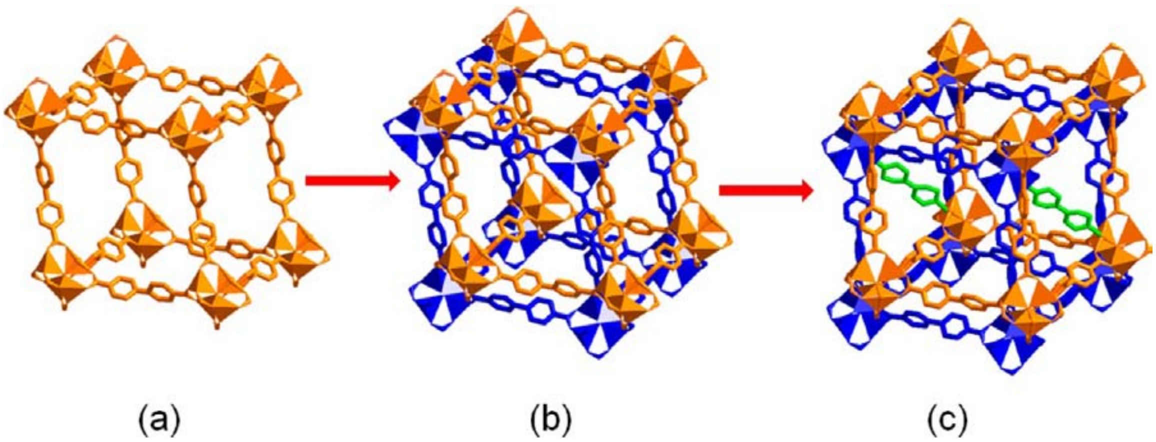

**Figure 6.** The consecutive representation of (a) 1-fold, (b) 2-fold, and (c) connection of two interpenetrated frameworks diagonally by 4,4′-bipyridine (hydrogen atoms and the $-CF_3$ groups are omitted for clarity).

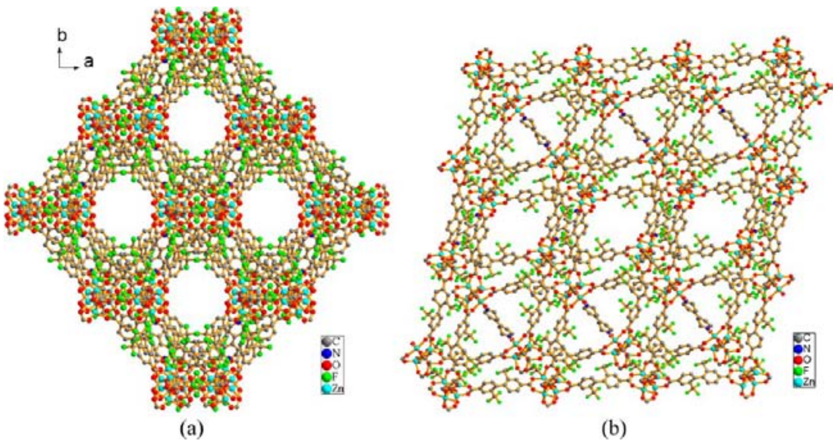

**Figure 7.** View of the 3D framework of **1** (a) along the *c* axis showing rectangular shaped channels decorated with pendent trifluoromethyl groups. (b) Rectangular channels along the (110) direction decorated with pendent trifluoromethyl groups (hydrogen atoms are omitted for clarity).

(excluding van der Waals radii). In the [110] direction also, another rectangular channel with the dimensions 7.91 × 4.54 Å$^2$ (excluding van der Waals radii) is also visible. Trifluoromethyl groups of the ligand bfbpdc$^{2-}$ are exposed into the channels that run along the *c* axis and the (110) direction, resulting in a highly polar pore surface (Figure 7). This 3D framework can be

