

## Electronic Supplementary Information

for

### **Reversible water uptake by a porous molecular crystal from metal complex of Gemini surfactant**

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## Supporting Figures

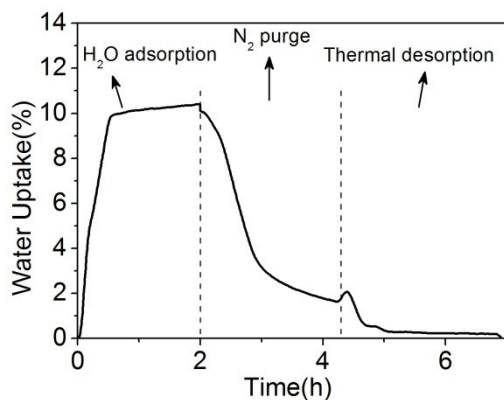


Figure S1. The detailed adsorption and desorption stages in one cycle for the thermogravimetric curves.

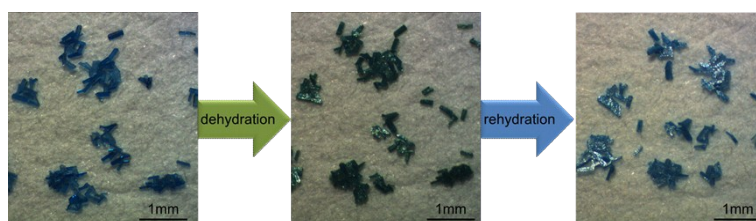


Figure S2. The change of the crystal appearance in the alternate dehydration/rehydration process.

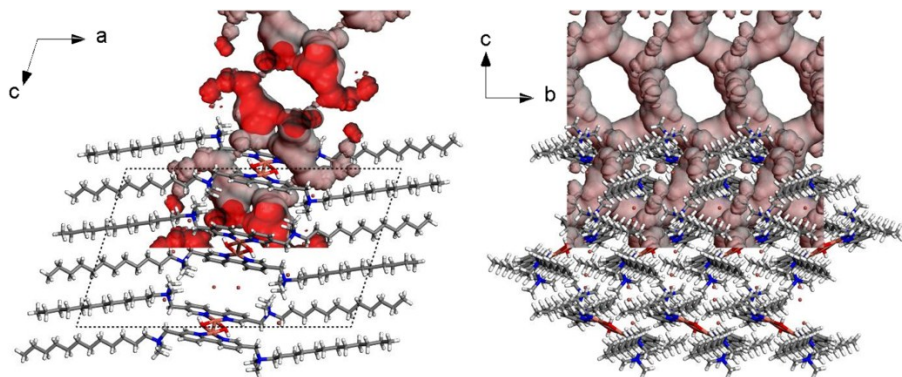


Figure S3. The solvent-accessible volume with an interconnected pore structure.

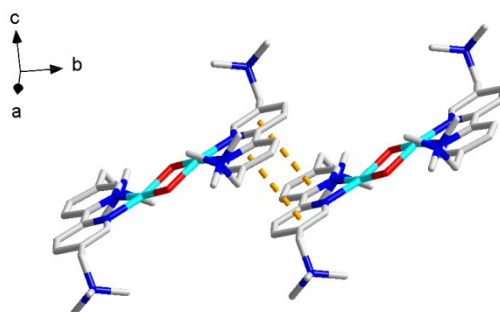


Figure S4. The  $\pi \cdots \pi$  interaction formed in the 1D column. The interaction is shown by yellow dash lines. All alkyl chains and H atoms are omitted for clarity.

