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Published in:
Chemical Communications

DOI:
10.1039/c4cc05833j

Link to publication

Citation for published version (APA):
Enhanced CO2 sorption and selectivity by functionalization of a NbO-type metal–organic framework with polarized benzothiadiazole moieties†

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A new NbO-type metal–organic framework ZJNU-40 incorporating highly polarized benzothiadiazole moieties exhibits a high CO2 uptake of 108 cm3 g−1 at 296 K and 1 atm, as well as good adsorption selectivities of CO2 over CH4 and N2 at room temperature, which is superior to that of the analogous MOF NOTT-101.

The escalating level of atmospheric CO2 is a subject of widespread public concern associated with global warming and climate change, and consequently, there remains an urgent need to selectively capture and sequester CO2 to reduce its greenhouse effect in the atmosphere. Most of the CO2 capture processes make use of liquid amine-based absorbents to chemically adsorb CO2; however, they suffer from the drawbacks of the corrosive nature of the solvents and high energy demand for solvent regeneration. In contrast, using porous materials to capture CO2 appears to be an energy-efficient alternative approach due to their low energy requirements, thus stimulating extensive efforts to find suitable adsorbents for removing CO2. In this regard, metal–organic frameworks (MOFs), an emerging class of porous materials, have shown charming properties with respect to CO2 storage and separation because their chemically adjustable organic and inorganic moieties can be carefully pre-designed to direct the molecular recognition of CO2.1 In fact, several MOFs with large CO2 storage capacity and high selectivity have been recently reported.2

Of various porous MOFs, the NbO-type MOF-505 series constructed from dicopper paddlewheels and diisophthalates has attracted tremendous attention because this class of MOF materials exhibit excellent gas sorption properties due to their high surface area, tunable pore size and open copper sites suitable for gas adsorption. Some of them exhibited high adsorption capacity for H2 and CH4.3 To improve the ability of NbO-type MOFs for CO2 capture and separation, great efforts have been devoted to tune the pore size/shape and/or engineer surface chemistry. It has been reported that the inclusion of some active binding sites into the framework such as NO2, amide, imide, and oxalamide is capable of increasing CO2 binding affinity.4 Since benzothiadiazole containing two nitrogen and one sulfur atoms is a polar, fused heterocyclic building block with the molecular dipole of 4.8 Debye estimated by Chemical 3D software, we plan to incorporate such a highly polarized benzothiadiazole unit as a spacer between two isophthalate moieties to develop a new tetracarboxylic acid (H4L, Scheme 1), and with which to target the corresponding NbO-type MOF designated as ZJNU-40. With a moderate surface area of 2209 m2 g−1, open metal sites (OMSs) of 1.52 nm−3, accessible donor sites, two types of nanoscopic cages, and a polarized cage surface within the framework, the activated ZJNU-40a exhibits high CO2 uptake capacity, as well as good adsorption selectivity of CO2 over CH4 and N2, which is superior to that of the analogous MOF NOTT-101 constructed from 1,4-benzenediisophthalate ligands of the same length as H4L.

The organic linker H4L, 5,5'-benzo[c1,2,5]thiadiazole-4,7-diyldiisophthalic acid, was readily synthesized by a Suzuki cross-coupling of 4,7-dibromobenzo[c1,2,5]thiadiazole and dimethyl (5-pinacolboranyl)isophthalate followed by hydrolysis and acidification. ZJNU-40 was obtained as blue rhombic crystals via a solvothermal reaction of the organic ligand and Cu(NO3)2·3H2O in a mixed solvent of N,N-diethylformamide (DEF) and H2O.

Scheme 1 The organic building block H4L used to construct the MOF ZJNU-40, with the local molecular dipole moment, highlighted in red, perpendicular to the molecular long axis.
under acidic conditions. The crystal structure was characterized by single-crystal X-ray diffraction studies, and the phase purity of the bulk material was verified by powder X-ray diffraction (PXRD, Fig. S1, ESI†). Based on the single-crystal X-ray diffraction structure determination, thermogravimetric analysis (TGA, Fig. S2, ESI†) and microanalysis, ZJNU-40 can be formulated as \[\text{[Cu}_2\text{L(H}_2\text{O})_2]\cdot4\text{DEF-H}_2\text{O}.\]

Single-crystal X-ray diffraction analysis revealed that ZJNU-40 is isoreticular to NOTT-101. As expected, a pair of copper centers are linked by four dicopper carboxylates to form a paddlewheel secondary building unit (SBU) serving as a 4-connected square-planar node, which is bridged by the 4-connected rectangular organic building blocks to form a three-dimensional (3D) noninterpenetrated 4,4-connected NbO-type network (Fig. 1). Alternatively, if the bridging organic linker is considered as having two 3-coordinated (3-c) branch points, then in combination with the 4-coordinated dicopper paddlewheels, the derived net is the one with the RCSR symbol for. Interestingly, the central benzothiadiazole sites remain unbound, and thus provide additional gas binding sites. If the centers of dicopper paddlewheel SBUs are taken as vertices of polyhedra, the framework of ZJNU-40 contains two distinct types of nanoscopic cages shown in Fig. 1b. The small octahedral cage consists of 12 ligands and 6 paddlewheel SBUs, and the diameter is about 12 Å, taking into account the van der Waals radii of the atoms; while the large cuboctahedral cage is constructed from 6 ligands and 12 paddlewheel SBUs with dimensions of ca. 9 × 18 Å. It is worth noting that the two cages are densely decorated with a big molecular dipole of benzothiadiazole functionalities.