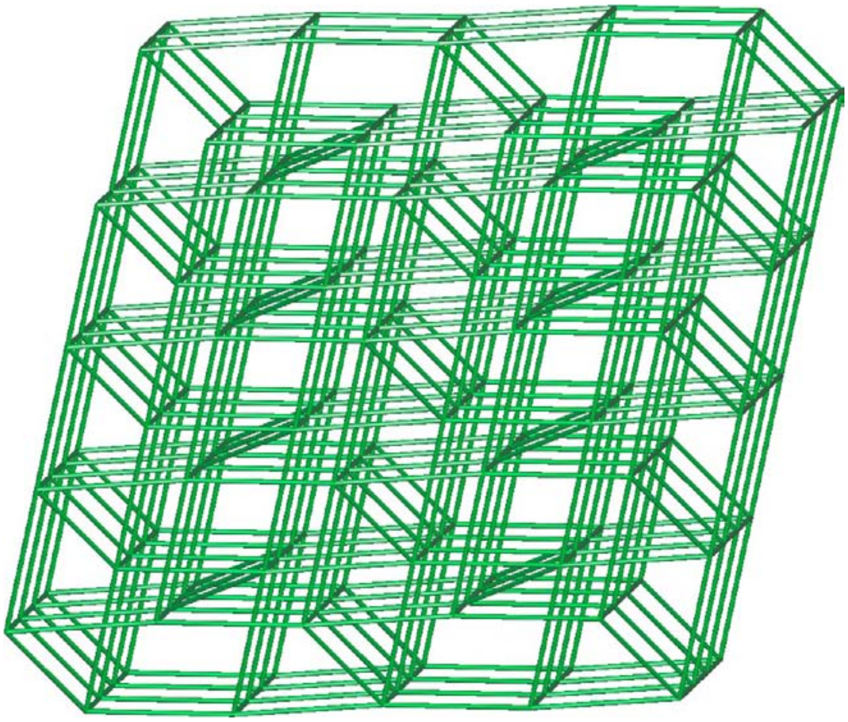

**Figure 8.** Schematic representation of the 7-connecting ***hxg-d*** net of **1**.

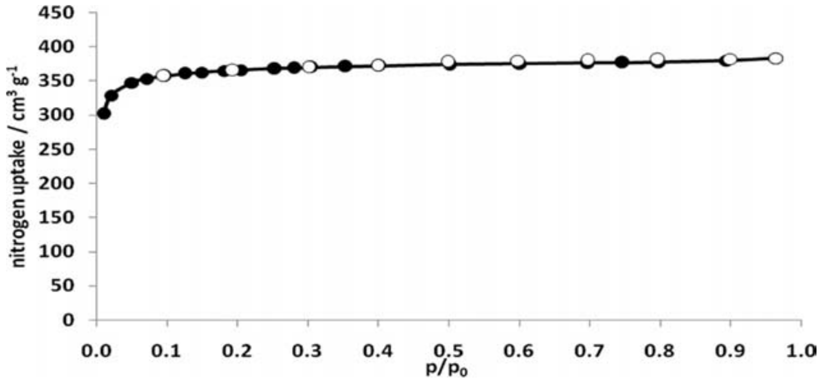

**Figure 9.** Nitrogen physisorption isotherm of activated **1** at 77 K (adsorption/desorption ●/○).

described as a 7-connected ***hxg-d*** net.[21] The point symbol of the net is $\{4^{16}.6^5\}$ (Figure 8).[22] Solvent accessible volume calculated from the crystal structure using the *PLATON* routine[16] is 49.1% of the total crystal volume.

## ■ ADSORPTION STUDIES

The 3D channel structure, high thermal stability, and structural rigidity besides maintaining the overall structure upon solvent removal make **1** a potential candidate for gas storage. To evaluate the porosity of activated **1**, gas adsorption measurements were carried out with $N_2$, $H_2$, $CH_4$, and $CO_2$ under different experimental conditions. The $N_2$ sorption isotherm at 77 K shows a type-I behavior, suggesting a microporous nature of the framework (Figure 9). The BET surface area on the basis of a $N_2$ adsorption isotherm is calculated to be 1450 m$^2$ g$^{-1}$ and the total pore volume as 0.59 cm$^3$ g$^{-1}$ (at $p/p_0 = 0.96$).

