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Azide-Functionalized Lanthanide-Based Metal−Organic Frameworks Showing Selective CO_2 Gas Adsorption and Postsynthetic Cavity Expansion

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Supporting Information

ABSTRACT: We report herein selective CO_2 gas adsorption by two azide-functionalized lanthanide-based metal−organic frameworks (MOFs). This work also demonstrates that azide-functionalized MOFs can be used for postsynthetic cavity expansion, further corroborated by enhanced gas-sorption data.

Over the past 2 decades, development in the field of porous metal−organic frameworks (MOFs), such as zeolite analogues, has experienced remarkable growth and is now an important market for the industrial sector.[1] Porous MOFs, because of their high surface area, tunable framework, and adjustable pore size, have emerged, inter alia, as promising candidates as absorbents for gas storage and separation.[2] Of particular interest is CO_2 sequestration, which has drawn a considerable amount of interest as an approach to mitigating climate change as well as because of its potential for the storage and purification of fuel and flue gases.[3] Recent reports further support the usefulness and advantages of MOFs for selective adsorption-based CO_2 separation.[4] For instance, owing to a limitless choice of building blocks, it is possible to construct tailor-made MOFs with immobilized functional groups such as $-NH_2$ or $-OH$ within the porous surface.[5] The presence of such immobilized functional groups on the porous surface facilitates direct interaction with the gas substrate, which in effect can play a pivotal role in enhancing gas-separation selectivity.[6]

The relationships between functionalized MOFs and CO_2 gas sorption have attracted extensive interest in recent years with the aim of understanding the fundamental factors governing the ligand−CO_2 affinity.[7] Subsequently, various ligand molecules with specific immobilized functionalities, such as $-NH_2$, $-OH$, $-CF_3$, $-COOH$, $-CH_3$, or halogen, have been explored.[8] Notwithstanding, the fact that there are hardly any examples of azide ($-N_3$)-functionalized MOFs prompted us to investigate the influence of the azide group on the gas-sorption behavior.[9]

The noncoordinating nature of the azide group and well-known coordination behavior of carboxylate groups led us to believe that 5-azidoisophthalic acid (N_3H_2-IPA) would be an ideal candidate for our investigation. Our initial attempts with transition metals do show some encouraging results; however, the compounds exhibit poor thermal stability and undergo decomposition immediately after loss of the azide group.[10] To bypass this stumbling block, we shift our focus to lanthanides, which are well-known to form thermally stable complexes with carboxylates. Indeed, the requisite thermal stability was achieved for the two lanthanide-based MOFs of interest, $[\{(N_3\text{-IPA})(N_3\text{-HIPA})(H_2O)_2Pr\}(H_2O)_2]_n$ (**SGR-Pr**) and $[\{(N_3\text{-IPA})_6(Gd)_4(DMF)_3(H_2O)_4\}(DMF)(H_2O)_2]_n$ (**SGR-Gd**; DMF = *N*,*N*-dimethylformamide). The structures of **SGR-Pr** and **SGR-Gd** were determined by single-crystal X-ray diffraction (XRD) analysis, the details of which including packing diagrams are given in the Supporting Information (SI).

The carboxylate groups in compound **SGR-Pr** coordinate to the metal ion in both chelating and bridging modes, and this results in an infinite 1D chain of metal ions that are subsequently linked by the acid molecules and results in a 2D grid network. The network contains 1D pore channels running along the *a* axis, partially occupied by the azide groups, which orient themselves away from the metal core and form a closed loop of four azide groups (Figure SI-1 in the SI). Compound **SGR-Gd**, which results in a complex 3D network, features a similar pore channel with free azide groups pointing into it. From the immobilized functional group−gas substrate interaction point of view, such arrangements of azide groups are of huge significance with greater exposure to gas substrates.

Thermogravimetric analysis (TGA) of **SGR-Pr** and **SGR-Gd** shows some common trends: both of them underwent two major mass losses at ca 100 and 180 °C. The weight loss at 100 °C can be linked to the loss of solvent molecules, whereas the weight loss at 180 °C is due to decomposition of the azide groups. The close resemblance of the TGA profile of the free ligand further supports this. Furthermore, retention of the framework integrity, an essential prerequisite for the gas-sorption experiments, was confirmed by a comparison of the powder XRD (PXRD) patterns collected at ambient conditions and at 110 °C (Figures SI-12 and SI-13 in the SI).

