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# Enhancement of CO<sub>2</sub> uptake and selectivity in a metal-organic framework by incorporation of thiophene functionality

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## Abstract

The complex  $[\text{Zn}_2(\text{tdc})_2\text{dabco}]$  ( $\text{H}_2\text{tdc}$  = thiophene-2,5-dicarboxylic acid; dabco = 1,4-diazabicyclooctane) shows a remarkable increase in  $\text{CO}_2$  uptake and  $\text{CO}_2/\text{N}_2$  selectivity compared to the non-thiophene analogue  $[\text{Zn}_2(\text{bdc})_2\text{dabco}]$  ( $\text{H}_2\text{bdc}$  = benzene-1,4-dicarboxylic acid; terephthalic acid).  $\text{CO}_2$  adsorption at 1 bar for  $[\text{Zn}_2(\text{tdc})_2\text{dabco}]$  is  $67.4 \text{ cm}^3\cdot\text{g}^{-1}$  (13.2 wt.%) at 298 K and  $153 \text{ cm}^3\cdot\text{g}^{-1}$  (30.0 wt.%) at 273 K. For  $[\text{Zn}_2(\text{bdc})_2\text{dabco}]$  the equivalent values are  $46 \text{ cm}^3\cdot\text{g}^{-1}$  (9.0 wt.%) and  $122 \text{ cm}^3\cdot\text{g}^{-1}$  (23.9 wt.%), respectively. The isosteric heat of adsorption for  $\text{CO}_2$  in  $[\text{Zn}_2(\text{tdc})_2\text{dabco}]$  at zero coverage is low ( $23.65 \text{ kJ}\cdot\text{mol}^{-1}$ ), ensuring facile regeneration of the porous material. The enhancement by the thiophene group on the separation of  $\text{CO}_2/\text{N}_2$  gas mixtures has been confirmed by both ideal adsorbate solution theory (IAST) calculations and dynamic breakthrough experiments. The preferred binding sites of adsorbed  $\text{CO}_2$  in  $[\text{Zn}_2(\text{tdc})_2\text{dabco}]$  have been unambiguously determined by *in situ* single crystal diffraction studies on  $\text{CO}_2$ -loaded  $[\text{Zn}_2(\text{tdc})_2\text{dabco}]$ , coupled with quantum chemical calculations. These studies unveil the role of the thiophene moieties in the specific  $\text{CO}_2$  binding *via* an induced dipole interaction between the  $\text{CO}_2$  and the sulfur center, confirming that enhanced  $\text{CO}_2$  capacity in  $[\text{Zn}_2(\text{tdc})_2\text{dabco}]$  is achieved without the presence of open metal sites. The experimental data and the theoretical insights suggest a viable strategy for improvement of adsorption properties of already known materials through incorporation of S-based heterocycles within their porous structures.

## Introduction

Carbon dioxide (CO<sub>2</sub>) release poses one of the biggest anthropogenic impacts to the environment. While broad implementation of low-carbon fuels and strategies will reduce CO<sub>2</sub> release, power plants, cement and steel production represent major industries that will continue to generate exhausts which require effective purification to remove CO<sub>2</sub> as well as other harmful gases.<sup>1</sup> CO<sub>2</sub> sequestration through selective adsorption is viewed as one of the most promising approaches due to its simple implementation, the absence of hazardous materials, tunable selectivity and low energy costs.<sup>2</sup> Thus, porous materials, such as metal-organic frameworks (MOFs), with the highest CO<sub>2</sub> adsorption capacity at relatively low partial pressures (< 5 bar) are valuable targets for such applications.<sup>3-10</sup> High adsorption selectivity and high uptake under ambient conditions may be enhanced in porous materials by the incorporation of specific binding sites at the pore surface. The main strategies for the incorporation of CO<sub>2</sub>-binding centers into MOF structures have been *via* the incorporation of basic centers such as amines functioning as Lewis bases,<sup>11-15</sup> and adsorption at coordinatively unsaturated metal cations as Lewis acid sites.<sup>16-21</sup> The former strategy is a development of the traditional approach of CO<sub>2</sub> capture by amines to form carbamates, and shows high uptakes and very good adsorption selectivity even under humid conditions, but also, significantly, increases the energy cost for regeneration of the adsorbate. The latter strategy employs CO<sub>2</sub> binding through the interaction to vacant metal sites. Despite a number of advantages such as moderate energy penalty for regeneration and tunability of the adsorption sites, such materials often only function under strictly anhydrous conditions as water competes effectively for binding at the unsaturated metal sites. Also the open metal sites usually reach saturation rapidly and thus lose their activity in selective guest binding. Since each strategy has its particular disadvantages, the development of porous materials with high adsorption selectivity, appreciable CO<sub>2</sub> uptake under ambient conditions, capable of working under humid environments and possessing a low regeneration penalty requires new approaches based on other types of inter- and supra-molecular interactions. With a handful of exceptions,<sup>19,22-32</sup> weak van der Waals and supramolecular interactions have not been widely considered as a driving force for specific CO<sub>2</sub> binding which could result in appreciable adsorption selectivity and improved storage capacity. We demonstrate herein that the incorporation of thiophene moieties with polarizable sulfur heteroatoms, capable of induced dipole-dipole interactions, results in a remarkable increase of the CO<sub>2</sub> binding affinity of the microporous MOF, [Zn<sub>2</sub>(tdc)<sub>2</sub>dabco]. This increases both the storage capacity and selectivity of the framework at ambient conditions by as much as 50%,

comparing thiophene with phenyl functionalization, and also maintains the heat of adsorption at a low level to minimize penalty costs for regeneration. The enhanced CO<sub>2</sub> binding property of the thiophene-containing MOF has also been confirmed by fixed-bed breakthrough separation of a CO<sub>2</sub>/N<sub>2</sub> mixture. More importantly, adsorbed CO<sub>2</sub> molecules within [Zn<sub>2</sub>(tdc)<sub>2</sub>dabco] have been directly observed and quantified by *in situ* single crystal diffraction experiments, revealing the preferential host-guest binding interaction in the pores. The mechanism of MOF-CO<sub>2</sub> binding has also been studied by quantum chemical calculations, giving detailed insights on the role of the sulfur atoms in the CO<sub>2</sub> supramolecular binding. These results provide a new viable strategy underpinning the development of MOF materials with improved uptake and selectivity for CO<sub>2</sub>.

## Materials and Methods

All chemicals were of analytical grade and were used without additional purification. DMF was dried over the activated molecular sieves (3Å) prior to use.

**Synthesis of [Zn<sub>2</sub>(tdc)<sub>2</sub>dabco]·4DMF (1).** To a mixture of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (120 mg, 404 μmol) and thiophene-2,5-dicarboxylic acid (H<sub>2</sub>tdc) (47 mg, 273 μmol) in DMF (5.3 ml) was added dabco (23 mg, 205 μmol) in DMF (4.0 ml) dropwise under rigorous stirring to avoid the formation of any precipitate. The resulting clear solution was heated at 100 °C for 20 h. The colorless block-shaped crystals were collected and washed with DMF. Yield: 0.093 mg (78% based on H<sub>2</sub>tdc). Elemental analyses. Calculated for [Zn<sub>2</sub>(tdc)<sub>2</sub>dabco]·4DMF·H<sub>2</sub>O: C, 40.3; H, 5.2; N, 9.4; S, 7.2. Found: C, 40.4; H, 5.0; N, 9.2; S, 7.4. Thermogravimetric analysis. Calculated for 4DMF: 33.4%. Found: 30.5%. FT-IR (KBr): 1667 cm<sup>-1</sup> (νC=O of DMF).