The hydrogen gas uptake studied of evacuated **1** up to 1 bar exhibits a typical reversible type-I isotherm with a capacity of 84 cm$^3$ g$^{-1}$ (at 77 K) and 37 cm$^3$ g$^{-1}$ (at 87 K; Figure 10). The uptake capacity is comparable to those of previously reported partially fluorinated or perflurinatrd MOFs.[6] The isosteric heat of $H_2$ adsorption ($Q_{st}$) value, determined by applying the Clausius−Clayperon equation to the isotherms obtained at 77 and 87 K, is approximately 7.9 kJ/mol at low coverages (Figure 11).[23] The value is higher than that for MOF-5 (4.5 kJ mol$^{-1}$),[8] IRMOF-8 (6.1 kJ mol$^{-1}$),[8] MIL-100 (6.3 kJ mol$^{-1}$),[24a] and PCN-6 (6.2 kJ mol$^{-1}$)[24b] but comparable to the MOFs having high $Q_{st}$ values, like PCN-69 (8.14 kJ mol$^{-1}$),[24c] MOF-74 (8.3 kJ mol$^{-1}$),[24d] and PCN-14 (8.6 kJ mol$^{-1}$).[24e] The enhancement in the binding strength is due to the presence of the exposed metal site and fluorine atoms in the pore surface of the framework. The high-pressure hydrogen sorption study was performed using a gravimetric measurement method at 77 K and a pressure up to 104 bar (Figure 12). The capacity of **1** to adsorb $H_2$ reaches the maximum 2.78 wt % at 41 bar, which is comparable to the highest capacity zeolites[25] and some other MOFs reported[26] in the literature (also see the Supporting Information, Table S1). The significant hydrogen storage capacity of **1** can

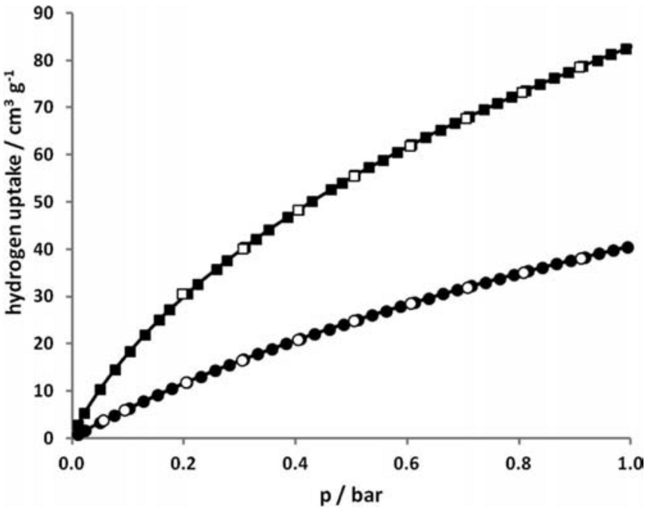

**Figure 10.** Hydrogen physisorption isotherms of activated **1** at 87 K (adsorption/desorption ●/○) and 77 K (adsorption/desorption ■/□).

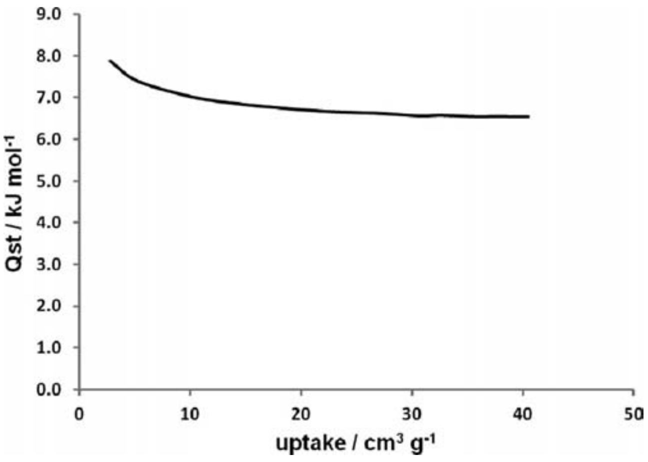

**Figure 11.** Isosteric heat of adsorption dependent on the hydrogen uptake.

probably be attributed to a combination of the high electrostatic interaction of $H_2$ to the exposed metal sites and the polar fluorinated pore surface of the framework. Perfluorinated compounds have been shown to exhibit favorable electrostatic interactions with $H_2$.[6]

