Mesoporous Metal-Organic Frameworks with Size-tunable Cages: Selective CO\textsubscript{2} Uptake, Encapsulation of Ln\textsuperscript{3+} Cations for Luminescence, and Column-Chromatographic Dye Separation

Ya-Qian Lan, Hai-Long Jiang, Shun-Li Li, and Qiang Xu\*.

Emerging as a new class of porous materials in the last two decades, metal-organic frameworks (MOFs) have been met with great interest owing to their tunable structures and porosities and a wide range of potential applications as functional materials.\[1,2]\ A key feature in MOFs is the porosity, which plays a crucial role in the functional properties, typically in gas/liquid sorption and separation and transport of catalytic substrates/products.\[1,3]\ The MOFs with tunable pore sizes ranging from non-pores to mesopores are regarded to bridge the gap between zeolites and mesoporous silica.\[4] In recent years much effort has been dedicated to develop MOFs with large and tunable pores, and there are a few mesoporous MOFs reported with various synthetic strategies.\[5,6]\ Increasing the length of bridging ligands has been adopted as a main strategy, but reduced porosity imposed by interpenetration is nevertheless almost unavoidable.\[7]\ Because of these difficulties it has been rarely reported to obtain a series of mesoporous MOFs that retain both structure and tunable mesopores upon suppressed interpenetration. To the best of our knowledge, only Schröder, Zhou, and Lin's groups have constructed a series of mesoporous Cu\textsubscript{2}/Zn-MOFs with fixed framework topology but varied pore sizes by systematically varying the length of the bridged ligands, where they have concerned the high gas uptake capabilities or catalytic enantioselectivities, while no selective gas sorption behavior was found for these pore size-tailored MOFs.\[8,9]\ Global warming caused by rapid accumulation of CO\textsubscript{2}, the predominant greenhouse gas, is emerging as a challenging environmental issue. Conventional technology for CO\textsubscript{2} removal usually requires high energy with environmental issues and physical adsorption of CO\textsubscript{2} on activated carbon or zeolites is feasible while their regeneration is very costly.\[10]\ It is imperative to develop an alternative strategy to effectively remove CO\textsubscript{2} with low cost and low energy consumption. Currently, MOFs are promising and being intensively investigated to address this challenge because their pore characteristics can be rationally adjusted for specific CO\textsubscript{2} selective adsorption\[10,11]\ and the alkyl ether fragment involved in the MOF framework was demonstrated to be beneficial to selective CO\textsubscript{2} uptake.\[12,13]\ In this work, we present a series of mesoporous MOFs with retained framework topology but tailored pore sizes, all of which exhibit high and selective CO\textsubscript{2}/N\textsubscript{2} adsorption as expected, by elaborate ligand design with flexible C–O–C bonds and successful controlling of interpenetration. Moreover, the MOF can serve as a host for encapsulating extra-framework lanthanide cations to exhibit mono- or bi-modal luminescence. In addition, by making use of the merits of the mesoporous pores, the MOFs are demonstrated to be useful for column-chromatographic separation for large dye molecules.

