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A Metal–Organic Framework with Highly Polar Pore Surfaces: Selective CO₂ Adsorption and Guest-Dependent On/Off Emission Properties

Prakash Kanoo, Ashta Chandra Ghosh, Soumya T. Cyriac, and Tapas Kumar Maji*^[a]

Abstract: A 3D porous Zn^{II} metal–organic framework $\{[\text{Zn}_2(\text{H}_2\text{dht})(\text{dht})_{0.5}(\text{azpy})_{0.5}]\cdot 4\text{H}_2\text{O}\}$ (**1**; H₂dht = dihydroxyterephthalate, azpy = 4,4'-azobipyridine) has been synthesised by employing 2,5-dihydroxyterephthalic acid (H₄dht), a multidentate ligand and 4,4'-azobipyridine by solvent-diffusion techniques at room temperature. The as-synthesised framework furnishes two different types of channels: one calyx-shaped along the [001] direction and another rectangle-shaped along the [101] direction occupied by guest water molecules. The dehydrated framework,

$\{[\text{Zn}_2(\text{H}_2\text{dht})(\text{dht})_{0.5}(\text{azpy})_{0.5}]\}$ (**1'**) provides 52.7% void volume to the total unit-cell volume. The pore surfaces of **1'** are decorated with unsaturated Zn^{II} sites and pendant hydroxyl groups of H₂dht linker, thereby resulting in a highly polar pore surface. The dehydrated framework **1'** shows highly selective adsorption of CO₂ over other

Keywords: adsorption • host–guest systems • metal–organic frameworks • microporous materials • zinc

gases, such as N₂, H₂, O₂ and Ar, at 195 K. Photoluminescence studies revealed that compound **1** exhibits green emission ($\lambda_{\text{max}} \approx 530$ nm) on the basis of the excited-state intramolecular proton-transfer (ESIPT) process of the H₂dht linker; no emission was observed in dehydrated solid **1'**. Such guest-induced on/off emission has been correlated to the structural transformation and concomitant breaking and reforming of the OH...OCO hydrogen-bonding interaction in the H₂dht linker in **1/1'**.

Introduction

Over the past several years, the chemistry of metal–organic frameworks (MOFs) or porous coordination polymers (PCPs) has been developing at an extraordinary rate.^[1] MOFs are widely regarded as promising functional materials for applications in gas storage,^[2] catalysis,^[3] separation,^[4] luminescence sensing,^[5] magnetism,^[6] and even as delivery vehicles for slow-release medicine.^[7] After these discoveries, one of the most appealing aims was to design multifunctional frameworks that combine a set of well-defined properties for specific applications in a single material. For the fabrication of such materials, use of a metal ion that possesses versatile coordination geometry and an organic linker with multiple functional groups would be a key approach. Among the numerous organic linkers devoted to the preparation of MOFs, it has been found that dicarboxylates are especially effective in generating diversified new systems with different dimensionality, porosity and coordination modes.^[8,9] 2,5-Dihydroxyterephthalic acid (H₄dht) is a versa-

tile linker because of the presence of two hydroxyl groups at the 2,5-position along with the two carboxylic groups at the 1,4-position, and it has recently been used for the construction of porous MOFs with different metal ions.^[10] Moreover, the H₄dht molecule is a bifunctional salicylic acid derivative and excited-state intramolecular proton transfer (ESIPT)-responsive organic molecule. By using this linker, we have recently demonstrated solvent-dependent tuneable multicolour emission properties in an Mg^{II}–H₂dht MOF in solution as well as in the solid state.^[11] MOFs have a fascinating feature of structural flexibility, which can lead to dramatic changes in the local coordination environment and thus emissive properties. It could therefore be used for molecular detection. Solvent-dependent changes in emission properties—that is, multicolour emission have been reported in MOFs—but solvent-specific on/off emission attributes in MOFs have not been much explored.^[12] Chen et al. reported modulation of luminescence based on Eu MOFs, and they showed an increase in luminescence intensity with dimethylformamide (DMF) but a decrease when exposed to acetone.^[13] For modification of pore surfaces and subsequent study of porous properties, our group has been engaged in the synthesis of MOFs based on a mixed-ligand system, such as carboxylates and several second spacers with different metal ions.^[14] The mixed-ligand MOFs display a tunable pore size and chemical environment and are found to be very flexible, which imparts many interesting properties like gated and stepwise adsorption, selective adsorption and so forth.^[15] In this context, the efficient storage and separation of CO₂ from air under atmospheric pressure has become an