Further, $CH_4$ adsorption was measured at 298 K at a pressure up to 140 bar (Figure 13). The excess gravimetric methane uptake (84 mg $g^{-1}$ at 87 bar) is lower compared to the best MOFs such as DUT-23 (266 mg $g^{-1}$ at 100 bar),[27] DUT-49 (291 mg $g^{-1}$ at 100 bar),[28] or MOF-210 (264 mg $g^{-1}$ at 80 bar).[29] However, the maximal volumetric methane storage capacity of **1** is comparable or higher in comparison to that of MOFs mentioned above due to the relatively high crystallographic density of **1** (1.065 g $cm^{-1}$; Supporting Information, Table S2). For example, the volumetric methane uptake of **1** is significantly higher (102 $cm^3$ $cm^{-3}$) compared to DUT-23 (83 $cm^3$ $cm^{-3}$), DUT-49 (79 $cm^3$ $cm^{-3}$) and MOF-210 (53 $cm^3$ $cm^{-3}$) at the same pressure of 35 bar and 298 K. For PCN-14, which is the best storage material in terms of volumetric uptake,[30] a volumetric methane storage capacity of 220 $cm^3$ $cm^{-3}$ at 35 bar has been reported, which surpasses the DOE methane storage target of 180 V/V (volume of gas stored per volume of storage cylinders) at 25 °C and 35 bar.[31]

The fluorine atom interspersed pore surface should also be desirable for $CO_2$ storage. The $CO_2$ physisorption isotherm of **1** shows a $CO_2$ uptake capacity of 315 $cm^3$ $g^{-1}$ at 195 K and 1 bar (Figure 14). To determine the isosteric heat of $CO_2$ adsorption ($Q_{st}$) value, $CO_2$ physisorption measurements were performed at different temperatures (262, 273, and 283 K) up to the relative pressure of 1 bar. The $CO_2$ uptakes for **1** are 20 $cm^3$ $g^{-1}$ (at 262 K), 14.9 $cm^3$ $g^{-1}$ (273 K), and 11 $cm^3$ $g^{-1}$ (283 K), respectively (Figure 15). The isosteric heat of $CO_2$ adsorption calculated using the virial method is 21.8 kJ $mol^{-1}$ at low coverage (Figure 16). Though the value is lower than some amine functionalized MOFs, like $NH_2$-MIL-53(Al) (50 kJ $mol^{-1}$),[32a] bio-MOF-11 (45 kJ $mol^{-1}$),[32b] and CAU-1 (48 kJ $mol^{-1}$)[32c] but comparable to that of MAF-26 (23 kJ $mol^{-1}$),[33a] MOF-253 (22 kJ $mol^{-1}$),[33b] and UMCM-150 (20.6 kJ $mol^{-1}$).[33c] High pressure $CO_2$ physisorption isotherms were measured at 273 and 298 K and are presented in Figure 17. The $CO_2$ adsorption isotherm of **1** shows a $g^{-1}$ (at 298 K and 50 bar). In contrast to the reported MOFs with a high $CO_2$ uptake of 575 $cm^3$ $g^{-1}$ (at 273 K and 28 bar) and 430 $cm^3$ uptake capacity (e.g., MOF-210,[29] 1220 $cm^3$ $g^{-1}$ at 50 bar; MOF-200,[29] 1240 $cm^3$ $g^{-1}$ at 50 bar; NU-100,[34a] 1039 $cm^3$ $g^{-1}$ at 40 bar), **1** still has a relatively high uptake (PCN-46,[34b] 470 $cm^3$ $g^{-1}$ at 30 bar; IRMOF-6,[35] 436 $cm^3$ $g^{-1}$ at 35 bar; IRMOF-3,[35] 418 $cm^3$ $g^{-1}$ at 35 bar).

The run of the water vapor physisorption isotherm reflects a very hydrophobic surface of **1**. The significant uptake can be reached only at a high relative humidity level ($p/p_0 > 0.9$; Figure 18). This outperforms even activated carbon, known to have a hydrophobic surface.