Currently, a number of MOF nets are found to be analogous to those of inorganic materials, for example, the MOFs with classical topologies of diamond, NbO, fluorite, PtS and corundum, etc.\[12,13]\ Among them, the (4,6)-connected MOFs, whose structural interpenetration is difficult because of the intrinsic structural features of corundum, are rarely reported.\[13]\ Therefore, it is likely to obtain corundum analogues having large pore sizes without interpenetration. Bearing this in mind, we have designed a series of tetratopic ligands with alterable lengths (namely, H\textsubscript{4}L\textsubscript{1}, H\textsubscript{4}L\textsubscript{2} and H\textsubscript{4}L\textsubscript{3}, Figure 1) for the first time. We combined them with a typical six-connected secondary building unit (SBU), Zn\textsubscript{4}O(CO\textsubscript{2})\textsubscript{6}, which is readily available under solvothermal conditions based on previous results.\[14]\ The reaction with these ligands and Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O in DMF or DEF/NMP under similar solvothermal conditions afforded three mesoporous MOFs, Zn\textsubscript{4}O(L\textsubscript{1})\textsubscript{1.5} (L\textsubscript{1}, 1; L\textsubscript{2}, 2; L\textsubscript{3}, 3), with the same (4,6)-connected corundum-type frameworks and hierarchical pore sizes, based on single crystal X-ray structural and elemental analyses.\[12,13]\ All three MOFs are isostructural and crystallize in the trigonal space group R-3c. The asymmetric unit contains unique Zn1 and Zn2 atoms having 1/3 and 1 occupancy factors, respectively, a central oxygen with 1/3 occupancy factor and a half L ligand. The Zn2 is coordinated to three same oxygens from carboxylates and one central oxygen, whereas Zn1 atom coordinates to three oxygens from three carboxylates and one central oxygen. The central oxygen atom connects with one Zn1 and three Zn2 atoms to form a Zn\textsubscript{4}O cluster, which is coordinated by six ligands to be a 6-connected node. Each tetratopic ligand connects with four Zn\textsubscript{2}O clusters, where each carboxylate group binds to one cluster. Such connectivity leads to an extended 3D highly porous framework with ideal (4,6)-connected corundum topology (Figure 2a). The resultant non-interpenetrated MOFs

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Dr. Y.-Q. Lan;[1] Dr. H.-L. Jiang;[2] Prof. Dr. Q. Xu
National Institute of Advanced Industrial Science and Technology (AIST)
Ikeda, Osaka 563-8577, Japan
E-mail: q.xu@aist.go.jp

Dr. Y.-Q. Lan, Dr. S.-L. Li
Faculty of Chemistry
Northeast Normal University
Changchun 130024, P. R. China

[1] These authors contributed equally to this work.

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and powder X-ray diffraction (PXRD) patterns show that only broadened peaks exist. The N$_2$ uptakes for 1-3 are very low at 77 K with respect to the calculated accessible surface area (Figure 3a), which usually happens to highly porous MOFs, presumably due to the distorted framework upon removal of the solvent molecules.\[^7d\] The adsorption isotherms of CO$_2$ and N$_2$ were measured up to 1 atm at 195, 273 and 298 K, respectively.\[^12\] Unexpectedly, the CO$_2$ uptakes for 1-3 are quite high while N$_2$ sorption at 195 K was very low and N$_2$ was hardly adsorbed at all at 273 and 298 K (Figure 3b–d). Strikingly, the CO$_2$ uptake of 3 is 85 cm$^3$/g at 298 K and 1 atm. It is worth noting that even though numerous MOFs have been reported, few exhibit a CO$_2$ uptake over such a value at 298 K and feature a quadrangular opening and two types of microporous and mesoporous cages (Figure 2b), the sizes of which gradually increase along with ligand extension in the fixed framework, as shown in Figure 1. With such an assembly, each microporous cage is surrounded by eight mesoporous cages (Figure 2c), which results in very high free porosities of 75.7, 83.7, and 84.6% in 1, 2, and 3, respectively. As far as we know, only very few MOFs are reported with accessible porosity values that approach or are over 85%\[^{1a,e,7c,d,13}\].

Based on the substantive weight loss from TG analyses\[^{12}\], there should be plentiful solvent molecules inside the MOF cages. Upon being subjected to solvent-exchange and desolvation treatments, the activated samples are almost amorphous and powder X-ray diffraction (PXRD) patterns show that only broadened peaks exist. The N$_2$ uptakes for 1-3 are very low at 77 K with respect to the calculated accessible surface area (Figure 3a), which usually happens to highly porous MOFs, presumably due to the distorted framework upon removal of the solvent molecules.\[^7d\] The adsorption isotherms of CO$_2$ and N$_2$ were measured up to 1 atm at 195, 273 and 298 K, respectively.\[^12\] Unexpectedly, the CO$_2$ uptakes for 1-3 are quite high while N$_2$ sorption at 195 K was very low and N$_2$ was hardly adsorbed at all at 273 and 298 K (Figure 3b–d). Strikingly, the CO$_2$ uptake of 3 is 85 cm$^3$/g at 298 K and 1 atm. It is worth noting that even though numerous MOFs have been reported, few exhibit a CO$_2$ uptake over such a value at 298 K and feature a quadrangular opening and two types of microporous and mesoporous cages (Figure 2b), the sizes of which gradually increase along with ligand extension in the fixed framework, as shown in Figure 1. With such an assembly, each microporous cage is surrounded by eight mesoporous cages (Figure 2c), which results in very high free porosities of 75.7, 83.7, and 84.6% in 1, 2, and 3, respectively. As far as we know, only very few MOFs are reported with accessible porosity values that approach or are over 85%\[^{1a,e,7c,d,13}\].