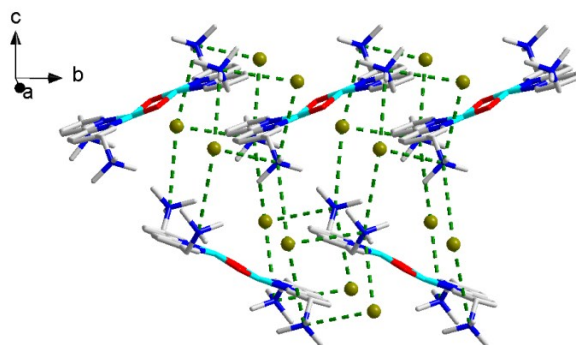


Figure S5. The electrostatic attraction both in the intra- and inter- column structures. Electrostatic attraction is marked by green dash line between quaternary ammonium head groups and Br ions (olive balls). All alkyl chains and H atoms are omitted for clarity.

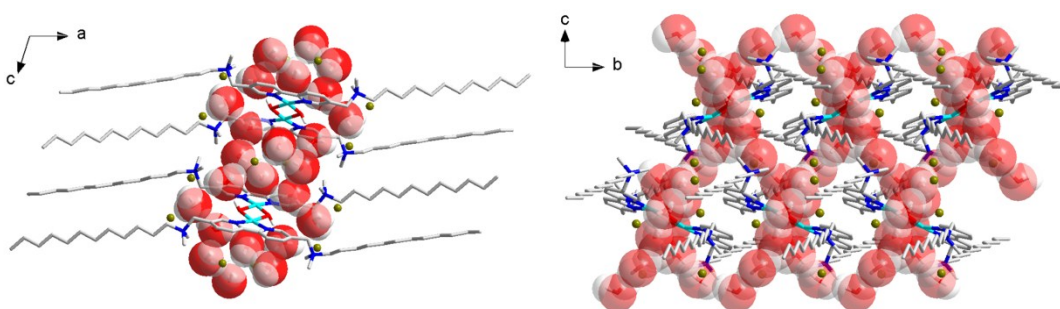


Figure S6. The crystal water filling the entire pore structure. All H atoms are omitted for clarity.

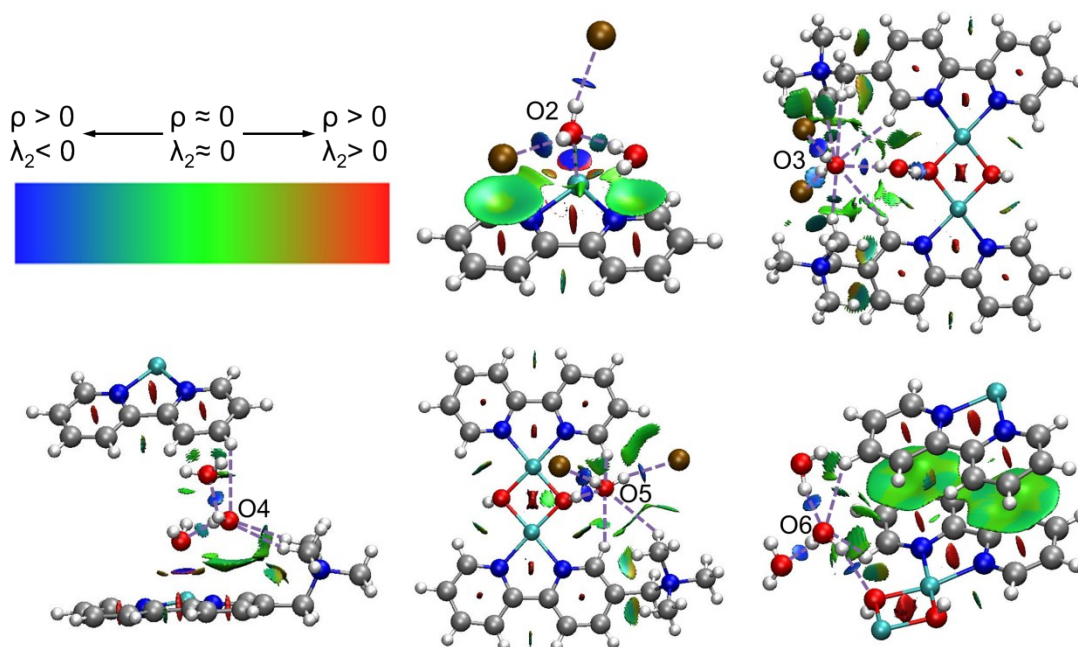


Figure S7. NCI analysis between water molecules and their surrounding groups. Blue indicates polarised attraction, green means van der Waals interaction and red stands for repulsion. Herein, purple dashed lines are used only for guiding the eye to show the interactions. Color for atoms: H, white; C, grey; N, blue; O, red; Br, olive; Cu, turquoise.

