

Enhanced Binding Affinity, Remarkable Selectivity, and High Capacity of CO₂ by Dual Functionalization of a *rht*-Type Metal–Organic Framework**

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As a new family of adsorbent materials, porous metal–organic frameworks (MOFs) have attracted enormous attention over the past decade.^[1] Having a large surface area,^[2] tunable pore size and shape,^[3] adjustable composition and functionalizable pore surface,^[4] MOFs show unique advantages and promises for potential applications in adsorption-based storage and separation technologies for small gas molecules such as H₂, CO₂, and CH₄.^[1b,d,5]

CO₂ capture from flue gases is of particular importance in reducing greenhouse gas emissions and in preserving environmental health. A flue gas mixture is composed of nitrogen, carbon dioxide, water vapor, oxygen, and other minor components such as carbon monoxide, nitrogen oxides, and sulfur oxides.^[1b,6] Separation of low-concentration CO₂ (about 10–15%) from nitrogen-rich streams remains a challenging task at the present time. Adsorption-based CO₂ capture and separation is considered an effective way and may have a real potential if adsorbents with both high CO₂ selectivity and

capacity near room temperature (up to 50°C) and in the low-pressure range can be developed.^[7] Recent studies have revealed a number of MOFs that show a high performance in capturing and separating CO₂ from N₂ and other small gases under conditions mimicking power plant flue gas mixtures.^[8]

To increase the gas uptake capacity, current efforts are devoted to enhancing the gas-binding affinity in MOFs.^[5] Strategies reported include framework interpenetration,^[9] ligand functionalization,^[1e,4b,10] construction of size/shape specific pores and polar pore walls,^[3,4b,11] and in particular, incorporation of open metal sites (OMSs).^[1d,8a,12] The *rht*-type MOFs built on supramolecular building blocks (SBBs)^[13] serve as excellent examples. The SBBs in *rht*-MOFs are constructed by linking three isophthalate moieties of dendritic hexacarboxylate ligands to 24 “square paddlewheel” M₂(COO)₄ units, forming a cuboctahedron cluster.^[12f,g,13a,14] Notably, all *rht*-MOFs possess a high concentration of OMSs and all are highly porous with large surface area and pore volume. A number of recent studies clearly show that their CO₂ uptake capacity is among the highest reported to date.^[12f,g,14,15]

However, with the isosteric heats of CO₂ adsorption in the range of 21–26 kJ mol^{−1} (Table 1), the CO₂ binding affinity in these OMS-rich structures is only moderate and not sufficiently high for optimum performance. To further enhance CO₂–MOF interactions, we have developed a strategy to incorporate two different types of functionality simultaneously in the MOF framework. In addition to a OMS-rich SBB, a ligand containing a high density of Lewis basic sites (LBSs) is synthesized and employed in the construction of new *rht*-type MOFs, taking into consideration the fact that LBS interacts strongly with CO₂.^[4b,11b,12g,16]

[Cu₃(TDPAT)(H₂O)₃]·10H₂O·5DMA (Cu-TDPAT) (**1**) is synthesized by using 2,4,6-tris(3,5-dicarboxylphenylamino)-1,3,5-triazine (H₆TDPAT), a LBS-rich hexacarboxylate ligand (see Scheme S1 in the Supporting Information). Based on our molecular simulation calculations, H₆TDPAT is most likely the shortest member of hexacarboxylic acids that can generate the same type of *rht*-type structures. As shown in Scheme S2 in the Supporting Information, any other shorter hexacarboxylates such as 3,3',3'',5,5',5''-benzene-1,3,5-triyl-hexabenzic acid (H₆BHB) will lead to an inter-SBB distance (4.9 Å) that is too short to accommodate two terminal water molecules. Thus, Cu-TDPAT may well be the smallest member of *rht*-nets and represents the first example of MOFs that possesses a high density of both OMSs (1.76 nm³)

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Table 1: Ligand and polyhedron sizes, porosities, density, and isosteric heats of Cu-TDPAT, Cu-TPBTM, NOTT-112, NU-100, and the isoreticular PCN-6X Series. All data except Cu-TDPAT are taken from Refs. [12f], [12g], [14e], and [15].