**Synthesis of [Zn<sub>2</sub>(tdc)<sub>2</sub>bpe]·2DMF (2) and [Zn<sub>2</sub>(tdc)<sub>2</sub>bpp]·2DMF (3)** was carried out using a similar procedure starting from Zn(NO<sub>2</sub>)<sub>2</sub>·6H<sub>2</sub>O (250 mg, 842 μmol), H<sub>2</sub>tdc (145mg, 843 μmol) and either 1,2-bis(4-pyridyl)ethane (bpe) (75mg, 408 μmol) or 1,3-bis(4-pyridyl)propane (bpp) (84mg, 424 μmol). The corresponding solids were dissolved in DMF (10 ml) with rigorous stirring and sonification. An unknown precipitate was removed from the reaction solution by centrifugation and the clear solution heated at 100 °C for 40 h. Block-shaped crystals of the product were collected and washed in DMF. The yields are 236 mg (69%) for **2** and 263 mg (73%) for **3**. Elemental analyses. Calculated for [Zn<sub>2</sub>(tdc)<sub>2</sub>bpe]·2DMF: C, 45.0; H,

3.8; N, 7.0; S, 8.0. Found: C, 45.0; H, 3.9; N, 7.0; S, 7.8. Calculated for  $[\text{Zn}_2(\text{tdc})_2\text{bpp}] \cdot 2\text{DMF}$ : C, 45.7; H, 4.0; N, 6.9; S, 7.9. Found: C, 45.3; H, 3.9; N, 6.8; S, 7.5. Thermogravimetric analysis for **2**. Calculated for 2DMF: 18.3%. Found: 17.8%. Thermogravimetric analysis for **3**. Calculated for 2DMF: 18.0%. Found: 17.4%. FT-IR (KBr): **2**, 1675  $\text{cm}^{-1}$ ; **3**, 1666  $\text{cm}^{-1}$  ( $\nu\text{C}=\text{O}$  of DMF).

**Synthesis of activated  $[\text{Zn}_2(\text{tdc})_2\text{dabco}]$  (**1a**).** The as-synthesized compound **1** was heated at 90 °C in *vacuo* for 10 h. The sample weight loss was 30.3%. Elemental analyses. Calculated for  $[\text{Zn}_2(\text{tdc})_2\text{dabco}] \cdot \text{H}_2\text{O}$ : C, 36.0; H, 3.0; N, 4.7; S, 10.7. Found: C, 36.2; H, 3.0; N, 4.8; S, 10.9.

**Synthesis of  $[\text{Zn}_2(\text{tdc})_2\text{bpe}]$  (**2**) and  $[\text{Zn}_2(\text{tdc})_2\text{bpp}]$  (**3**):** The as-synthesized crystals of **2** or **3** were heated at 100 °C in *vacuo* for 6 h. The sample weight loss was found to be 18.4% for **2** and 17.7% for **3**. Elemental analyses. Calculated for  $[\text{Zn}_2(\text{tdc})_2\text{bpe}]$ : C, 44.0; H, 2.5; N, 4.3; S, 9.8. Found: C, 43.7; H, 2.4; N, 4.2; S, 9.5. Calculated for  $[\text{Zn}_2(\text{tdc})_2\text{bpp}] \cdot \frac{2}{3}\text{H}_2\text{O}$ : C, 44.1; H, 2.9; N, 4.1; S, 9.4. Found: C, 44.5; H, 2.7; N, 4.2; S, 9.0.

## Results and discussion

### Synthesis and crystal structure analysis

The coordination polymer  $[\text{Zn}_2(\text{tdc})_2\text{dabco}] \cdot 4\text{DMF}$  (**1**) was prepared by solvothermal reaction of  $\text{Zn}(\text{NO}_3)_2$ , thiophene-2,5-dicarboxylic acid ( $\text{H}_2\text{tdc}$ ) and dabco in hot DMF (100 °C) to give rectangular colorless stick-like single crystals. The stability of **1** was found to be very similar to many Zn(II) carboxylate MOFs. The crystalline material **1** is stable in organic media, but decomposes rapidly in water. The as-synthesized crystals **1** can be handled in air for several hours without any impact on crystallinity. Single crystal X-ray diffraction confirms that **1** crystallizes in tetragonal space group  $P\bar{4}2_1c$  and incorporates binuclear paddle-wheel nodes  $[\text{Zn}_2(\text{OOCR})_4]$  (Fig. 1a) bound by four carboxylate groups of  $\text{tdc}^{2-}$  anions to form a slightly squeezed layer of square-grid topology with a corrugated overall structure (Fig. 1b). The remaining available coordination site at the square pyramidal Zn(II) cations are bound by N-donors of the dabco ligands, which connect  $[\text{Zn}_2(\text{tdc})_2]$  layers into a 3D porous framework with a scaffold-like primitive cubic topology **pcu** (Fig. 1c). The rotation of the dabco ligands results, as expected, in severe disorder of the carbon atoms of the  $\text{CH}_2\text{CH}_2$  moieties, and the rigid angular shape of the  $\text{tdc}^{2-}$  anion forces notable distortions of the paddle-wheel unit such that the Zn-Zn axis is twisted from the *c* crystallographic direction of the unit cell by *ca.* 16°. The van der Waals aperture of the channels running along the 4-fold axis is  $5 \times 8 \text{ \AA}$  corresponding to the

shape of the squeezed square window of the  $[\text{Zn}_2(\text{tdc})_2]$  layer (Fig. 1d). These corrugated layers stack along the  $c$  direction in an alternating ABAB fashion, forming two different types of smaller windows across the 4-fold axis. The narrower window has van der Waals dimensions of  $2.5 \times 5 \text{ \AA}$  formed by two closely located  $\text{tdc}^{2-}$  moieties. The wider  $3.5 \times 5 \text{ \AA}$  window is formed by two  $\text{tdc}^{2-}$  arcs bent outwards from each other with an interatomic S...S distance of  $8.5 \text{ \AA}$  (Fig. 1e). It is worth noting that the slight tilting of the thiophene groups [*i.e.*, the orientation of the heteroatom (*vide supra*)] results in two different types of pore environment (Fig. 1b). Regardless of this tilting, both types of channels have similar aperture and are set up for diffusion of gas molecules with potential interaction with the sulfur atoms of the thiophene moieties.

In a similar manner, two additional microporous zinc(II) thiophene-2,5-dicarboxylates  $[\text{Zn}_2(\text{tdc})_2\text{bpe}] \cdot 2\text{DMF}$  (**2**) and  $[\text{Zn}_2(\text{tdc})_2\text{bpp}] \cdot 2\text{DMF}$  (**3**) were synthesized using 1,2-bis(4-pyridyl)ethane (bpe) and 1,3-bis(4-pyridyl)propane (bpp) as N-donor bridging ligands, respectively. During the course of this work the synthesis and structure of **2** was reported.<sup>33</sup> In **2** and **3** the structure of the  $[\text{Zn}_2(\text{tdc})_2]$  corrugated layer remains unchanged compared to **1**, and these layers are connected through longer N-donor linkers (Fig. 2). The elongation of the bridging ligand does open up the possibility for framework interpenetration, which is not possible for **1** incorporating shorter dabco ligands.<sup>34</sup> As a result the structure **1** is a single non-interpenetrated net, while **2** and **3** show doubly-interwoven structures with **pcu** topology. Despite the interpenetration, both **2** and **3** contain microporous volume filled with solvent molecules in the as-synthesized materials. We should also note that in spite of our numerous attempts to obtain similar structures with 4,4'-bipyridyl or *trans*-bis(4-pyridyl)ethylene bridging ligands we could not crystallize any product thus far. The problem could be related to steric constraint of substantially skewed  $[\text{Zn}_2(\text{OOCR})_4]$  paddle-wheel building units, which cannot be inter-connected by structurally rigid linear ligands. Dabco is an apparent exception due to its aliphatic nature and the formation of rather strong metal-ligand coordination bonds. The micropores of the as-synthesized materials **1-3** are filled by DMF solvent molecules which were located from the X-ray diffraction data. The FT-IR spectra and the chemical and thermogravimetric analyses confirm the nature and composition of the guest molecules. According to TGA data the DMF molecules can be removed by heating the material to 170–190 °C, while the irreversible thermolysis of the metal-organic framework takes place near 300 °C for **1** and **2**, or 330 °C for **3**.