The permanent porosity was unambiguously established by the N\textsubscript{2} sorption isotherm at 77 K. Prior to gas sorption analysis, the as-prepared ZJNU-40 was solvent-exchanged with dry acetone and then evacuated at 373 K under dynamic vacuum, generating the activated ZJNU-40a. The integrity of the framework was confirmed by powder X-ray diffraction (Fig. S1, ESI†). The nitrogen sorption isotherms at 77 K reveal a typical reversible type-I sorption behavior (Fig. S3, ESI†), characteristic of microporous materials. Based on the N\textsubscript{2} sorption isotherms, Brunauer-Emmett-Teller (BET) and Langmuir surface areas were estimated to be 2209, and 2328 m\textsuperscript{2} g\textsuperscript{-1}, respectively (Fig. S4, ESI†). The pore volume calculated from the maximum amount of N\textsubscript{2} adsorbed is 0.88 cm\textsuperscript{3} g\textsuperscript{-1}. These values are lower than those of NOTT-101 due to the presence of the thiadiazole moieties pointing to the pore, but are comparable to those of some copper-based NbO-type frameworks such as NOTT-105, NOTT-125a, PCN-16, NU-135, UTSA-80, SNU-50, NJU-Bai14a and HNUST-2a (Table S2, ESI†).

Establishment of permanent porosity prompts us to examine its utility as an adsorbent for CO\textsubscript{2} capture and separation. Accordingly, CO\textsubscript{2}, CH\textsubscript{4} and N\textsubscript{2} sorption isotherms were collected up to 1 atm at two different temperatures of 273 K and 296 K. As shown in Fig. 2, the isotherms are completely reversible and show no hysteresis. At 1 atm, ZJNU-40a exhibited a CO\textsubscript{2} uptake of 170 and 108 cm\textsuperscript{3} (STP) g\textsuperscript{-1} at 273 and 296 K, respectively, corresponding to about 40 and 26 CO\textsubscript{2} molecules per unit cell. Remarkably, this gravimetric CO\textsubscript{2} adsorption capacity at room temperature is significantly higher than that of NOTT-101 (83 cm\textsuperscript{3} g\textsuperscript{-1}), and is among the highest reported for isoreticular Cu-based NbO-type MOFs (Table S2, ESI†): MOF-505 (73 cm\textsuperscript{3} g\textsuperscript{-1}), NOTT-101 (83 cm\textsuperscript{3} g\textsuperscript{-1}), NOTT-102 (72 cm\textsuperscript{3} g\textsuperscript{-1}), UTSA-40 (73 cm\textsuperscript{3} g\textsuperscript{-1}), NU-135 (79 cm\textsuperscript{3} g\textsuperscript{-1}), SNU-50 (80 cm\textsuperscript{3} g\textsuperscript{-1}), NOTT-125a (93 cm\textsuperscript{3} g\textsuperscript{-1}), HNUST-1 (93 cm\textsuperscript{3} g\textsuperscript{-1}), NJU-Bai14a (100 cm\textsuperscript{3} g\textsuperscript{-1}), and Cu\textsubscript{2}(dbip)\textsubscript{2} (122 cm\textsuperscript{3} g\textsuperscript{-1}). In sharp contrast to CO\textsubscript{2}, ZJNU-40a can adsorb only limited amounts of CH\textsubscript{4} and N\textsubscript{2}, indicating that ZJNU-40a has potential application in the separation of CO\textsubscript{2}-CH\textsubscript{4} and CO\textsubscript{2}-N\textsubscript{2} mixtures.

