Electronic Supplementary Material (ESI) for Dalton Transactions.

A two-dimensional porous framework: solvent-induced structural transformation and selective adsorption towards malachite green

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Supporting Information (in 16 pages)

Contents

1. General Materials and Methods

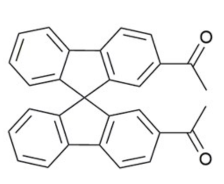
All reagents were commercially available and used as received without further purification unless otherwise stated. 9,9'-Spirobi[9H-fluorene] (Puyang Huicheng Electronic Material Co., Ltd, 99%), Aluminum Chloride (SCRC, 99%), Acetyl Chloride (SCRC, 99%), Dichloromethane (SCRC, 99.5%), Carbon disulfide (SCRC, 99.5%), Sodium hydroxide (Aladdin, ACS, 97%), Sodium hydrogen sulfite (SCRC, 99.5%), Bromine (SCRC, 99.5%), 1,4-Dioxane (SCRC, 99.5%).

NMR spectra were recorded on a Bruker 500 FT-NMR spectrometer. Mass spectra were recorded on Agilent GC6890-5975I mass spectrometer. Elemental analysis was estimated on an Elementar Vario EL-III element analyzer. FT-IR data were recorded on a Thermo Nicolet Avatar 370 FTIR Spectrometer. TGA data were obtained from a NETZSCH STA 409 PC Luxx Simultaneous Thermal Analyzer with a heating rate of 10 °C / min under N_2 atmosphere. The powder X-ray diffraction patterns (PXRD) were obtained from a Rigaku D/Max2550V/PC or D/Max2200V/PC X-ray Powder Diffractometer with Cu-Kα radiation (λ = 0.15418 nm). Simulation of the PXRD patterns was carried out on the program PLATON. UV-vis spectra measurements were conducted on a Shimadzu UV-2501PC or Persee TU-1900 Spectrophotometer.

2. Synthesis of ligand and complex

2.1. Synthesis of $\mathbf{H_2L}$

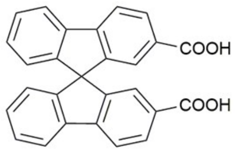
Scheme S1. Synthesis of $\mathbf{H_2L}$.



2,2'-Ac$_2$SBF

2,2'-Diacetyl-9,9'-Spirobi[9H-fluorene] (2,2'-Ac$_2$SBF): **2,2'-Ac$_2$SBF** was synthesized according to the literature methods [S1 and S2] with a slight modification as follows: the mixture of 9,9'-Spirobi[9H-fluorene] (6.00 g, 19.0 mmol) and anhydrous $AlCl_3$ (20.00 g, 150.0 mmol) in CS_2 (60 mL) was stirred at RT for 30 min under anhydrous condition, and acetyl chloride (3.60 mL, 51.4 mmol) dissolved in CS_2 (10 mL) was added through a dropping funnel over an hour. The mixture was further stirred for 3 h, and then heated to reflux overnight, poured into ice-water, acidified with dilute HCl, and extracted with of DCM (3 × 100 mL). The combined organic phase was dried over Na_2SO_4, and purified by flash column chromatography on silica gel (DCM : petroleum ether = 1:3) to afford **2,2'-Ac$_2$SBF** as a white solid (5.50 g, 72%). ^{1}H NMR: (500 MHz, $CDCl_3$): δ 8.02 (dd, J = 8.1, 1.6 Hz, 1H), 7.93 (dd, J = 8.5, 5.6Hz, 2H), 7.42 (td, J = 7.6, 0.9Hz, 1H), 7.30 (d, J =

1.4 Hz, 1H), 7.18 (td, *J* = 7.5, 1.0Hz, 1H), 6.72 (d, *J* = 7.6 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR: (125 MHz, DMSO-d$_6$): *δ* 197.6, 149.3, 148.5, 146.8, 140.6, 136.9, 129.4, 129.3, 128.4, 124.3, 123.9, 121.3, 120.2, 65.9, 26.8. EI-MS: m/z (%) 400 [M$^+$] (100). FT-IR (KBr, 4000-400 cm^{-1}) 3423 (m), 3050 (w), 1677 (m), 1605 (m), 1569 (w), 1455 (w), 1414 (w), 1354 (m), 1282 (m), 1258 (m), 1221 (m), 1071(w), 951 (w), 843 (w), 733 (m), 596 (w), 503 (w), 465 (w), 416 (w).