The guest-free sample  $[\text{Zn}_2(\text{tdc})_2\text{dabco}]$  (**1a**) was obtained by thermal activation of the as-synthesized crystals **1** in *vacuo*. Compared with the as-synthesized **1**, the activated **1a** is more susceptible to airborne moisture, but no sign of degradation of the X-ray powder diffraction pattern or gas adsorption properties was observed for **1a** exposed to air for 1h. The crystalline material was sufficiently robust to sustain the activation procedure so we were able to characterize the solvent-free open structure **1a** by single-crystal X-ray diffraction. The space group was found to be *I4/mmm* (tetragonal) and the local coordination of the metal cations as well as the overall **pcu** connectivity remains unchanged from **1** (Fig. 3a). The only notable difference is that the anionic  $\text{tdc}^{2-}$  linkers are more linear in the guest-free structure **1a**, resulting in a higher symmetry and a more regular structure with rectangular channels of van der Waals aperture  $6.5 \times 6.5$  Å (Fig. 3b). This straightening of the organic ligands results in an overall expansion of the guest-free structure **1a**, compared to the solvated material **1**. The total unit cell volume increases during the activation by *ca.* 3%. Notably, the structural changes between **1** and **1a** are fully reversible as the guest free compound **1a** shrinks back when placed in DMF solvent to re-form **1**. It is worth noting that the analogous compound based on terephthalate  $\text{bdc}^{2-}$  bridging ligands  $[\text{Zn}_2(\text{bdc})_2\text{dabco}] \cdot x(\text{solv})$  (**4**) features the same reversible structural changes upon the framework activation and re-solvation, though the degree of volume expansion/contraction of the unit cell in **4** is somewhat greater (3–5%) depending on the nature of the solvent.<sup>35,36</sup>

### Gas adsorption studies

Activation of the interpenetrated compounds **2** and **3** was achieved by heating the compounds *in vacuo* at 100 °C for 6 h. The complete removal of the guest DMF molecules without framework collapse was confirmed by powder X-ray diffraction (PXRD), TGA, chemical analyses and IR spectroscopy. Some shift of the PXRD peaks to higher  $2\theta$  angles upon de-solvation of **3** indicates a shrinkage of the partially flexible framework.  $\text{N}_2$  adsorption measurements for the activated samples at 77 K showed reversible type I isotherms, characteristic of microporous materials, with pore volumes of 0.19 and 0.20  $\text{cm}^3 \cdot \text{g}^{-1}$  and BET surface areas of 447 and 407  $\text{m}^2 \cdot \text{g}^{-1}$  for **2** and **3**, respectively (See ESI). The relatively low porosity for these compounds is not surprising given the observed two-fold interpenetrated structures for these species.



The stability and permanent porosity of the guest free compound **1a** was confirmed by PXRD and gas adsorption measurements. The N<sub>2</sub> isotherm at 77 K reveals a type I reversible isotherm (Fig. 4) with a pore volume of 0.68 cm<sup>3</sup>·g<sup>-1</sup> and BET surface area of 1553 m<sup>2</sup>·g<sup>-1</sup>. The pore volume is similar to the expected value of 0.63 cm<sup>3</sup>·g<sup>-1</sup> calculated from the gravimetric density of the framework **1a** (0.94 g·cm<sup>-3</sup>) and its guest accessible volume (0.59 v/v) according to the PLATON SOLV routine.<sup>37</sup> This is entirely consistent with the complete activation of the material and the overall stability of the porous structure under these conditions. The pore-size distribution, calculated from the N<sub>2</sub> isotherm, gives a sharp peak near 8 Å, which corresponds to the van der Waals diameter of the cubic cages in **1a** (ca. 8–9 Å). The pore volume of **1a** and its specific surface area are very close to those reported earlier for the terephthalate analogue [Zn<sub>2</sub>(bdc)<sub>2</sub>dabco] (**4a**) (0.75 cm<sup>3</sup>·g<sup>-1</sup> and 1450 m<sup>2</sup>·g<sup>-1</sup>, respectively).<sup>38</sup> Consistent with these surface area data, the H<sub>2</sub> adsorption for **1a** (245 cm<sup>3</sup>·g<sup>-1</sup> and 2.23 wt.% at 77K and 1 bar) is slightly higher than for **4a** (2.0 wt.%) under similar conditions.

The reported CO<sub>2</sub> adsorption measurements for **4a**,<sup>39,40</sup> as well as our data (see ESI) indicate rather moderate gas uptake of 9.0 wt.% (46 cm<sup>3</sup>·g<sup>-1</sup>) at 298K and 1 bar, and 23.9 wt.% (122 cm<sup>3</sup>·g<sup>-1</sup>) at 273 K and 1 bar. In contrast, CO<sub>2</sub> adsorption in **1a**, which generally shows similar porosity as **4a**, reveals a significant increase of ca 50% in uptake under the same conditions. The maximum CO<sub>2</sub> adsorption in **1a** at 1 bar reaches as high as 13.2 wt% (67.4 cm<sup>3</sup>·g<sup>-1</sup>) at 298 K and 1 bar, and 30.0 wt% (153 cm<sup>3</sup>·g<sup>-1</sup>) at 273 K and 1 bar (Fig. 5). At a pressure of 0.15 bar, which is relevant to the flue gas processing, the CO<sub>2</sub> uptakes of **1a** are 18.5 wt.% and 8.5 wt.% at 273 and 298 K, respectively.

The isosteric heat of adsorption for CO<sub>2</sub> in **4a** at zero coverage, calculated from the isotherms at 273 and 298 K using the Clausius-Clapeyron equation is 19.52 kJ·mol<sup>-1</sup> consistent with literature data.<sup>41</sup> The heat of the adsorption of CO<sub>2</sub> for **1a** is noticeably higher at 23.65 kJ·mol<sup>-1</sup>, reflecting presumably stronger binding of CO<sub>2</sub> to the thiophene ring. The modest adsorption enthalpy of **1a** highlights the absence of the strong binding centers in **1a** with open metal sites and active amines reported to increase the heat of adsorption to 35–45 kJ·mol<sup>-1</sup> and 50–100 kJ·mol<sup>-1</sup>, respectively.<sup>5,6</sup> Despite the negative impact to the selectivity,<sup>42</sup> the low heat of the adsorption in **1a** decreases the energy penalty for the regeneration of the porous material in a temperature-swing process.