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important issue for science, industry and the environment.^[16] Selective adsorption of CO₂ from gas mixtures is essential for natural gas purification and CO₂ segregation. Such selectivity depends either on the adsorption energy of CO₂ or on the geometry and polarity of the frameworks.^[16d,e] Moreover, the design and synthesis of MOFs have the advantage of tailoring the framework structure by incorporating polar groups, which subsequently affects adsorption selectivity. Therefore, the introduction of polar parts, such as unsaturated metal sites, hetero atoms or polar functional groups, to the internal surface of porous frameworks is a very effective technique to enhance adsorption selectivity and enthalpy of adsorption for CO₂ with a large quadrupole moment.^[16d,e,17] Herein, we report the synthesis, structural characterisation and multifunctional properties of a 3D microporous Zn^{II} framework $\{[\text{Zn}_2(\text{H}_2\text{dht})(\text{dht})_{0.5}(\text{azpy})_{0.5}(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}\}$ (**1**) obtained by using 2,5-dihydroxyterephthalic acid (H₄dht) and 4,4'-azobipyridine (azpy) linkers at RT. The dehydrated framework, $\{[\text{Zn}_2(\text{H}_2\text{dht})(\text{dht})_{0.5}(\text{azpy})_{0.5}]\}$ (**1'**), shows selectivity and high affinity towards CO₂ over other gases. Moreover, **1** exhibits green emission in the solid state based on ESIPT processes in the H₂dht linker, which was found to be off in the desolvated state (**1'**) and reappears with different intensities depending upon the solvent molecules.

Results and Discussion

Crystal structure description of $\{[\text{Zn}_2(\text{H}_2\text{dht})(\text{dht})_{0.5}(\text{azpy})_{0.5}(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}\}$ (1**):** Compound **1** crystallises in the monoclinic crystal system with space group *C2/c*, and structural determination reveals a 3D coordination framework bridged by H₂dht/dht and azpy linkers. The asymmetric unit of **1** contains two crystallographically independent Zn^{II} centres (Zn1 and Zn2), one molecule of H₂dht, half molecules of dht and azpy (Figure 1), one coordinated water and four guest water molecules. Zn1 is tetrahedral and is coordinated to four oxygen atoms: O2, O3, O4 from carboxylate groups of three different H₂dht/dht ligands and the O1 oxygen from the hydroxyl group of another dht ligand. Zn1–O bond lengths and O–Zn1–O angles are in the range of 1.891(10)–1.993(13) Å and 97.0(5)–118.3(5)°, respectively, suggesting distortion in the tetrahedral geometry. The Zn2 centre is octahedral and is coordinated to three oxygen atoms (O5, O7, O8) from carboxylate groups of three different H₂dht/dht ligands, the O1 oxygen from the hydroxyl group of a dht ligand and the

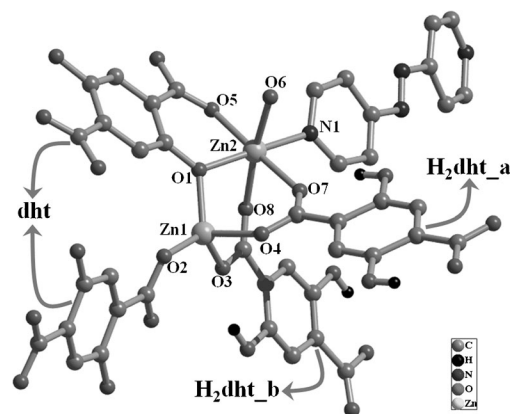


Figure 1. View of the coordination environment around Zn1 and Zn2 in **1**.

O6 oxygen from a water molecule. The sixth coordination, N1, results from the azpy ligand. The O1 oxygen from the hydroxyl group of dht bridges two metal centres (Zn1 and Zn2). Zn2–O bond lengths and O–Zn2–O angles around Zn2 are 2.011(9)–2.164(15) Å and 86.3(4)–176.3(5)°, respectively. Zn1...Zn2 separation in the framework is 3.214 Å. To get an understanding about how the 3D framework structure is generated, a three-step building process can be envisaged (Figure 2). Symmetrically, there are three different ligands in **1**: H₂dht_a, dht and H₂dht_b (Figure 1). H₂dht_a and azpy linkers link Zn^{II} atoms alternately to build a zig-zag, chainlike structure along the *c* axis (Figure 2a). Both the linkers coordinate to Zn^{II} in an unusually curved fashion, not usually observed for this kind of strut. Two such chains sit atop one other to form convex-type motifs (Figure 2b) that are connected by dht ligands along the *a* axis to generate a 2D network in the *ac* plane (Figure 2c and Figure S2 in the Supporting Information). The third dht ligand, H₂dht_b, acts as a pillar and connect the 2D networks along

