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Central metal dependent modulation of induced-fit gas uptake in molecular porphyrin solids†

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Induced-fit accommodation of a variety of gaseous molecules including non-polar molecules has been demonstrated in porphyrin-based supramolecular architectures for the first time. Moreover, the gas uptake behaviour can be modulated by the central cation of porphyrin.

A great deal of attention has been paid to advanced porous frameworks such as metal-organic frameworks (MOFs),1, 2 porous organic polymers (POPs),3, 4 and hydrogen-bonded frameworks (HBFs).5 These materials can be designed and synthesized by the methodologies of organic and/or coordination chemistry, unlike conventional disordered porous materials, such as porous carbons and porous silicas. Among a variety of building units, porphyrin has fascinating advantages of chemical/thermal stability, robust nature, facile synthesis, and ubiquitous biological functions such as light-harvesting, oxygen transportation, and catalysis.6, 7 Thus, porphyrin-based porous frameworks which possess gas-accessible permanent porosities have been intensively developed as the forms of MOFs,8-16 POPs,17-20 and HBFs.21, 22

On the other hand, organic solids composed by van der Waals forces are also expected as another type of gas-sorptive materials. There are two mechanisms for gas uptake: (1) physisorption in permanent nanospaces at inter-molecular spaces and/or internal nanospaces existing inside cage-shaped,23 or ring-shaped,25 molecules, and (2) accommodating guests by the rearrangement of molecular orientation, called ‘induced-fit’ accommodation.26, 27 In (2), even non-porous solids can accommodate gas molecules, and moreover, complex gas uptake behaviour by hybrid mechanism of (1) and (2) has been also reported.28-30 These sorptive van der Waals solids (SVSs) have potential advantages, such as solution processability, applicability of ‘mix and match’ strategy, and a high guest responsiveness, compared to framework-based porous materials.31, 32 Thus, porphyrin-based porous cage molecules have been also reported recently.32 On the other hand, induced-fit gas uptake in porphyrin-based SVSs has not been reported, while it has been possible in solution.33 Herein, we demonstrate it in porphyrin-based SVSs, cyclic porphyrin dimers (CPDs),34, 35 and moreover, the on-off porosity switching can be modulated simply by changing the central cation of CPDs.

As shown in Fig. 1a, CPD bearing diacetylene linkers and 4-pyridyl groups is used as a basic molecular framework in this work. Figs. 1b and 1c show the crystal structures of free base (M = 2H; 1a)35 and Ni(II)-metalated (M = Ni; 2a)34 CPDs, accommodating o-dichlorobenzene and toluene inside the CPD rings, respectively. Four pyridyl groups on the side edges of the porphyrin planes weakly interact with each other, and CPDs form a self-assembled nanotube structure shown in Figs. 1b and 1c. Thus, CPDs possess the ability of forming guest-accommodating structures by crystallisation from solution. This work aims to study gas uptake, and therefore, guest-free forms of 1a and 2a were prepared by using easily removable chloroform as the final solvent for their synthesis. The obtained solids are denoted as 1b and 2b, respectively. Absence of guest molecules was confirmed by 1H-NMR (Fig. S1†) and thermogravimetry (Fig. S2†). As is found from very small adsorption amounts of CO2 at 298 K in 1b and 2b (Fig. 1d), these guest-free forms are densely-packed solids without noticeable permanent porosity. Fig. S3† shows the powder X-ray diffraction (PXRD) patterns of 1a, 1b, 2a, and 2b. 1b displays a few intense and sharp peaks, along with broad and weak peaks, indicating that the CPD packing structure includes

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some disorder. Thus, it is not possible to determine the exact crystal structure of 1b. On the other hand, 2b is a well-crystalline solid with the densely packing structure as shown in Fig. 1e. The inside space of a CPD molecule is occupied by pyridine groups of the neighboring molecules (Fig. 1f), and thus, 2b does not possess permanent porosity. The predominant Intermolecular Interactions are weak van der Waals forces in 1b and 2b, and it is expected that gas molecules may trigger the rearrangement of CPD orientation through the induced-fit mechanism, especially in 1b which has the looser packing structure.