Having confirmed retention of the framework integrity, the samples were activated for gas-sorption studies. The microcrystals of each MOF were soaked in a 1:1 dry dichloromethane

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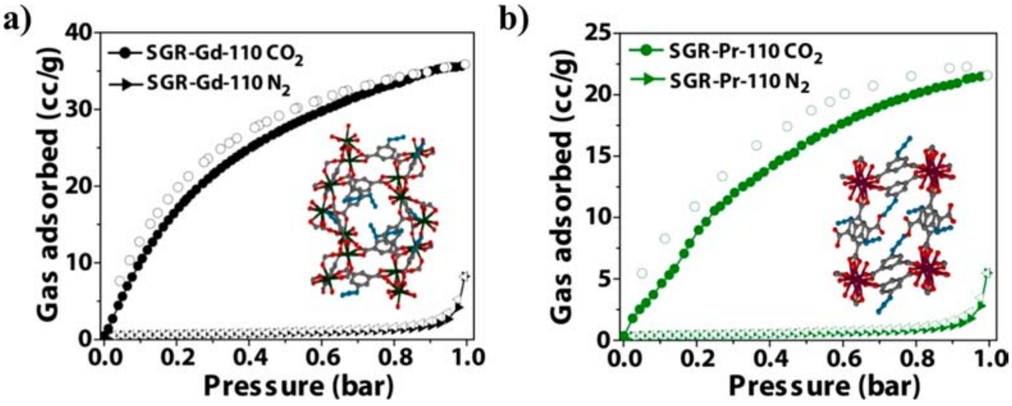

Figure 1. (a) Gas adsorption isotherms of **SGR-Gd** showing selective CO_2 gas sorption (black circles) over N_2 (black triangles) at 273 K. (b) Typical type I gas adsorption isotherms of **SGR-Pr** showing selective CO_2 gas sorption (green circles) over N_2 (green triangles) at 273 K. The filled and open circles represent adsorption and desorption, respectively.

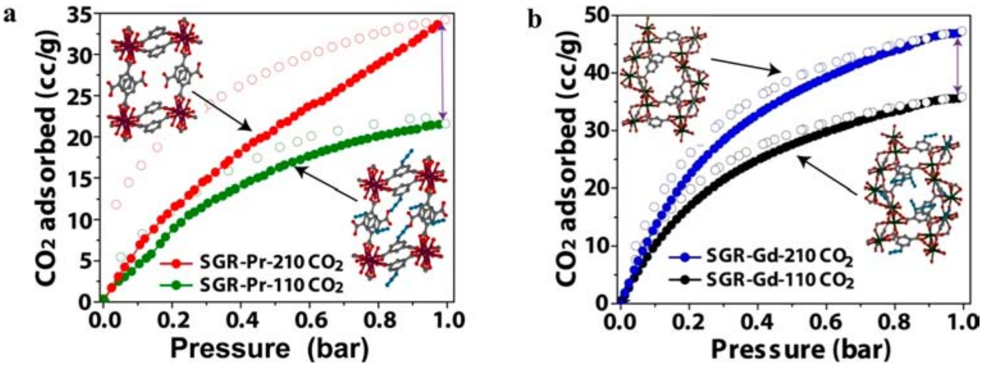

Figure 2. CO_2 gas adsorption isotherms for (a) **SGR-Gd** and (b) **SGR-Pr**, illustrating increased amounts of gas uptakes after activation of the MOFs at higher temperature.

and methanol mixture for 12 h. A fresh 1:1 dry dichloromethane and methanol mixture was subsequently added, and the crystals were allowed to stay for an additional 48 h to remove coordinated and free solvates (methanol, H_2O, and DMF) present in the framework. The sample was dried overnight under a dynamic vacuum ($\sim 10^{-3}$ Torr) at room temperature. To remove coordinated solvents, the samples **SGR-Gd** and **SGR-Pr** were heated at 110 °C for 12 h under a dynamic vacuum (**SGR Gd-110** and **SGR-Pr-110**).

The presence of moderate pores, as is evident from the single-crystal structures for both MOFs, prompted us to determine their surface areas and explore their gas-sorption behavior. The N_2 adsorption isotherms for both **SGR-Pr-110** and **SGR-Gd-110** exhibit typical type II sorption behavior with moderate surface area.

