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adsorbent that exhibits benzene/cyclohexane selectivity[†]

Guest-induced gate-opening in a flexible MOF

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We report the synthesis of a 2-fold interpenetrated primitive cubic (**pcu**) topology network, **X-pcu-11-Zn**, formulated as $[Zn_2(DMTDC)_2(dpb)]$ (H₂DMTDC = 3,4-dimethylthieno[2,3-*b*]thiophene-2,5-dicarboxylic acid; dpb = 1,4-di(pyridin-4-yl)benzene). Upon removal of solvent molecules from the as-synthesised form, **X-pcu-11-Zn-** α , transformation from a large-pore "open" phase to a narrow pore phase, **X-pcu-11-Zn-** β , occurred. The β -phase subsequently exhibited guest-induced switching as evidenced by a 2-step type F-IV² adsorption isotherm for N₂ at 77 K and a 3-step profile with two gate-opening pressures for CO₂ at 195 K. Dynamic vapour sorption studies revealed selective sorption of methanol, ethanol, and CH₃CN over H₂O at 298 K. Furthermore, **X-pcu-11-Zn-** β selectively adsorbed benzene over cyclohexane concomitant with a gate-opening effect driven by structural transformations. Importantly, the transformations between the guest-free and guest-loaded structures were found to be reversible over six adsorption/desorption cycles. Single-crystal X-ray diffraction analysis of the benzene-loaded phase indicates that selective benzene binding can be attributed to π - π and C-H··· π aromatic packing interactions.

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Introduction

Metal-organic frameworks (MOFs)¹ or porous coordination polymers (PCPs)² are an evolving class of porous materials that are of interest for key commodity separations, especially for difficult-to-separate hydrocarbons.³ Flexible MOFs (FMOFs), a subset of MOFs, are stimuli-responsive soft porous crystalline solids that undergo structural transformations in response to external stimuli such as pressure, heat, light, cation/anion exchange, or guest (gas/vapour/solvent) uptake/removal.⁴⁻⁷ FMOFs are characterised by atypical stepped or "S-shaped" isotherms that are concomitant with gate-opening phenomena. Hysteresis can be associated with these breathing or swelling processes.^{8,9} These stimuli-responsive structural transformations can result in useful properties in the context of gas storage and separation,^{10,11} guest capture and release,¹² and molecular sensing,^{13–15} in some cases setting benchmark performance.¹⁶

Separation of benzene (Bz) and cyclohexane (Cy) is a challenge for the chemical and petrochemical industries. Cy is primarily obtained through the catalytic hydrogenation of Bz and unreacted Bz must be removed from the reactor's effluent stream to generate high-purity Cy. However, this separation is challenging due to their similar boiling points (Bz, 80.1 °C; Cy, 80.7 °C), molecular geometries (Bz, $3.3 \times 6.6 \times 7.3 \text{ Å}^3$; Cy, $5.0 \times$ 6.6 \times 7.2 Å³), and Lennard–Jones collision diameters.^{17,18} The similar boiling points and the formation of azeotropes render distillation processes poorly effective. Currently, the predominant industrial methods for separating Bz/Cy mixtures are extractive distillation and azeotropic distillation, both of which have high energy footprints and are accompanied by process complexity and high operating costs.¹⁹⁻²¹ It is therefore desirable to develop separation methods that are easier and more energy-efficient for the separation of Bz and Cy. A similar challenge exists for alcohol/water separations.