H$_2$L

9,9'-Spirobi[9H-fluorene]-2,2'-Dicarboxylic acid (H$_2$L): **H$_2$L** was synthesized according to known procedures [S1 and S2] with a slight modification as follows: NaOH (4.00 g, 100.0 mmol) and H_2O (20 mL) were stirred at 0 °C, and Br_2 (1.6 mL, 30.5 mmol) was added. The yellow solution was further stirred at 0 °C for half an hour, and then **2,2'-Ac$_2$SBF** (2.00 g, 5.0 mmol) dissolved in 1,4-Dioxane (27 mL) was added slowly. The addition was controlled to initiate the reaction at an early stage. The yellow mixture was stirred at 0 °C for 3 h, and another 3 h at RT. The clear solution was treated with $NaHSO_3$ (0.67 g, 6.3 mmol), and acidified with concentrated HCl. The white precipitate was collected by suction filtration and recrystallized from ethanol to afford **H$_2$L•EtOH•H$_2$O** as a white crystalline solid (1.70 g, 73%). ^{1}H NMR: (500 MHz, DMSO-d$_6$): δ 12.95 (s, 2H), 8.20 (d, *J* = 7.9 Hz, 2H), 8.17 (d, *J* = 7.7 Hz, 2H), 8.05 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.51 (td, *J* = 7.6, 0.7 Hz, 2H), 7.25 (td, *J* = 7.6, 0.9 Hz, 2H), 7.10 (d, *J* = 0.5 Hz, 2H), 6.72 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR: (125 MHz, DMSO-d$_6$): 166.8, 148.3, 145.7, 140.2, 130.3, 129.8, 129.4, 128.6, 124.0, 123.8, 121.7, 120.9, 65.1. EI-MS: m/z (%) 404 [M$^+$] (100). Elemental analysis (%) Calcd for **H$_2$L•EtOH•H$_2$O** ($C_{29}H_{24}O_6$): C, 74.35; H, 5.16, Found: C, 74.89; H, 5.32. FT-IR (KBr, 4000-400 cm^{-1}) 3055 (s), 2890 (m), 2645 (m), 2556 (m), 1685 (vs), 1610 (s), 1493 (w), 1459 (m), 1421 (s), 1299 (s), 1265 (s), 1226(s), 1161 (m), 1120 (w), 1083 (w), 1005 (w), 909 (m), 841 (m), 809 (w), 754 (s), 721 (m), 673 (w), 640 (m), 567 (w), 512 (w), 416 (w).

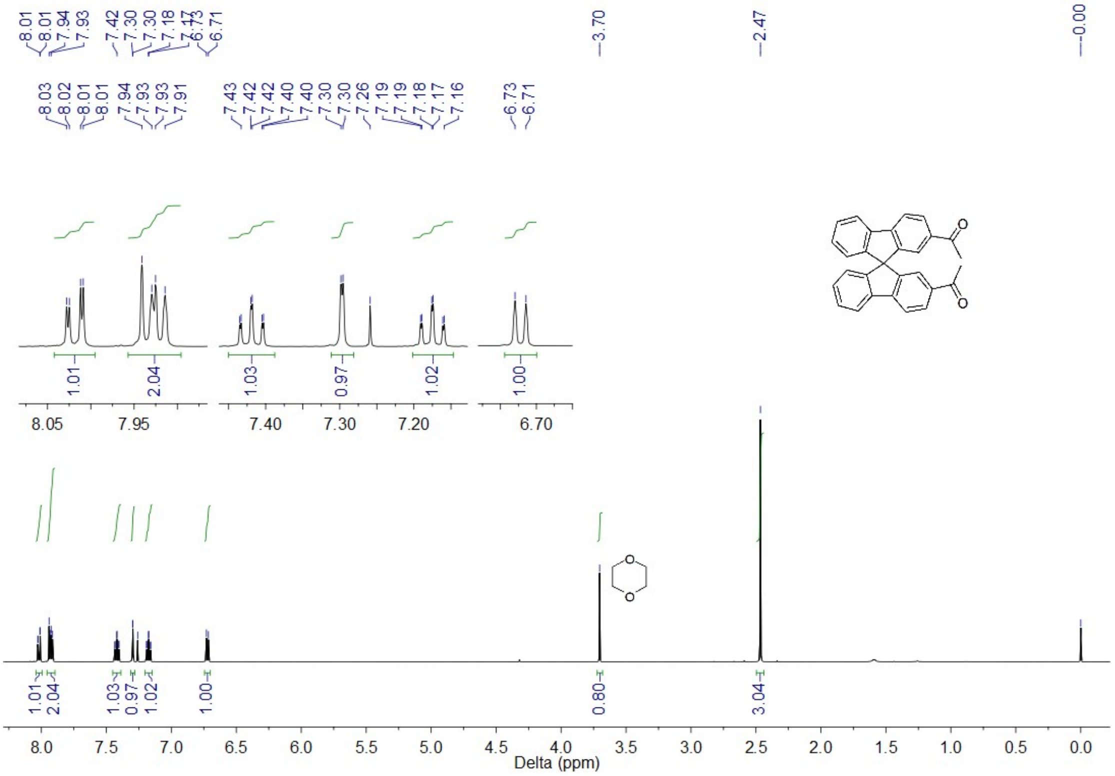


Figure S1. ^{1}H NMR spectra of **2,2'-Ac$_2$SBF**.