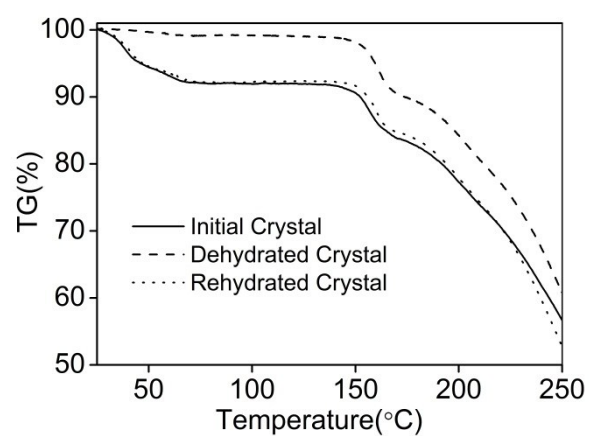


Figure S8. The TG curves of the initial, dehydrated and rehydrated crystals.

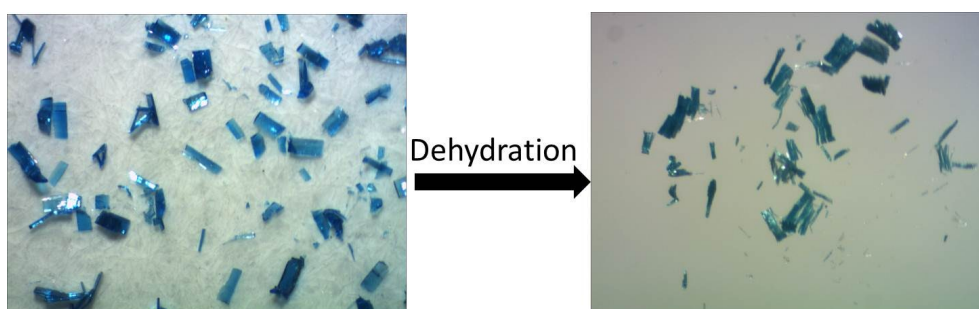


Figure S9. An optical microscope image of the cracking crystals of the dehydrated phase in contrast with the initial crystals.