To enable selective separation between sorbates with similar physicochemical properties, the development of physisorbents with tight binding sites has proven to be fruitful as exemplified by CO₂ and C₂H₂ selective adsorbents.^{22,23} For Bz/ Cy, π - π , H- π , and H-bonding interactions are likely to drive selective Bz binding and could also induce structural transformations.²⁴⁻²⁹ FMOFs comprised of aromatic linker



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ligands would be expected to offer suitable pore chemistry for Bz binding and, because of inherent flexibility, offer the possibility of induced-fit binding for Bz that is reminiscent of enzyme–substrate binding.^{26–29} This principle was demonstrated by Kitagawa's group in an FMOF featuring a flexible undulating channel that exhibited selective adsorption of Bz over Cy *via* gate-opening triggered by CH- π interactions.²⁶ Chen *et al.* reported a flexible MOF with a similar mechanism for selective adsorption of Bz,²⁷ whereas Ghosh *et al.* reported an FMOF with a π -electron deficient ligand that exhibited Bz/Cy recognition and structural transformation induced by Bz.²⁸

In this study, we report a new 2-fold interpenetrated FMOF, $[Zn_2(DMTDC)_2(dpb)]$ (**X-pcu-11-Zn**), comprising two aromatic π -conjugated ligands (Scheme 1): 3,4-dimethylthieno[2,3-*b*] thiophene-2,5-dicarboxylic acid (H₂DMTDC) and 1,4-di



Scheme 1 X-pcu-11-Zn- α is composed of H₂DMTDC and dpb ligands and exhibits a primitive cubic (pcu) topology with 2-fold interpenetration.

(pyridin-4-yl)benzene (dpb). **X-pcu-11-Zn** was found to undergo reversible structural transformations between its assynthesized large pore "open" phase, **X-pcu-11-Zn-** α , and its activated narrow pore phase, **X-pcu-11-Zn-** β . These transformations were characterised by single-crystal X-ray diffraction (SCXRD) as well as gas and vapor adsorption to provide insight into the Bz binding mechanism.

Results and discussion

Synthesis and crystal structure

Solvothermal reaction of H2DMTDC and dpb with Zn (NO₃)₂·6H₂O in DMF at 105 °C yielded colourless, block crystals of $[Zn_2(DMTDC)_2(dpb)]$ ·5DMF·0.5H₂O, X-pcu-11-Zn- α (full synthetic details are available in the ESI[†]). SCXRD revealed that **X-pcu-11-Zn-\alpha** had crystallised in the triclinic space group P1. The resulting coordination network comprises dinuclear Zn(II) tetracarboxylate paddlewheels (Fig. 1a) linked via DMTDC ligands to form a square lattice (sql) network (Fig. 1b). The sql nets are pillared by dpb linkers to generate a pcu topology (Fig. 1c). X-pcu-11-Zn- α is a member of the DMOF-1 family which already has several members with extended (X-) ligands, X-pcu-n-Zn (e.g. n = 5, 6, 7, 8), that exhibit 2-fold offset interpenetration (Fig. 1d).³⁰⁻³² X-pcu-11-**Zn-\alpha** features ultramicroporous 3D channels with effective pore diameters of *ca*. 2.3 × 2.5, 3.3 × 5.4, and 4.5 × 6.8 \AA^2 along the a-, b-, and c-axes, respectively (Fig. S1-S3[†]). The calculated guest-accessible volume is 49.8%. TGA revealed that as-synthesized X-pcu-11-Zn- α loses guest molecules (observed:



Fig. 1 Crystal structures of the α and β forms of **X-pcu-11-Zn** reveal zinc "paddlewheel" clusters (a and e), **sql** nets constructed by the clusters and DMTDC ligands (b and f), and two-fold interpenetrated structures (c, g, d and h). Hydrogen atoms are omitted for clarity. C (gray), Zn (green), O (red), N (blue), and S (yellow).

30.02%; calculated: 30.05%) on reaching 150 $^{\circ}$ C and is thermally stable below 320 $^{\circ}$ C (Fig. S8†).

