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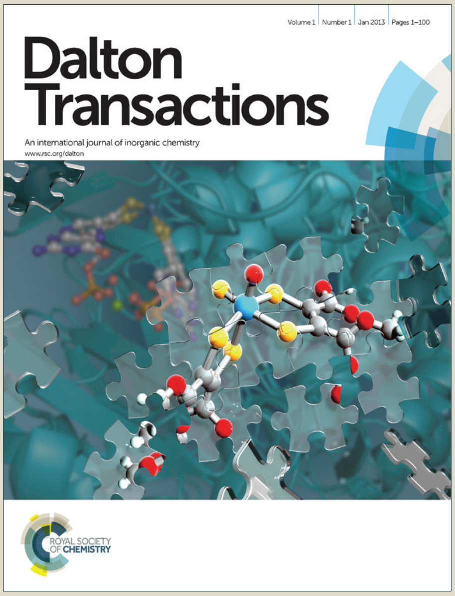

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ARTICLE TYPE

Tuning of Gate Adsorption: Modification of a Flexible Metal-Organic Framework by Secondary Organic Ligands

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For realizing selective adsorption of targeted molecules, a flexible metal-organic framework (MOF) was modified with monodentate secondary ligands. Although the modified MOF retains CO_2 adsorptivities with a vertical adsorption uptake, the material also shows gate adsorptibities of a specific gas molecule that the pristine MOF does not adsorb.

Metal-organic frameworks (MOFs) or porous coordination polymers have gathered much attention and considerable effort has been devoted to explore the synthesis of unique framework structures with high performance in wide fields such as gas adsorption, storage, separation, and catalysis.[1-4] MOFs are composed of metal ions/metal oxide clusters and organic linkers, and proper selection of the building units enables us to construct MOFs with regulated pore structures. Among them, flexible MOFs have gathered much attention because they can change their structures through guest accommodation, leading to selective adsorption/separation properties.[5-9] One of the known selective adsorption phenomena is gate adsorption, which is first reported on a flexible 2D copper MOF by Li and Kaneko in 2001.[10] The CO_2 adsorption isotherms on the MOF shows almost negligible uptake at low pressure and sudden uptake appears at a specific pressure with rectangular shape of a hysteretic loop. Since the first discovery, many MOFs showing gate adsorption have been synthesized in a wide variety of framework dimensionalities. For example, Kitaura *et al*. showed gate adsorption of methanol on a 3D pillared-layer MOF in 2002[11] and we reported gate adsorption of CO_2 on a 1D MOF in 2012.[12] These MOFs have advantages in energy saving to recover the adsorbed gas molecules because of desorption of the adsorbed gases at moderate pressures.[13]

Recently, several attempts to tune gate adsorption were reported. Cheng *et al*. treated the 2D copper MOF with solvents such as methanol, ethanol, and propanol and successfully tuned CO_2 gate adsorption/desorption pressure.[14] Fukushima *et al*. also tuned gas adsorption properties on a 2D interdigitated MOF using the concept of ligand-based solid solution.[15] However, gas species adsorbed on flexible MOFs are material-dependent and it is still a significant challenge to synthesize MOFs that can adsorb a targeted gas species under a specific condition. Adsorption of targeted molecular species extends potential of MOFs and there is no doubt about important breakthrough of porous materials for effective adsorption/separation. Aiming at gate adsorption of a targeted molecular species, modification of MOFs with small amounts of secondary organic ligands was attempted, which enables us to open up a new way to tune gate adsorptivity. As secondary ligands, monodentate ligands containing a pyridyl ring, which is a characteristic structural unit in a primary organic ligand of 4,4′-bipyridine (bpy), were used. By using both the primary and secondary organic ligands simultaneously in sample preparation, we modified both outer surface and inside of the MOF grains with the secondary ligands. It should be noted that the modified MOF with almost negligible amount of the secondary ligands acquired new adsorption ability; the modified MOFs adsorb a specific gas species that the pristine MOF does not adsorb. This simple methodology should be applicable for various porous MOFs to tune gas adsorptivities.