Given that the MOFs have open metal sites along with immobilized functional groups pointing into pores as well as interlayer spaces, we were naturally interested in evaluating their absorbent potential. It is worth mentioning that insertion of the polar functional groups and the presence of open metal sites have been proven to have a good impact on enhancing the CO_2 adsorption properties. Furthermore, considering the moderate surface area and comparable pore size with a kinetic diameter of CO_2 (3.30 Å), we decided to check the selective gas-sorption possibilities of **SGR-Gd** and **SGR-Pr**. Accordingly, adsorption measurements of both MOFs were carried out for N_2 and CO_2 at 273 K. As illustrated in Figure 1, both **SGR-Pr-110** and **SGR-Gd-110** exhibit selective CO_2 gas adsorption over N_2. **SGR-Gd-110** shows a typical type I isotherm, and as the pressure approaches to 1 atm, the adsorption of CO_2 reaches a plateau at 1.59 mmol/g. On the other hand, **SGR-Pr-110** absorbs 0.96 mmol/g of CO_2 with similar type I adsorption curves. It is noteworthy here that the above CO_2 sorption results are comparable with well-known MOFs like ZIF-9, ZIF-100, and other porous materials like zeolites and carbons.[11]

Interestingly, the azide-functionalized MOFs provide us with a unique opportunity to explore the so-called *postsynthesis cavity expansion*, a new approach put forward by Telfer and coworkers that can generate/enhance the porosity even from a nonporous MOF and is independent of solvent molecule inclusion.[12] The strategy is to use a ligand molecule that contains a noncoordinating functional group, an innocuous bystander, which can be cleaved selectively from the rest of the ligand molecule while leaving the remaining part of the ligand intact. The successful execution of this method therefore offers a two-step challenge: first, to synthesize a MOF using a ligand that contains a labile functional group; second, to ensure that the MOF is stable after removal of the functional group. Coincidentally, with the presence of noncoordinated, thermolabile azide functional groups and high thermal stability, **SGR-Pr** and **SGR-Gd** perfectly suit the purpose.

Unfortunately, both MOFs lost their crystalline nature upon heating at 210 °C. Nonetheless, the postsynthetic thermolysis of azide groups can be confirmed from the IR spectra of **SGR-Pr** and **SGR-Gd**, which were recorded at ambient conditions as well as after heating at 110 and 210 °C. The sharp characteristic bands (2131 and 2129 cm^{-1} for **SGR-Pr** and **SGR-Gd**, respectively) for the azide groups were present even after heating at 110 °C but were absent after heating at 210 °C (Figures SI-7 and SI-8 in the SI). This was further corroborated from elemental analysis data, which show a lower percentage of nitrogen atoms for the samples heated at 210 °C.

Having confirmed thermolysis of the azide groups, the obvious question then arose as to whether the porosity could be enhanced by this new technique. In order to check that, the surface areas for both MOFs were determined after their activation at 210 °C (**SGR-Pr-210** and **SGR-Gd-210**) for N_2 gas adsorption. A comparison of these surface areas with those of **SGR-Pr-110** and **SGR-Gd-110** (as tabulated in Table-SI-2 in the SI) will put this into perspective. The results are in excellent agreement with our assumptions and reveal enhancement of the surface area after heating at 210 °C.

An enhancement in the surface area should also be reflected in the gas-sorption data. To our astonishment, this is indeed the case for the CO_2 gas-sorption results of **SGR-Pr-210** and **SGR-Gd-210**. As illustrated in Table SI-2 in the SI, both show higher gas uptake than their low-temperature counterparts. **SGR-Pr-210** adsorbs 1.52 mmol/g of CO_2 compared to 0.96 mmol/g of CO_2 for **SGR-Pr-110**. On the other hand, **SGR-Gd-210** shows a much higher 2.10 mmol/g of CO_2 uptake than that of 1.59 mmol/g for **SGR-Gd-110**. Interestingly, the gas-sorption selectivity for CO_2 over N_2 was also retained for the respective higher-temperature samples (**SGR-Pr-210** and **SGR-Gd-210**; Figure 2). It should be noted that the repeatability of CO_2 adsorption behavior was confirmed by reproducing the same isotherm three times for **SGR-Pr-210** and **SGR-Gd-210** at 273 K and 1 atm of pressure (Figures SI-18 and SI-19 in the SI).

Thermolysis of the azide groups simply raises the prospect of generating more porosity in the framework because decomposition of the azide group would effectively increase the circumference of the pore channel. Therefore, the higher gas uptake values for high-temperature samples can be envisaged as corroborating evidence to the *postsynthesis cavity expansion* technique.

In conclusion, we have successfully synthesized two lanthanide-based MOFs with immobilized azido functional groups. Both MOFs exhibit selective CO_2 gas sorption. This work also demonstrates an interesting postsynthesis cavity expansion method using thermolysis of the azide groups for enhancement of the porosity, further corroborated by increased surface area and selective CO_2 gas-sorption results.

Caution! *Low-molecular-weight azides are potentially explosive and should be handled with great care and in small quantities.*

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis of ligands and MOFs, IR, elemental analysis data, X-ray crystallographic data, CIF files, additional packing diagrams, TGA plots, PXRD patterns, and additional gas-sorption results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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