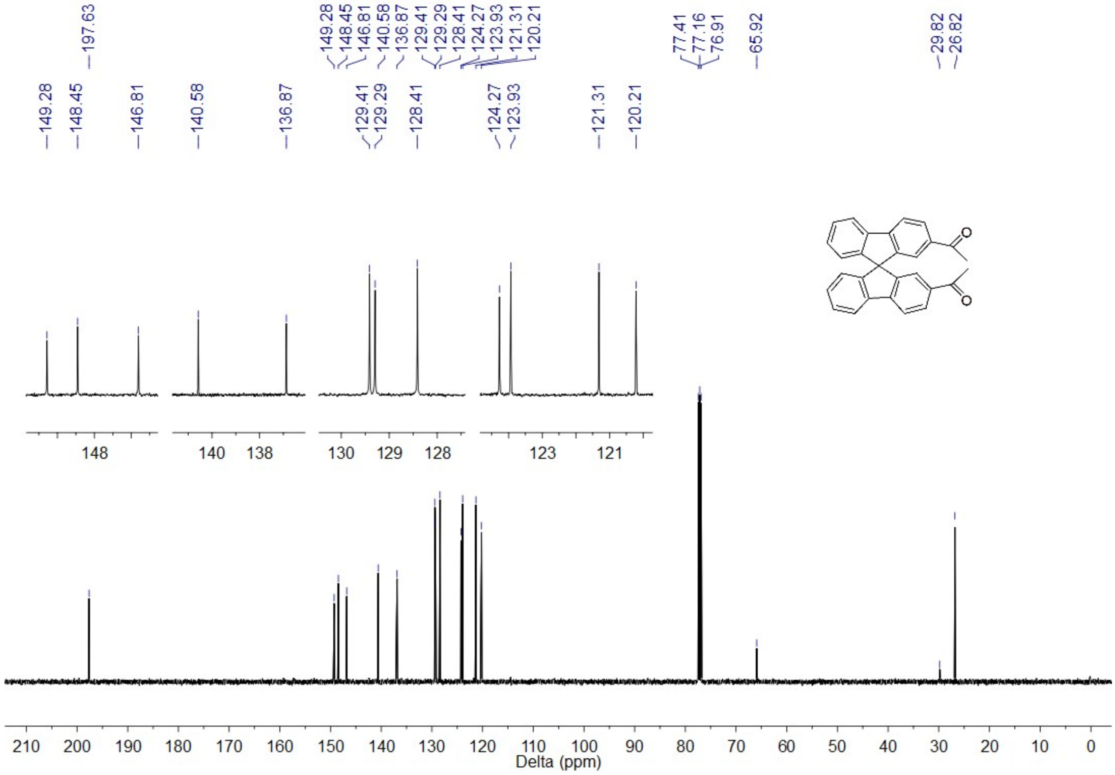


Figure S2. ^{13}C NMR spectra of **2,2'-Ac$_2$SBF**.