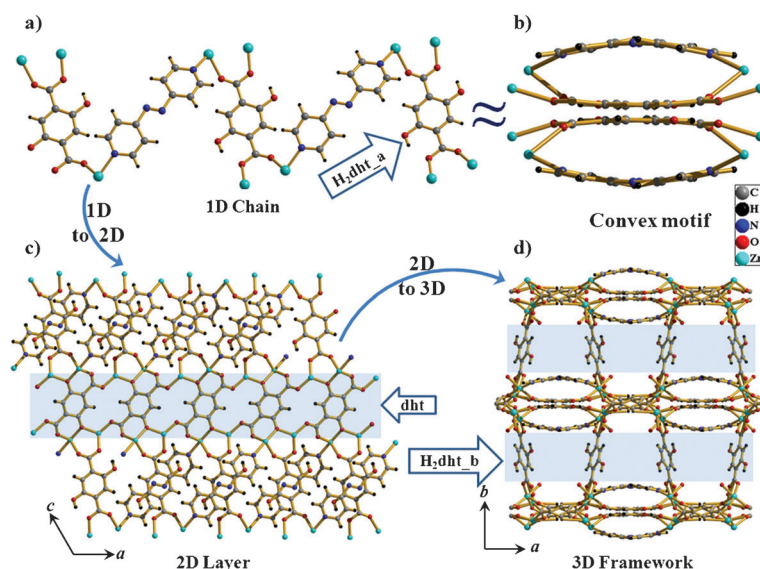


Figure 2. A simplified demonstration of assembly of **1** from a 1D chain to a 3D framework structure.

the [010] direction to build a 3D framework structure (Figure 2d). Structural analysis with TOPOS software^[18] that considers Zn1 and Zn2 (coordinated water removed) to be a single node reveals a 5-nodal 2,4,5-c net (Figure 3) with

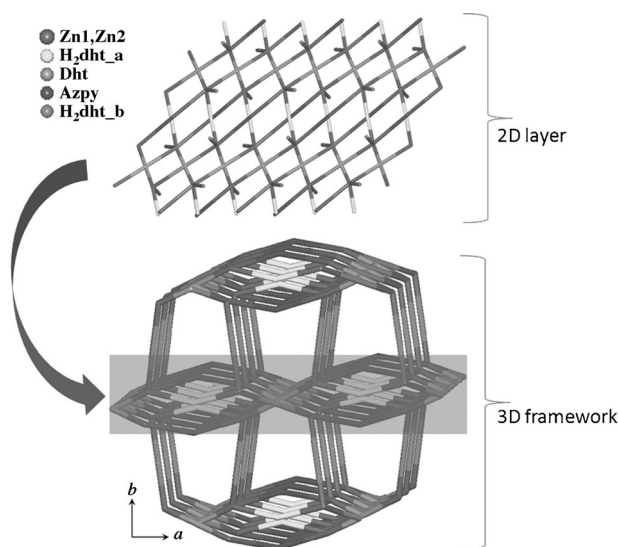


Figure 3. The drawing shows the different types of connectivity in the framework of **1** after simplifying Zn1 and Zn2 (coordinated water removed) as a single node.

stoichiometry (2-c)(4-c)6(5-c) and the corresponding Schläfli symbol for the net is $\{4.8^8.10\}2\{4^2.8^4\}\{8\}3$. The 3D framework houses two types of channels along the [001] and [101] directions occupied by guest water molecules (Figure 4 and Figure S3 in the Supporting Information). The dimensions of the calyx-shaped channels along the [001] direction are approximately (6.6×4.4) Å, and the rectangle-shaped channels along the [101] direction are around (4×6.7) Å.^[19] The interiors of both the channels are decorated with unsaturated metal sites (UMSs) and –OH groups of the H₂dht ligand that make the pore surface highly polar. Calculation using PLATON^[20] suggests that after removal of coordinated and guest water molecules, the framework possesses a large void volume of around 3265.5 Å³, which is about 52.7% of the total unit-cell volume.

