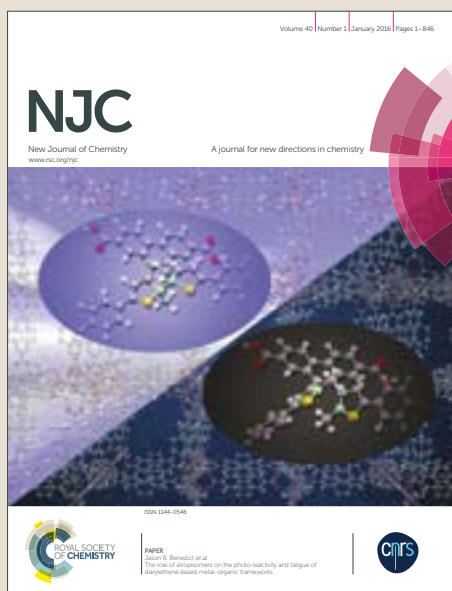


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Supramolecular structural transformation of N, N'-bis(4-pyridylmethyl)-naphthalene diimide and fluorescence water sensing

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Abstract: A supramolecular structure based on N, N'-bis(4-pyridylmethyl)-naphthalene diimide exhibits reversible phase transitions in a single-crystal-to-single-crystal process. Such temperature induced SC-SC transformations are driven by intermolecular π - π interactions and hydrogen bond interaction. Interestingly, the dynamic supramolecular structure shows selective adsorption and fluorescence water sensing.

Introduction

In recent years, the design and synthesis of supramolecular organic frameworks (SOFs) have captured the attention of chemists because of their potential applications in the areas of drug delivery, selective catalysis, cell mimicking, nanotechnology, fluorescence sensor, gas sorption and separation.¹⁻³ SOFs can be readily self-assembled from two or more organic species by noncovalent interactions such as hydrogen-bonding, halogen-bonding, cation- π interactions, π - π interactions and van der Waals forces.⁴⁻⁵ The components of supramolecular organic frameworks define the shape, size, properties of the resultant supramolecular aggregate, and play a vital role in the functioning of the SOFs as well as in their structural morphology.⁶ The π - π stacking has the relatively low stabilization energy about 10 kJ mol⁻¹ and can lead to rapid interconversion to structures, which often plays important roles in functional molecules.⁷⁻⁸ The naphthalene diimides are a compact, neutral, planar, electron deficient class of aromatic

compound capable of self-organisation and being incorporated into larger multicomponent assemblies through intercalation.⁹ Due to their planar aromatic nature, naphthalene diimides exhibit stacking in the solid-state with distances commensurate with π - π stabilisation.¹⁰ Since introduction of heteroatom nitrogen in the aromatic ring increases the stabilization energy, significantly, the pyridine dimer has 6 kJ mol⁻¹ higher stabilization energy than the benzene dimer,¹¹ 4-pyridylmethyl groups was placed on the diimide nitrogens to produce highly ordered π -stacking structures.¹² The π - π interactions absorb the strain energy by adjusting their intermolecular distances and keep the crystal packing stable even after large deformation.¹³ The single-crystal-to-single crystal (SCSC) transformation is preferred, since it allows direct visualization of how the crystal structure is changed during the transformation process.¹⁴⁻¹⁵ These direct insights further the understanding of the subtle interaction between the guest molecules and the host. Materials with reversible SCSC structure transformations and characteristic responses toward specific external stimuli are vitally important for applications in selective adsorption and sensing for small molecules, molecular switches, and catalysis.¹⁶⁻¹⁷

Herein, we report about the remarkable structural features and physical properties of an hydrate crystal form of N, N'-bis(4-pyridylmethyl)-naphthalene diimide(4-pmntd), which shows reversible SCSC structure transformations and

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Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1507742-1507744. Copies of the data can be obtained free of charge from www.ccdc.cam.ac.uk/contents/retrieving.html

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characteristic responses toward water. Furthermore, the selective adsorption and fluorescence sensing for water were also studied, in the solid state.