### Gas adsorption selectivity and gas separation studies

Together with the CO<sub>2</sub> uptake, the CO<sub>2</sub>/N<sub>2</sub> adsorption selectivity is one of the most important parameters for the practical application of porous materials in the purification of the industrial exhausts.<sup>43</sup> The adsorption data (see ESI) allowed us to calculate the CO<sub>2</sub>/N<sub>2</sub> selectivity factors for **1a** and **4a** at 298 K by three commonly used methodologies *via* i. the ratio of the adsorbed gas volume, ii. the ratio of the Henry's constants, and iii. using ideal adsorbed solution theory (IAST). The selectivity, calculated as the ratio of the adsorbed gas volumes by **1a** at 1 bar, is  $V(\text{CO}_2)/V(\text{N}_2) = 15.1$  (Fig. 5). By considering a typical flue gas composition of 0.15 bar CO<sub>2</sub> and 0.75 bar N<sub>2</sub>, the normalized<sup>37</sup> selectivity of adsorption at this composition can be calculated  $S_{\text{ads}} = 11.4$ . The corresponding numbers for **4a** are  $V(\text{CO}_2)/V(\text{N}_2) = 10.2$  and  $S_{\text{ads}} = 9.4$ . The Henry's constants ( $K_H$ ) were derived from the linear approximation of the low pressure part of the isotherms, and based on the obtained values of  $K_H$  for **1a** and **4a**, and the selectivity factors at 298 K were calculated to be 12.5 and 8.9, respectively. The IAST<sup>44</sup> calculations for **1a** resulted in a selectivity factor of 11.2 for an equimolar CO<sub>2</sub>/N<sub>2</sub> mixture, while for **4a** this factor is 9.2. Thus, comparison of the above selectivity factors for **1a** and **4a** concludes that substitution of a phenyl group to thiophene on going from **4a** to **1a** enhances the CO<sub>2</sub>/N<sub>2</sub> adsorption selectivity by 20 to 50%, depending upon the methodology used. Finally, it is important to note that even though the obtained selectivity factors for **1a** are lower than those for MOFs with strong CO<sub>2</sub> binding centers, a selectivity above 8 is high enough to be considered for practical applications.<sup>45</sup>

The potential of utilising these MOFs for CO<sub>2</sub> separation has also been confirmed in breakthrough experiments in which an equimolar mixture of CO<sub>2</sub>/N<sub>2</sub> was flowed over a packed bed of **1a** at 298 K and 1.0 bar (Fig. 6). To validate the role of thiophene group in enhanced CO<sub>2</sub> binding, corresponding breakthrough experiment has also been conducted on the phenyl-functionalized material **4a** under the same conditions. As predicted by the selectivity calculations, a complete separation has been achieved in both cases, with N<sub>2</sub> being the first to elute through the bed, whereas CO<sub>2</sub> was retained. On saturation, CO<sub>2</sub> breaks through from the bed and reaches saturation rapidly. As shown in Fig. 6, dimensionless breakthrough plots offer a direct comparison between **1a** and **4a** on the performance of separation of the CO<sub>2</sub>/N<sub>2</sub> mixture. Significantly, **1a** shows a pronouncedly better separation than **4a** ( $\Delta\tau = 130$  and  $87$  for **1a** and **4a**, respectively). Additionally, the enhanced CO<sub>2</sub> storage capacity by the thiophene functionalization in **1a** has been confirmed by its notably delayed (almost a factor of 2) breakthrough of CO<sub>2</sub> ( $\tau = 250$  and  $143$  for **1a** and **4a**, respectively). These results confirm the potential application of **1a** on CO<sub>2</sub>/N<sub>2</sub> separation.

## Theoretical studies

Achieving such an outstanding affinity towards CO<sub>2</sub> in the absence of strong Lewis basic centers or coordinatively unsaturated metal sites prompted us to thoroughly investigate the nature of the CO<sub>2</sub> binding in **1a**. The main difference between **1a** and **4a** is the chemical environment of the microporous surface as the channels in **1a** are decorated by sulfur atoms from the thiophene-2,5-dicarboxylate linkers. In the absence of any stronger intermolecular interactions (such as donor-acceptor bonds or H-bonds) the CO<sub>2</sub> guest molecules have to interact with the porous host through somewhat weaker dipole-dipole interactions. The sulfur atom is more susceptible to polarization and thus for the induced dipole interactions with the quadrupole of CO<sub>2</sub>. Comparison of [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(bpdc)<sub>6</sub>] with [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(bt dc)<sub>6</sub>] (bpdc<sup>2-</sup> = biphenyl-4,4'-dicarboxylate, bt dc<sup>2-</sup> = bithiophenedicarboxylate) shows, depending on the temperature, a 32 to 78% increase for the gravimetric CO<sub>2</sub> uptake for the latter thiophene-containing structure.<sup>25</sup> It was suggested that differences in the electrostatic surface potentials for bpdc<sup>2-</sup> and bt dc<sup>2-</sup> accounted for this difference, but no direct chemical explanation was given. In order to understand the role of the tdc<sup>2-</sup> ligand in CO<sub>2</sub> adsorption in **1a**, we undertook grand canonical Monte Carlo (GCMC) simulations (see ESI). These reveal unambiguously that CO<sub>2</sub> is preferentially adsorbed near the tdc<sup>2-</sup> linker at low loading (Fig. 7a) and that thiophene plays a key role in the adsorption of CO<sub>2</sub> at low pressure. The CO<sub>2</sub>...tdc<sup>2-</sup> interaction was probed further by DFT simulations, which confirmed that the carbon-sulfur bond provides an excellent binding site for CO<sub>2</sub> (Fig. 7b,c), with calculated binding energies ranging from -15.7 to -18.3 kJ·mol<sup>-1</sup>, *ca.* 3-10 kJ·mol<sup>-1</sup> stronger than reported binding energies for CO<sub>2</sub> with benzene-based moieties.<sup>46-48</sup> The shortest S...C interatomic distance in the energy-optimized thiophene...CO<sub>2</sub> complex is 3.51 Å (Fig. 7c), equal to the sum of the van der Waals radii of sulfur and carbon. The simulated heat of CO<sub>2</sub> adsorption in **1a** (24.2 kJ·mol<sup>-1</sup>) coincides with the experimental value (23.65 kJ·mol<sup>-1</sup>), giving consistency between the theory and the experiment. The lower value of heat of adsorption of CO<sub>2</sub> for **4a** (19.6 kJ·mol<sup>-1</sup>),<sup>39</sup> calculated by DFT, suggests and generalizes the idea that the inclusion of thiophene-based ligands in MOFs provides a route to materials with an increased affinities for CO<sub>2</sub>.

## Determination of the binding sites for adsorbed CO<sub>2</sub>

We also sought to determine the preferred binding sites of adsorbed CO<sub>2</sub> molecules in the extended pore structure of **1a** by *in situ* synchrotron X-ray single-crystal diffraction. Desolvated sample of **1a** shows complete retention of the framework structure and removal of the free guest solvent molecules from the pore (Fig. 8a). Two types of pores can be clearly observed and are denoted as  $\alpha$  and  $\beta$  with a pore diameter of 7.1 Å and 7.8 Å (taking into consideration of van der Waal radii), respectively. The S centers of all thiophene groups point into pore  $\alpha$ , whereas pore  $\beta$  is primarily functionalized with –CH moieties on the thiophene. The desolvated **1a** was then loaded with CO<sub>2</sub> at a pressure of 1.0 bar at 273 K and diffraction data collected at time  $t = 0.25, 1, \text{ and } 2$  hours to capture the dynamic information of site population. It is worth mentioning that the kinetics of gas uptake in single crystals could be notably different to that of powder sample typically used in isotherm experiments. Analysis of the diffraction data indicates an absence of notable structural phase change of **1a** upon CO<sub>2</sub> inclusion. Sequential Fourier difference map analysis of the diffraction data revealed the position of the adsorbed CO<sub>2</sub> molecules in all three structures (Fig. 8 b–d).