Thermal and PXRD analysis: To evaluate the thermal stability of the as-synthesised framework **1**, thermogravimetric analysis (TGA) was carried out in the temperature range of 30–650 °C (Figure 5). The TGA plot reveals a stepwise loss of guest and coordinated water molecules in the temperature range 30–210 °C (exp 15.3%, calcd 14.8%). Rapid loss at low temperature indicates that the guest water molecules are loosely bound in the framework. The desolvated compound (**1'**) is thermally stable up to 290 °C and then decomposes to an unidentified product. The powder X-ray diffraction (PXRD) patterns of compound **1** were recorded in different states and are shown in Figure 6. The desolvated compound, $[\text{Zn}_2(\text{H}_2\text{dht})(\text{dht})_{0.5}(\text{azpy})_{0.5}]$ (**1'**), shows significant changes in the PXRD pattern, which suggests structural

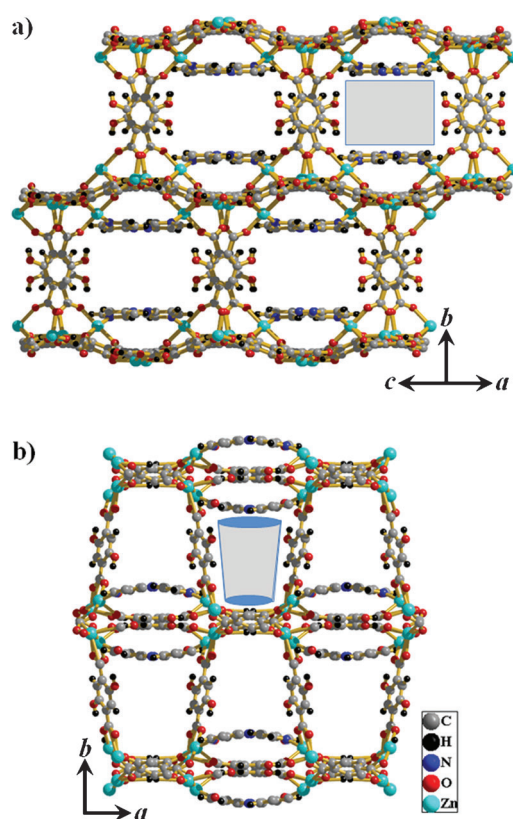


Figure 4. View of a) rectangle- and b) calyx-shaped channels along the [101] and [001] directions in **1**.

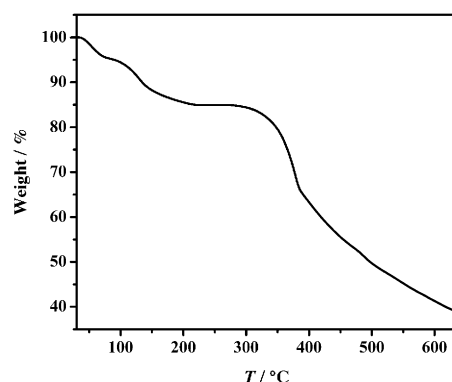


Figure 5. TGA plot of compound **1** measured under a nitrogen atmosphere (heating rate 5 °C min^{−1}).

transformation upon removal of guest and coordinated water molecules. To check the reversibility, **1'**, was exposed to water vapour for three days and then the PXRD pattern was recorded. The dissimilarity in the pattern between water-exposed **1'** and **1** indicates the framework is not completely reversible with respect to dehydration–rehydration process (Figure 6).

Adsorption study: Because we were inspired by the high void volume of the desolvated framework, **1'** was tested for its gas adsorption capacity. Despite an adequate effective

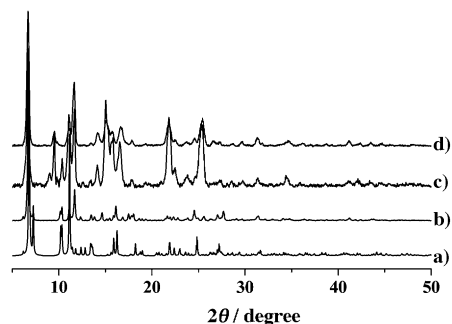


Figure 6. PXRD pattern of compound **1** under different states: a) simulated from single-crystal data, b) as-synthesised sample, c) heated at 200°C under vacuum for 6 h and d) water-exposed sample. The very good correspondence between simulated and as-synthesised patterns indicates the high purity of the synthesised sample.

pore size, to our surprise an N₂ (3.64 Å) adsorption study at 77 K with **1'** showed a type-II adsorption profile, thereby suggesting only surface adsorption (Figure 7). The exclusion