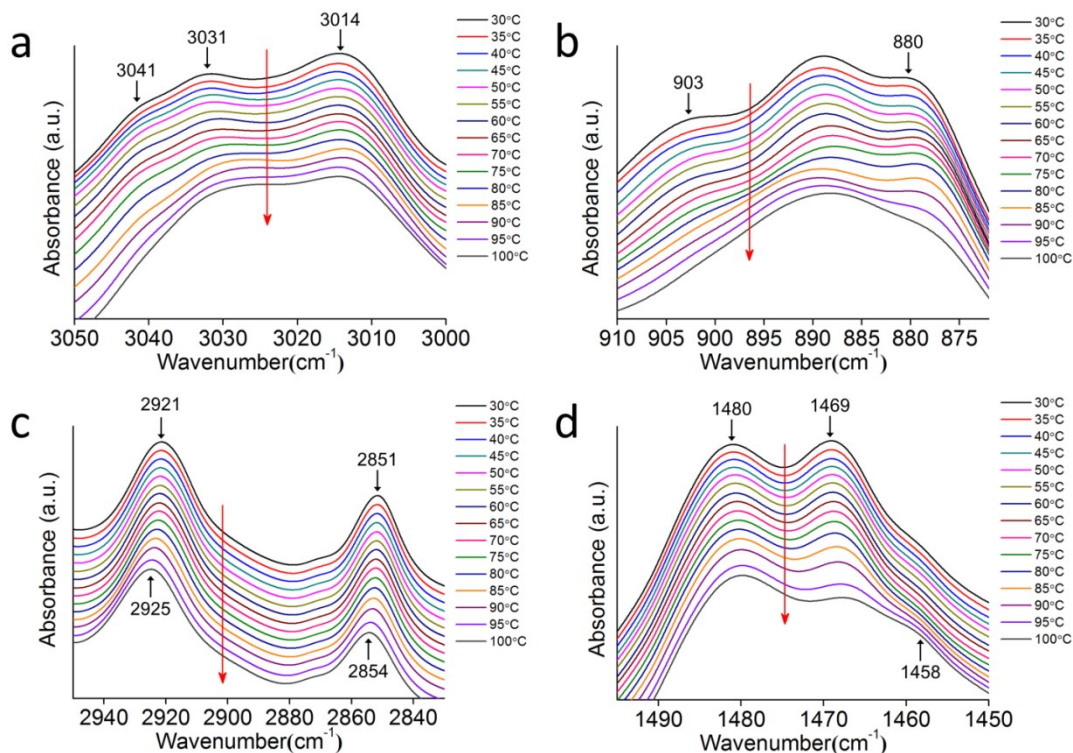


Figure S10. The temperature-dependent in situ FT-IR spectra in the process of dehydration. The red arrows represent the direction of the increasing temperature. The temperature of the sample cell is elevated from 30 to 100 °C at a 1 °C/min heating rate. The depicted curves from up to down denote a change in the temperature from 30 to 100 °C with a 5 °C interval

Figure S10a. A legible peak at around 3014  $\text{cm}^{-1}$  is attributed to the C-H stretching vibration of the bipyridine ring. Two weak but discernable peaks appear at 3031  $\text{cm}^{-1}$  and 3041  $\text{cm}^{-1}$  at the lower temperature, which can be explained by the fact that the formation of C-H $\cdots$ O interactions between bipyridine ring and water change the C-H bond length of the bipyridine ring, increases the vibration frequency and finally results in the blue-shifting peak. As the temperature increases, the intensity of the former peak gradually diminished and the latter peak finally disappeared, indicating that the content of water decreases in the dehydration process. The peak at 3031  $\text{cm}^{-1}$  does not completely disappear upon the dehydration. This is a likely consequence of the fact that  $\mu$ -OH has an unavoidable influence of on the bipyridine ring via intramolecular hydrogen bonds.

Figure S10b. Simultaneously, the C-H bending-vibration peaks of bipyridine rings can be understood in the same way. The peaks at 903  $\text{cm}^{-1}$  and 880  $\text{cm}^{-1}$  are the result of blue shifts of the C-H bending frequency caused by C-H $\cdots$ O interactions between bipyridine ring and water. As the crystal water decreases gradually in the process of the dehydration, the blue-shift peaks gradually disappear.

Figure S10c. With the increase of temperature, the anti-symmetric and symmetric stretching vibration peaks of methylene blue-shift from 2921 and 2851  $\text{cm}^{-1}$  to 2925 and 2854  $\text{cm}^{-1}$  respectively, indicating that the alkyl chains arrangement changes from a highly-ordered zigzag conformation into a relatively disordered structure.

Figure S10d. The dehydration affects the  $-\text{CH}_2-$  scissoring vibration band at ca.  $1470\text{cm}^{-1}$ . Although the  $\text{C}=\text{C}$  and  $\text{C}=\text{N}$  stretching vibration bands of the pyridine ring appear at the  $1480\text{ cm}^{-1}$  and  $1469\text{ cm}^{-1}$ , respectively, which may has an effect on the band judgment, the change in the  $-\text{CH}_2-$  scissoring vibration can be obviously observed, as the temperature is elevated. Here, such a change in the relatively peak intensity at  $1469$  and  $1458\text{ cm}^{-1}$  (the former is lowered and the latter is risen) is a likely result of the change in the packing behavior for alkyl chains in crystal.