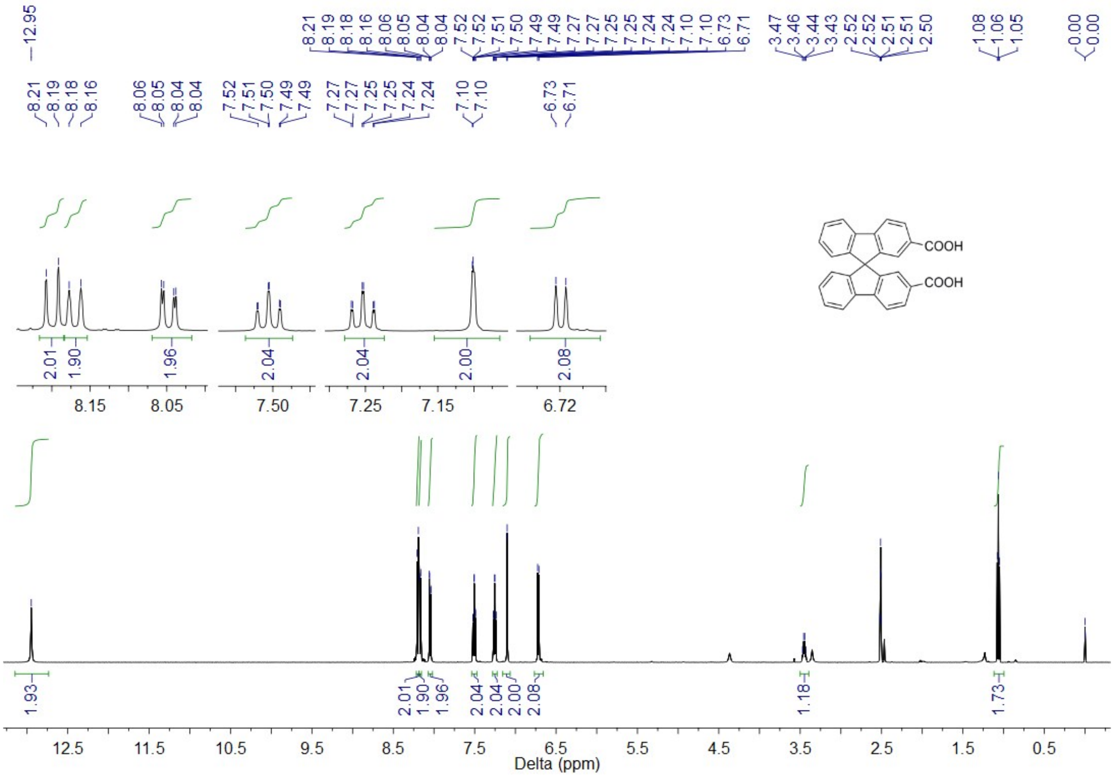


Figure S3. ^{1}H NMR spectra of $\mathbf{H_2L}$.

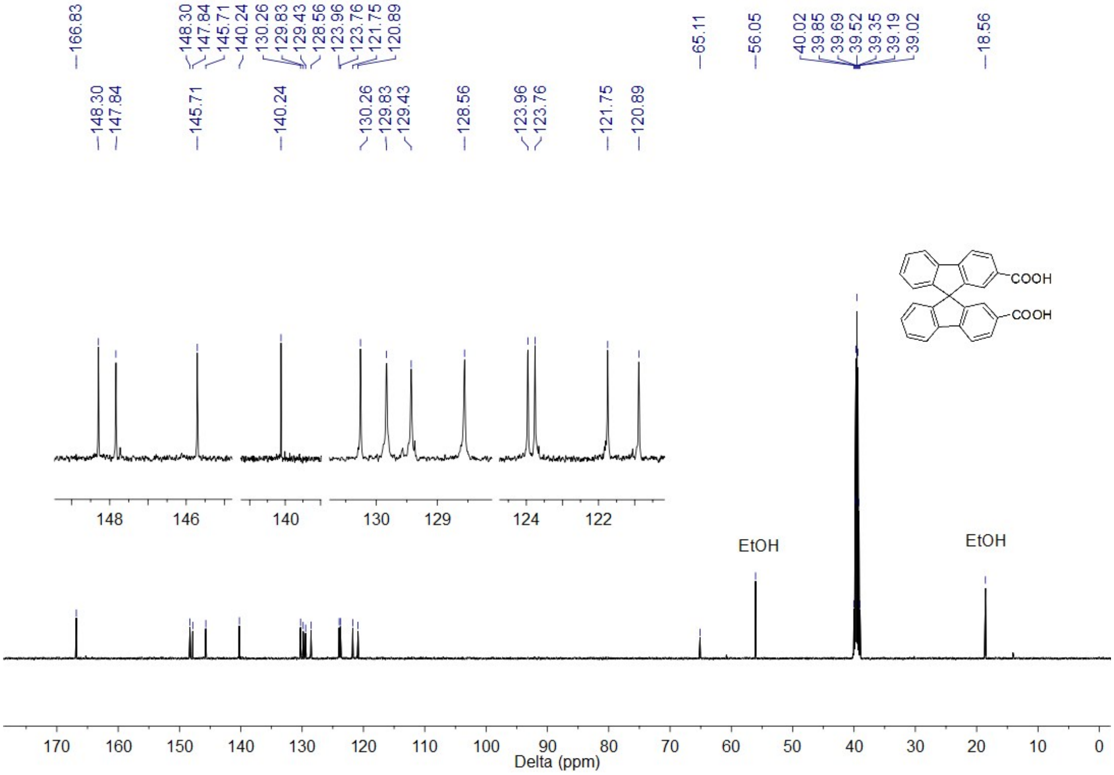


Figure S4. ^{13}C NMR spectra of $\mathbf{H_2L}$.