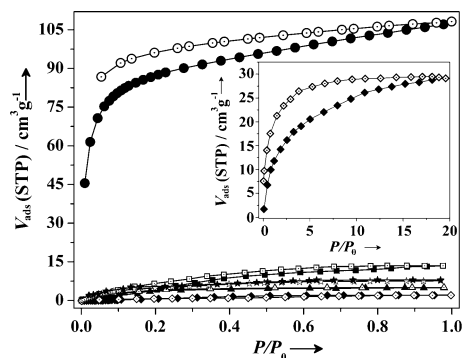


Figure 7. Gas adsorption isotherms for **1'**; CO₂ (circles), Ar (squares), O₂ (diamonds) at 195 K and N₂ (triangles) and H₂ (stars) at 77 K. Inset shows the CO₂ adsorption isotherm measured at 298 K and 20 bar. (closed symbols indicate adsorption and open symbols indicate desorption; P_0 is the saturated vapour pressure of the adsorbates at measurement temperatures).

of N₂ molecules by **1'** could be twofold: 1) N₂ molecules probably interact strongly with the pore windows, which blocks other molecules from passing into the pore; and 2) the pore surfaces decorated with Zn^{II} UMSS and –OH groups of the H₂dht ligand cannot provide sufficient energy of adsorption for inert molecules, such as N₂. Measurement of isotherms with other gases, such as H₂ (2.89 Å) at 77 K and Ar (3.5 Å) and O₂ (3.46 Å) at 195 K, also did not reveal any significant uptake. Interestingly, however, an adsorption study with CO₂ (3.3 Å) gas at 195 K revealed a steep uptake in the low-pressure region and the profile displays a type-I curve that is typical of microporous materials. The final uptake volume from the profile was found to be 108 mL g^{−1} (21.2 wt %), which corresponds to 2.5 molecules of CO₂ per formula unit of **1'**. The Langmuir surface area calculated from the CO₂ adsorption study for **1'** turned out to be 613 m² g^{−1}. This type of selectivity and favouritism of CO₂

over other gases is unique because it has important implications the separation of mixtures of gases. The notable affinity toward CO₂ in contrast to N₂/Ar/O₂/H₂ by **1'** is probably because of the quadrupolar nature of the CO₂ molecule (quadrupole moment of CO₂: -1.4×10^{-39} Cm²). After removal of coordinated water molecules, framework **1'** contains Zn^{II} UMSS and hence becomes the interaction centre for polar molecules. The presence of polar heads Zn^{II} and –OH groups of the H₂dht ligand gives rise to an electric field in the host framework, which interacts with the quadrupole moment of CO₂ to provide extra energy for adsorption.^[15d] The strong interaction of CO₂ with **1'** is also reflected in the high value of isosteric heat of adsorption, q_{st}, ϕ , (33.4 kJ mol^{−1}) as calculated by the Dubinin–Radushkevich^[21] (DR) equation. CO₂ adsorption measurement at high pressure and RT also reveals a type-I profile with an uptake value of 30 mL g^{−1} (5.9 wt %). We have also carried out a solvent-vapour (H₂O, EtOH, C₆H₆ at 298 K and MeOH at 293 K) adsorption study to further confirm the polar nature of the compound (Figure 8). As the polarity of the adsor-

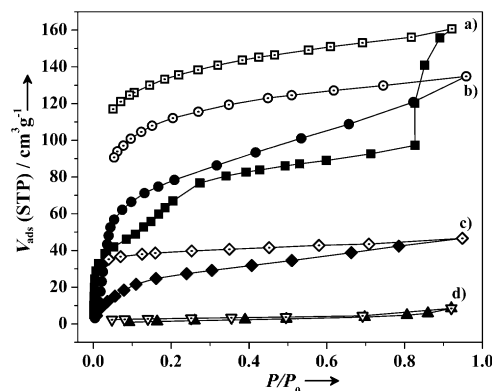


Figure 8. Solvent-vapour adsorption isotherms of **1'**: a) MeOH at 293 K and b) H₂O, c) EtOH and d) C₆H₆ at 298 K. P_0 is the saturated vapour pressure of the adsorbates at measurement temperatures.

bates decreases, a gradual decrease in uptake (up to $P/P_0 \approx 0.8$) was observed in the solvent adsorption isotherms; as shown in Figure 8, H₂O exhibits the highest uptake, whereas no adsorption was encountered with C₆H₆. The H₂O adsorption profile shows a steep uptake at low P/P_0 and then a gradual increase in the high-pressure region with the final uptake of 135 mL g^{−1}, which corresponds to 3.1 molecules of H₂O per formula unit of **1'**. A similar behaviour was observed in the MeOH profile as well that suggests adsorption of 2.2 molecules of MeOH per formula unit (97 mL g^{−1}); however, an exception was noticed at high pressure and the isotherm displays a two-step adsorption behaviour. The distinct observation in MeOH isotherm can be correlated with some structural transformation at high pressure, a well-established phenomenon in framework materials, and is further supported by large hysteresis in the isotherm. The final uptake for MeOH adsorption is 161 mL g^{−1} (3.7 mol mol^{−1}). The EtOH molecule, which has an accessible kinetic diameter for adsorption in the pores of **1** but less polarity than