The modified MOFs were synthesized from $Cu(BF_4)_2 \cdot 6H_2O$ and bpy and monodentate ligands (4-picoline: PI or 4-tertiary-butylpyridine: TBP) with the molar ratio of 1:2:x in water/ethanol (1:1 v/v) mixture, where x is 0.15 (unless otherwise stated) or 0.25. The modified MOFs are hereafter denoted as CuMOF-PI or CuMOF-TBP, when picoline or tertiary-butylpyridine was used as secondary organic ligands, respectively. As a reference material, a pristine material (denoted as CuMOF) was prepared with a similar procedure except no addition of the secondary organic ligands. The pristine CuMOF shows a gate adsorption of CO_2 and is proved to be identical to the previously reported one.[16,17]

Synchrotron X-ray diffraction (XRD) patterns of CuMOF-PI and CuMOF-TBP are compared with a pattern of CuMOF as the reference (Fig. S1, ESI†). The estimated unit cell parameters in CuMOF are a = 16.5019(6) Å, b = 11.1281(4) Å, c = 14.2960(4) Å, β = 115.367(2)° in monoclinic crystal system and space group $C2/c$ (No. 15). The unit cell parameters are close to that reported by Blake *et al*., and the space group is the same.[18] There are slight deviation between the crystallographic parameters because of the thermal expansion behaviour of the MOF, which is also confirmed by synchrotron XRD experiments between 100 K and 303 K (Fig. S2, ESI†). The crystal structure of CuMOF reveals 1D chain motifs to form a quasi-3D network structure weakly bound through hydrogen bondings (Fig. S3, ESI†).[18] Basically, the modification with the secondary ligands gives negligible influence on XRD, FT-IR, TG, and CHN elemental analysis results (Table S1, Fig. S4 and S5, ESI†). In the FT-IR spectra of the modified CuMOFs, there are very weak absorption peaks that are assigned to the secondary organic ligands used. Because of the weakness of absorption signals, it is difficult to evaluate the secondary ligands quantitatively by the FT-IR results.

NMR is a highly sensitive and sophisticated method to detect organic molecules quantitatively. Therefore, ^{1}H-NMR technique was used to detect small amount of the secondary ligands in the modified CuMOFs (Fig S6, ESI†). The primary ligand bpy was clearly detected in an acid–decomposed and extracted solution of the modified CuMOFs and used as the reference. In both cases of CuMOF-PI and CuMOF-TBP, weak signals assigned to the secondary ligands were observed (Table S2, ESI†). The NMR spectrum of CuMOF-PI showed signals at δ = 2.3, 7.2, and 8.5 with reasonable integration ratio, which correspond to the methyl proton and beta- and alpha-protons of the pyridyl rings in PI, respectively, indicating the presence of the secondary organic ligand. The integral ratio of PI/bpy in CuMOF-PI is estimated as 0.003, which corresponds to 0.11wt% of PI in CuMOF-PI. In CuMOF-TBP, signals of bpy and TBP were observed at reasonable chemical shifts with an integration ratio of 0.002. The NMR results clearly indicate the presence of PI or TBP in each modified CuMOF, although the amount of PI or TBP is extremely small compared to the main ligand of bpy, which is consistent with TG, FT-IR, and CHN elemental analysis.

Carbon dioxide gas adsorption properties were examined on the modified CuMOFs (Fig. S7, ESI†). Both CuMOF-PI and CuMOF-TBP show an abrupt uptake at a relative pressure and sudden desorption at a pressure below the uptake pressure, forming rectangular shape of a hysteretic loop, which is the characteristic shape of CO_2 gate adsorption on CuMOF. Slight deviation in the adsorption/desorption pressures is observed compared to those of CuMOF; P/P_0 = 0.011 and 0.0079 on both the modified CuMOFs and, on the other hand, 0.010 and 0.0073 on CuMOF, respectively. The adsorption amounts of CO_2 per one Cu atom on CuMOF, CuMOF-PI, and CuMOF-TBP are 2.2, 2.1, and 2.0, respectively. These adsorption results indicate that the modification with slight amounts of the secondary ligands do not disturb the CO_2 gate adsorptivity on the flexible MOF.