2.2. Synthesis of **SHU-1**, **SHU-1a** and **SHU-1b**

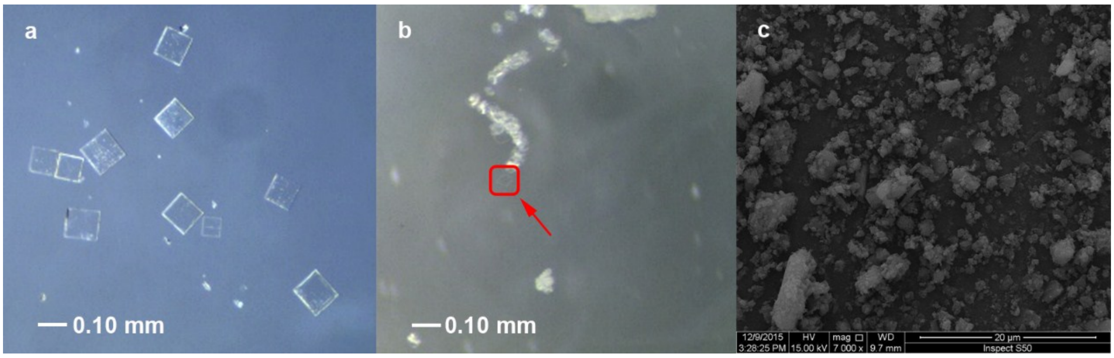


Figure S5. (a) Photographic image of **SHU-1**; (b) photographic image of **SHU-1a**, a single crystal has been highlighted by a red box and a red arrow; (c) SEM image of **SHU-1b**.

SHU-1: $H_2L\cdot EtOH\cdot H_2O$ (80.8 mg, 0.20 mmol) was stirred in the mixture of DMF (2.5 mL) and methanol (2.5 mL), and calcium nitrate (66.0 mg, 0.28 mmol) was added. The mixture was further stirred for 1 h, transferred into a 25 mL Teflon-lined stainless steel autoclave, sealed tightly, heated in an oven at 120 °C for 100 h, and then allowed to cool to RT at a rate of 3 °C / h. Colorless plate-like crystals of **SHU-1** were collected, washed with the mixture of DMF and methanol (V/V, 1/1), and dried in air. Yield: 99.0 mg (81%).

Elemental analysis (%) Calcd for $[(CH_3)_2NH_2]_2[C_{108}H_{64}Ca_4O_{21}]\cdot 6DMF$ or $[(CH_3)_2NH_2]_2[(Ca_4O)\mathbf{L}_4(H_2O)_4]\cdot 6DMF$: C, 65.37; H, 5.15; N, 4.69; Found: C, 65.17; H, 4.57; N, 4.54. FT-IR (KBr, 4000-400 cm^{-1}) 3421 (s), 3068 (m), 2935 (m), 1664 (s), 1598 (s), 1551 (s), 1494 (m), 1389 (vs), 1297 (w), 1261 (m), 1164(w), 1100 (m), 1074 (m), 1014 (w), 911 (w), 909 (m), 849 (m), 765 (m), 671 (m), 646 (m), 564 (m), 501 (m), 416 (m).

The large-scale preparation of **SHU-1** was carried out in a parallel manner. Different batches of samples were collected, washed with and stored in in the mixture of DMF and methanol. The phase purity was confirmed by PXRD.

SHU-1a: Crystals of **SHU-1** (32.1 mg) were soaked in dry methanol (20 mL) for 48 h without any disturbance. Colorless tiny plate-like crystals of **SHU-1a** were collected and washed with methanol. Yield: 27.9 mg (86%).

Elemental analysis (%) Calcd for $C_{30}H_{26}CaO_7\cdot CH_3OH\cdot 2H_2O$ or $[Ca\mathbf{L}(CH_3OH)_3]\cdot CH_3OH\cdot 2H_2O$: C, 61.37; H, 5.65; Found: C, 61.96; H, 4.58. FT-IR (KBr, 4000-400 cm^{-1}) 3606 (m), 3394 (m), 3067 (m), 2927 (w), 1592 (s), 1551 (s), 1491 (m), 1458 (m), 1416 (s), 1391 (s), 1301 (w), 1267 (w), 1158 (w), 1112 (w), 1071 (w), 1005 (w), 910 (w), 849 (w), 795 (w), 759 (m), 728 (m), 682 (w), 645 (w), 561 (w), 498 (m), 419 (w).

SHU-1b: Crystals of **SHU-1** (30.8 mg) were soaked in deionized water (20 mL) for 12 h. White powder of **SHU-1b** was collected and dried in air. Yield: 19.5 mg (73%).

Elemental analysis (%) Calcd for $C_{27}H_{20}CaO_7\cdot H_2O$ or $[Ca\mathbf{L}(H_2O)_3]\cdot H_2O$: C, 63.03; H, 4.31;

Found: C, 63.34; H, 4.19. FT-IR (KBr, 4000-400 cm^{-1}) 3618 (m), 3384 (m), 3064 (m), 1663 (w), 1592 (s), 1545 (s), 1493 (w), 1456 (m), 1419 (s), 1389 (s), 1299 (w), 1266 (w), 849 (w), 761 (s), 731 (w), 680 (w), 679 (w), 646 (w), 556 (w), 499 (w), 417 (w).

