Enhancement of CO₂ Uptake and Selectivity in a Metal–Organic Framework by the Incorporation of Thiophene Functionality

Vsevolod A. Bolotov, Konstantin A. Kovalenko, Denis G. Samsonenko, Xue Han, Xinran Zhang, Gemma L. Smith, Laura J. Mc Cormick, Simon J. Teat, Sihai Yang, Matthew J. Lennox, Alice Henley, Elena Besley, Vladimir P. Fedin, Danil N. Dybtsev, and Martin Schröder

Nikolaev Institute of Inorganic Chemistry (NIIC), Siberian Branch of the Russian Academy of Sciences, 3 Ac. Lavrentiev Avenue, Novosibirsk 630090, Russian Federation
Novosibirsk State University, 2 Pirogova Street, Novosibirsk 630090, Russian Federation
School of Chemistry, University of Manchester, Manchester M13 9PL, U.K.
Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States
Centre for Advanced Separations Engineering, Department of Chemical Engineering, University of Bath, Bath BA2 7AY, U.K.
School of Chemistry, University of Nottingham, Nottingham NG7 2RD, U.K.

Supporting Information

ABSTRACT: The complex [Zn₂(tdc)₂dabco] (H₂tdc = thiophene-2,5-dicarboxylic acid; dabco = 1,4-diazabicyclooctane) shows a remarkable increase in carbon dioxide (CO₂) uptake and CO₂/dinitrogen (N₂) selectivity compared to the nonthiophene analogue [Zn₂(bdc)₂dabco] (H₂bdc = benzene-1,4-dicarboxylic acid; terephthalic acid). CO₂ adsorption at 1 bar for [Zn₂(tdc)₂dabco] is 67.4 cm³·g⁻¹ (13.2 wt %) at 298 K and 153 cm³·g⁻¹ (30.0 wt %) at 273 K. For [Zn₂(bdc)₂dabco], the equivalent values are 46 cm³·g⁻¹ (9.0 wt %) and 122 cm³·g⁻¹ (23.9 wt %), respectively. The isosteric heat of adsorption for CO₂ in [Zn₂(tdc)₂dabco] at zero coverage is low (23.65 kJ·mol⁻¹), ensuring facile regeneration of the porous material. Enhancement by the thiophene group on the separation of CO₂/N₂ gas mixtures has been confirmed by both ideal adsorbate solution theory calculations and dynamic breakthrough experiments. The preferred binding sites of adsorbed CO₂ in [Zn₂(tdc)₂dabco] have been unambiguously determined by in situ single-crystal diffraction studies on CO₂-loaded [Zn₂(tdc)₂dabco], coupled with quantum-chemical calculations. These studies unveil the role of the thiophene moieties in the specific CO₂ binding via an induced dipole interaction between CO₂ and the sulfur center, confirming that an enhanced CO₂ capacity in [Zn₂(tdc)₂dabco] is achieved without the presence of open metal sites. The experimental data and theoretical insight suggest a viable strategy for improvement of the adsorption properties of already known materials through the incorporation of sulfur-based heterocycles within their porous structures.

INTRODUCTION
Carbon dioxide (CO₂) release poses one of the biggest anthropogenic impacts to the environment. While broad implementation of low-carbon fuels and strategies will reduce CO₂ release, power plants, cement, and steel production represent major industries that will continue to generate exhausts that require effective purification to remove CO₂ as well as other harmful gases. CO₂ sequestration through selective adsorption is viewed as one of the most promising approaches because of its simple implementation, the absence of hazardous materials, tunable selectivity, and low energy costs. Thus, porous materials, such as metal–organic frameworks (MOFs), with the highest CO₂ adsorption capacity at relatively low partial pressures (<5 bar) are valuable targets for such applications. 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 CO₂ binding centers into MOF structures have been via the incorporation of basic centers such as amines functioning as Lewis bases and adsorption at coordinatively unsaturated metal cations as Lewis acid sites. The former strategy is a development of the traditional approach of CO₂ capture by amines to form carbamates and shows high uptake 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 CO₂ binding
through interaction to vacant metal sites. Despite a number of advantages such as a 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. Because each strategy has its particular disadvantages, the development of porous materials with high adsorption selectivity and appreciable CO₂ 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 supramolecular interactions. With a handful of exceptions, weak van der Waals and supramolecular interactions have not been widely considered as a driving force for specific CO₂ 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 CO₂ binding affinity of the microporous MOF [Zn₂(tdc)₂dabco] (H₂tdc = thiophene-2,5-dicarboxylic acid; dabco = 1,4-diazabicyclooctane). This increases both the storage capacity and selectivity of the framework at ambient conditions by as much as 50%, in a comparison with phenyl functionalization, and also maintains the heat of adsorption at a low level to minimize penalty costs for regeneration. The enhanced CO₂ binding property of the thiophene-containing MOF has also been confirmed by fixed-bed breakthrough separation of a CO₂/N₂ mixture. More importantly, adsorbed CO₂ molecules within [Zn₂(tdc)₂dabco] 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–CO₂ binding has also been studied by quantum-chemical calculations, giving detailed insight into the role of the sulfur atoms in CO₂ supramolecular binding. These results provide a new viable strategy underpinning the development of MOF materials with improved uptake and selectivity for CO₂.