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![Figure 1](https://www.materialsviews.com/commun/images/content/advmat.11.05015.m112.jpg)

**Figure 1.** A view of 1-3 constructed by Zn$_4$O(CO$_2$)$_6$ SBU and extendable tetratopic ligands, showing main features of quadrangular openings and two types of microporous and mesoporous cages marked with respective sizes. The large yellow spheres represent the largest van der Waals spheres that fit in the cavities without touching the frameworks. All hydrogen atoms have been omitted for clarity.
by naked eye as a qualitative indication of lanthanide sensitization. The characteristic sharp emission bands are corresponding to the respective encapsulated lanthanide cations and simultaneously doping with $\text{Eu}^{3+}$ and $\text{Tb}^{3+}$ in the MOF exhibited their multiband emissions (Figure 4a–c). Notably, both the $\text{Eu}^{3+}$ and $\text{Tb}^{3+}$ doped MOF samples have shown very long $\text{Ln}^{3+}$ lifetimes of 0.63 and 1.75 ms, respectively, while the luminescence $\text{Eu}^{3+}/\text{Tb}^{3+}$ lifetime in co-doped MOF is much shorter (1.65 ns). Despite this limitation, the co-doped MOF displayed bimodal luminescence and the $\text{Eu}^{3+}/\text{Tb}^{3+}$ percentage-tuned intermediate colors of the doped MOF samples can also be observed by naked eye (Figure 4d).

Moreover, given such high CO$_2$ uptake and almost non-adsorption for N$_2$, the CO$_2$/N$_2$ selectivity at ambient conditions is exceptionally high. We attribute the high CO$_2$ absorption and excellent CO$_2$/N$_2$ selectivity to highly flexible frameworks involving C–O–C alkyl ether fragments.

Lanthanide(III) ions have been introduced into the pores of 1, for which the sample was soaked in DMF solutions of nitrate salts of $\text{Eu}^{3+}$ or $\text{Tb}^{3+}$. The successful $\text{Ln}^{3+}$ loading does not influence the crystalline integrity of 1, as demonstrated by PXRD profiles. Upon excitation with a standard UV lamp ($\lambda_{\text{ex}} = 365$ nm), the $\text{Eu}^{3+}$ and $\text{Tb}^{3+}$-doped samples emitted their respective red and green colors, which can be readily observed by naked eye as a qualitative indication of lanthanide sensitization. The characteristic sharp emission bands are corresponding to the respective encapsulated lanthanide cations and simultaneously doping with $\text{Eu}^{3+}$ and $\text{Tb}^{3+}$ in the MOF exhibited their multiband emissions (Figure 4a–c). Notably, both the $\text{Eu}^{3+}$ and $\text{Tb}^{3+}$ doped MOF samples have shown very long $\text{Ln}^{3+}$ lifetimes of 0.63 and 1.75 ms, respectively, while the luminescence $\text{Eu}^{3+}/\text{Tb}^{3+}$ lifetime in co-doped MOF is much shorter (1.65 ns). Despite this limitation, the co-doped MOF displayed bimodal luminescence and the $\text{Eu}^{3+}/\text{Tb}^{3+}$ percentage-tuned intermediate colors of the doped MOF samples can also be observed by naked eye (Figure 4d).