3. Single Crystal X-ray Crystallography of SHU-1 and SHU-1a

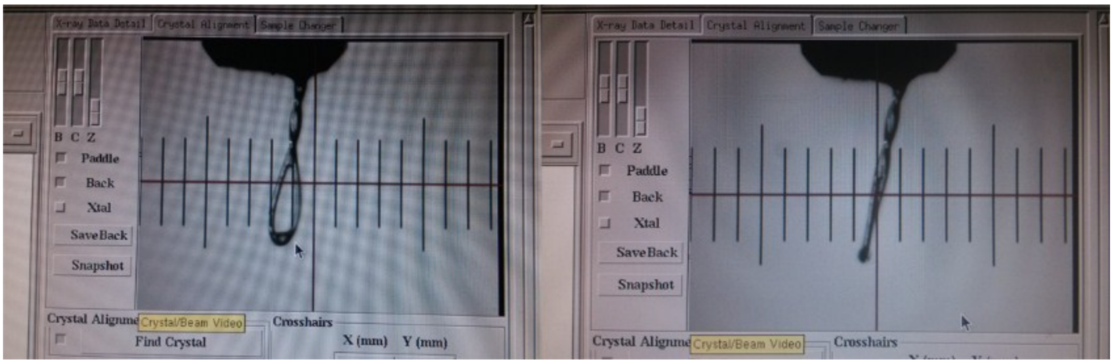


Figure S6. Crystal Mounting of **SHU-1a**.

Single-crystal X-ray diffraction data of **SHU-1_296 K** was collected on a Bruker-AXS APEX-II CCD X-ray diffractometer equipped with a fine-focus sealed-tube X-ray source (graphite monochromated Mo-Kα radiation, λ = 0.71073 Å). Suitable single crystals were mounted in oil on glass fibers at RT for data collections. Absorption corrections were applied via SADABS routine. [S3a]

Single-crystal X-ray diffraction data of **SHU-1_100 K** and **SHU-1a** was collected on an X-ray diffractometer equipped with a MarCCD-165 detector (λ = 0.75000 or 0.72000 Å), at Beamline 3W1A and 1W2B of Beijing Synchrotron Radiation Facility (BSRF). Suitable single crystals were mounted on a Nylon loop with Paratone-N oil for diffraction at 100 or 105 K. Absorption corrections were carried out by HKL2000. [S3b]

The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement. [S4] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2 × U_{eq} of the attached atom. The unit cell contains a large region of highly disordered solvent molecules, which could not be modeled as satisfactory discrete atomic sites, and therefore PLATON/SQUEEZE [S5] was employed to remove these electron densities. Crystallographic data has been deposited in the Cambridge Crystallographic Data Center with CCDC Number: 1424463, 1552733 and 1470061. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/data_request/cif.

The final formulae were estimated from elemental analysis, TGA data and the SQUEEZE results. The crystallographic data and structure refinement details are summarized in **Table S1**. The contents of the solvent region are not included in the refinement model and **Table S1**.

The SQUEEZE results are given as follows:

SHU-1_296 K

```
loop_
   _platon_squeeze_void_nr
   _platon_squeeze_void_average_x
   _platon_squeeze_void_average_y
   _platon_squeeze_void_average_z
   _platon_squeeze_void_volume
   _platon_squeeze_void_count_electrons
   _platon_squeeze_void_content
    1   -0.004 -0.002   0.000        871         72 ''
    2   0.000   0.000   0.326        219         28 ''
    3   -0.081   0.498   0.500        871         72 ''
    4   0.000   0.000   0.674        220         28 ''
    5   0.500   0.500   0.174        220         28 ''
    6   0.500   0.500   0.826        219         28 ''
_platon_squeeze_void_probe_radius                    1.20
_platon_squeeze_details                             ?
```

SHU-1_100 K

```
loop_
   _platon_squeeze_void_nr
   _platon_squeeze_void_average_x
   _platon_squeeze_void_average_y
   _platon_squeeze_void_average_z
   _platon_squeeze_void_volume
   _platon_squeeze_void_count_electrons
   _platon_squeeze_void_content
    1 -0.004   0.000   0.000        1322        279 ''
    2 -0.218   0.496   0.500        1322        279 ''
_platon_squeeze_void_probe_radius                    1.20
_platon_squeeze_details                             ?
```