At the first dataset of CO<sub>2</sub>-loaded **1a**, only one binding site, (CO<sub>2</sub><sup>I</sup>) was located within the pore  $\alpha$  of **1a**·(CO<sub>2</sub>)<sub>0.40</sub>. CO<sub>2</sub><sup>I</sup> (occupancy = 0.20) is located near the {Zn<sub>2</sub>} paddle-wheel stabilised by dipole interactions to the paddle-wheel and hydrogen bonds to the –CH groups (Fig. S6). Upon the second data collection, **1a**·(CO<sub>2</sub>)<sub>1.56</sub>, the occupancy of CO<sub>2</sub><sup>I</sup> increases to 0.43, accompanied by the appearance of a second binding site (CO<sub>2</sub><sup>II</sup>) with an occupancy of 0.352. CO<sub>2</sub><sup>II</sup> was located in pore  $\beta$  and is close to the thiophene group (Fig. S7). Interestingly, the CO<sub>2</sub>–thiophene interatomic distance found in the X-ray diffraction data (3.49 Å) is highly consistent with that (3.51 Å) obtained in the DFT calculation. On additional equilibrium time ( $t = 2$  h), **1a**·(CO<sub>2</sub>)<sub>1.63</sub>, the occupancies of CO<sub>2</sub><sup>I</sup> and CO<sub>2</sub><sup>II</sup> drop slightly to 0.38 and 0.29, respectively, indicating a re-distribution of adsorbed CO<sub>2</sub> molecules. The rest of adsorbed CO<sub>2</sub> molecules fill into a third site (CO<sub>2</sub><sup>III</sup>) with an occupancy of 0.14 (Fig. S8). CO<sub>2</sub><sup>III</sup> was found in pore  $\alpha$ , forming intermolecular dipole interaction with CO<sub>2</sub><sup>I</sup> in a “T-shape” manner. Additional diffraction data collection at  $t > 2$  h yielded same crystal structures as **1a**·(CO<sub>2</sub>)<sub>1.63</sub>, indicating the presence of adsorption equilibrium. Thus, two out of the three CO<sub>2</sub> binding sites are found within the sulfur-rich pore  $\alpha$  of **1a**, confirming the critical role of this heteroatom functionalization in carbon dioxide adsorption. Indeed, the observation of direct host-guest interaction between the thiophene and CO<sub>2</sub><sup>II</sup> represents the first experimental evidence of CO<sub>2</sub> binding to a sulfur-rich functional group in MOFs.

## Conclusions

Three isorecticular porous MOFs based on  $[\text{Zn}_2(\text{OOCR})_4]$  paddle-wheels, connected through thiophene-2,5-dicarboxylate moieties and N-donor linkers (L)  $[\text{Zn}_2(\text{tdc})_2\text{L}]$  have been synthesized and characterized. Apart from some structural distortions these frameworks are very similar to the prototypic Zn(II) terephthalate material  $[\text{Zn}_2(\text{bdc})_2\text{dabco}]$  and has similar porosity in terms of pore size, volume and specific surface area. However, substitution of a phenyl group with thiophene substantially increases adsorption of  $\text{CO}_2$  as well as  $\text{CO}_2/\text{N}_2$  separation selectivity as evidenced by thorough gas isotherm measurements and breakthrough experiments. The thiophene-lined  $[\text{Zn}_2(\text{tdc})_2\text{dabco}]$  possesses a very good  $\text{CO}_2$  uptake under ambient condition even though it features neither basic amine functions nor open metal sites, which is reflected by a low isosteric heat of adsorption. The *in situ* synchrotron X-ray diffraction data and quantum chemical calculation confirm the role of the thiophene heterocycle and, particularly, sulfur atoms in binding  $\text{CO}_2$  via induced dipole interactions. These results emphasize the feasibility of van der Waals interactions to effective  $\text{CO}_2$  binding while maintaining low heat of adsorption within a hydrophobic porous material. More importantly, the incorporation of heterocycles into porous structures may represent a viable route to improving the adsorption properties of already known materials.

## ASSOCIATED CONTENT

Supplementary information available: the details of the analytical methods, X-ray single crystal experiments, CIF files, gas adsorption measurements, GCMC and DFT calculation, additional figures and plots. CCDC 1503063-1503066 and 1568882-1568885 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center at [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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### Competing financial interests

The authors declare no competing financial interests.

