Thermosensitive gating effect and selective gas adsorption in a porous coordination nanocage†

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A porous coordination nanocage functionalized with 24 triisopropylsilyl groups exhibits a remarkable thermosensitive gate opening phenomenon and demonstrates a molecular sieving effect at a certain temperature range, which can be used for gas separation purposes.

Adsorption-based gas separation plays an important role in industry.[1] By judiciously choosing adsorbents with appropriate surface property and pore size, gas separation can be achieved in an energy-conserving and environmentally friendly approach. Three mechanisms have been proposed for this process: steric, kinetic, and equilibrium effect.[1] The steric separation, in which only small adsorbates can diffuse into the adsorbents, is widely encountered in zeolite molecular sieves due to their uniform aperture size in the crystalline structure.[1] During this process, a size match between the adsorbent' aperture and the adsorbate is required. However, such optimized aperture size is not always readily available when the size difference between adsorbates being separated is small. In this case, a molecule sieve with adjustable mesh size is required. We have reported mesh-adjustable molecular sieves (MAMSs), which are based on metal–organic frameworks (MOFs) and have tunable mesh size directly proportional to temperature.[2] It is proposed that the escalating thermal vibration of the bulky groups in the amphiphilic ligands at higher temperature accounts for such thermosensitive gate opening.

Porous coordination nanocages, also known as metal–organic polyhedra (MOP) or nanoballs, are newly emerging porous materials and have found applications as plasticizer, gas sponge, ion channel, coatings, and building units.[3] Their porosity comes from the inner void of these discrete nanocages, although it is possible that the spacing between these nanocages contributes to their porosity as well.[3c,4] We hypothesize that by covering the nanocage with bulky group outside, the opening towards the inner void can be reduced. As a result, these bulky groups may function as gates and give the nanocage thermosensitive gate opening property as well. The ligand precursor for preparing such nanocage is 5-((triisopropylsilyl)ethynyl)isophthalic acid (TEI) (Fig. 1a). It has the isophthalate moiety that can readily participate in the formation of porous coordination nanocage,[5] leaving the bulky triisopropylsilyl (TIPS) groups covering the outside. The initial solvothermal reactions between TEI and copper salts yielded amorphous precipitate that denied any further characterization. Inspired by the fast formation kinetics of these nanocages,[6] we adopted an alternative approach, in which TEI was first deprotonated by a sterically hindered base (2,6-lutidine) and then reacted with $Cu(NO_3)_2 \cdot 2.5H_2O$ (see ESI† for details). Recrystallization from chloroform/DMF afforded single crystal suitable for X-ray crystallography study.‡ As has been anticipated, the crystal of CuTEI is composed of large discrete porous coordination nanocages constructed from the Cu paddlewheel clusters bridged by the isophthalate moieties (Fig. 1b, Fig. S1, ESI†).[5] Like its Cu(*m*-BDC) analogue,[5] CuTEI has 8 triangular and 6 square windows. The yellow sphere at the centre of this nanocage representing its void has a diameter of around 11 Å.

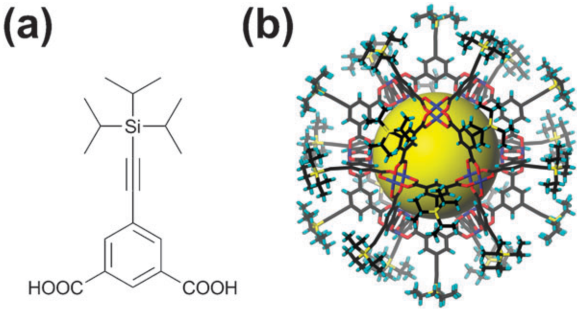

Fig. 1 (a) Ligand TEI. (b) The porous coordination nanocage CuTEI.

Gas sorption measurements were carried out to check CuTEI's porosity. Before these measurements, CuTEI was heated at 120 °C under dynamic vacuum overnight, an activation condition that is vigorous enough to remove any residual solvents. As shown in Fig. 2f, N_2 has barely any sorption at 77 K, and is accompanied by a large hysteresis loop between the adsorption and desorption isotherm branches. Compared to that of N_2, the H_2 isotherm shows a much higher uptake at 77 K and a pronounced hysteresis loop (Fig. 2a) as well. When the temperature is raised by 10 °C to 87 K, however, the overall H_2 uptake increases as well, a phenomenon that is very rare in exothermic physisorption process. In addition, the large hysteresis loop observed at 77 K is greatly diminished. Raising the temperature further to 113 K leads to the lowest H_2 uptake among the three and barely any hysteresis is observable. The same trend is observed in methane sorption isotherms (Fig. 2e). The lower temperature (113 K) gives lower gas uptake and larger hysteresis. Raising the temperature (142 K) yields a large increase in gas uptake. With increasing temperatures (179 K, 195 K and 273 K) the gas uptake