Experimental

General procedures

All materials were reagent grade, obtained from commercial sources, and used without further purification. Solvents were dried by standard procedures. The 4-pmntd was prepared from the reaction of 1,4,5,8-naphthalenedianhydride with 4-(aminomethyl)pyridine according to previous literatures.^{12g}

Synthesis

[4-pmntd·2H₂O] (1). A mixture of MnCl₂ · 4H₂O (19.8 mg, 0.1 mmol), 4-pmntd (6 mg, 0.0125 mmol), NaSCN (8.5 mg, 0.1 mmol) in H₂O (1.0 mL), and CHCl₃ 12.0 mL) was stirred and then sealed in a 20 mL Teflon-lined autoclave. The autoclave was heated to 110 °C and held at that temperature for 7 days, followed by cooling to room temperature. Orange crystals of **1** were collected in 25% yield based on the 4-pmntd. Anal. Calcd for C₂₆H₁₈N₄O₅: C, 66.95; H, 3.89; N, 12.01%. Found: C, 66.75; H, 4.02; N, 11.86%. IR (KBr, cm⁻¹): 3440vs, 1706m, 1667s, 1605w, 1580w, 1451w, 1416w, 1375w, 1340m, 1245m, 1116s, 1082s, 768m, 565m. Phase purity was verified by powder XRD. Preparation of [4-pmntd] (**2**) and dense [4-pmntd] (**3**). Subsequently, the desolvated crystal [4-pmntd] (**2**) was obtained by heating a single crystal **1** at 100 °C under air for a period of 12 h. Then the single crystal **2** exposed to air for seven days resulted in contraction to the close packed structure crystal [4-pmntd] (**3**).

Physical measurements

Elemental analyses (C, H, N) were carried out with a Perkin-Elmer 240C elemental analyzer. FT-IR spectra were recorded from KBr pellets in the range of 4000–400 cm⁻¹ on a VECTOR 22 spectrometer. UV-Visible absorption spectra were recorded on a UV-2501PC UV-Visible Spectrophotometer. The powder X-ray

diffraction (PRXD) was recorded on a Bruker D8 ADVANCE diffractometer (CuKα, 1.5418 Å) at 40 kV and 40 mA. Thermal analyses and DSC were performed on a TGA V5.1A Dupont 2100 instrument from room temperature to 800 °C with a heating rate of 10 °C min⁻¹ in the air, and the data are consistent with the structures. The adsorption isotherms of CO₂ (at 195 K), N₂ and H₂ (at 77 K) were measured by using BELmax 00027 adsorption equipment (BEL Japan). The methanol (298 K), alcohol (298 K) and toluene (298 K) vapor were measured with a BELSORP-max automatic volumetric sorption apparatus. An exactly measured amount of the sample was introduced into the gas sorption instrument after the sample was pre-desolvated in a Schlenk tube at 120 °C under vacuum for 24 h. The adsorbate was placed into the sample tube, then the change of the pressure was monitored and the degree of adsorption was determined by the decrease of the pressure at the equilibrium state. The sorption properties were analyzed using Autosorb 1 for Windows 1.24 software.

X-ray crystallography

The diffraction data were collected on a Oxford Gemini S Ultra diffractometer equipped with Cu-Kα radiation (λ = 1.54178 Å) for compounds **1**, **2**, and **3** by using φ and ω scans. Analytical adsorption corrections were applied for compounds **2** and **3**. Multiscan adsorption corrections were applied for all others. The structures were solved by the direct methods (SHELXS) and refined by the full matrix least-squares method against Fo² using the SHELXTL software.¹⁸ The coordinates of the non-hydrogen atoms were refined anisotropically. Most of hydrogen atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms, and the water hydrogen atoms have been not added. Details of the crystal parameters, data collections and refinement for the three compounds are summarized in Table 1. Further details are provided in Supporting Information. The CCDC 1507742–1507744 are for the compounds **1**, **2**, **3**, respectively.