X-pcu-11-Zn-\alpha underwent single-crystal-to-single-crystal (SCSC) transformation after heating at 120 °C for 12 h to form **X-pcu-11-Zn-\beta** (Fig. S11[†]). SCXRD revealed that the β -form is a contorted version of the α -form with the same connectivity (Fig. 1e and f) but with centred rather than offset interpenetration (Fig. 1g). X-pcu-11-Zn- β crystallized in the orthorhombic space group Ibca with a 32.0% shrinkage in unit-cell volume relative to the α -form (Table S1[†]). X-pcu-11-Zn- β exhibits 1D channels with an effective pore diameter of *ca*. 2.1 \times 2.6 Å² along the *a*-axis (Fig. S4[†]). TGA and IR studies indicated that guest molecules had indeed been removed (Fig. S8 and S10[†]) and PLATON calculations revealed that the β -phase has only 4.9% solvent-accessible space. TGA of X-pcu-11-Zn-β showed no weight loss until decomposition at 320 °C (Fig. S8†). The structural transformation associated with guest release is reversible, with PXRD data revealing that the β -form had reverted to the α -form when soaked in DMF at room temperature for one day (Fig. S11[†]).

Analysis of the crystal structures reveals that the transformation between the large pore and narrow pore phases involves distortion of the **sql** nets and a sliding motion of the two interpenetrated nets (Fig. 1 and Fig. S7, Table S2†). In the α -phase, the metal–carboxylate junction Zn2=O2 > C approaches linearity with dihedral angles (Table S2 and Fig. S5†) between the Zn2=O2 plane and the carboxylate group O2 > C ranging from 1.0° to 8.4° for **X-pcu-11-Zn-\alpha**. Conversely, in the β -phase, the metal–carboxylate junctions bend with dihedral angles ranging from 18.1° to 30.1° for **X-pcu-11-Zn-\beta**. There are no π - π interactions (centroid–centroid distance <4.0 Å) or C–H- π interactions in either structure, but C–H···O hydrogen bonding exists in both phases (Table S3†).

Gas adsorption

That **X-pcu-11-Zn-\beta** was prepared from a large pore phase motivated us to determine if switching or breathing would occur when **X-pcu-11-Zn-\alpha** is exposed to gases. As shown in Fig. 2, the β -form is nonporous to N₂ (kinetic diameter: 3.64 Å)



Fig. 2 Gas sorption isotherms of **X-pcu-11-Zn-β**. Solid and open symbols represent adsorption and desorption branches, respectively.

at low pressure $(P/P_0 < 0.1)$, consistent with its narrow pore dimensions $(2.1 \times 2.6 \text{ Å}^2)$ and expected weak framework-N₂ interactions. β exhibited a 2-step adsorption profile for N₂ at 77 K, with saturation occurring after the second step. The first step, with an onset pressure of approximately $P/P_0 = 0.10$, is indicative of gas-induced gate-opening (switching) behaviour, suggesting a structural transformation from a non-porous phase to an intermediate pore phase. The resulting increase of overall pore volume at a threshold pressure of N₂ can result in a negative sorption step as seen in Fig. 2.33 The intermediate phase existed until $P/P_0 = 0.46$. Upon further increasing the pressure to $P/P_0 = 1.0$, the framework transformed to the large pore α -form with an uptake of 337 cm³ g⁻¹. The pore volume calculated by assuming liquid filling of saturated N2 is 0.52 cm³ g⁻¹, consistent with the void volume of **X-pcu-11-Zn-** α calculated from the crystal structure (0.50 cm³ g⁻¹). These data suggest that X-pcu-11-Zn-β had reverted X-pcu-11-Zn-α under these sorption conditions. To the best of our knowledge, X**pcu-11-Zn-\beta** is the first example of switching between closed and two open phases showing a two-step type F-IV² isotherm⁸ (Table S7^{\dagger}) with high capacity (>300 cm³ g⁻¹) although other switching sorbents exhibit one-step type F-IV^s isotherms (e.g. DUT-8(Ni),³⁴ rtl-[Cu(HIsa-azdmpz)]³⁵ and ELM-11 ³⁶) or even a five-step type F-IV⁵ isotherm (Co(bpe)) with an uptake $>300 \text{ cm}^3 \text{ g}^{-1}.^{37}$

