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Gate effects in a hexagonal zinc-imidazolate-4-amide-5-imidate framework with flexible methoxy substituents and CO₂ selectivity†

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A new imidazolate-4-amide-5-imidate based MOF, IFP-7, is generated, having flexible methoxy groups, which act as molecular gates for guest molecules. This allows highly selective CO₂ sorption over N₂ and CH₄ gases.
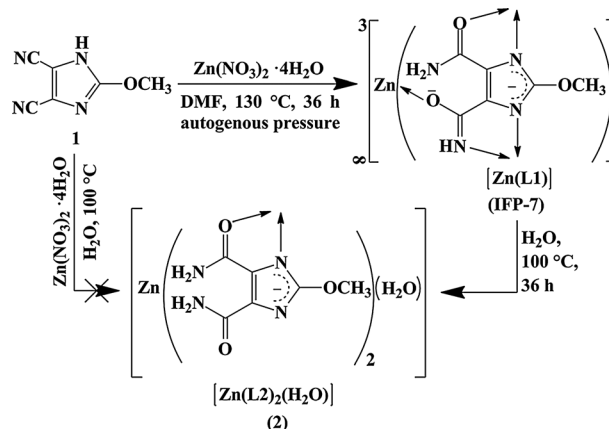
Metal–Organic Frameworks (MOFs) have emerged as a unique class of crystalline materials because of their potential for structural and functional design along with pertinent applications like gas storage[1–8] and gas separation.[8–20] MOFs are envisioned as materials for capturing CO_2 from flue gas in connection with global warming.[2,8,15] Flue gas contains not only CO_2 but also N_2, H_2, O_2, and H_2O. Hence, selective adsorption properties of MOFs for CO_2/H_2 and CO_2/N_2 are important for pre-combustion and post-combustion CO_2 capture, respectively.

MOFs should exhibit high CO_2 adsorption capacity at ambient temperature,[9,10] high selectivity for CO_2 over other gases,[14–17] and high hydrothermal stability to be excellent CO_2 capture materials. To enhance the CO_2 capture with MOFs, various strategies have been developed such as pore-surface functionalization with amines,[14,16] making the network flexible,[17] using organic ligands with flexible joints[12] and side chains,[18] creating accessible metal sites[15] and rotatable pillared-layer based frameworks,[19] and exposing Lewis base sites.[20] The structural flexibility, causing the closed–open structural transformation, is the key factor in obtaining a 'gate effect', which enhances the selectivity by responding to specific guest molecules. Flexible crystalline materials can provide an ideal

sorption system with highly selective recognition properties that enable the selective storage of a particular target molecule.[18]

Considering all of these points, here we report a MOF $\{[Zn(L1)]\cdot xH_2O \cdot yDMF\}_n$ (L1 = 2-methoxyimidazolate-4-amide-5-imidate) named IFP-7 (Imidazolate Framework Potsdam) which has flexible methoxy substituents. The reaction of 4,5-dicyano-2-methoxy-imidazole (**1**) with $Zn(NO_3)_2 \cdot 4H_2O$ in *N,N'*-dimethylformamide (DMF) yielded the *in situ* functionalized 2-methoxyimidazolate-4-amide-5-imidate based material IFP-7 (Scheme 1, for details see ESI†). The structure of IFP-7 was determined by a combination of Powder X-ray Diffraction (PXRD) and structure modelling and was confirmed by solid-state direct polarization ¹H Magic Angle Spinning (MAS) NMR, ¹³C{¹H} Cross Polarization (CP) MAS NMR and IR spectroscopy. The structural model of IFP-7 was constructed by using the single-crystal X-ray structure determination for IFP-1,[21] and was further optimized by using a density functional theory *ab initio* method (see ESI†).