Because PI and TBP have methyl or tertiary-butyl groups, they must have positive interaction with molecules with alkyl groups. It is assumed that 2,2-dimethylbutane (DMB) is an appropriate probe molecule to evaluate a specific interaction between the adsorbate and the secondary organic ligands. Adsorption isotherms of DMB are shown in Fig. 1a. Both CuMOF-PI and CuMOF-TBP show almost no adsorption below P/P_0 = 0.4, and sudden uptakes occurred at around P/P_0 = 0.4 – 0.6 with large hysteretic loops. Although there are some deviation in the uptake pressures depending on sample lots, the sudden adsorption uptake is observed on all the modified samples. It should be noted that the pristine CuMOF has no uptake of DMB up to P/P_0 = 1, indicating that the modification with negligible amount of the secondary ligands induces the DMB adsorption. The adsorption amounts of DMB on both the modified CuMOFs at P/P_0 = 1 correspond to approximately one molecule per one Cu atom, which is almost the half of CO_2 adsorption at 273 K under one bar. By considering the molecular volumes of DMB (96 Å^3) and CO_2 (24 Å^3) estimated by ChemOffice software, the pore space occupied by DMB molecules is almost twice as large as that by CO_2 molecules in the modified CuMOF because of the bulkiness of DMB molecules.

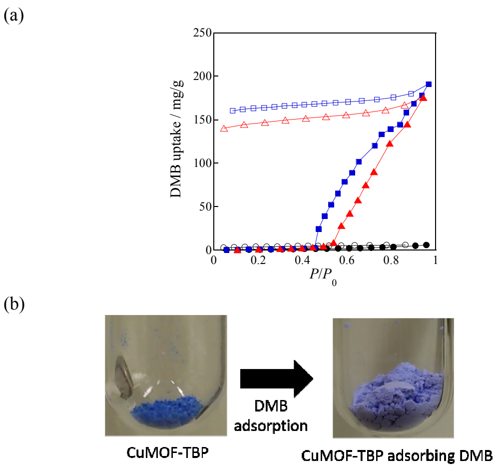

Fig. 1 (a) 2,2-dimethylbuthane adsorption isotherms at 273 K on CuMOF (black), CuMOF-PI (red), and CuMOF-TBP (blue). Open and filled symbol represent adsorption and desorption, respectively. (b) Photograph of colour change of CuMOF-TBP by 2,2-dimethylbuthane adsorption.

The DMB adsorption is also recognized by colour change (from blue to purple) and apparent severalfold volume expansion (Fig. 1b). It is well known that change of coordination environment around transition metals has an influence on coordination fields, and results in colour change of materials. In MOFs, apparent colour change is sometimes observed, which is often due to coordinative adsorption/desorption of molecules at open metal sites.[19] In this work, it is interesting to observe the colour change even in the modified CuMOFs in which the coordination sites of Cu(II) ions are fully occupied. The drastic volume change is interpreted as a result of an expansion of 2D layers of the CuMOF framework through accommodation of DMB molecules.[16]

Hysteretic loops at low relative pressures are often observed in adsorption isotherms on flexible MOFs.[20] Therefore, it is plausible that the modified CuMOFs also adsorb DMB molecules accompanied by structural transformation. To elucidate the adsorption mechanism XRD experiments were performed on the modified CuMOFs with DMB vapour loaded at a room temperature. The XRD experiments clearly indicated that CuMOF-PI and CuMOF-TBP showed structural transformation through DMB adsorption to form a similar phase which is considerably different from that of a CO_2-adsorbed sample,[16] indicating that transformation to a new phase occurred accompanied by the DMB adsorption (Fig. S8, ESI†). Interestingly, the DMB-adsorbed state of both CuMOF-PI and CuMOF-TBP are highly stable and keep the states *ca.* one month under atmospheric conditions, although CO_2-adsorbed state of the modified CuMOF is unstable and transforms to a form that can adsorb no gas including CO_2 within a few minutes at the same condition. The adsorbed DMB molecules on the modified CuMOFs are removed by heating at 383K under vacuum as confirmed by XRD and FT-IR (Fig. S9 and S10, ESI†), and the DMB adsorption can be repeated. The modification with tiny amount of the secondary ligands not only induces new gas adsorptivity but also provides an ability to retain DMB gas molecules.