Unlike N₂ adsorption at 77 K, the adsorption isotherm of CO₂ for **X-pcu-11-Zn-** β at 195 K consists of three adsorption/desorption steps. The initial uptake of CO₂ reached a saturated uptake of 33 cm³ g⁻¹. The Langmuir surface area calculated for the first CO₂ sorption step is 200 m² g⁻¹. The next step, which we attribute to gate-opening, occurred at $P/P_0 = 0.10$ with saturated uptake reaching 125 cm³ g⁻¹. The Langmuir surface area calculated from the second-step of CO₂ sorption is 754 m² g⁻¹. At the second gate-opening pressure ($P/P_0 = 0.70$), the CO₂ uptake further increased to 267 cm³ g⁻¹ at $P/P_0 = 1.0$. The Langmuir surface area was calculated to be 1677 m² g⁻¹ (see section 10†).³⁸ **X-pcu-11-Zn-** β represents a rare example of 3-step CO₂ adsorption with high capacity (>250 cm³ g⁻¹) (Table S8†). After N₂ and CO₂ desorption, **X-pcu-11-Zn-** β retained its original structure (Fig. S12†).

Vapour sorption

Dynamic vapour sorption measurements were conducted at 298 K to further study the dynamic properties of **X-pcu-11-Zn-β**. Fig. 3 illustrates the adsorption/desorption isotherms of **X-pcu-11-Zn-β** for H₂O, MeOH, EtOH and CH₃CN at 298 K. **X-pcu-11-Zn-β** preferentially adsorbed aliphatic organic molecules over water vapor despite the smaller kinetic diameter of H₂O compared to that of the organic molecules. For MeOH and EtOH, gate-opening pressures were found to be $P/P_0 = 0.7$ for MeOH and 0.6 for EtOH, with uptakes of 211 and 140 cm³ g⁻¹, respectively, at $P/P_0 = 0.96$. In contrast, the isotherm for CH₃CN shows a 3-step adsorption process, with gate-opening pressures at $P/P_0 = 0.18$ and 0.66, and an uptake of 194 cm³ g⁻¹ at $P/P_0 = 0.96$. These gate-opening phenomena are consistent with guest-induced structural transformations for MeOH, EtOH and



Fig. 3 H_2O , MeOH, EtOH, and MeCN sorption isotherms measured at 298 K. Solid and open symbols represent adsorption and desorption branches, respectively.

CH₃CN, whereas H_2O did not induce such transformations (Fig. S13[†]), indicating that **X-pcu-11-Zn** is hydrophobic.

To investigate the adsorption behaviour of larger organic molecules on X-pcu-11-Zn-β, single-component adsorption isotherms for benzene (Bz) and cyclohexane (Cy) were collected at 298 K. As shown in Fig. 4, X-pcu-11-Zn- β adsorbed Bz (92 cm³) g^{-1}) but exhibited minimal adsorption for Cy (5 cm³ g⁻¹) at P/ $P_0 = 0.99$. This uptake amount corresponds to 3.56 Bz molecules per formula unit. Although Bz is larger than MeOH, EtOH, and MeCN, its gate-opening adsorption pressure starts at a lower relative pressure $(P/P_0 = 0.10)$, which may be attributed to host-guest interactions arising from the π system and the more acidic C(sp²)-H moieties in Bz compared to C(sp³)-H bonds. PXRD patterns of **X-pcu-11-Zn-β** exposed to Bz for 12 h reveal distinct changes compared to the patterns of unexposed **X-pcu-11-Zn-\beta**, whereas the PXRD patterns remained unchanged under Cy vapour for the same duration (Fig. 5). PXRD data suggest that the structure of X-pcu-11-Zn-β after exposure to Bz for 12 h matches well with that of X-pcu-11-Zn- α calculated from SCXRD data, indicating that Bz had induced structural transformation from the β to the α phase, while Cy did not induce such a change (Fig. 5). This makes X-pcu-11-**Zn-\beta** a candidate for selective adsorption of Bz over Cy.



Fig. 4 Bz and Cy sorption isotherms measured at 298 K.



Fig. 5 PXRD patterns of X-pcu-11-Zn under different conditions.