Table 1. Crystallographic data for **1**, **2**, and **3**

Compound	1	2	3
Formula	C ₂₆ H ₁₆ N ₄ O ₄ ·2H ₂ O	C ₂₆ H ₁₆ N ₄ O ₄	C ₂₆ H ₁₆ N ₄ O ₄
Fw	480.43	448.43	448.43
T(K)	293(2)	373(2)	293(2)
Wavelength(Å)	1.54178	1.54178	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	C2/c	C2/c	P-1
a(Å)	27.561(3)	22.760(8)	5.588(3)
b(Å)	4.6812(2)	4.6927(12)	7.545(4)
c(Å)	21.646(4)	21.335(8)	11.984(6)
α(deg)	90	90	77.113(11)
β(deg)	128.914(17)	115.96(5)	88.392(13)
γ(deg)	90	90	87.412(12)
V(Å ³)	2173.0(4)	2048.8(12)	492.0(5)
Z	4	4	1
ρ _{calcd} (g cm ⁻³)	1.468	1.454	1.514
μ(mm ⁻¹)	0.895	0.831	0.105
Reflnscollected/unique	4658 / 1611	4003 / 1507	4205 / 1916
GOF	1.040	1.074	1.001
R _i [I > 2σ(I)]	0.0383	0.1265	0.0669
ωR2 [all data]	0.1045	0.2899	0.1164

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}}{1}, \quad \text{where } w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP], \quad P = (F_o^2 + 2F_c^2)/3$$

Results and discussion

Structure description of compound 1

The cocrystal composed of 4-pmntd and water was determined by X-ray crystallographic analysis. Figure 1 shows the molecular packing of the compound **1**. The π - π interaction between the adjacent naphthalene rings overlap with a 3.34 Å interplanar distance propagates into the direction of the b-axis and makes stacking column structures. The pyridine ring planes of two adjacent molecules in **1** hardly overlapped at all, so there was

nearly no π - π interaction between the adjacent pyridine rings.

Hydrogen bonded water molecules reside in the channels of the 4-pmntd host framework connected via water $\cdots$ pyridine H bonding (Figure 2).

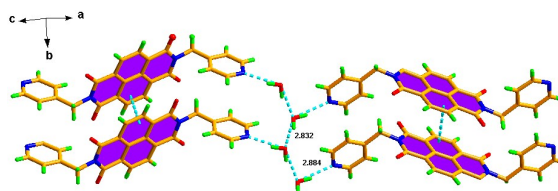


Fig. 1 The structure of compound 1.

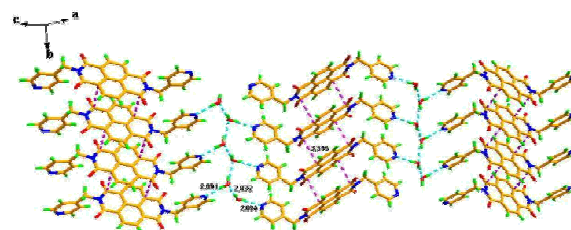


Fig. 2 The 2D network through π - π interaction and hydrogen bond of compound 1.

A single-crystal-to-single-crystal transformation between 1, 2, and 3

We suppose that the hydrate crystal form **1** may release the water molecules without causing a collapse of the crystal structure because of the presence of strong π - π interactions. To explore this possibility, orange single crystal **1** was heated and then analyzed. The result of temperature-dependent XRPD measurements exhibit that the framework is robust, and can be maintained even without any solvent molecules being present at 100 °C (Fig. S1). The desolvated crystal [4-pmntd] (**2**) was obtained by heating the single crystal **1** at 100 °C under an air atmosphere for a period of 2 h. The X-ray structure of **2** indicates that the adjacent naphthalene ring planes overlapped with each other by about 20%, and the perpendicular distance between them was measured to be approximately 3.39 Å, which corresponds to the formation of π - π interaction between the adjacent naphthalene rings (Fig. 3). There was also no π - π interaction between the adjacent pyridine rings. In **2**, four 4-pmntd molecules are hydrogen bonded via O(-C=O) atom $\cdots$ pyridine H bonding to form a rectangular grid of 9.1×3.7 Å voids in the ac-plane, and the naphthalene rings of adjacent layers stack to make empty