The PXRD pattern of the optimised IFP-7 structure is in very good agreement with the experimental data (Fig. S3, ESI†). IFP-7 belongs to the isoreticular IFP series.[21,22] ¹H MAS and ¹³C{¹H} CP MAS NMR spectra of as-synthesized IFP-7 (Fig. S2, ESI†) indicate the presence of

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† Electronic supplementary information (ESI) available: Detailed experimental procedure, IR spectra, theoretical calculations, NMR spectra, PXRD patterns, TGA traces, a table displaying X-ray data of Zn-complex [Zn(L2)₂(H₂O)] (**2**) and gas adsorption data of IFP-7. CCDC 925826. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc42156b

Scheme 1 Syntheses of IFP-7 and transformation to a monomeric Zn-complex [Zn(L2)₂(H₂O)] (**2**).
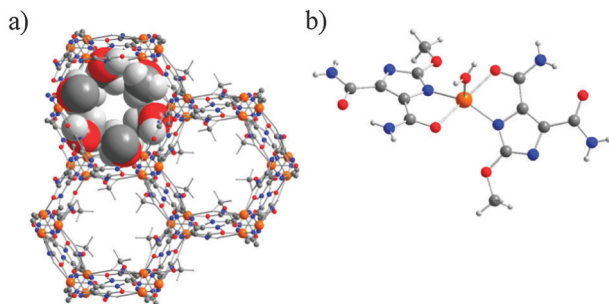
Fig. 1 (a) Hexagonal channels in IFP-7, the methoxy substituents at the linker L1 are presented in a space filling mode. The structure is based on density functional *ab initio* calculations. (b) Crystal structure of the momomeric Zn-complex [Zn(L2)$_2$(H$_2$O)] (**2**) [orange Zn, blue N, red O, dark gray C, light gray H].

a 2-methoxyimidazolate-4-amide-5-imidate linker. Moreover, ^{13}C NMR reveals the *in situ* functionalization of the cyano groups with two peaks at 167 and 170 ppm for the carbon atoms of amide and imidate groups, respectively.

The theoretically estimated structure of IFP-7 possesses 1D hexagonal channels (Fig. 1a). The flexible methoxy groups protrude into the open channels. The channel diameter was calculated by considering the van der Waals radii and the accessible diameter of the channels in IFP-7 was estimated to be 2.1 Å.

The TGA trace shows that after removal of the solvent, IFP-7 is stable up to 300 °C (Fig. S8, ESI†). PXRD patterns of activated IFP-7 exhibit diffraction peaks similar to those of the as-synthesized sample. This indicates that the porous framework maintained the crystalline integrity without solvent molecules (Fig. S3, ESI†).