To gain insight into this adsorption behaviour, single crystals of Bz@X-pcu-11-Zn were obtained by soaking X-pcu-11-Zn- α in benzene (Bz). PXRD analyses indicate that Bz-loaded Xpcu-11-Zn is indeed isostructural with X-pcu-11-Zn-α as calculated from SCXRD data (Fig. 5). The single crystal structure of Bz-loaded X-pcu-11-Zn reveals the presence of 3.5 Bz molecules per molecular unit, consistent with the uptake from the Bz adsorption isotherm. In the crystal structure of Bz@X-pcu-11-Zn, the framework resembles that of X-pcu-11-Zn- α with similar unit cell parameters (Table S1[†]). As shown in Fig. 6 and Tables S4, S5,[†] multiple π - π and C-H··· π aromatic interactions exist between the benzene molecules and the X-pcu-11-Zn framework, which likely drive the phase transformation of **X-pcu-11-Zn-β**. The selectivity of **X-pcu-11-Zn-β** for Bz can be attributed to this host-guest binding. Furthermore, the PXRD pattern of X-pcu-11-Zn-ß after Bz capture also matches well with the calculated pattern from the crystal structure of Bz@X-



Fig. 6 The $\pi \cdots \pi$ and C-H $\cdots \pi$ interactions between benzene molecules and the framework in **Bz@X-pcu-11-** α viewed along the crystallographic *b*-axis.

pcu-11-Zn- (Fig. 5), indicating that the crystal structure transforms from **X-pcu-11-Zn-** β to **Bz@X-pcu-11-Zn** upon Bz adsorption. The ¹H NMR spectra of **X-pcu-11-Zn-** β exposed to Bz and Cy vapours for 12 h showed that **X-pcu-11-Zn-** β adsorbs 3.48 Bz and 0.04 Cy molecules per molecular unit (Fig. S19 and S20†), respectively. Additionally, TGA data were collected for Bz and Cy vapour adsorption by **X-pcu-11-Zn-** β . As shown in Fig. S9,† the TGA curves for **X-pcu-11-Zn-** β that had been exposed to Bz for 12 h reveal a weight loss of 22.61% below 115 °C, corresponding to 3.26 Bz molecules per molecular unit, again consistent with the SCXRD analysis results. In contrast, there is negligible weight loss (2.61%) for **X-pcu-11-Zn-** β after exposure to Cy vapor for 12 h before reaching 300 °C. This pronounced adsorption difference suggested to us that **X-pcu-11-Zn-** β can be utilised for the separation of Bz and Cy.

To evaluate the adsorption kinetics of X-pcu-11-Zn-β for benzene (Bz) and cyclohexane (Cy) vapours, ¹H NMR spectroscopy was employed (details are available in the ESI[†]). Samples that had been exposed to Bz and Cy vapours were soaked in CDCl₃ to extract adsorbed Bz and Cy, respectively. As depicted in Fig. 7a, the amount of Bz adsorbed by X-pcu-11-Zn- β increased over time, reaching saturation after approximately 1 h at room temperature. At saturation, **X-pcu-11-Zn-β** adsorbed about 3.48 Bz molecules per unit, while the uptake of Cy was negligible. The adsorption kinetics for Bz were analysed by using pseudo-first-order and pseudo-second-order kinetic models (see section 15 of the ESI[†]). As shown in Fig. S23, S24 and Table S6,[†] the adsorption kinetics can be best described by the pseudo-first-order model for X-pcu-11-**Zn-\beta**. This suggests that the adsorption process may be governed by physisorption rather than chemisorption. The structural changes induced by Bz adsorption were found to be



Fig. 7 (a) Time-dependent single-component solid-vapour sorption plots of X-pcu-11-Zn- β under ambient conditions; (b) the uptake of Bz by X-pcu-11-Zn- β after 6 recycles; (c) time-dependent binary-component solid-vapour adsorption plots of X-pcu-11-Zn- β in Bz/Cy equimolar mixture vapour according to ¹H-NMR spectroscopy data; and (d) gas chromatography of X-pcu-11-Zn- β in equimolar Bz and Cy mixtures for 1 h.

reversible; adsorbed Bz was removed by heating **Bz@X-pcu-11-Zn** at 120 °C under vacuum (Fig. S14†). So-formed **X-pcu-11-Zn-** β retained its ability to adsorb Bz with no loss of performance after six cycles (Fig. 7b) and PXRD data revealed that **Xpcu-11-Zn-** β maintained phase stability (Fig. S14†).