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channels along the b-axis. To study the host-guest interactions of pyridine-base H-bond, brief immersion of single crystal **2** into water results in complete rehydration and formation of hydrated crystal [4-pmntd·2H₂O](**1**), including two guest water molecules. The single-crystal X-ray structure determination of **1** revealed that hydrogen bonded water molecules reside in the tubular framework of the 4-pmntd host connected via water...pyridine H bonding (Ow1-Hc...Ow1 2.83 Å, Ow1-Hb...N1 2.89 Å). The π - π interaction between the adjacent naphthalene rings overlap with a 3.35 Å interplanar distance and the adjacent pyridine rings has no π - π interaction. Interestingly, a single crystal **2** exposed to air for seven days changed its shape and shrank of about 8% (Fig. S2). Single crystal X-ray diffraction showed that it is a new anhydrous crystalline form [4-pmntd](**3**) exhibiting a zigzag chain arrangement of molecules via pyridine rings π - π interaction. A strong π - π interaction occurs among adjacent pyridine planes, which are overlapped almost face-to-face with a distance between them of approximately 3.71 Å (Fig. 4); however, there is also weak π - π interaction between the adjacent naphthalene rings with a distance of approximately 4.16 Å and overlapped with each other by about 10%. Thus a 2D network is formed through π - π interaction.¹⁹

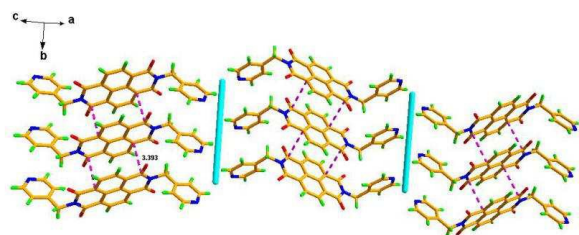


Fig. 3 The void framework of compound **2** up on removal of guest molecules.

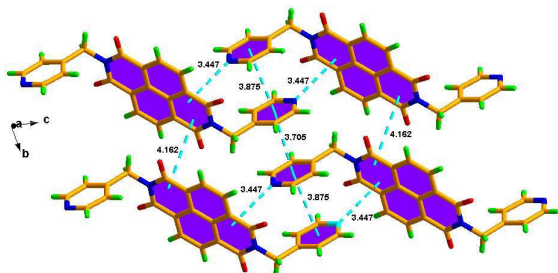


Fig. 4 The dense packing of compound **3**.

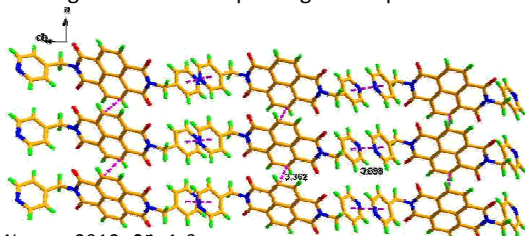


Fig. 5 The 2D network through π - π interaction of compound **3**.

Structural diversity

It is generally believed that most organic crystals tend to collapse as the guest solvent molecules being removed for the magnitude of local stress depends on the organic host frameworks. In the present crystals **1-3**, the difference between the **1** and **2** is rather small, only the distance of adjacent naphthalene ring planes expanding 0.04 Å, so the crystal can preserve the three-dimensional order by small adjustments in the unit cell. The adjacent naphthalene rings' interaction is considered to play an important role as buffer stacking layers in the crystal, in which π - π interaction absorb the strain energy by adjusting their intermolecular distances and keep the crystal packing stable even after large deformation.²⁰ when **2** is immersed in water, the water molecules filled the empty channels of **2**, hydrogen bonded water molecules reside in the tubular framework of the 4-pmntd host connected via water molecules and water...pyridine H bonding (Ow1-Hc...Ow1 2.83 Å, Ow1-Hb...N1 2.89 Å), which stabilized the organic host framework, so **2** converted to the two-hydrate form **1**. Single crystals **2** expose to air for seven days, for the magnitude of local stress, the frameworks contraction and adjacent pyridine rings get close to each other, form a strong π - π interaction, result in formation a zigzag chain close arrangement structure **3**.