Thus, we have examined adsorption isotherms of a variety of gases on 1b and 2b (Fig. 2). Non-logarithmic diagrams for Figs. 2a-c are shown in Fig. S4†. As for N₂ adsorption at 77K (Fig. 2a), the same measurement was repeated twice. At the first measurement, 1b shows a specific adsorption isotherm in which sudden gas uptake occurs at $P/P_0 = 0.01-0.03$, and a desorption branch does not overlap the adsorption. The second isotherms agree well with the first results, indicating that the specific gas uptake is reversible without irreversible permanent structure change/destruction. These are the typical behaviour at the induced-fit gas accommodation. Indeed, the change of the 1b packing structure was confirmed by in situ PXRD measurement as shown later. On the other hand, 2b accommodates a smaller amount of N₂ at $P/P_0$ near 1, and the desorption isotherm is not closed, also showing the behaviour of the induced-fit gas accommodation, although the uptake pressure and the amount are very different from those of 1b. Thus, the difference of the central cation can significantly change the gas uptake property. The results for Ar at 87 K (Fig. 2b) are basically similar to those of N₂ at 77 K (Fig. 2a). The different gas-uptake properties in 1b and 2b can be ascribed to their different molecular packings depending on the central cations. In 2b, CPD molecules are closely packed (Figs. 1e and 1f), and each CPD molecule more hardly moves against the stimulus by N₂ or Ar, whereas the CPD molecules in 1b can...
easily move because of their relatively loose packing.

Fig. 2c shows the CO$_2$ adsorption-desorption isotherms at 195 K, and 1b exhibits the induced-fit behaviour. Unlike at 298 K, lower temperature is favour for physisorption and it is thus found that the temperature is also an important factor for the induced-fit accommodation. To confirm the structure change of 1b upon the CO$_2$ uptake, in situ PXRD analysis was carried out at the several data points highlighted in Fig. 2c. The results are shown in Fig. 3a. At the pressure range below $P/P_0 = 0.018$, 1b gradually accommodates CO$_2$ up to 2.24 mmol g$^{-1}$ (Fig. 2c), corresponding to ca. 3 mol mol$^{-1}$ (3 CO$_2$ molecules per one CPD molecule; Fig. S5†). During this period, the peaks of the PXRD patterns become weak as well as broaden, and their positions are shifted to lower angle, indicating gradual disordering of the CPD arrangement together with expansion of the packing structure. The d-spacing calculated from the most intense peak (Fig. 3a, inset) is increased from 1.41 nm ($P/P_0 = 0$) to 1.44 nm ($P/P_0 = 0.018$). Such structure change slightly generates inter-molecular spaces into which CO$_2$ can invade. At $P/P_0$ between 0.018 and 0.031, a rapid uptake occurs up to ca. 5 mol mol$^{-1}$, and the PXRD pattern shows a drastic change (Fig. 3a). Thus, it is confirmed that the rearrangement of CPD molecules occurs by the induced-fit accommodation. Above $P/P_0 = 0.031$, 1b gradually uptakes CO$_2$ molecules up to 10–11 mol mol$^{-1}$, and PXRD peaks gradually become sharper and more intense without significant shift of their positions. The d-spacing calculated from the most intense peak (Fig. 3a, inset) is only slightly increased from 1.48 nm ($P/P_0 = 0.031$) to 1.49 nm ($P/P_0 = 0.018$). Such structure change shows a largest uptake for CO$_2$ (195 K) with $V_{total} = 0.34$ cm$^3$ g$^{-1}$, 1b shows a largest uptake for ethanol (298 K) with $V_{total} = 0.31$ cm$^3$ g$^{-1}$.

The crystalline structures of 1b and 2b upon accommodating gas molecules are analysed by PXRD as shown in Figs 3b and c. For 1b, the inclusion crystal structures can be roughly classified into three groups: (1) N$_2$ and CO$_2$, (2) H$_2$O, methanol, and ethanol, and (3) o-dichlorobenzene (1a). Also for 2b, it is found from Fig. 3c that inclusion of H$_2$O, methanol, or ethanol forms the similar crystalline phase which is different...
from the one formed by toluene (2a). Thus, CPD molecules has an ability of forming several different inclusion crystals depending on the host molecules, and the induced-fit behaviour can be greatly modulated simply by changing the porphyrin central cations. A gas uptake ability of 1b was further examined by a variety of gases, and found that the gas uptake behaviour greatly varies depending on the type of gases (Fig. S7). Thus, this work demonstrates an interesting possibility of porphyrin-based SVSs towards versatile applications based on the selective gas uptake ability of CPDs.

In summary, induced-fit gas uptake has been demonstrated in porphyrin-based sorptive van der Waals solids (SVSs), cyclic porphyrin dimers (CPDs). Depending on the central cations of CPDs, the induced-fit behaviour can be remarkably modulated. This means that it is possible to tune the selectivity of gas uptake even by very minor change of the host molecular structure. From the tunable selectivity of gases and the versatile function of porphyrin moiety, porphyrin-based SVSs are expected as new class of gas sorptive materials.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

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Textual abstract

Induced-fit gas uptake in supramolecular sorbent materials has attracted great interest from its potential for versatile applications which cannot be achieved by classical physisorption in porous solids. In this work, we report the induced-fit gas uptake in porphyrin-based supramolecular architecture, and moreover, the on-off porosity switching can be modulated simply by changing the central cation of porphyrin.

Graphical abstract

![Graphical abstract](image_url)