Ideal Adsorbed Solution Theory (IAST) was used to calculate the adsorption selectivities and CO\textsubscript{2} uptake of ZJNU-40 and NOTT-101 for the following binary gas mixtures: 50/50 CO\textsubscript{2}/CH\textsubscript{4}, 5/95 CO\textsubscript{2}/CH\textsubscript{4}, and 15/85 CO\textsubscript{2}/N\textsubscript{2}. These mixtures mimic biogas treatment, natural gas upgrading, and post-combustion capture applications, respectively. Fig. S8 (ESI†) presents IAST calculations for CO\textsubscript{2} uptake from 50/50 CO\textsubscript{2}/CH\textsubscript{4}, 5/95 CO\textsubscript{2}/CH\textsubscript{4}, and 15/85 CO\textsubscript{2}/N\textsubscript{2} gas mixtures maintained under isothermal conditions at 296 K in ZJNU-40a and NOTT-101. It can be seen that ZJNU-40a has much higher selectivity towards CO\textsubscript{2} for all three mixture compositions. Fig. S9 (ESI†) presents IAST calculations for CO\textsubscript{2} uptake from 50/50 CO\textsubscript{2}/CH\textsubscript{4}, 5/95 CO\textsubscript{2}/CH\textsubscript{4}, and 15/85 CO\textsubscript{2}/N\textsubscript{2} gas mixtures maintained under isothermal conditions at 296 K in ZJNU-40a, and NOTT-101.
Again, ZJNU-40a has a much higher CO₂ uptake in all three cases. The combination of higher CO₂ uptake capacity and higher adsorption selectivity of CO₂ over CH₄ and N₂ will lead to a better separation performance of ZJNU-40a.

To further compare the separation performance of ZJNU-40a and NOTT-101, we perform transient breakthrough simulations using the methodology described in the literature. The details are provided in ESI.† Fig. 3 compares 50/50 CO₂/CH₄ mixture breakthrough characteristics as a function of the dimensionless time in an adsorber packed with ZJNU-40a and NOTT-101 and maintained at 296 K. In these calculations the total pressure is maintained at 200 kPa. The breakthrough of CO₂ occurs at a later time with ZJNU-40a, indicating that this material has a better separation performance. Furthermore, based on the material balance on the fixed bed adsorber, the productivities of methane with a purity of 99.95%+ are calculated to be 2.84 mol per kg of ZJNU-40a, and 1.78 mol per kg of NOTT-101 (Fig. S11 and 12, ESI†). This implies that ZJNU-40a has a 50% higher productivity than NOTT-101. Likewise, when separation of 5/95 CO₂/CH₄ mixtures at 296 K and a total pressure of 200 kPa is considered, the productivities of methane with a purity of 99.95%+ are calculated to be 5.80 mol per kg of ZJNU-40a, and 3.62 mol per kg of NOTT-101 (Fig. S13 and 14, ESI†). These productivity values are higher than the corresponding ones for 50/50 CO₂/CH₄ mixtures because a lower amount of CO₂ needs to be captured. For 5/95 CO₂/CH₄ mixtures, ZJNU-40a has a 60% higher productivity than NOTT-101. As for the separation of 15/85 CO₂/N₂ gas mixtures at 296 K and a total pressure of 100 kPa, the productivities of N₂ with a purity of 99.95%+ can be determined to be 3.29 mol per kg of ZJNU-40a, and 2.08 mol per kg of NOTT-101 (Fig. S15 and 16, ESI†). Taken together, these breakthrough calculations clearly demonstrate that ZJNU-40a has a better separation performance than NOTT-101.

To understand the gas-framework interaction, the coverage dependent adsorption enthalpies were calculated using the Clausius–Clapeyron equation by fitting the adsorption isotherms taken at 273 and 296 K to the Langmuir expression. As expected (Fig. S17, ESI†), ZJNU-40a exhibits a higher CO₂ binding affinity than CH₄ and N₂ throughout the adsorption process. ZJNU-40a has a slightly lower isosteric heat of CO₂ adsorption than NOTT-101, indicating that the binding sites can play even more important roles than the interaction strengths in enhancing carbon dioxide uptake and thus gas separation selectivities. Such phenomena are even more clearly demonstrated in unique UTSA-16 because of its extraordinarily high carbon dioxide capture and separation. 24 The introduction of the heterocyclic functional sites and the smaller pore sizes within ZJNU-40a have played the most important roles for its better performance than NOTT-101 for carbon dioxide capture and separation.

In summary, we have synthesized a new NbO-type MOF, ZJNU-40, by utilizing a unique tetracarboxylate containing benzothiadiazole as a polarized functional site. With moderately high BET surface area, two types of nanoscopic cages, open metal sites, accessible donor sites, and smaller pore spaces within the framework, the activated ZJNU-40a exhibits higher CO₂ uptake capacity as well as better adsorption selectivity of CO₂ over CH₄ and N₂, and thus better CO₂ capture performance than the isoreticular NOTT-101. This work demonstrated that incorporation of a polarized heteroaromatic ring into the framework provides a promising route to improve CO₂ gas sorption and selectivity and thus to produce materials with enhanced CO₂ separation performance.

This work was supported by the National Natural Science Foundation of China (No. 21301156), Open Research Fund of Top Key Discipline of Chemistry in Zhejiang Provincial Colleges and Key Laboratory of the Ministry of Education for Advanced Catalysis Materials (ZJHX201313), and Grant AX-1730 from the Welch Foundation (B.C.).

Notes and references
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