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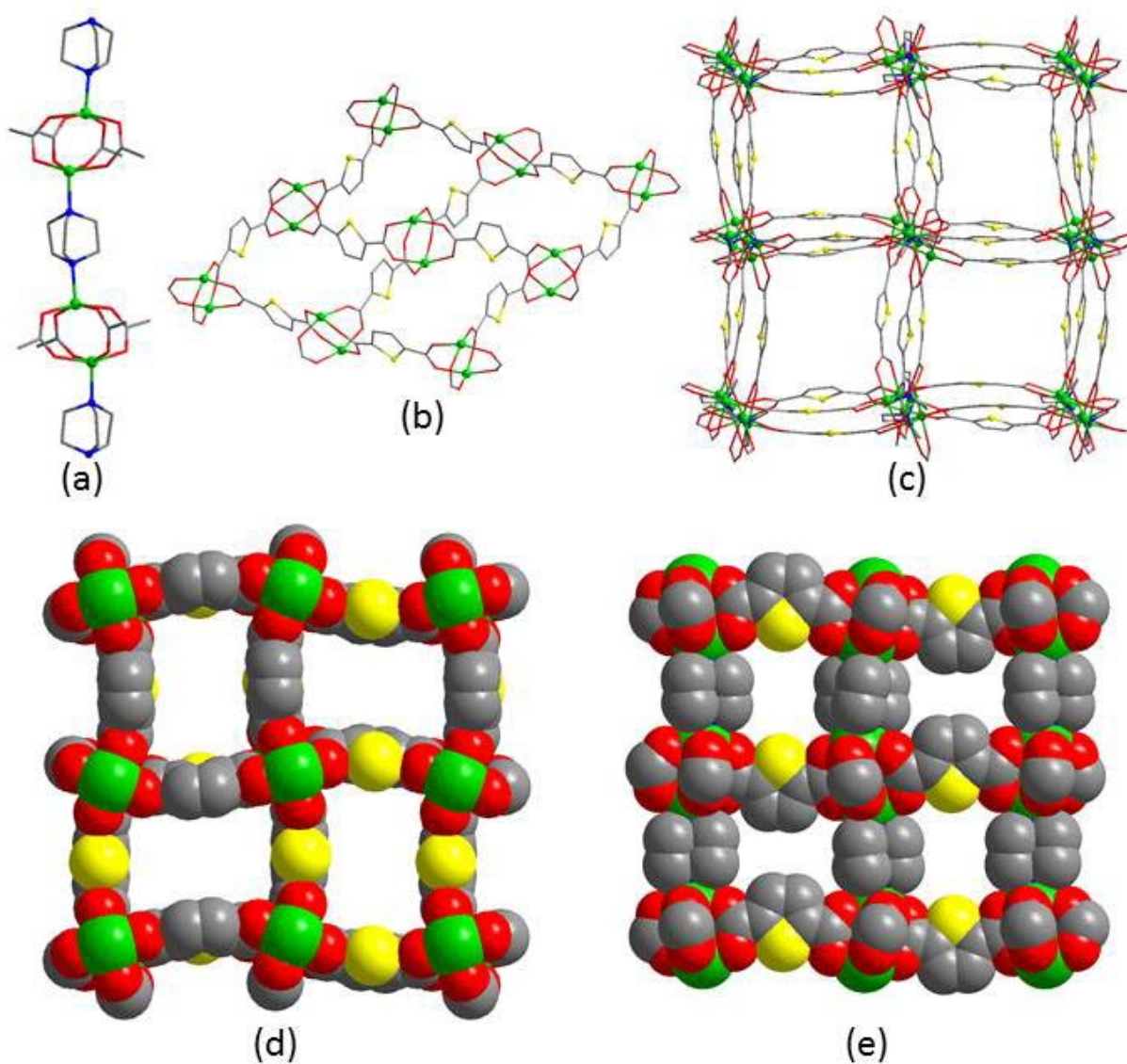
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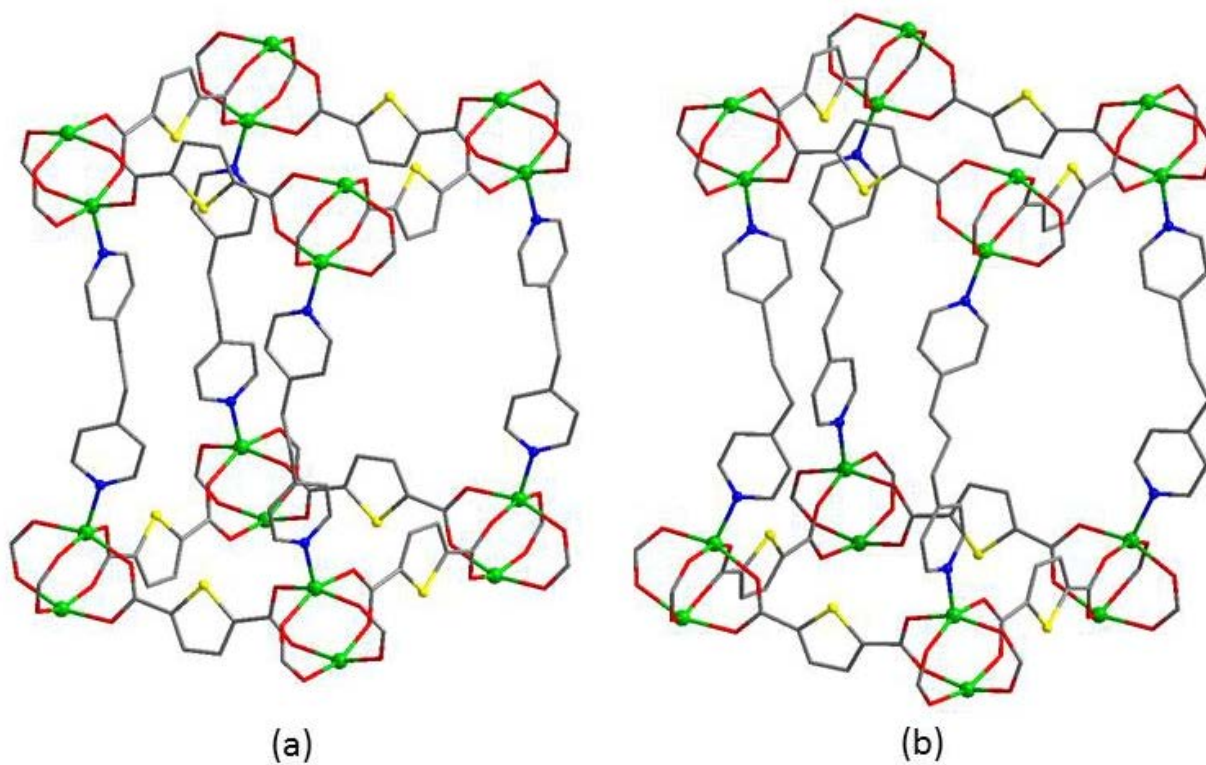
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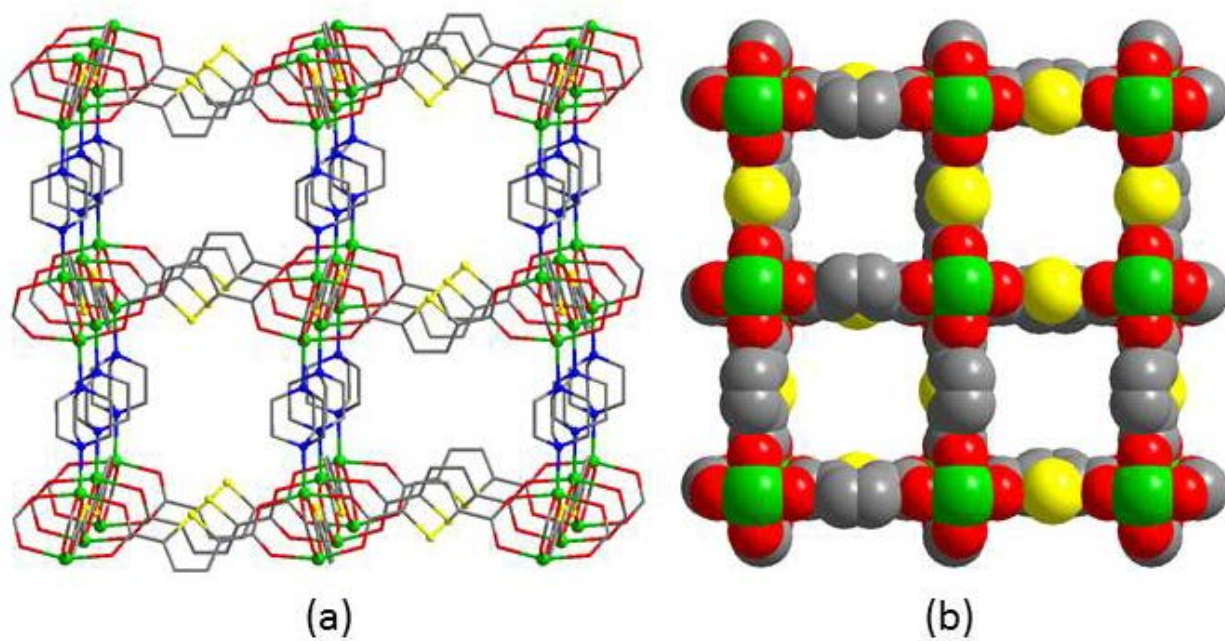
## Figures and Legends