	Cu-TDPAT	Cu-TPBTM	PCN-61	NOTT-112	PCN-66	PCN-68	NU-100
L [Å] ^[a]	5.0	6.5	6.9	8.6	9.7	11.2	13.71
cub- O_h size [Å]	12	12	12	12	12	12	12
T- T_d size [Å]	9.1	11.6	11.8	13.1	12	14.8	17
T- O_h size [Å]	17.2	18.7	18.8	21.1	20.6	23.2	29.2
BET SA [m ² g ⁻¹]	1938	3160	3000	3800	4000	5109	6605
Pore volume [cm ³ g ⁻¹] ^[b]	0.93	1.27	1.36	1.62	1.63	2.13	2.82
Density [g cm ⁻³]	0.782	0.627	0.56	0.503	0.45	0.38	0.273
OMS Density (per nm ³)	1.76	1.27	1.22	0.92	0.81	0.70	0.45
H ₂ uptake [wt %] ^[c]	2.65	—	2.25	2.3	1.79	1.87	2.2
Q_{st} (H ₂) [kJ mol ⁻¹] ^[d]	8.29	—	6.36	5.64	6.22	6.09	6.1
CO ₂ uptake [wt %] ^[e]	6.2	2.8	1.6	—	0.88	0.44	1.6
Q_{st} (CO ₂) [kJ mol ⁻¹] ^[f]	42.2	26.3	21.0	—	26.2	21.2	—

[a] L is defined as the distance (Å) between the center of the ligand and the center of a terminal benzene ring (see Scheme S1 in the Supporting Information). [b] Pore volumes were calculated from N₂ isotherms. [c] 77 K, 1 atm. [d] Q_{st} of H₂ is defined as the isosteric heat of H₂ adsorption and calculated at zero coverage. [e] 298 K, 0.1 atm. [f] Q_{st} of CO₂ is the isosteric heat of CO₂ adsorption and calculated at zero coverage.

and LBSs (3.52 nm³). In fact, it has the highest OMS density among all known *rht*-MOFs of the same type (Table 1). Gas adsorption studies show that Cu-TDPAT has a significantly improved CO₂ affinity, as well as the highest CO₂ uptake capacity and selectivity under conditions that mimic flue gas mixtures over all other members of the series.

The three isophthalate moieties in TDPAT are linked through copper paddlewheel units to form cuboctahedral SBBs, which are covalently bonded through the isophthalate moieties (at position-1) to yield a (3,24)-connected *rht*-type network of **1** (Figure 1 and Figure S1 in the Supporting Information). Similar to other reported (3,24)-connected nets, there are three types of cages in **1**, namely, cuboctahedron (cub- O_h), truncated tetrahedron (T- T_d), and truncated octahedron (T- O_h ; see Figure S2 in the Supporting Information). The inner spheres of these three cages are smaller than those of all other *rht*-type structures, with 1.2, 0.91, and 1.72 nm in diameter, respectively, as H₆TDPAT is the smallest ligand among all hexacarboxylic acids (Table 1).

Compound **1** is highly porous with exceptional water and thermal stability. The total accessible volume after removal of

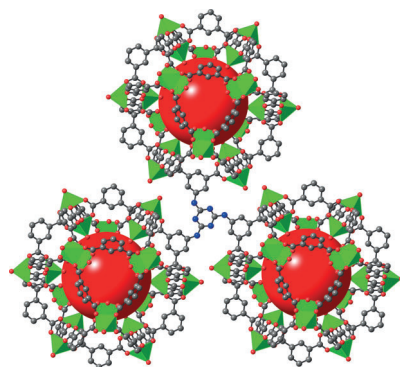


Figure 1. Structure of **1**. A portion of the (3,24)-connected *rht*-net built on the shortest linker TDPAT is shown.

the guest and coordinated solvent molecules is 70.2 % using the PLATON/VOID routine,^[17] and the calculated density of the desolvated framework is 0.782 g cm⁻³. Thermogravimetric (TG) and powder X-ray diffraction (PXRD) analysis at various temperatures show that the framework is stable up to 285 °C (see Figures S3 and S4 in the Supporting Information). The water/moisture stability was tested in boiling water (1 day) and in air (30 days). The framework remained intact as clearly indicated by the PXRD patterns of the samples taken after these tests (see Figure S5 in the Supporting Information).

Permanent porosity of activated Cu-TDPAT was confirmed by N₂ adsorption-desorption isotherms at

77 K which show a reversible type-I isotherm (see Figure S6 in the Supporting Information). The Langmuir and BET surface area calculated based on data at the low-pressure region ($P/P_0 = 0.05$ – 0.2)^[18] are 2608 and 1938 m² g⁻¹, respectively. The total pore volume calculated from the N₂ isotherms is 0.93 cm³ g⁻¹, in good agreement with the value obtained from single-crystal data.