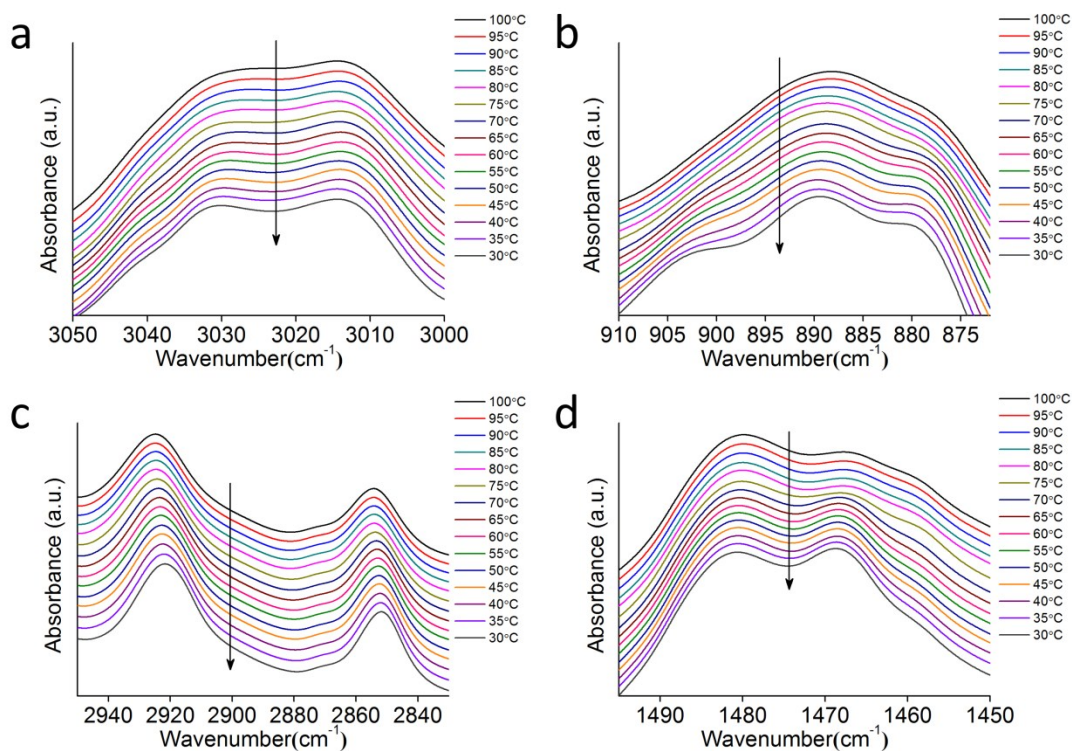


Figure S11. The temperature-dependent *in situ* FT-IR in the process of rehydration. The black arrows represent the direction of temperature decrease. The depicted curves from up to down denote a change in the temperature from 100 to 30  $^{\circ}\text{C}$  with a 5  $^{\circ}\text{C}$  interval

## Supporting Tables

Table S1. Crystal data and structure refinement for PMC-bpy

Crystal reference	PMC-bpy
Empirical formula	C80 H166 Br6 Cu2 N8 O12
Formula weight	2038.74
Temperature	130 K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	a = 30.2435(5) Å $\alpha = 90^\circ$ b = 9.4252(2) Å $\beta = 107.5450(10)^\circ$ c = 18.2742(3) Å $\gamma = 90^\circ$
Volume	4966.75(16) Å <sup>3</sup>
Z	2
Density (calculated)	1.363 Mg/m <sup>3</sup>
Absorption coefficient	3.788 mm <sup>-1</sup>
F(000)	2132
Crystal size	0.2 x 0.11 x 0.03 mm <sup>3</sup>
Theta range for data collection	1.532 to 69.592°.
Index ranges	-36 ≤ h ≤ 35, -11 ≤ k ≤ 10, -20 ≤ l ≤ 21
Reflections collected	26082
Independent reflections	8946 [R(int) = 0.0527]
Completeness to theta = 67.679°	97.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7532 and 0.4104
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	8946 / 0 / 506
Goodness-of-fit on F <sup>2</sup>	1.025
Final R indices [I > 2σ(I)]	R1 = 0.0562, wR2 = 0.1537
R indices (all data)	R1 = 0.0633, wR2 = 0.1608
Extinction coefficient	n/a
Largest diff. peak and hole	1.816 and -1.619 e.Å <sup>-3</sup>