Activated IFP-7 is expected to show gas-sorption selectivity towards small polar molecules due to its polar and flexible methoxy side chains.[17] The gas sorption isotherms of IFP-7 are recorded for N$_2$, H$_2$, CH$_4$, and CO$_2$ gases at various temperatures and 1 bar (Fig. 2 and Table 1). IFP-7 barely adsorbs N$_2$ at 77 K, but adsorbs a significant amount of CO$_2$ at 195 K (Fig. 2a). The kinetic diameters of N$_2$, H$_2$, CH$_4$, and CO$_2$ are 3.64, 2.89, 3.8, and 3.3 Å, respectively. The IFP-7 pore aperture of 2.1 Å is too narrow for N$_2$ adsorption at 77 K. Upon increasing the temperature to 195 K, the sorption capacity increases slightly (11 cm^3 g^{-1}). At 77 K, the low thermal energy of the methoxy substituents locks the pore aperture windows like a molecular gate. At 195 K, the thermal motion of the flexible methoxy chains increases, which makes it easier for N$_2$ molecules to penetrate into the channels. A further increase in temperature to 273 K or 298 K decreases the N$_2$ sorption capacity (3.8 cm^3 g^{-1}, at 273 K) again, as expected for thermodynamic reasons (Fig. 2b and Table 1). Moreover, IFP-7 exhibits H$_2$ uptake of 50.3 cm^3 g^{-1} with broad desorption hysteresis. A similar type of desorption hysteresis was observed in NOTT-200.[23] However, the adsorption at higher relative pressure is irreversible due to small pore openings, which gives rise to an open loop hysteresis (Fig. 2a). The smaller H$_2$ molecule can pass through the gates formed from the methoxy groups.[24] The sorption isotherms can deviate from ideal equilibrium experiments as pronounced kinetic effects occur because of the small channel size and the gate effect. The H$_2$ sorption isotherm shown in Fig. 2a confirms that 98% of the adsorbed H$_2$ is trapped in the framework when the pressure is reduced
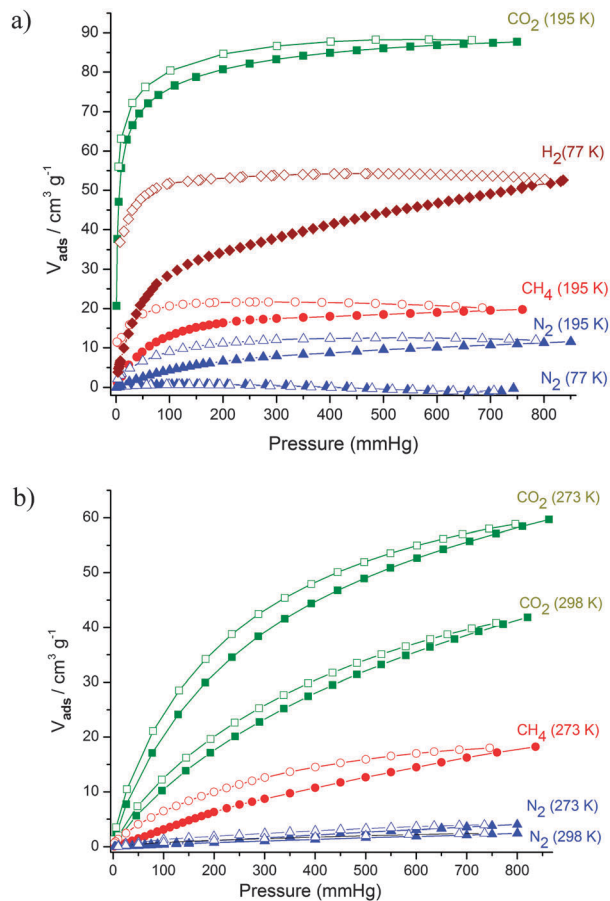

Fig. 2 Gas sorption isotherms for activated IFP-7. Adsorption and desorption branches are indicated by closed and open symbols, respectively.

Table 1 Adsorbed gas volumes [V_{ads} (cm^3 g^{-1})] in activated IFP-7 at 1 bar, in comparison with [Zn$_2$(BME-bdc)$_2$-bipy]$_n$ (ref. 18)

Gas	T/K	IFP-7	[Zn$_2$(BME-bdc)$_2$-bipy]$_n$
CO$_2$	195	87.7	156
	273	56.9	52
	298	40	33
CH$_4$	195	19.7	60
	273	17.0	7
	298	4.9	6
N$_2$	77	—	∼0.1
	195	11.0	16
	273	3.8	∼0.1
	298	2.3	∼0.1
H$_2$	77	50.3	—

from 840 mmHg to 100 mmHg, and 70% of the adsorbed H$_2$ remains when the pressure is further reduced to 7 mmHg.