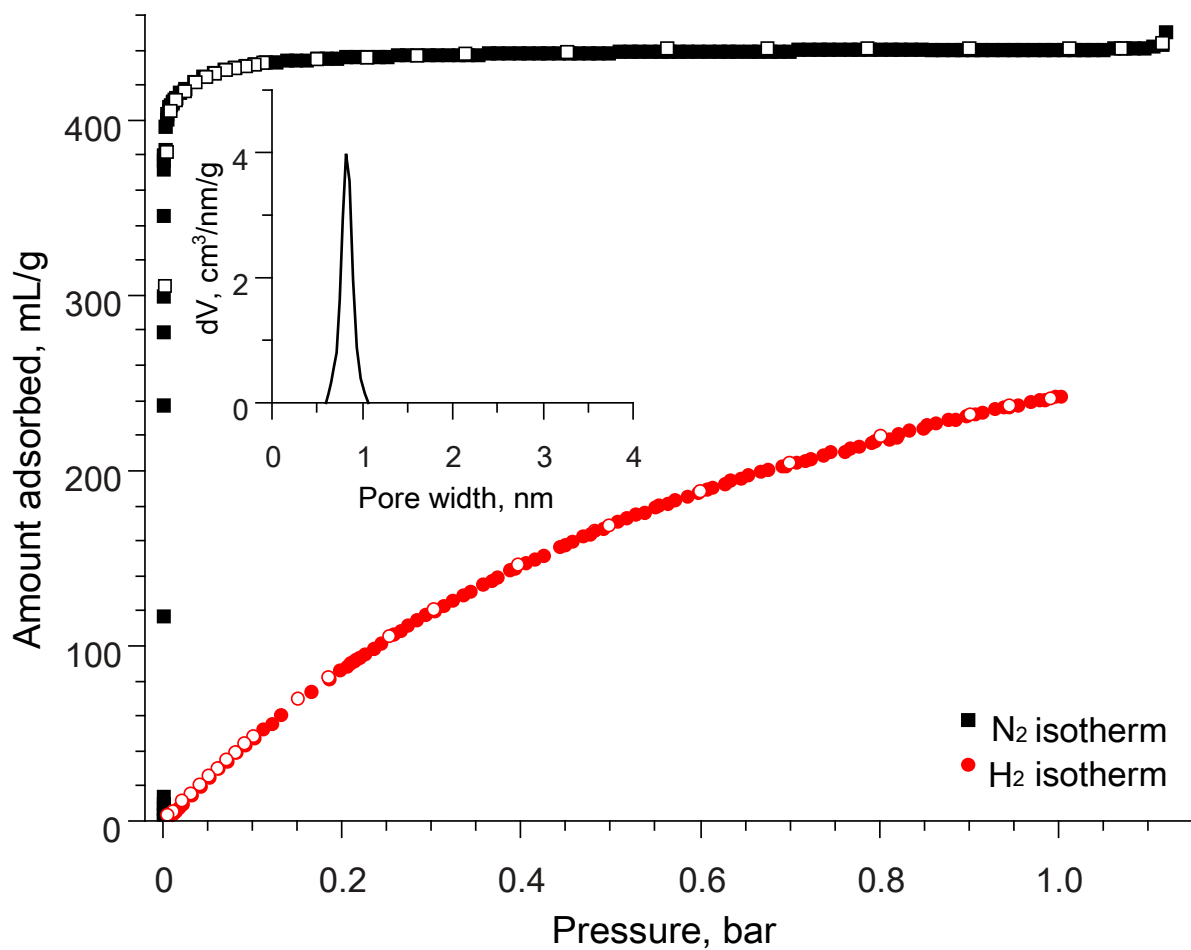
**Figure 1.** View of the structure of the as-synthesized [Zn<sub>2</sub>(tdc)<sub>2</sub>dabco]·4DMF (**1**). The view of the [Zn<sub>2</sub>(OOCR)<sub>4</sub>] paddle-wheels, connected by dabco ligands (a). The structure of the [Zn<sub>2</sub>(tdc)<sub>2</sub>] layer (b). Projection of the crystal structure of **1** along the 4-fold axis (c). The aperture of channels along the 4-fold axis (d). The aperture of channels across the 4-fold axis (e). Zn – green, S – yellow, O – red, N – blue, C – grey, hydrogen atoms are not shown.



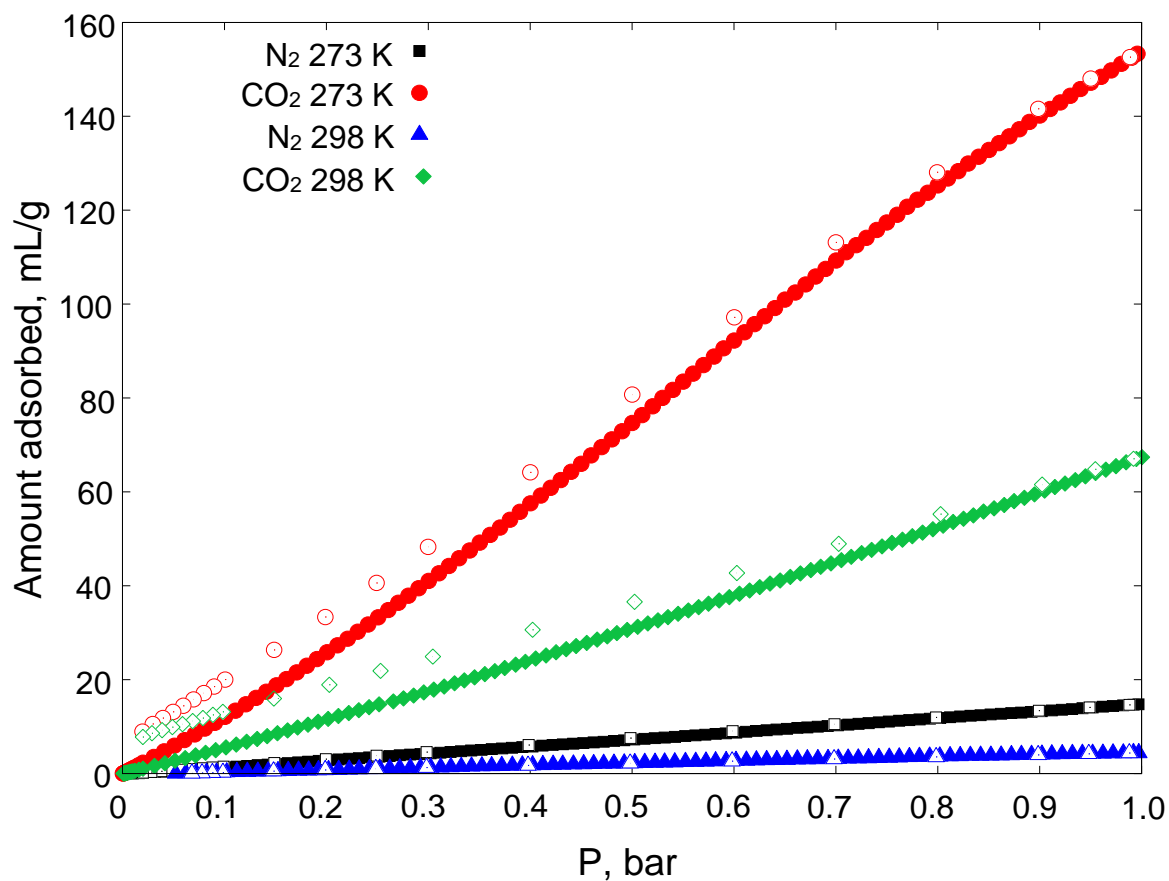
**Figure 2.** Views of the single nets of  $[\text{Zn}_2(\text{tdc})_2\text{bpe}]\cdot 2\text{DMF}$  (**2**)<sup>28</sup> (a) and  $[\text{Zn}_2(\text{tdc})_2\text{bpp}]\cdot 2\text{DMF}$  (**3**) (b). Zn – green, S – yellow, O – red, N – blue, C – grey, hydrogen atoms are not shown.