To explore the potential of **X-pcu-11-Zn-\beta** for separating Bz and Cy mixtures, a time-dependent binary-component sorption experiment was conducted with **X-pcu-11-Zn-β** exposed to an equimolar Bz/Cy vapor mixture (details are available in the ESI[†]). In contrast to single-component adsorption, binary-component Bz/Cy adsorption resulted in co-adsorption, 2.10 Bz and 0.97 Cy molecules per formula unit, respectively, after 12 h of exposure to equimolar Bz/Cy (Fig. 7c). The separation ratio of the Bz/Cy mixture was calculated to be 2.16. Although the Bz/Cy selectivity is smaller than other flexible MOFs (Table S9[†]) such as $[Zn(TCNQ-TCNQ)bpy]_n^{26}$ and CID-23,³⁹ this value is comparable or better than several rigid MOFs such as MOF-5,40 HKUST-1,41 and CUB-30.42 Binary-component Bz/Cy adsorption by gas chromatography revealed that X-pcu-11-Zn-β reached saturation for Bz and Cy within 1 h (Fig. S22[†]), and had adsorbed 76.52% Bz and 23.48% Cy after 1 h (Fig. 7d). The molar ratio of Bz/Cy (3.2:1) from gas chromatography is comparable to that obtained from ¹H NMR analyses. As expected, the PXRD pattern of X-pcu-11-Zn-β changed upon exposure to the Bz/Cy mixture, matching the calculated pattern from the SCXRD data of Bz@X-pcu-11-Zn (Fig. S15[†]). These results indicate that **X-pcu-11-Zn-\beta** is a soft crystalline material with moderate selectivity for adsorption of Bz from a 1:1 Bz/Cy mixture, the selectivity being ascribed to the structural transformation induced by Bz adsorption.

Conclusions

In summary, we report a flexible, 2-fold interpenetrated coordination network, X-pcu-11-Zn, with π -conjugated thiophenecontaining dicarboxylate and benzene-bridged bipyridine ligands. X-pcu-11-Zn exhibited reversible structural transformations between large pore and narrow pore phases. For N2 adsorption, a 2-step N₂ F-IV² isotherm at 77 K was observed with an uptake of 337 cm³ g⁻¹. A 3-step CO_2 sorption isotherm was observed at 195 K with the uptake exceeding 260 cm³ g⁻¹. To our knowledge, X-pcu-11-Zn is the first example of switching between closed and two open phases showing a two-step F-IV² isotherm with high capacity (>300 cm³ g⁻¹). Vapor sorption experiments revealed that X-pcu-11-Zn is selective for methanol, ethanol, and CH₃CN over H₂O, characterized by stepped vapour sorption isotherms and significant hysteresis. Most notably, it selectively adsorbs Bz over Cy, with gateopening concomitant with structural transformations. The transformations between the guest-free and guest-containing structures are reversible, with X-pcu-11-Zn maintaining its ability to adsorb benzene without performance loss after six cycles. SCXRD studies indicated that the selective adsorption is driven by host-guest interactions, including multiple π - π and C-H··· π aromatic interactions, which induce structural

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transformation and gate-opening upon benzene sorption. This study highlights that two-fold interpenetrated flexible MOFs with π -conjugated ligands, which have many possible variants, offer potential to selectively adsorb/separate Bz over Cy driven by Bz-selective binding sites.

Data availability

The data supporting the findings of this study are available in the ESI† or from the authors upon request.

Conflicts of interest

The authors declare no competing financial interest.

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