## MATERIALS AND METHODS

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

### Synthesis of [Zn₂(tdc)₂dabco]·4DMF (1)
To a mixture of Zn(NO₃)₂·6H₂O (120 mg, 404 μmol) and thiophene-2,5-dicarboxylic acid (H₂tdc; 47 mg, 273 μmol) in DMF (5.3 mL) was added dropwise dabco (23 mg, 205 μmol) in DMF (4.0 mL) 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 H₂tdc). Elem anal. Calcd for 1·H₂O: 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. TGA. Calcd for 4DMF: 33.4%. Found: 30.5%. FT-IR (KBr, νC=O of DMF): 1667 cm⁻¹.

The synthesis of [Zn₂(tdc)₂bpe]·2DMF [2; bpe = 1,2-bis(4-pyridyl)ethane] and [Zn₂(tdc)₂bpp]·2DMF [3; bpp = 1,3-bis(4-pyridyl)propane] was carried out using a similar procedure starting from Zn(NO₃)₂·6H₂O (120 mg, 404 μmol) and thiophene-2,5-dicarboxylic acid (H₂tdc; 47 mg, 273 μmol) in DMF (5.3 mL) and either bpe (23 mg, 205 μmol) or bpp (23 mg, 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 were 236 mg (69%) for 2 and 263 mg (73%) for 3. Elem anal. Calcd for 2: 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. Calcd for 3: C, 45.7; H, 4.0; N, 3.9; S, 3.9; S, 7.5. TGA for 2. Calcd for 2DMF: 18.3%. Found: 17.8%. TGA for 3. Calculated for 2DMF: 18.0%. Found: 17.4%. FT-IR (KBr, νC=O of DMF): 2, 1675 cm−1; 3, 1666 cm−1.

Synthesis of Activated [Zn2(tdc)2dabco] (1a). The as-synthesized compound 1 was heated at 90 °C in vacuo for 10 h. The sample weight loss was 30.3%. Elem anal. Calcd for 1a·H2O: 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 Activated [Zn2(tdc)2bpe] · 2DMF (2) and [Zn2(tdc)2bpp] · 2DMF (3). The as-synthesized crystals of 2 and 3 were heated at 100 °C in vacuo for 6 h. The sample weight losses were found to be 18.4% for 2 and 17.7% for 3. Elem anal. Calcd for 2: 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. Calcd for 3: C, H2O: 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 1 was prepared by the solvothermal reaction of Zn(NO3)2, H2tdc, and dabco in hot DMF (100 °C) to give rectangular colorless single crystals. The stability of 1 was found to be very similar to that of many zinc(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 the crystallinity. Single-crystal X-ray diffraction confirms that 1 crystallizes in the tetragonal space group P421c and incorporates binuclear paddlewheel nodes [Zn2(OOCR)2] 3 (Figure 1a) bound by four carboxylic groups of tdc− anions to form a slightly squeezed layer of square-grid topology with a corrugated overall structure (Figure 1b). The remaining available coordination site at the square-pyramidal zinc(II) cations are bound by nitrogen-donor donors of the dabco ligands, which connect [Zn2(tdc)2] layers into a 3D porous framework with a scaffoldlike primitive cubic topology pcu (Figure 1c). Rotation of the dabco ligands results, as expected, in severe disorder of the carbon atoms of the CH2CH2 moieties, and the rigid angular shape of the tdc− anion forces notable distortions of the paddlewheel unit such that the Zn–Zn axis is twisted from the a 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 × 8 Å, corresponding to the shape of the squeezed square window of the [Zn2(tdc)2] layer (Figure 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 × 5 Å formed by two closely located tdc− moieties. The wider 3.5 × 5 Å window is formed by two tdc− arcs bent outward from each other with an interatomic S···S distance of 8.5 Å (Figure 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 environments (Figure 1b). Regardless of this tilting, both types of channels have similar apertures and are set up for the 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, 2 and 3, were synthesized using 1,2-bis(4-pyridyl)ethane (bpe) and 1,3-bis(4-pyridyl)propane (bpp) as nitrogen-donor bridging ligands, respectively. During the course of this work, the synthesis and structure of 2 were reported.33 In 2 and 3, the structure of the [Zn2(tdc)2]− corrugated layer remains unchanged compared to 1, and these layers are connected through longer N-donor linkers (Figure 2). Elongation of the bridging ligand does open up the possibility for framework interpenetration, which is not possible for 1 incorporating shorter dabco ligands.34 As a result, structure 1 is a single noninterpenetrated net, while 2 and 3 show doubly interwoven structures with pcu topology. Despite 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
unchanged from metal cations as well as the overall pcu connectivity remained synthesized of the as-synthesized crystals by single-crystal X-ray di... moisture, but no sign of degradation of the powder X-ray observed for I to be that the anionic tdc2 molecules. According to the TGA data, the DMF molecules can be removed by heating the material to 170°C for 6 h. Complete removal of the guest DMF molecules without framework collapse was confirmed by PXRD, TGA, chemical analyses, and IR spectroscopy. Some shifting of the PXRD peaks to higher 2θ angles upon desolvation of 3 indicates shrinkage of the partially flexible framework. N2 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 cm3·g−1 and BET surface areas of 447 and 407 m2·g−1 for 2 and 3, respectively (see the Supporting Information). The relatively low porosity for these compounds is not surprising given the observed 2-fold-interpenetrated structures for these species.