The CO₂ low-pressure adsorption-desorption isotherms were measured at 273, 288, and 298 K (0–1 atm). Compound **1** has a very high CO₂ adsorption capacity. At 298 K, the uptake amount is 132 cm³ g⁻¹ (STP = standard temperature and pressure; 25.8 wt %, 103 v/v) and 31.3 cm³ g⁻¹ (STP; 6.2 wt %, 24.5 v/v) at 1.0 and 0.1 atm, respectively. At 273 K, they are 227 cm³ g⁻¹ (STP; 44.5 wt %, 177 v/v) and 52.8 cm³ g⁻¹ (STP; 10.4 wt %, 41.3 v/v) at 1.0 and 0.1 atm, respectively (see Table 1, Figure 2 and Figure S7 in the Supporting Information). These values are substantially higher than all previously reported *rht*-type structures (Table 1), and significantly larger than that of the best performing zeolitic imidazolate frameworks (ZIFs), namely ZIF-78 (60.2 v/v, at 298 K and 1 atm),^[4b] and that of zeolite 13X (20.7 wt %, at 298 K and 1 atm),^[19] one of the best sorbents for CO₂ separation.

To evaluate the extent of CO₂–MOF interactions, isosteric heats (Q_{st}) of CO₂ adsorption were calculated by the virial^[20] method using experimental isotherm data at three temperatures. The Q_{st} values (based on the Clausius–Clapeyron equation) were also obtained directly from experimental data at low loadings by interpolation (AS1Win 2.01).^[8c] No fitting was involved in the latter case. The data plotted in Figure S8 in the Supporting Information show excellent agreement by the two methods. Compound **1** shows a very high adsorption enthalpy (42.2 kJ mol⁻¹ at zero loading), indicative of strong adsorbate–adsorbent interactions. The Q_{st} values over the entire CO₂ loading range are appreciably higher compared with all other *rht*-type structures reported thus far, following the same trend as the uptake amounts at low pressure. As all *rht*-type MOFs contain a high density of OMSs, this unusually

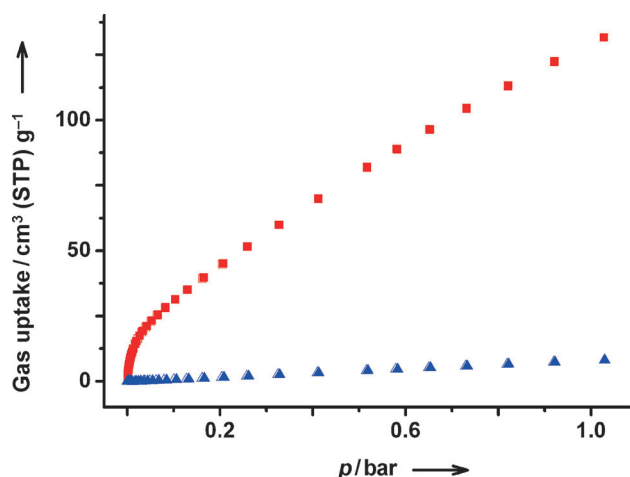


Figure 2. CO₂ and N₂ sorption isotherms of Cu-TDPAT at 298 K (adsorption: filled; desorption: open; CO₂: red squares; N₂: blue triangles).

high CO₂ binding affinity can be attributed to the fact that **1** is the only member that also carries a high density of LBSs and that has the smallest cages.

To further understand the nature of interactions between CO₂ and the framework, we performed room-temperature IR absorption measurements. Three distinct IR absorption bands of adsorbed CO₂ in **1** are identified, as shown in Figure S21 in the Supporting Information.^[21] The appearance of multiple CO₂ IR bands indicates that there are more than one strong adsorbing center. The bands at $\tilde{\nu} = 2335$ and 2342 cm^{-1} , red-shifted by $\tilde{\nu}$ of about -14 and -7 cm^{-1} from the unperturbed value of CO₂ asymmetric stretch ($\tilde{\nu} = 2349\text{ cm}^{-1}$), are attributed to CO₂ adsorption sites at the LBS and phenyl rings, respectively.^[22] The slightly blue-shifted band at $\tilde{\nu} = 2351\text{ cm}^{-1}$ ($\tilde{\nu} \approx +2\text{ cm}^{-1}$ shift) is attributed to CO₂ interacting through its oxygen with the unsaturated metal centers in a linear adsorption configuration.^[23] The lower intensity of the band at $\tilde{\nu} = 2351\text{ cm}^{-1}$ as compared to that of $\tilde{\nu} = 2335\text{ cm}^{-1}$ indicates that less CO₂ is present for that specific site, consistent with the fact that **1** has a higher density of LBSs (3.52 nm^3) than that of OMSs (1.76 nm^3). These assignments are consistent with observed changes in the vibrations of **1** upon CO₂ loading (see Figure S21 in the Supporting Information, right panel).