SHU-1a

```
loop_
   _platon_squeeze_void_nr
   _platon_squeeze_void_average_x
   _platon_squeeze_void_average_y
   _platon_squeeze_void_average_z
   _platon_squeeze_void_volume
   _platon_squeeze_void_count_electrons
   _platon_squeeze_void_content
    1   0.250   0.750   0.434        101         16 ''
```

```
 2   0.250   0.750   0.934        101          16 ' '
 3   0.250   0.750   0.103         39           0 ' '
 4   0.250   0.750   0.603         39           0 ' '
 5   0.750   0.250   0.066        100          16 ' '
 6   0.750   0.250   0.566        100          16 ' '
 7   0.750   0.250   0.397         38           0 ' '
 8   0.750   0.250   0.897         38           0 ' '
_platon_squeeze_void_probe_radius                  1.20
_platon_squeeze_details                           ?
```

Table S1. Crystal data and structure refinement for **SHU-1** and **SHU-1a**.

	SHU-1_296 K	**SHU-1_100 K**	**SHU-1a**
Identification code	CCDC 1424463	CCDC 1552733	CCDC 1470061
Empirical formula	$C_{108}H_{64}Ca_4O_{21}$	$C_{108}H_{64}Ca_4O_{21}$	$C_{30}H_{26}CaO_7$
Formula weight	1857.91	1857.91	538.59
Temperature (K)	296(2)	100(2)	105(2)
Wavelength (Å)	0.71073	0.75000	0.72000
Crystal system, space group	Tetragonal	Tetragonal	Orthorhombic
Unit cell dimensions	*I*4/m	*I*4/m	*P*ccn
a (Å)	13.3902(12)	13.5460(19)	10.263(2)
b (Å)	13.3902(12)	13.5460(19)	15.960(3)
c (Å)	35.510(7)	34.908(7)	33.531(7)
$\alpha = \beta = \gamma$ (º)	90	90	90
V (Å^3)	6366.8(17)	6405(2)	5492.3(19)
Z	2	2	8
Calculated density (mg/m^3)	0.969	0.963	1.303
Absorption coefficient (mm^{-1})	0.224	0.255	0.274
F(000)	1920	1920	2256
Crystal size(mm^3)	0.07×0.06×0.03	0.10×0.10×0.05	0.05×0.05×0.01
θ range for data collection (º)	1.63 to 25.00	2.44 to 27.50	2.36 to 25.00
Limiting indices	$-15 \leqslant h \leqslant 9$, $-15 \leqslant k \leqslant 15$, $-40 \leqslant l \leqslant 42$	$-16 \leqslant h \leqslant 16$, $0 \leqslant k \leqslant 16$, $-42 \leqslant l \leqslant 42$	$0 \leqslant h \leqslant 12$, $-18 \leqslant k \leqslant 18$, $-39 \leqslant l \leqslant 39$
Reflections collected	16181	11487	14681
Independent reflections	2864 [R_{int} = 0.1505]	3190 [R_{int} = 0.0458]	4651 [R_{int} = 0.1724]
Completeness to θ	99.9 % (25.00°)	99.9 % (26.74°)	99.7 % (25.00°)
Refinement method	Full-matrix least-squares on F^2		
Data / restraints / parameters	2864 / 1/ 159	3190 / 3 / 160	4651 / 2 / 359
Goodness-of-fit on F^2	0.971	1.077	1.057
Final R indices [I>2σ(I)]	R_1 = 0.0852, wR_2 = 0.2069	R_1 = 0.0490, wR_2 = 0.1367	R_1 = 0.0858, wR_2 = 0.2028
R indices (all data)	R_1 = 0.1896, wR_2 = 0.2407	R_1 = 0.0633, wR_2 = 0.1447	R_1 = 0.1371, wR_2 = 0.2403
Largest diff. peak and hole (eÅ^{-3})	0.799 and -0.720	1.324 and -0.299	0.603 and -0.481

a. $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ b. $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$

4. Thermogravimetric Analysis and Powder X-ray Diffraction Measurement

4.1 Thermogravimetric Analysis

Thermogravimetric analysis was conducted in the temperature range RT to 600°C with a heating rate of 10 °C / min under N_2 atmosphere.

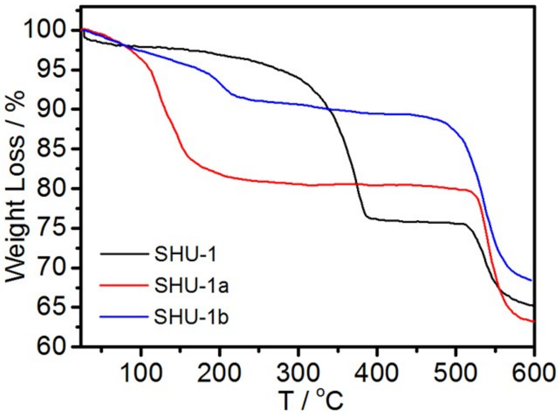


Figure S7. TGA curves of **SHU-1**, **SHU-1a** and **SHU-1b**.