The stability and permanent porosity of the guest-free compound 1a were confirmed by PXRD and gas adsorption measurements. The N2 isotherm at 77 K reveals a type I reversible isotherm (Figure 4) with a pore volume of 0.68 cm3·g−1 and a BET surface area of 1553 m2·g−1. The pore volume is similar to the expected value of 0.63 cm3·g−1 calculated from the gravimetric density of the framework 1a (0.94 g·cm−3) and its guest accessible volume (0.59 v/v) according to the...
PLATON SOLV routine. 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_2 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_2(bdc)_2dabco] (4a; 0.75 cm^3·g^-1 and 1450 m^2·g^-1, respectively). Consistent with these surface area data, the H_2 adsorption for 1a (2.0 wt%) under similar conditions.

The reported CO_2 adsorption measurements for 4a, as well as our data (see the Supporting Information) indicate a moderate gas uptake of 9.0 wt% (46 cm^3·g^-1) at 298 K and 1 bar and of 23.9 wt% (122 cm^3·g^-1) at 273 K and 1 bar. In contrast, CO_2 adsorption in 1a, which shows a porosity similar to that of 4a, reveals a significant increase of ca. 50% in uptake under the same conditions. The maximum CO_2 adsorption in 1a at 1 bar reaches 13.2 wt% (67.4 cm^3·g^-1) at 273 K and 1 bar. At a pressure of 0.15 bar, which is relevant to the flue gas processing, the CO_2 uptakes of 1a are 18.5 and 8.5 wt% at 273 and 298 K, respectively.

The isosteric heat of adsorption for CO_2 in 4a at zero coverage, calculated from the isotherms at 273 and 298 K using the Clausius–Clapeyron equation, is 19.52 kJ·mol^-1, consistent with the literature data. The heat of adsorption of CO_2 for 1a is noticeably higher at 23.65 kJ·mol^-1, reflecting presumably stronger binding of CO_2 to the thiophene ring. The modest adsorption enthalpy of 1a highlights the absence of strong binding centers in 1a, with open metal sites and active amines reported to increase the heat of adsorption to 35–45 and 50–100 kJ·mol^-1, respectively. Despite the negative impact to the selectivity, the low heat of adsorption in 1a decreases the energy penalty for regeneration of the porous material in a temperature-swing process.

Gas Adsorption Selectivity and Gas Separation Studies. Together with CO_2 uptake, the CO_2/N_2 adsorption selectivity is one of the most important parameters for the practical application of porous materials in the purification of the industrial exhausts. The adsorption data (see the Supporting Information) allowed us to calculate the CO_2/N_2 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) ideal adsorbed solution theory (IAST). The selectivity, calculated as the ratio of the adsorbed gas volumes by 1a at 1 bar, is V(CO_2)/V(N_2) = 15.1 (Figure 5). By considering a typical flue gas composition of 0.15 bar of CO_2 and 0.75 bar of N_2, the normalized selectivity of adsorption at this composition can be calculated as S_{ads} = 11.4. The corresponding numbers for 4a are V(CO_2)/V(N_2) = 10.2 and S_{ads} = 9.4. The Henry’s constants (K_H) were derived from the linear approximation of the low-pressure part of the isotherms, and on the basis of the obtained values of K_H for 1a and 4a the selectivity factors at 298 K were calculated to be 12.5 and 8.9, respectively. The IAST calculations for 1a resulted in a selectivity factor of 11.2 for an equimolar CO_2/N_2 mixture, while for 4a, this factor is 9.2. Thus, a comparison of the above selectivity factors for 1a and 4a concludes that substitution of a phenyl group to thiophene upon going from 4a to 1a enhances the CO_2/N_2 adsorption selectivity by 20–50%, depending on 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_2 binding centers, a selectivity above 8 is high enough to be considered for practical applications.