H₂O and MeOH, does not display steep uptake in the low-pressure region. Also, the total uptake of EtOH (47 mL g⁻¹; 1 mol mol⁻¹) is less than the H₂O and MeOH uptake. The higher and steeper uptake in H₂O and MeOH isotherms than the EtOH isotherm suggests a stronger interaction between the framework and the guest molecules (H₂O and MeOH). The high value of βE_0 (≈ 10.5 kJ mol⁻¹), which reflects adsorbate–adsorbent interaction, calculated from the H₂O adsorption isotherm by the DR equation^[21] also indicates that polar molecules interact strongly with the framework **1**'.

Luminescence properties: Compound **1** was found to be fluorescent in the solid state and a broad emission was observed in the PL spectra in the visible region (Figure 9). Re-

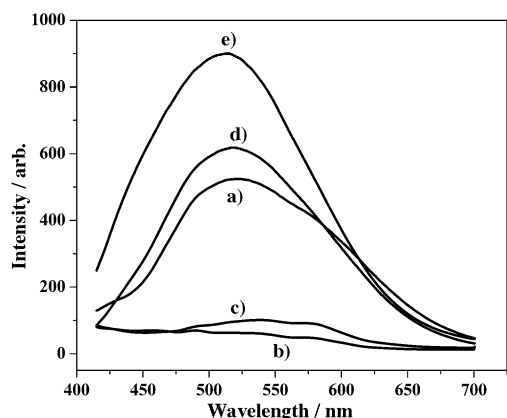


Figure 9. Solid-state emission spectra of **1** in different states: a) compound **1**, b) **1**', c) **1**' ground with EtOH, d) **1**' ground with MeOH and e) **1**' ground with DMF (excitation wavelength 390 nm).

cently, we have demonstrated tunable emission in solution as well as in the solid state in an Mg–H₂dht MOF based on the excited-state intramolecular proton transfer (ESIPT)-responsive linker H₄dht.^[11] As-synthesised solid **1** exhibits a Stokes-shifted green emission ($\lambda_{\text{max}} \approx 530$ nm), which can be attributed to the ESIPT process since in the framework two free –OH groups of the H₂dht ligands are hydrogen-bonded with the carboxylate oxygen atoms (Figure S5 in the Supporting Information). Surprisingly, we observed almost no emission when water molecules were removed from **1** to produce **1**'. We correlate this observation with the framework dynamics because significant change is observed in the PXRD pattern of **1**' relative to **1**. The removal of a coordinated water molecule from the octahedral Zn^{II} centre would severely distort the coordination environment around the metal and the corresponding Zn₂(CO₂) part. This probably leads to reorientation of the aromatic ring of the H₂dht linker with the Zn₂(CO₂) part in such a manner that the OH...OCO hydrogen-bonding interaction is disrupted and hence the ESIPT process is as well. Therefore no emission was observed in **1**'. This type of reorientation of the aromatic ring and the corresponding changes in geometry upon removal of the coordinated solvent molecule in the Zn^{II}-based

MOF [Zn₃(ntb)₂(EtOH)₄]_n·4*n* EtOH (ntb = 4,4',4''-nitrotrimesic acid) has been previously demonstrated by Suh et al., and such changes have been characterised by the single-crystal structural determination after removal of the solvent molecules.^[22] Due to the instability of the single crystal after dehydration of **1**, the validity of our hypothesis has been confirmed by looking at the –OH stretching frequencies in the IR spectra of **1**, **1**' and the H₄dht ligand (Figure 10). As-synthesised framework **1** displays a broad

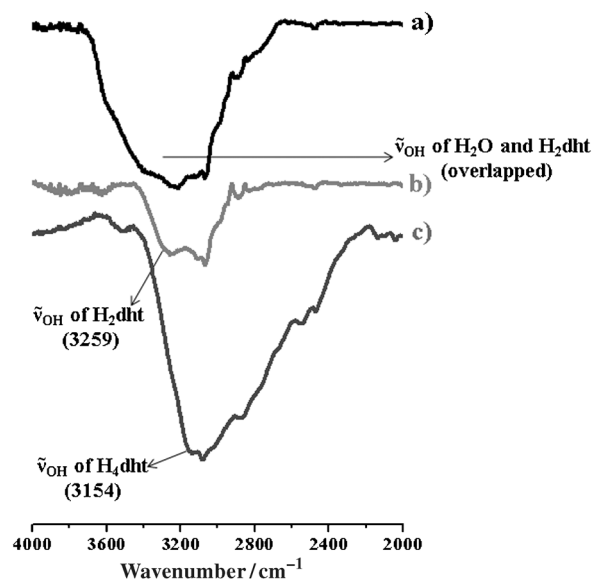


Figure 10. IR spectra of a) as-synthesised **1**, b) dehydrated **1**' and c) H₄dht ligand recorded in KBr.