The high Q_{st} values place **1** among a small group of all MOFs having the record high CO₂ binding affinity, including amino-MIL-53 (Al; 38.4 kJ mol^{-1}),^[16b] bio-MOF-11 (45 kJ mol^{-1}),^[16c] and MOF-74-Mg (47 kJ mol^{-1}),^[8a] The value is also close to that of NaX (48.2 kJ mol^{-1}), a zeolite that is used in commercial separation processes based on pressure swing adsorption (PSA).^[21]

In addition to its high uptake capacity and strong adsorption enthalpy for CO₂, **1** also shows high adsorption selectivity of CO₂ over N₂ at 298 K. At 1 atm, the separation ratio for CO₂/N₂ calculated based on single-component gas adsorption isotherms is 16 v/v, higher than those of MOF-74-Mg (12 v/v)^[8a] and ZIF-78 (about 13 v/v)^[4b] under the same conditions. At 0.16 atm (a pressure close to the CO₂ concentration in a power plant flue gas stream), the value is 34 v/v for

1, second to the highest value reported for MOF-74-Mg (49 v/v). To imitate the separation behavior of **1** under a more real-world setting, the CO₂/N₂ selectivity in a binary mixture was calculated employing the ideal adsorbed solution theory (IAST) method^[5b,22] with the experimental single-component isotherms fitted by the dual-site Langmuir (DSL) model.^[23] At a total pressure of 1 atm and CO₂ concentration of 10% (partial pressure of 0.1 atm), a remarkable selectivity of about 79 is predicted by IAST (see Figure S9 in the Supporting Information).

To evaluate the performance of compound **1** in a real gas mixture, we carried out a series of breakthrough experiments to determine its CO₂ separation capacity from a CO₂/N₂ mixture under kinetic flow conditions (see Figures S11 and S12 in the Supporting Information). The results show that **1** can effectively capture CO₂ from the mixed gas with an uptake of 6.7 wt% before breakthrough, comparable to that of MOF-74-Mg in a similar CO₂/CH₄ breakthrough experiment.^[12d] Moreover, compound **1** saturated with CO₂ can be fully regenerated under relatively mild conditions. Successive breakthrough experiments revealed that **1** retains a constant capacity of 5.7 wt% upon repeated regenerations at 80 °C (see the Supporting Information). These values reflect the kinetic aspect of separation, suggesting that **1** is a promising candidate for CO₂ capture and separation from gas mixtures.

The high-pressure gas (CO₂, H₂, CH₄) adsorption of **1** has also been studied. The adsorption data indicate that **1** shows extremely high gas uptake capacity [CO₂ (excess): 310 v/v, 298 K, 48 bar; H₂ (total): 6.77 wt%, 52.8 g L⁻¹, 77 K, 67 bar; CH₄ (total): 181 v/v, 298 K, 35 bar]. These values place it among the leading MOF materials to date for CO₂, H₂, and CH₄ storage. Detailed information is provided in the Supporting Information (see Figure S13–20 in the Supporting Information).

In summary, the smallest member of *rht*-type MOFs, Cu-TDPAT built on a hexacarboxylate ligand with imino triazine backbone, shows a greatly enhanced CO₂ binding affinity compared with all other isorecticular *rht*-MOFs and remarkable selectivity of CO₂ over N₂ under conditions that mimic flue gas mixtures. The high adsorption affinity and capacity are attributed to the dual functionalization of the framework by concurrent incorporation of high density of open metal sites and Lewis basic sites. In addition, narrower pores in Cu-TDPAT are likely to be the other contributing factor leading to the stronger CO₂-framework interactions with respect to other similar *rht*-type MOFs. Coupled with its exceptionally high water and thermal stability, Cu-TDPAT may have real promise for adsorption-based small gas separations, in particular CO₂ capture from power plant flue gases.

Experimental Section

The crystal data for Cu-TDPAT are: C₂₇H₁₈Cu₃N₆O₁₅, $M = 857.09$, tetragonal, space group $I4/m$, $a = 26.860(4)$, $b = 26.860(4)$, $c = 37.753(8)$, $V = 27238(8)$, $Z = 16$, $F_{000} = 6864$, $R_1 = 0.0621$, and $wR_2 = 0.1513$. Full experimental details are given in the Supporting Information.

CCDC 831219 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge

Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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