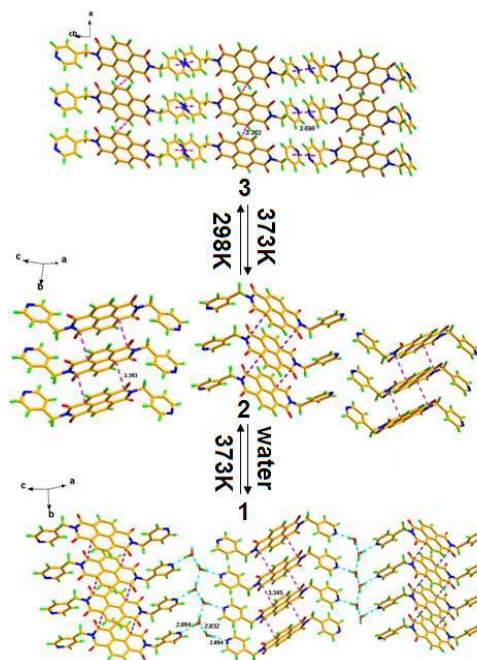


Fig. 6 Reversible single-crystal-to-single-crystal transformations between **1**, **2** and **3**.

Thermal stability

The stepwise thermogravimetric curve of **1** indicates that the release of the guest water molecules occurred at the range from 60 to 120°C, and give the desolvated form, **2**, which is stable up to 360°C (calcd 7.4%; found 7.8%). Therefore, the desolvation can be accomplished by heating at the temperature range between 120 and 360°C. On further heating, the compound decomposes to form unidentified products (Fig. S3). The water release occurs stepwise in the range of 70 to 120°C, the first step is from 70°C to 100°C and the second step is from 100°C to 120°C, as it is pointed out also by DSC. (Fig. S4).

Sorption properties of **2**

To study the effect of structural transformation and verify the porosity of **2**, the gas sorption properties were measured for N₂ (kinetic diameter = 3.64 Å), H₂ (2.8 Å), and CO₂ (3.3 Å) gases. All adsorption isotherms of **2** show type I behavior as expected for materials with micropores (~5 Å). (Fig. 7). Interestingly, **2** can absorb an amount of CO₂ at 1 atm and 195 K [21.8 cm³ g⁻¹ (STP)], exhibiting highly selective sorption of CO₂ over N₂ [2.4 cm³ g⁻¹ (STP)] and H₂ [2.6 cm³ g⁻¹ (STP)]. It was also observed that there is some sort of hysteresis between CO₂ sorption/desorption curves, which might originate from the strong interactions of CO₂ molecules with the host solid **2** and/or a dynamic structural transformation from desolvated to guest occupied structure. The different adsorption capabilities for gases can be ascribed to the existence of a larger quadrupolar moment for CO₂ (quadrupolar moment = 4.30 × 10²⁶ esu cm²) than N₂ (1.52 × 10²⁶ esu cm²) and H₂ (0.662 × 10²⁶ esu cm²), thereby providing stronger framework-partial-charge/quadrupole interactions for CO₂.¹² We reasoned that the pyridine nitrogen atom of the organic components in **2** also might enhance the selectivity for adsorbed CO₂ molecules.

Sorption experiments with different solvents were also carried out at 298 K (Fig. 8). For water vapor adsorption, an increase in the amount of adsorbed vapor under low pressure (0 < P/P₀ < 0.13) indicates initial adsorption of 1 molecule of water per 4-pmtd molecule unit, and then at 0.13 < P/P₀ < 0.14, a rapid increase of adsorption with 1 molecules of water per 4-pmtd molecule unit, and the third stepwise sorption at 0.14 < P/P₀ < 1.0 is an adsorption with 6 molecules of water per unit pore. It was found that the

desorption curve did not trace the adsorption curve any longer, which has a large hysteresis. According to the interesting phenomenon, we deduced that one water molecule is firstly adsorbed in the H bonding pyridine nitrogen sites, the secondly 1 molecule of water fast enter the channels through H bonding interaction between water molecules, and thirdly 6 molecules of water are adsorbed in the channels. The water molecules strongly interact with the organic host framework through H bonding interaction, and therefore, desorption becomes difficult and shows a hysteresis profile. The water adsorption of **2** has dynamic adsorption property wherein the organic host framework was changed according to the guest molecules entering. The methanol (kinetic diameter = 3.6 Å) vapor adsorption curve shows that after an initial adsorption with about a molecule of methanol at P/P₀ < 0.45 per unit pore, another molecule of methanol adsorption occurred at 0.45 < P/P₀ < 1.0. In the case of MeOH, one methanol molecule could be firstly adsorbed in the pyridine nitrogen sites and the following molecules of methanol are adsorbed in channels' surface by H-bonding interactions with the pyridine groups of the ligand, which results in a two stepwise adsorption profile. The stepwise sorption curves of **2** for water and methanol show a hysteretic sorption behavior correlating with the diversity of the binding sites. However, the absorption experiments with ethanol, n-propanol, isopropanol, n-butanol, benzene (5.3 Å) at 298 K show these molecules cannot enter the channels of **2** for the large size. The selective sorption of water over methanol, ethanol, n-propanol, isopropanol, n-butanol, benzene in **2** is due both to a size effect, which helps smaller guest molecules to enter the channels, and to selective H-binds within the hydrophilic channels, which favours alcohol solvents (Fig. 8).