band in the region 3600–3150 cm⁻¹, which is the result of the overlap of several –OH stretching frequencies with a contribution from guest and coordinated H₂O molecules and the hydrogen-bonded –OH group of the H₂dht linker. In the H₄dht ligand, the –OH groups are hydrogen-bonded with the carboxylate group and the corresponding peak appears at 3140 cm⁻¹, whereas in **1**' the band that corresponds to the –OH group is observed at 3259 cm⁻¹. Such a significant increase in the stretching frequency from 3140 to 3259 cm⁻¹ suggests that the –OH groups of the H₂dht linker in **1**' are no longer hydrogen-bonded with the carboxylate (–OCO) part. The dehydrated framework **1**' was ground together with H₂O, MeOH or DMF, and the corresponding photoluminescence studies revealed that a similar green emission was regenerated with same maxima as **1** but no emission was observed with EtOH-ground sample. This unprecedented solvent-selective on/off emission property could be attributed to restoration of the ESIPT process, which facilitates the inclusion of solvent (H₂O/MeOH/DMF) molecules in **1**'. A similar process does not take place upon EtOH inclusion. Such guest-induced structural transformation has been realised by the differences in the PXRD patterns of solvent-ground samples and compound **1**. Significant differences in the PXRD pattern of the EtOH-ground sample relative to

other solvent-ground samples suggest that the framework dynamics are different with less polar EtOH molecules, which is further supported by adsorption studies as a smaller uptake was observed in the EtOH isotherm than in the H₂O and MeOH isotherms. It is worth mentioning that solvent-ground samples of **1'** do not lead to any collapse of the overall framework structures because similar CO₂ uptake was observed in the DMF-ground sample.

Conclusion

In conclusion, we have synthesised a new, highly thermally stable and flexible 3D microporous metal-organic framework of Zn^{II} by using a mixed-ligand system. Detailed structural analysis of **1** reveals an unusual curved binding mode of the H₂dht and azpy linker, which is not usually observed in such systems. Removal of water molecules, guest and coordinated, creates porosity and unsaturated sites in the framework. The uncoordinated pendant -OH groups of the H₂dht linker and unsaturated Zn^{II} sites make pore surfaces of **1'** highly polar in nature. This ensures selective capture of CO₂ gas molecules over N₂/H₂/O₂/Ar and hence would be promising for separating gas mixtures. Optical studies revealed that compound **1** exhibits reversible fluorescence property upon dehydration and rehydration in the solid state; the fluorescence can be tuned by changing the solvent molecules and it may thus find application as a potential solvent sensor.

Experimental Section

Materials and methods: All the reagents and solvents employed were commercially available and used as supplied without further purification. Zn(NO₃)₂·6H₂O and 2,5-dihydroxyterephthalic acid were obtained from Aldrich Chemical Co. 4,4'-Azobipyridine was synthesised following the literature procedure.^[23] Elemental analysis was carried out using a Thermo Fischer Flash 2000 elemental analyser. IR spectra were recorded using a Bruker IFS 66V/S spectrophotometer with KBr pellets in the 4000–400 cm⁻¹ region. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA850 instrument in the temperature range of 30–650 °C under nitrogen atmosphere (flow rate of 50 mL min⁻¹) at a heating rate of 5 °C min⁻¹. PXRD patterns were recorded using a Bruker D8 Discover instrument with CuK_α radiation. UV/Vis and fluorescence spectra were recorded using a Perkin-Elmer Lambda 900 spectrophotometer and a Perkin-Elmer LS 55 spectrophotometer, respectively.

Gas adsorption measurements: Adsorption studies of CO₂, Ar and O₂ at 195 K and N₂ and H₂ at 77 K with the dehydrated sample of **1** prepared at 433 K under high vacuum were carried out using a Quantachrome Quadrasorb-SI analyser. The high-pressure CO₂ adsorption isotherm was measured at 298 K for **1'** on a fully computer-controlled volumetric Belsorp-HP (Bel Japan) high-pressure instrument. The carbon dioxide gas used for the measurements was of scientific/research grade with 99.999% purity. For the measurements, approximately 100 mg (≈250 mg for high pressure) of the sample was taken in a sample holder and degassed at 433 K under a 10⁻¹ Pa vacuum for about 12 h. The dead volume of the sample cell was measured using helium gas of 99.999% purity. Non-ideal corrections were made by applying virial coefficients at the measurement temperature.