The potential of utilizing these MOFs for CO_2 separation has also been confirmed in breakthrough experiments in which an equimolar mixture of CO_2/N_2 was flowed over a packed bed of 1a at 298 K and 1.0 bar (Figure 6). To validate the role of the thiophene group in enhanced CO_2 binding, a corresponding
breakthrough experiment has also been conducted on the phenyl-functionalized material 4a under the same conditions. As predicted by the selectivity calculations, complete separation has been achieved in both cases, with N2 being the first to elute through the bed while CO2 was retained. Upon saturation, CO2 breaks through from the bed and reaches saturation rapidly. As shown in Figure 6, dimensionless breakthrough plots offer a direct comparison between 1a and 4a on the performance of separation of the CO2/N2 mixture. Significantly, 1a shows a pronouncedly better separation than 4a (Δτ = 130 and 87 for 1a and 4a, respectively). Additionally, the enhanced CO2 storage capacity by thiophene functionalization in 1a has been confirmed by delayed (by almost a factor of 2) breakthrough of CO2 (τ = 250 and 143 for 1a and 4a, respectively). These results confirm the potential application of 1a upon CO2/N2 separation.

**Theoretical Studies.** Achieving such an outstanding affinity toward CO2 in the absence of strong Lewis basic centers or coordinatively unsaturated metal sites prompted us to thoroughly investigate nature of the CO2 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 hydrogen bonds), the CO2 guest molecules have to interact with the porous host through somewhat weaker dipole–dipole interactions. The sulfur atom is more susceptible to polarization and to induced dipole interactions with the quadrupole of CO2. A comparison of [Zr6O4(OH)4(bpdc)6] with [Zr6O4(OH)4(btdc)6] (bpdc2− = biphenyl-4,4′-dicarboxylate; btdc2− = bithiophenedicarboxylate) shows, depending on the temperature, a 32–78% increase of the gravimetric CO2 uptake for the latter thiophene-containing structure. It was suggested that differences in the electrostatic surface potentials for bpdc2− and btdc2− accounted for this difference, but no direct chemical explanation was given. In order to understand the role of the tdc2− ligand in CO2 adsorption in 1a, we undertook grand canonical Monte Carlo (GCMC) simulations (see the Supporting Information). These reveal unambiguously that CO2 is preferentially adsorbed near the tdc2− linker at low loading (Figure 7a) and that thiophene plays a key role in the adsorption of CO2 at low pressure. The CO2−tdc2− interaction was probed further by density functional theory (DFT) simulations, which confirmed that the C=S bond provides an excellent binding site for CO2 (Figure 7b,c), with calculated binding energies ranging from −15.7 to −18.3 kJ·mol−1, ca. 3–10 kJ·mol−1 stronger those reported for CO2 with benzene-based moieties. The shortest S···C interatomic distance in the energy-optimized thiophene···CO2 complex is 3.51 Å (Figure 7c), equal to the sum of the van der Waals radii of sulfur and carbon. The simulated heat of CO2 adsorption in 1a (24.2 kJ·mol−1) coincides with the experimental value (23.65 kJ·mol−1), giving consistency between the theory and experiment. The lower value of the heat of adsorption of CO2 for 4a (19.6 kJ·mol−1) calculated by DFT, suggests and generalizes the idea that the inclusion of thiophene-based ligands in MOFs provides a route to materials with increased affinities for CO2.

**Determination of the Binding Sites for Adsorbed CO2.** We also sought to determine the preferred binding sites of...
adsorbed CO$_2$ molecules in the extended pore structure of 1a by in situ synchrotron single-crystal X-ray diffraction. A desolvated sample of 1a shows complete retention of the framework structure and removal of the guest-free solvent molecules from the pore (Figure 8a). Two types of pores can be clearly observed and are denoted as $\alpha$ and $\beta$ with pore diameters of 7.1 and 7.8 Å (taking into consideration the van der Waals radii), respectively. The sulfur 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$_2$ at a pressure of 1.0 bar at 273 K and diffraction data collected at time $t$ = 0.25, 1, and 2 h to capture the dynamic information on the site population. It is worth mentioning that the kinetics of gas uptake in single crystals can be different from that of the powder sample typically used in isotherm experiments. Analysis of the diffraction data indicates the absence of a notable structural phase change of 1a upon CO$_2$ inclusion. Sequential Fourier difference map analysis of the diffraction data revealed the positions of the adsorbed CO$_2$ molecules in all three structures (Figure 8b–d).