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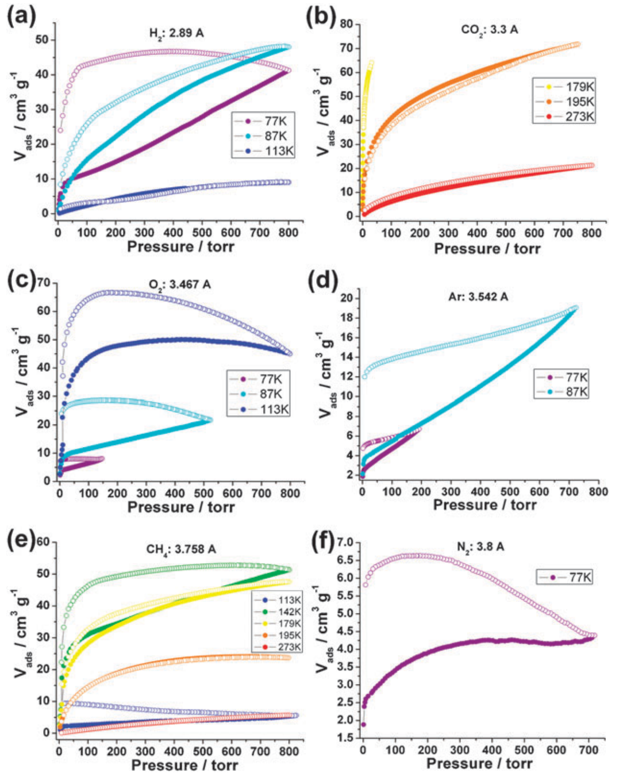

Fig. 2 Gas sorption isotherms of CuTEI under various temperatures.

decreases and the hysteresis loop is less noticeable. Evidently there exists a thermosensitive gating effect, *i.e.*, at a certain temperature range, increasing temperature will lead to larger pores to accommodate more adsorbates.

In order to understand the above experimental data, molecular simulations were performed using perfect CuTEI crystal as the model. The GCMC simulations were carried out to determine the CH_4 and Ar adsorption isotherms at different temperatures. We note that the experimental data are consistently about an order of magnitude lower than the simulated results (Fig. S3, ESI†). Such apparently lower experimental data indicate either a structural change in the CuTEI crystal during the activation process, or a substantially low diffusivity of adsorbates within CuTEI under the testing temperature. In order to verify the second possibility, Molecular Dynamics (MD) simulations were carried out to determine the self-diffusivity of CH_4 at different temperatures for a variety of loadings (Fig. S4a, ESI†). Self-diffusivities decrease slightly with increased loading, which is consistent with other porous materials.[7] Comparison of the self-diffusivities of CH_4 in CuTEI at 300 K with the MD simulation data for MOFs (MOF-5, CuBTC), and zeolites (FAU, MFI) available in the published literature indicates that the self-diffusivity of CH_4 in CuTEI is slightly lower than that in open structures such as MOF-5, CuBTC, and FAU, but is significantly higher than that in MFI zeolite that has a medium-pore size of 5.6 Å (Fig. S4b, ESI†).[7,8] Based on the simulation data, we can conclude that the diffusion of CH_4 in CuTEI is comparable to that in large-pore zeolites and MOFs.

The above simulations, however, overlook two factors that are of paramount importance in interpreting the above-mentioned anomalous gas sorption behavior. The first one is the thermal vibration of TIPS group. The CuTEI structure was considered to be rigid in the simulations. However, TIPS groups are highly likely to function as gates by undergoing thermal vibration within CuTEI, giving this material the thermosensitive gate opening property that is identical with the MAMSs. The second one is the structural change. All the simulations were based on perfect CuTEI crystal structure. During the activation process, nevertheless, the discrete CuTEI molecule tends to move around due to the lack of a strong holding force. Such movement leads to an amorphous structure (Fig. S5, ESI†). As a result, channels and openings toward the inner void in the perfect crystal model are partially reduced and blocked by the close packing of adjacent nanocages and extruded TIPS groups in the activated sample, yielding abundant "kinetically closed pores".[9] In these pores, the pore space becomes inaccessible by adsorbate at low temperature. This is due to the lower kinetic energy of the adsorbate molecule at low temperatures, which cannot overcome potential barriers at the aperture of pores that can otherwise accommodate them.[9] Calculation indicates that the real equilibrium time needed for the sorption process in those kinetically closed pores is much longer than the experimental time scale, which explains why some of the isotherms shown in Fig. 2 have abnormally higher desorption amounts than adsorption amounts.[9] Apparently, increasing the temperature will have two effects in CuTEI's gas sorption. First, it increases the adsorbate' diffusivity due to increased kinetic energy, which we attribute to kinetic effect. Second, it weakens the adsorbate/adsorbent affinity and decreases P/P_0 at a certain pressure, which we attribute to thermodynamic effect. The kinetic effect will boost the gas uptake while the thermodynamic effect will lower it. Overall gas uptake is the balance between these two effects. At a low temperature range, the kinetic effect outperforms the thermodynamic, and that's why the uptake of H_2, O_2 and Ar in CuTEI is higher at 87 K than at 77 K. At higher temperature ranges, the thermodynamic effect becomes dominant, which leads to lower gas uptake observed for H_2 at 113 K and CH_4 at 179 K and above. The CO_2 sorption is a special case. Under these testing temperatures (179 K, 195 K, and 273 K), CO_2 molecules have sufficient kinetic energy to diffuse within CuTEI freely, and the kinetic effect becomes trivial. As a result, no hysteresis is observed and the overall sorption behavior is controlled solely by the thermodynamic effect.