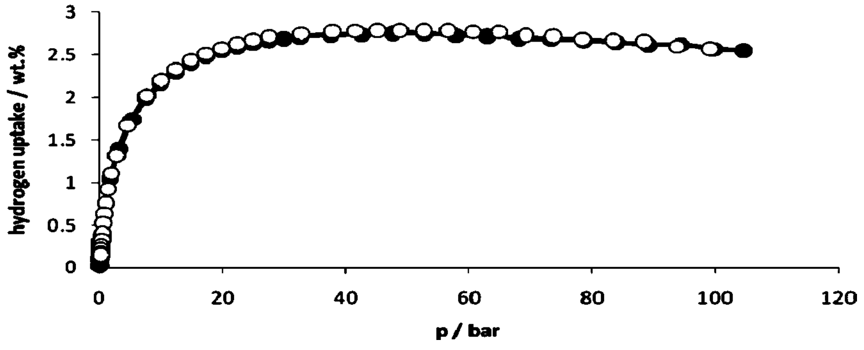

**Figure 12.** Hydrogen physisorption isotherms of activated **1** at 77 K up to 104 bar (adsorption/desorption ●/○).

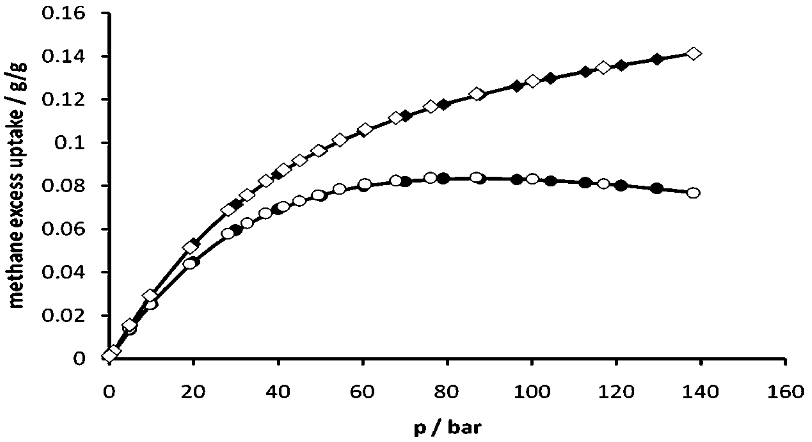

**Figure 13.** Methane excess (adsorption/desorption ●/○) and total (adsorption/desorption ◆/◇) physisorption isotherms of activated **1** at 298 K.

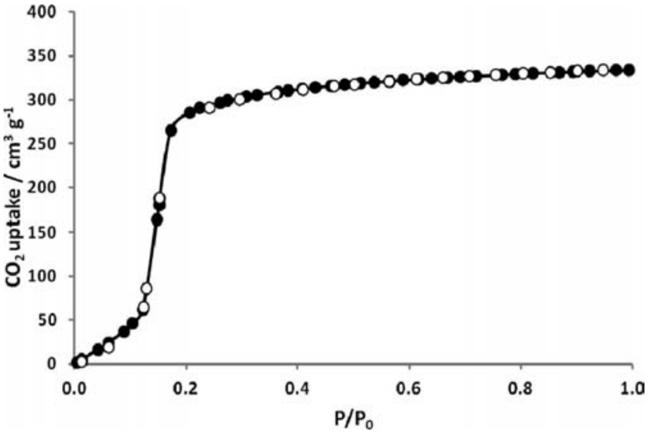

**Figure 14.** Carbon dioxide physisorption isotherms of activated **1** at 196 K (adsorption/desorption ●/○).

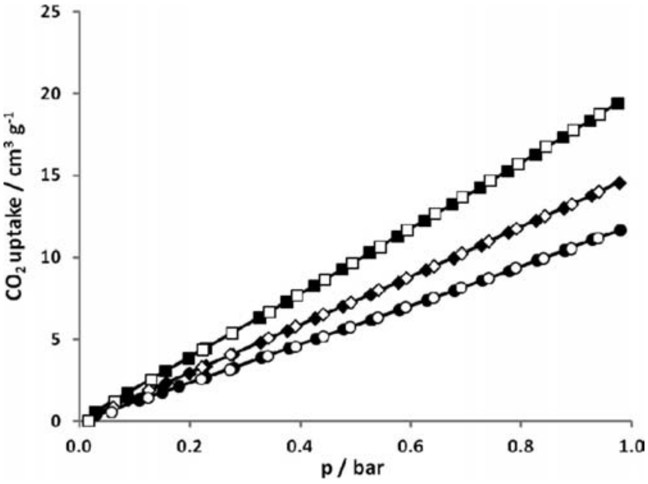

**Figure 15.** Carbon dioxide physisorption isotherms of activated **1** up to 1 bar at 283 K (circles), 273 K (diamonds), and 262 K (squares).