Table S2. The H-Bond interactions between water, counter ions and host molecules <sup>a</sup>

D-H...A	<i>d</i> (D-H)/Å	<i>d</i> (H...A)/Å	<i>d</i> (D...A)/Å	∠(DHA)/deg
O-H...O				
O1-H1...O5a	0.85	1.86	2.71	179
O4-H4A...O6a	0.86	2.14	2.85	139
O4a-H4Ba...O2	0.86	2.35	3.20	163
O6a-H6Aa...O3b	0.86	2.05	2.92	175
O6a-H6Ba...O1b	0.86	2.16	2.89	141
O-H...Br				
O2-H2A...Br2	0.87	2.33	3.19	166
O2-H2B...Br2a	0.87	2.47	3.22	144
O3b-H3Ab...Br3c	0.84	2.38	3.22	172
O3b-H3Bb...Br1b	0.85	2.55	3.33	154
O5a-H5Aa...Br2	0.86	2.44	3.30	170
O5a-H5Ba...Br1	0.87	2.41	3.28	170
C-H...O				
C1-H1A...O5a	0.94	2.87	3.56	130
C1b-H1Ab...O3b	0.94	2.88	3.73	150
C1b-H1Ab...O6a	0.94	2.99	3.54	118
C8d-H8d...O4	0.95	2.91	3.53	123
C8d-H8d...O6a	0.95	2.70	3.43	133
C10-H10...O3b	0.95	2.98	3.88	160
C10b-H10b...O5a	0.94	3.04	3.61	120
C11b-H11Ab...O3b	0.99	2.80	3.65	144
C12-H12A...O4a	0.97	2.88	3.69	140
C13-H13A...O5a	0.97	2.94	3.47	115
C13-H13C...O4a	0.98	2.34	3.30	166
C13b-H13Ab...O3b	0.97	2.62	3.55	159
C28-H28C...O3b	0.98	2.51	3.44	157
C-H...Br				
C4d-H4d...Br2	0.94	2.70	3.50	141
C11b-H11Ab...Br3c	0.99	3.00	3.84	143
C12d-H12Cd...Br1	0.98	2.99	3.90	153
C26b-H26Bb...Br1	0.98	2.81	3.73	155
C27-H27C...Br2a	0.98	3.05	3.94	151
C27d-H27Ad...Br3c	0.98	2.88	3.79	154
C28-H28A...Br2a	0.98	2.96	3.85	150
C29d-H29Ad...Br3c	0.99	2.93	3.84	152

<sup>a</sup> Symmetry codes: (a) 1-x,-0.5+y,0.5-z; (b) 1-x,-y,1-z; (c) 1-x,0.5+y,0.5-z; (d) x,1+y,z.



Table S3. The unit cell parameters of the dehydrated crystal from the indexing and space group determination.

Crystal reference	Dehydrated Crystal	
Empirical formula	C80 H146 Br6 Cu2 N8 O2	
Formula weight	1858.6	
Crystal system	triclinic	
Space group	P 1 or P -1	
Unit cell dimensions	a = 30.1613 Å	$\alpha = 101.300^\circ$
	b = 8.8460 Å	$\beta = 103.731^\circ$
	c = 8.5433 Å	$\gamma = 94.725^\circ$
Volume	2151.385 Å <sup>3</sup>	
Z	1	