This abnormal gas sorption behavior (at certain temperature ranges, higher temperatures give higher gas adsorption) was reported in MAMSs and other MOFs with flexible motif and was attributed to the thermal vibration of these flexible motifs functioning as gates.[2a,b,10] However, the same behavior was observed in coal, zeolite, and rigid MOFs as well.[11] Under these circumstances, it is more appropriate to attribute this phenomenon to the increased kinetic energy of adsorbates at the higher temperature. It is hard to determine which factor dominates the gas sorption behavior in CuTEI, and both seem feasible. Theoretical study indicates longer equilibrium time would be needed for the adsorbate to diffuse into the kinetically closed pore.[9,12] Accordingly, by extending the equilibrium time, gas uptake should be increased as well. To confirm that, N_2 sorption isotherms at 77 K was recollected at an eightfold

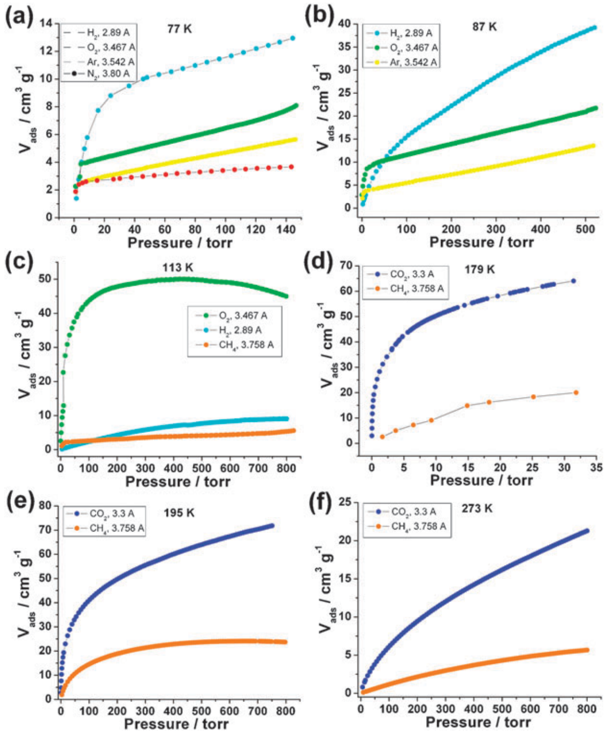

Fig. 3 Thermosensitive molecular sieving effect in CuTEI.

longer equilibrium time, and there is indeed a dramatic increase of N_2 uptake, especially at the lower pressure range (<10 Torr) (Fig. S6, ESI†). Apparently, kinetically closed pores play an important role in the gas sorption behavior of CuTEI.

Since the energy barrier of the aperture's potential can be overcome by the adsorbate's higher chemical potential at high pressure, we propose the kinetic effect can be suppressed under high pressure, leaving only the thermodynamic effect. This is proved by high pressure H_2 adsorption in CuTEI at 77 K and 87 K (Fig. S7a, ESI†), where the maximal H_2 uptake is higher at 77 K than at 87 K. This opposes the low pressure data (Fig. 2a) and confirms our hypotheses. Besides, the high pressure H_2 sorption kinetic study indicates it takes much longer to reach equilibrium for both adsorption and desorption at 77 K than at 87 K, indicating the small aperture's strong retarding effect on hydrogen's self-diffusivity in CuTEI at low temperature (Fig. S7b, ESI†).

By plotting different gas uptake data at the same temperature together, one can see a distinct molecular sieving effect, especially at 77 K and 87 K, where the gas that is more strongly adsorbed is the smallest one, while the larger gas exhibits weaker sorption (Fig. 3). It is worth noting that CuTEI exhibits preferential sorption of CO_2 over CH_4 persistently under all the testing temperatures (179 K, 195 K, 273 K and 298 K). The CO_2/CH_4 adsorption selectivity in CuTEI was estimated *via* the ideal adsorbed solution theory (IAST) using the adsorption data at 298 K, which is found to be comparable with the CO_2/CH_4 selectivity in MOFs (MOF-5, CuBTC) and zeolites (FAU, MFI) based on GCMC simulation results.[13] This selective gas adsorption property makes CuTEI an appealing candidate for gas separation purposes.

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Notes and references

‡ Crystal data for CuTEI: trigonal, space group $R\bar{3}m$, $a = b = 51.642(5)$, $c = 33.245(4)$ Å, $V = 76783(14)$ Å^3, $Z = 18$, synchrotron radiation, $\lambda = 0.42318$ Å. CCDC 779616. Atoms of the ligand were highly disordered and therefore could not be located. The nanocage was modeled based on the locations of the heavy atoms that were found.

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