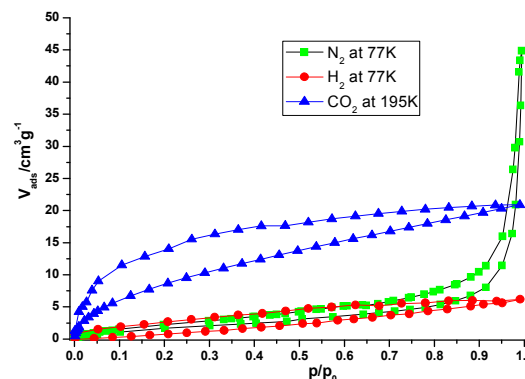
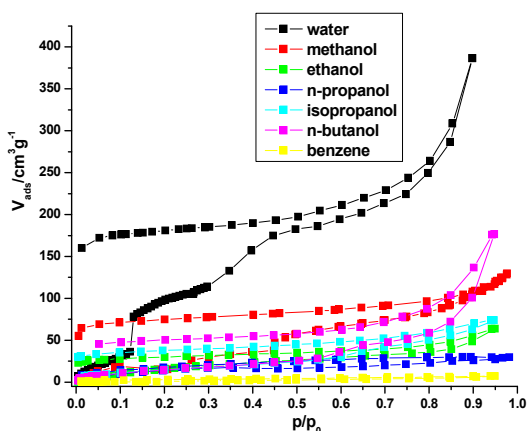
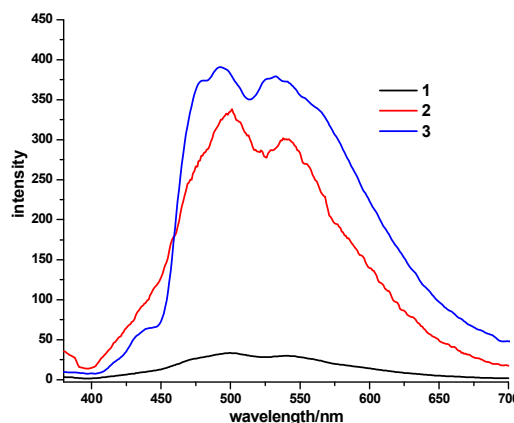


Fig.7 Gas adsorption/desorption isotherms of **2**Fig. 8 Different solvents vapor adsorption/desorption isotherm at 298 K for **2**

Fluorescence property

The fluorescence emission spectra of the 4-pmtd in chloroform solution shows an intense emission band at 440nm with a shoulder around 412 nm upon excitation at 360nm (Fig. S5). With increasing concentration of the 4-pmtd solution, the intensity of the short-wavelength emission gradually enhances and becomes dominant. The UV-visible absorption spectra of the compound **3** in solid-state is shown in Fig.S6. The absorption band 360 nm is attributed to the $\pi-\pi^*$ transition absorption of aromatic ring. The normalized solid-state fluorescence spectra of compounds **1-3** are shown in Fig. 9. The intensity of this fluorescence was found to vary much from that of the solid-state sample. The presence of water molecules for **1** weakened the solid-state fluorescence intensity of 4-pmtd, each hydrogen-bonded dimer unit is held together by the $\pi-\pi$ stacking interaction of naphthalene rings. It is well known that the $\pi-\pi$ stacking of planar molecules may facilitate the formation of detrimental excimeric species and lead to fluorescence quenching in the solid-state.²¹ Powdered **2** shows solid-state luminescence at 475nm, 540nm which undergoes a red shift to 480nm, 550nm in the **3**. The pyridine planes of two adjacent molecules in **2** hardly overlapped at all, there was nearly no $\pi-\pi$ interaction in **2**, but there was a strong $\pi-\pi$ interaction between the adjacent pyridine planes overlapped almost in a face-to-face stack, so the increase in exciton coupling and orbital overlap between neighbouring molecules from **2** to **3** is an important factor for the red-shifted fluorescence, increased exciton coupling and orbital overlap could lead to a strong red shift of the emission of the lowest state of the coupled