At the first data set of CO$_2$-loaded 1a, only one binding site (CO$_2^I$) was located within pore $\alpha$ of 1a−(CO$_2$)$_{0.60}$ CO$_2^I$ (occupancy = 0.20) is located near the {Zn$_2$} paddlewheel stabilized by dipole interactions to the paddlewheel and hydrogen bonds to the −CH groups (Figure S6). Upon the second data collection, 1a−(CO$_2$)$_{1.56}$ CO$_2^I$ with an occupancy of 0.32. CO$_2^II$ was located in pore $\beta$ and is close to the thiophene group (Figure S7). Interestingly, the CO$_2$−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. Upon additional equilibrium time ($t$ = 2 h) of 1a−(CO$_2$)$_{1.63}$ the occupancies of CO$_2^I$ and CO$_2^II$ drop slightly to 0.38 and 0.29, respectively, indicating a redistribution of the adsorbed CO$_2$ molecules. The rest of the adsorbed CO$_2$ molecules fill into a third site (CO$_2^III$) with an occupancy of 0.14 (Figure S8). CO$_2^III$ was found in pore $\alpha$, forming an intermolecular dipole interaction with CO$_2^I$ in a “T-shaped” manner. Additional diffraction data collection at $t > 2$ h yielded the same crystal structures as that of 1a−(CO$_2$)$_{1.63}$ indicating the presence of an adsorption equilibrium. Thus, two out of three CO$_2$ binding sites are found within the sulfur-rich pore $\alpha$ of 1a, confirming the critical role of this heteroatom functionalization in CO$_2$ adsorption. Indeed, the observation of a direct host–guest interaction between the thiophene and CO$_2^I$ represents the first experimental evidence of CO$_2$ binding to a sulfur-rich functional group in MOFs.

### CONCLUSIONS

Three isoreticular porous MOFs based on [Zn$_2$(OOCR)$_4$] paddlewheels, connected through thiophene-2,5-dicarboxylate moieties and nitrogen-donor linkers (L) [Zn$_2$(tdc)$_2$L], have been synthesized and characterized. Apart from some structural distortions, these frameworks are very similar to the prototypic zinc(II) terephthalate material [Zn$_2$(bdc)$_2$]dabco) and have similar porosities in terms of the pore size, volume, and specific surface area. However, substitution of a phenyl group with thiophene substantially increases the adsorption of CO$_2$ as well as the CO$_2$/N$_2$ separation selectivity, as is evidenced by thorough gas isotherm measurements and breakthrough experiments. The thiophene-lined 1a possesses very good CO$_2$ uptake under ambient conditions 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 CO$_2$ via induced dipole interactions. These results emphasize the feasibility of van der Waals interactions to effective 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

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b00138.

Details of the analytical methods, single-crystal X-ray diffraction experiments, gas adsorption measurements, GCMC and DFT calculations, and additional figures and plots (PDF)

### Accession Codes

CCDC 1503063−1503066 and 1568882−1568885 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

### AUTHOR INFORMATION

#### Corresponding Authors

*E-mail: dan@niic.nsc.ru.

*E-mail: M.Schroeder@manchester.ac.uk.

#### ORCID

Laura J. M¢Cormick: 0000-0002-6634-4717

Elena Besley: 0000-0002-9910-7603

Martin Schröder: 0000-0001-6992-0700

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

We thank the EPSRC, ERC, and University of Manchester for funding. The NIIC team is grateful to the Russian Science Foundation (Grant 14-23-00013) and Federal Agency for Scientific Organizations for financial support. We thank the University of Nottingham for HPC facilities. M.S. acknowledges the Russian Ministry of Science and Education for the award of a Russian Megagrant (Grant 14.Z50.31.0006). We are especially grateful to the Advanced Light Source for access to Beamline 11.3.1. This research used resources of the Advanced Light Source, which is a DOE Office of Science User Facility under contract no. DE-AC02-05CH11231. The development of the gas cell used in this work was partially funded by the Center for Gas Separations Relevant to Clean Energy Technologies, an Energy Frontier Research Center funded by U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Award DE-SC0001015.
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