The CO$_2$ sorption measurements at 195, 273 and 298 K show typical type I isotherms with high uptake (Fig. 2 and Table 1). The uptake of CO$_2$ by IFP-7 at 298 K and 1 bar is 40 cm^3 g^{-1} (7.85 wt%) which is higher than those of the previously reported flexible zinc MOFs with tetrahedral linkers.[25] A similar high uptake was recently found by Yaghi and co-workers for ZIF-69 and ZIF-82, which were

synthesized by using imidazolates containing the functional groups Cl and CN.[26] At 195 K, a steep increase in the CO_2 uptake takes place in the low-pressure region (10–110 mmHg), and a small hysteresis is visible in all the desorption branches. Such hysteretic behavior is typical for this kind of flexible MOF.[12,18] The hysteresis can be attributed to slow kinetics of desorption. However, the fact that CO_2 (kinetic diameter of 3.3 Å) is adsorbed by IFP-7 suggests that CO_2 interacts with the flexible MOF and opens the molecular gate due to its high polarizability and quadrupole moment. To further understand the adsorption properties, the isosteric heats of adsorption were calculated from the CO_2 adsorption isotherms at 273 K and 298 K (Fig. 2b). At zero loading the Q_{st} value ($-\Delta H$) for IFP-7 is 42.6 kJ mol^{-1} (Fig. S12, ESI†), which is comparable to those of other MOFs.[2,27] Upon increasing the loading the Q_{st} value decreases to 25.8 kJ mol^{-1}. The high Q_{st} value of IFP-7 can be attributed to the highly polar framework and the effect of the small pore size.

In general, at 195 K, MOFs exhibit higher uptake capacity for CO_2 than for CH_4 since CO_2 (T_c = 304.19 K) is subcritical and thus more condensable than CH_4 (T_c = 190.09 K) which is supercritical. Still, flexible MOFs can often effectively include CH_4 with its high electric dipole polarizability (2.59 Å^3). For example, flexible MOF SNU-M10 adsorbs 123.5 cm^3 g^{-1} of CO_2 and 27.5 cm^3 g^{-1} of CH_4 at 195 K.[17]

From the ratios of the initial slopes in the Henry region of the adsorption isotherms of IFP-7 (Fig. S13–S15 in ESI†), the sorption selectivity for CO_2 over N_2 and for CO_2 over CH_4 was estimated. The adsorption selectivity of IFP-7 at 298 K and 1 bar for CO_2/N_2 is 26:1 (37:1 at 273 K; 467:1 at 195 K), which is higher than those of BPL carbon, ZIF-68–70, -79, -81, but lower than those of ZIF-78, -82 at 298 K and 1 bar, and for CO_2/CH_4 is 14:1 (7:1 at 273 K; 132:1 at 195 K) which is higher than those of BPL carbon and the above-mentioned ZIFs.[26] The gas sorption behavior of IFP-7 is comparable with that of a honeycomb-like zinc-dicarboxylate–bipyridine framework with flexible methoxyethoxy chains, [Zn$_2$(BME-bdc)$_2$(bipy)]$_n$ (see Table 1).[18]

Additionally, the chemical stability of IFP-7 was analyzed by suspending IFP-7 for 5 days in boiling methanol, benzene and water (see ESI†), conditions that reflect extreme operational parameters of typical industrial chemical processes. After such extensive treatments, IFP-7 maintained its fully crystalline integrity in methanol and benzene as confirmed by powder X-ray diffraction (see ESI†). But in boiling water, after 24 h the material irreversibly transformed to a monomeric Zn-complex, [Zn(L2)$_2$(H$_2$O)] (2), where L2 is 2-methoxyimidazolate-4,5-diamide (see Scheme 1, Fig. 1b and ESI† for details). We assume that the polar water molecules attack the unsaturated pentacoordinated Zn center of IFP-7 structure.

In conclusion, we have synthesized a microporous Zn-imidazolate-4-amide-5-imidate framework, IFP-7, having flexible methoxy substituents. This is the first example where a flexible methoxy substituent shows the gate opening behavior in a MOF. Because of the presence of methoxy functional groups at the hexagonal channels, IFP-7 acted as a molecular gate for N_2 gas. Due to

polar methoxy groups and channel walls, a wide hysteresis isotherm was observed during H_2 uptake. The IFP-7 exhibits high selectivity for CO_2 over N_2 and CH_4 recommending the possible applications in capturing CO_2 from flue gases or purification of natural gas by CO_2/CH_4 separation.

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