chromophores.^{14a} Therefore, the powder fluorescence emission of 4-pmtd in the aggregate solid state could be changed by altering its molecular stacking mode.^{14b} The supramolecular fluorescence host system **2** might be expected to exhibit solvent water dependent solid state fluorescence properties. Dispersing **2** in 2 mL of water weakened the luminescence, as molecules of 4-pmtd aggregate as in the hydrate crystal form **1** (Fig. S7); dispersing **2** in 2 mL of MeOH, EtOH, CH₃CN, THF, acetone and benzene solvent enhanced the luminescence, 4-pmtd molecules aggregate to give an amorphous state (Fig. S8). Interestingly, the emission intensity of compound **2** decreased dispersing in 2 mL of water. To further understand this phenomenon, the same experiments were performed with the introduction of methanol, ethanol, acetonitrile, acetone, tetrahydrofuran and benzene (Figure 10). When compound **2** is dispersed in 2 mL of these solvents, the fluorescence intensity increased, that is different from the effect of adding water solvent. We speculate that the variation arises because water molecules can enter the small channels, leading to strongly H-bonding interactions between pyridine and water molecules, which decreased fluorescence intensity. We have discovered a novel example of naphthalene diimide fluorescence in the molecule 4-pmtd, which exhibits distinctly different fluorescence emission in its three crystals. It was found that water molecule H-bonds and $\pi-\pi$ interaction between the neighbouring molecules weakened or induced the shift in fluorescence emission. This fluorescence switchable feature of 4-pmtd may have potential for application in water-sensing materials.

Fig. 9 solid-state luminescence (λ_{ex} =365nm) of compounds **1-3**

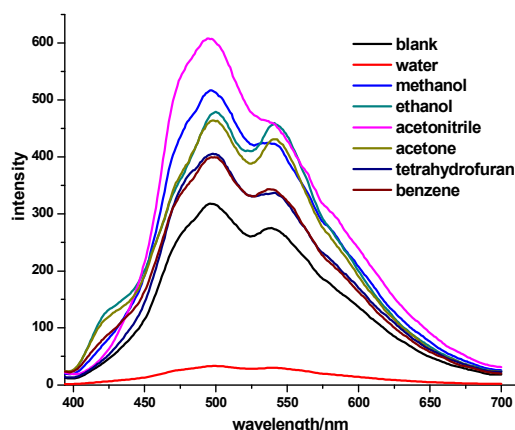


Fig. 10 The emission spectra of compound **2** indispersing in 2 mL of various solvents

Conclusions

In summary, the supramolecular organic structure shrank and expanded induced by temperature that exhibits outstanding performance as selective adsorption of CO₂ over N₂, H₂. The supramolecular organic structure shows a sorption selectivity for water over methanol, ethanol, n-propanol, isopropanol, n-butanol, benzene guests owing to the effect of shape exclusion. Notably, this feature of obvious fluorescence quenching induced by the presence of water is highly promising for detecting water molecules through a simple fluorescence sensing mechanism.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No.21403191), the Natural Science Foundation of Guangdong Province (No. 2014A030307010), Special funds for public welfare research and capacity building in Guangdong Province (No. 2015A010105031 and 2016A010103042).

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Abstract Graphical

Supramolecular structural transformation of N, N'-bis(4-pyridyl-methyl)-naphthalene diimide and fluorescence sensing water

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Temperature induced phase transitions in a supramolecular structure. The supramolecular organic structure exhibits reversible dehydration/rehydration in a single-crystal-to-single-crystal process and selectively adsorption of CO₂ over N₂, H₂. Moreover, The supramolecular organic structure shows a sorption selectivity for water and fluorescence sensing water.