To examine the influence of the secondary ligands in more details, modified CuMOFs were prepared using different amount of the secondary organic ligands (x = 0.25) (Fig. S11-S13, ESI†). In the case of CuMOF-PI (x = 0.25), no CO_2 adsorption occurred at 273 K. However, the CuMOF-PI (x = 0.25) ground in a mortar surprisingly indicated CO_2 gate adsorptivity close to that of pristine CuMOF (Fig. 2) This result is interpreted that the grinding treatment makes slight structural change and the inner surface of CuMOF exposed by breaking down the crystal grains, which brings the crystal particles active for CO_2 gate adsorption. On the other hand, CuMOF-TBP (x = 0.25) without grinding showed CO_2 gate adsorption at 273 K, which is identical to that of CuMOF. Assuming the coordination characteristics of the monodentate ligands, it is reasonable that the secondary ligands should preferentially modify the outer surface of the CuMOF. However, the difference of CO_2 adsorptivity between CuMOF-PI (x = 0.25) and CuMOF-TBP (x = 0.25) clearly reveals the difference in modification manner of the MOFs. It follows from these results that the outer surface of CuMOF-TBP is relatively less modified with the secondary ligands than CuMOF-PI, implying importance of molecular adsorption on the outer surface of CuMOF for the gate adsorption.[21]

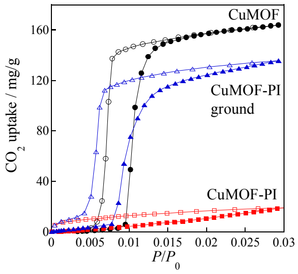

Fig. 2 Carbon dioxide adsorption isotherms at 273 K on ground CuMOF (black), CuMOF-PI (x = 0.25) (red), and CuMOF-PI (x = 0.25) ground (blue).

Water adsorption experiments give a light for better understanding of the modified CuMOFs (Fig. S14, ESI†). It is known that CuMOF adsorbs two water molecules per one Cu atom as a part of the crystal structure and transforms to a structure with no open pore to accommodate any other molecules.[22] However, both CuMOF-PI and CuMOF-TBP adsorb larger amount of water than CuMOF; 2.7 and 2.4 H_2O molecules per one Cu atom for CuMOF-PI and CuMOF-TBP, respectively. This result indicates the formation of pore space to accommodate more water molecules, which may be derived from the defects in the crystal structure formed by the coordination of the secondary organic ligands.

In conclusion, adsorption properties of a copper based metal-organic framework (CuMOF) are successfully tuned by very small amount of secondary organic ligands (picoline and tertiary-butylpyridine). Although CO_2 gate adsorptivity was retained through the modification with the secondary ligands, the modified CuMOFs strongly adsorb and accommodate 2,2-dimethylbutane which pristine CuMOF does not adsorb at the same condition.

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† Electronic Supplementary Information (ESI) available: Additional experimental details, figures of XRD patterns, crystal structures, TG, FT-IR, and adsorption isotherms, tables of elemental analysis and H^1-NMR results, and photographs. See DOI: 10.1039/b000000x/

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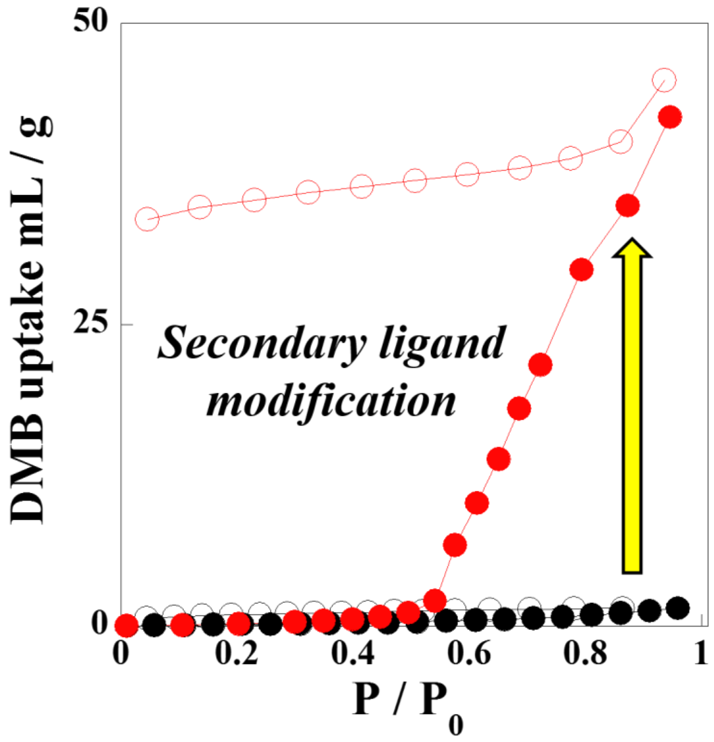
Graphical abstract



Modification with secondary organic ligands on a MOF induces gate adsorptivities of a specific gas molecule that the pristine MOF does not adsorb.