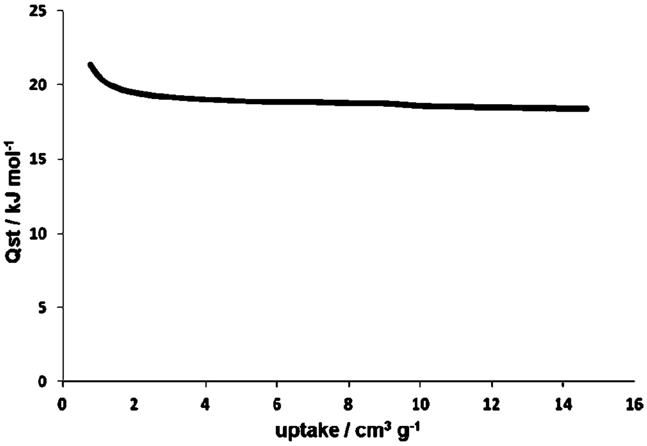

**Figure 16.** Isosteric heat of adsorption dependent on the carbon dioxide uptake.

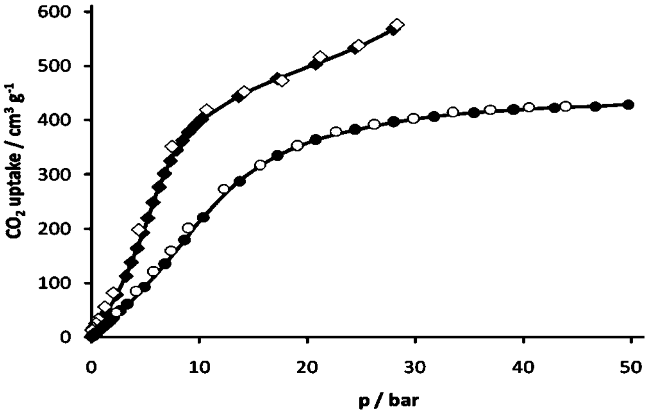

**Figure 17.** $CO_2$ excess physisorption isotherms of **1** measured at 273 K (adsorption/desorption ◆/◇) and 298 K (adsorption/desorption ●/○).

In conclusion, we have successfully synthesized a partially fluorinated linear ligand that forms a highly stable 3D framework with a $\{Zn_4O^{6+}\}$ SBU in the presence of the coligand 4,4′-bipyridine where trifluoromethyl groups are present in the channels. The presence of these trifluoromethyl groups make the channel hydrophobic in nature and stable in the presence of moisture. The MOF is also thermally quite stable as shown by VTPXRD and TGA data. The integrity of this framework is maintained upon removal of the guest DMF and water molecules. One water molecule bound to one of the Zn(II) ions of the SBU is also lost upon heating, rendering it

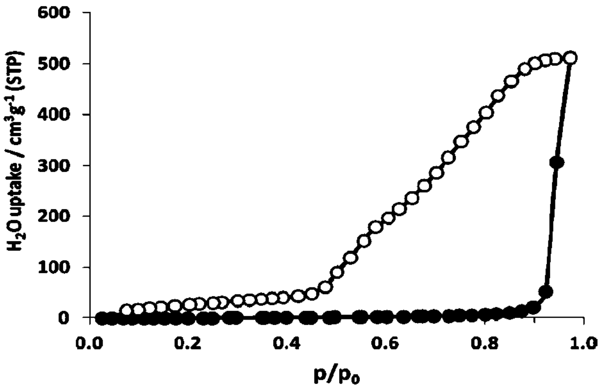

**Figure 18.** Water vapor physisorption isotherms of activated **1** at 298 K (adsorption/desorption ●/○).

coordinatively unsaturated. Thus a porous structure with a coordinatively unsaturated metal center is formed, rendering it an excellent system for the adsorption of different gases. Presently we are looking at the structural variations of different linkers to synthesize porous MOFs with better gas adsorption capacity.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

X-ray crystallographic data in CIF format; table for selected bonds and distances for **1**; complete data for IR, TGA analysis, and PXRD; and tabulated physisorption isotherms. This material is available free of charge via the Internet at http://pubs.acs.org/.

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### Notes

The authors declare no competing financial interest.

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