Figure 2. The structural overview for 3 as a representative. a) The natural tiling of the corundum-type network. b) Combined featured opening and two types of cages. c) View of the 3D network along the c-axis. The central small cage marked as green ball was hidden by the upper yellow ball.

Figure 3. N$_2$ sorption isotherms for 1-3 at 77 K a), and CO$_2$ and N$_2$ sorption isotherms for b) 1, c) 2, and d) 3 at 195, 273 and 298 K.
Figure 4. Excitation and emission spectra of a) Eu$^{3+}$, b) Eu$^{3+}$/Tb$^{3+}$, and c) Tb$^{3+}$ doped 1. d) The Eu$^{3+}$/Tb$^{3+}$-doped 1 illuminated with 365 nm laboratory UV light. The samples were prepared by doping 100 mg MOF with 2 mmol Ln$^{3+}$ in 5 mL DMF. From left to right, Eu$_{1}$/Tb$_{0}$, Eu$_{0.8}$/Tb$_{0.2}$, Eu$_{0.7}$/Tb$_{0.3}$, Eu$_{0.6}$/Tb$_{0.4}$, Eu$_{0.3}$/Tb$_{0.7}$, and Eu$_{0}$/Tb$_{1}$.

Figure 5. (top left) UV-vis spectra of the DMF solution containing BR1 and FG3 dyes, in which crystals of 3 were soaked. The continuing decrease of characteristic absorbance for BR1 reveals its successful incorporation whereas unchanged peak of FG3 suggests its exclusion by the MOF cages. (bottom left) UV-vis spectra of the effluent during the dye mixture of BR1 and FG3 passing through the MOF chromatographic column. (right) Photograph records for 3-filled column-chromatographic separation process for BR1 and FG3 dyes, in which (1) 3-filled column, (2-6) separation process with gradually changed color, and (7) complete separation with only BR1 retained.
Experimental Section

Crystal data for compound 1: C_{111}H_{69}O_{29}Zn_{8}, M = 2752.84, trigonal, a = 26.880(4) Å, c = 85.169(4) Å, V = 53293(10) Å³, T = 293(2) K, space group R-3c, Z = 6, \( \rho_{\text{calc}} = 0.515 \text{ g cm}^{-3} \), \( F_{000} = 8412, 87702 \) reflections measured, 10646 independent reflections (\( R_{\text{int}} = 0.1337 \)). The final RI values were 0.0497 (\( I > 2\sigma(I) \)). The final \( wR(F^2) \) values were 0.0879 (\( I > 2\sigma(I) \)). The goodness of fit on \( F^2 \) was 0.966.

Crystal data for compound 2: C_{135}H_{120}O_{50}Zn_{8}, M = 3065.27, trigonal, a = 32.3599(13) Å, c = 100.8246(11) Å, V = 91435(5) Å³, T = 293(2) K, space group R-3c, Z = 6, \( \rho_{\text{calc}} = 0.334 \text{ g cm}^{-3} \), \( F_{000} = 9420, 41192 \) reflections measured, 3762 independent reflections (\( R_{\text{int}} = 0.1819 \)). The final RI values were 0.0841 (\( I > 2\sigma(I) \)). The final \( wR(F^2) \) values were 0.2116 (\( I > 2\sigma(I) \)). The goodness of fit on \( F^2 \) was 0.964.

Crystal data for compound 3: C_{135}H_{120}O_{50}Zn_{8}, M = 2999.20, trigonal, a = 33.1396(6) Å, c = 96.086(18) Å, V = 91385(24) Å³, T = 293(2) K, space group R-3c, Z = 6, \( \rho_{\text{calc}} = 0.326 \text{ g cm}^{-3} \), \( F_{000} = 9132, 79050 \) reflections measured, 7890 independent reflections (\( R_{\text{int}} = 0.1488 \)). The final RI values were 0.0594 (\( I > 2\sigma(I) \)). The final \( wR(F^2) \) values were 0.1102 (\( I > 2\sigma(I) \)). The goodness of fit on \( F^2 \) was 0.962.

CCDC 834530-834532 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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[12] See the Supporting Information.