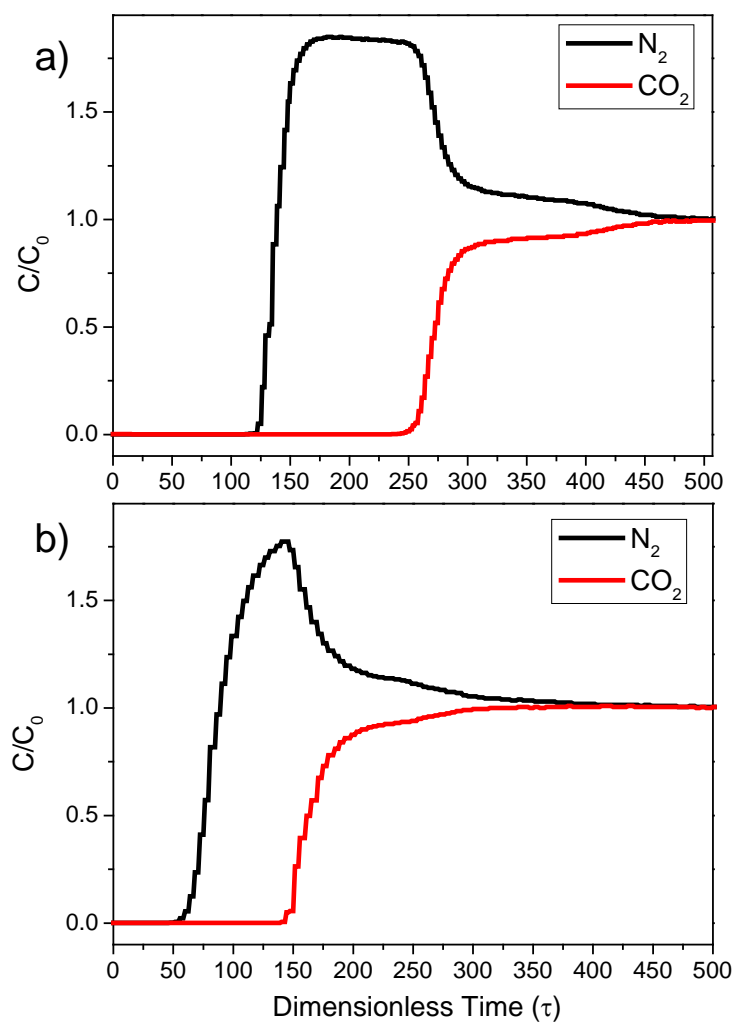
**Figure 3.** View of the crystal structure of the activated [Zn<sub>2</sub>(tdc)<sub>2</sub>dabco] (**1a**). Wireframe presentation viewed along the [Zn<sub>2</sub>(tdc)<sub>2</sub>] layers (a). Van der Waals model view along the 4-fold axis (b). Zn – green, S – yellow, O – red, N – blue, C – grey, hydrogen atoms are not shown.



**Figure 4.** N<sub>2</sub> (black squares) and H<sub>2</sub> (red circles) isotherms for [Zn<sub>2</sub>(tdc)<sub>2</sub>dabco] (**1a**) at 77K. Adsorption – full symbols, desorption – open symbols. Inset: pore size distribution curve.

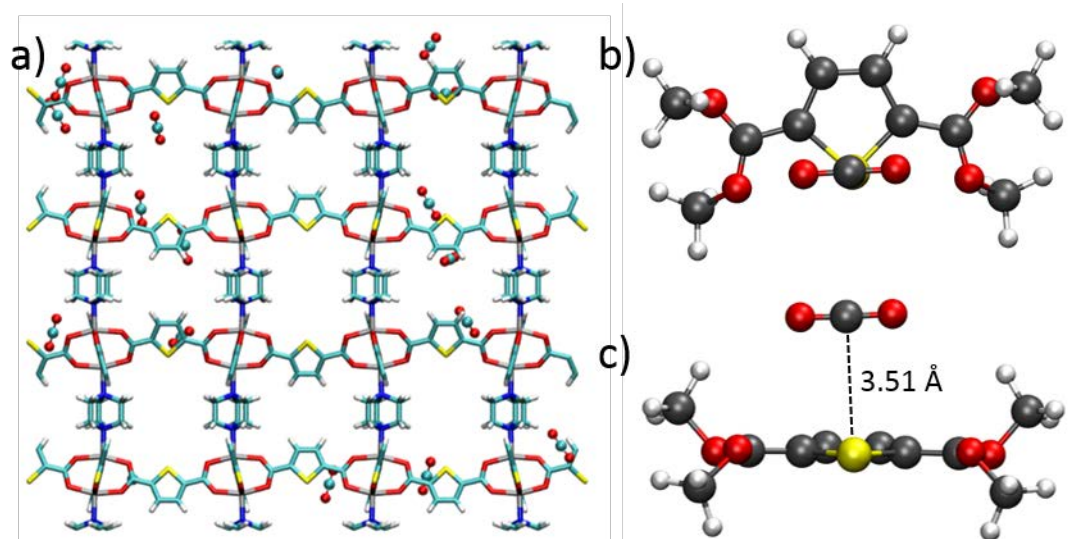


**Figure 5.**  $N_2$  and  $CO_2$  adsorption (full symbols) and desorption (open symbols) isotherms on  $[Zn_2(tdc)_2dabco]$  (**1a**) at 273 K and 298 K.

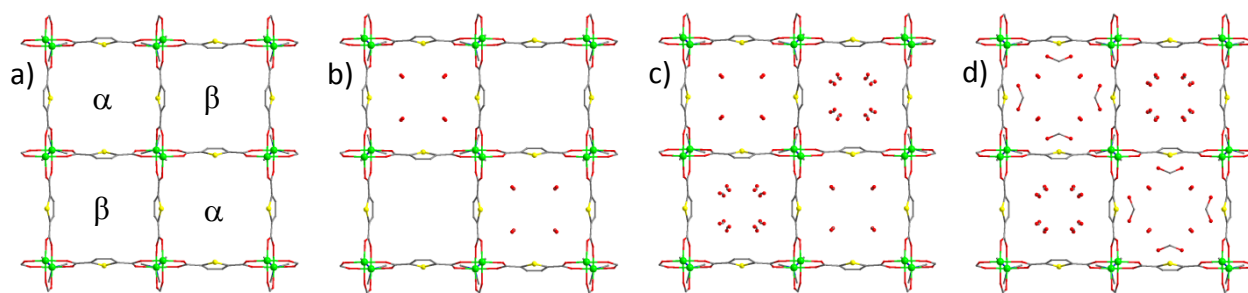


**Figure 6.** Dimensionless breakthrough curves for  $N_2/CO_2$  mixture (1:1) for **1a** (a) and **4a** (b) at 25 °C and 1 bar.





**Figure 7.** Snapshot from GCMC simulation at low pressure in which the majority of CO<sub>2</sub> molecules were found to be located near to the thiophene ring (a). The DFT-optimized lowest-energy binding site for CO<sub>2</sub> viewed from above the tdc<sup>2-</sup> fragment (b,c).



**Figure 8.** X-ray crystal structures for [Zn<sub>2</sub>(tdc)<sub>2</sub>dabco] (**1a**) as a function of CO<sub>2</sub> loading (projection along the *c* direction). The gas-free activated structure **1a** featuring sulfur-rich ( $\alpha$ ) and sulfur-poor ( $\beta$ ) channels, respectively (a). Views of the binding site for adsorbed CO<sub>2</sub> molecules at gradually increased population of CO<sub>2</sub> in the channels of **1a** (b, c, d).

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