Vapour adsorption measurements: The adsorption isotherms of different solvents (H₂O, EtOH and C₆H₆ at 298 K and MeOH at 293 K) were measured by using a Belsorp Aqua-3 volumetric adsorption instrument from Bel Japan. The adsorbent sample (≈100 mg) was placed into the sample chamber (≈12 mL) maintained at $T \pm 0.03$ K, which had been pre-treated at 433 K with a vacuum level of 10⁻¹ Pa for about 12 h prior to measurement of the isotherms. The adsorbate was charged into the sample tube, and then the change in pressure was monitored and the degree of adsorption was determined by the decrease in pressure at the equilibrium state. All operations were computer-controlled and automatic.

Synthesis of 1: 2,5-Dihydroxyterephthalic acid (H₂dht) (0.162 g, 0.75 mmol) was dissolved in water (5 mL) by adding KOH (0.084 g, 1.5 mmol). 4,4'-Azobipyridine (azpy) (0.25 mmol, 0.046 g) was dissolved in 2-methoxyethanol (45 mL). The solutions of H₂dht and azpy were mixed together and stirred for 30 min to prepare the ligand solution. Zn(NO₃)₂·6H₂O (1 mmol, 0.297 g) was dissolved in MeOH (50 mL), and this Zn^{II} solution (2 mL) was slowly and carefully layered with the above mixed-ligand solution by using buffer solution (1 mL; 1:1 of 2-methoxyethanol and MeOH). Reddish-brown block-shaped crystals were obtained after 15 d. The crystals were separated and washed with a 2-methoxyethanol/MeOH (1:1) mixture and air-dried. Yield: 81%; FTIR (KBr pellet, 4000–400 cm⁻¹): $\tilde{\nu}$ = 3150–3650 (O–H), 3052 Ar(C–H), 1603 Ar (C=C), 1447–1509 cm⁻¹ Ar(C=N) (see Figure S1 in the Supporting Information); elemental analysis calcd (%) for C₁₇H₁₉Zn₂N₂O₁₄: C 33.69, H 3.16, N 4.62; found: C 33.13, H 3.01, N 4.25. Bulk amount of the compound was synthesised in powder form by the direct mixing of the corresponding ligand solution with a solution of Zn^{II} in methanol. The very good correspondence between simulated and bulk-phase PXRD patterns indicates the high purity of the sample, which was also further confirmed by the results of elemental analysis.

Single-crystal X-ray diffraction: A suitable single crystal of **1** was mounted on a thin glass fibre with commercially available super glue. X-ray single-crystal structural data were collected using a Bruker Smart-CCD diffractometer equipped with a normal-focus, 2.4 kW, sealed-tube X-ray source with graphite-monochromated MoK_α radiation (λ = 0.71073 Å) operating at 50 kV and 30 mA. Crystal data were collected at 100 K. The program SAINT^[24] was used for integration of diffraction profiles; absorption correction was made with the SADABS program.^[25] The structure was solved by SIR92^[26] and refined by full-matrix least-squares methods using SHELXL-97.^[27] The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed by HFIX and placed in their ideal positions. Potential solvent-accessible area or void space was calculated using the PLATON^[20] multi-purpose crystallographic software. All crystallographic and structure-refinement data of **1** are summarised below. Selected bond distances and angles are given in Table S1 in the Supporting Information. All calculations were carried out using SHELXL-97,^[27] PLATON,^[20] SHELXS 97^[28] and the WinGX system, Ver 1.70.01.^[29]

Crystal data for 1: C₁₇H₁₉Zn₂N₂O₁₄; M_r = 606.94; monoclinic, space group C2/c; a = 20.5126(15), b = 25.971(3), c = 13.9517(9) Å; β = 123.508(3)°; V = 6197.3(10) Å³; Z = 8; T = 150 K; λ (MoK_α) = 0.71073 Å; ρ_{calcd} = 1.278 g cm⁻³; μ = 1.603 mm⁻¹. A total of 23 455 reflections were collected, of which 2525 were unique (R_{int} = 0.112); R_1 = 0.0828 for 1889 independent reflections with $I > 2\sigma(I)$, wR_2 = 0.2751 for all data.

CCDC-821671 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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