4.2 Powder X-ray Diffraction Measurement

Powder X-ray Diffraction Measurement was carried out with a scan speed of 8°/min in 2*θ*.

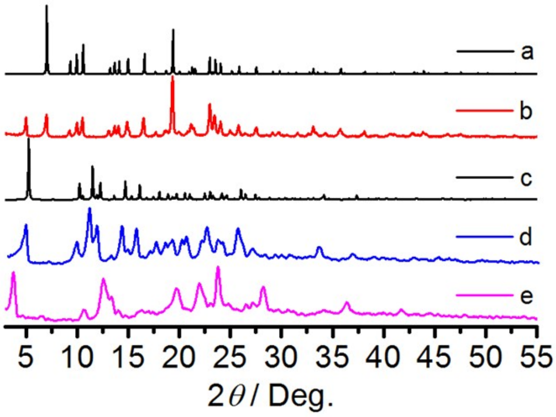


Figure S8. PXRD patterns of **SHU-1**, **SHU-1a** and **SHU-1b**. (a) **SHU-1** simulated, (b) **SHU-1** as synthesized, (c) **SHU-1a** simulated, (d) **SHU-1a** as synthesized, (e) **SHU-1b** as synthesized.

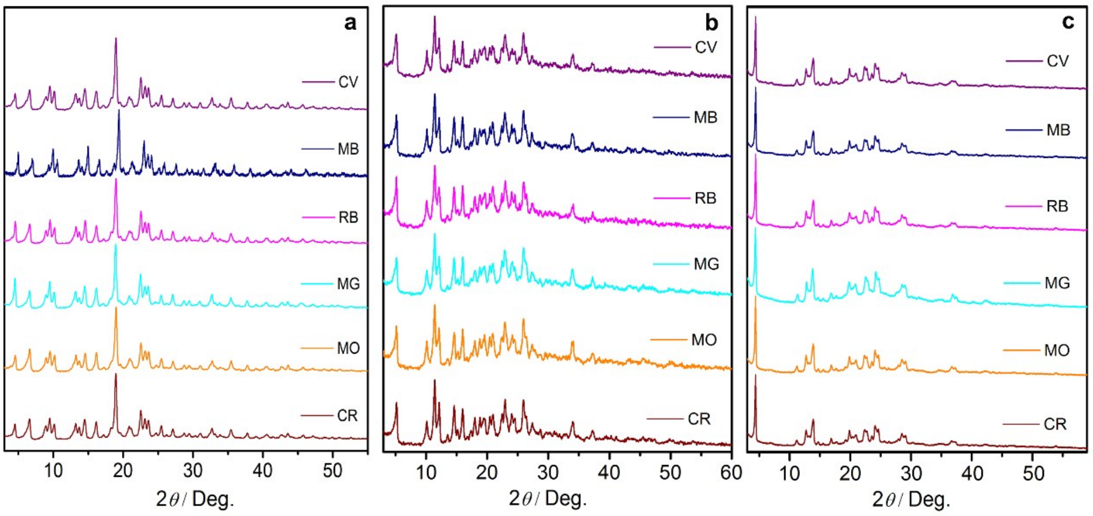


Figure S9. PXRD patterns of (a) **SHU-1**, (b) **SHU-1a**, (c) **SHU-1b** after dye adsorption. CV, crystal violet; MB, methylene blue; RB, rhodamine-B; MG, malachite green; MO, methyl orange and CR, Congo red.

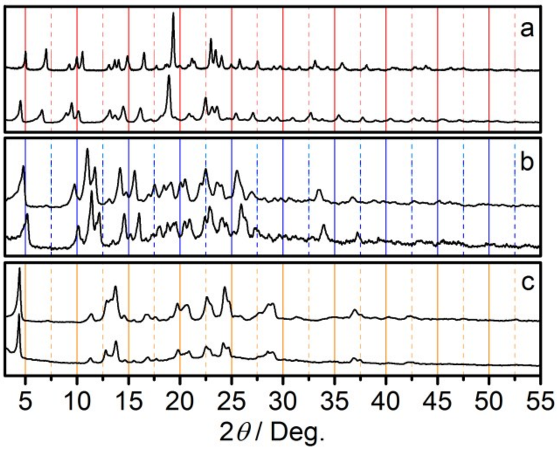


Figure S10. PXRD patterns of (a) **SHU-1** before (upper panel) and after (lower panel) MG adsorption; (b) **SHU-1a** before (upper panel) and after (lower panel) MG adsorption; (c) **SHU-1b** before (upper panel) and after (lower panel) MG adsorption.

5. Dye Adsorption

A weighed adsorbent (ca. 30.0 mg) was added into a Teflon lined screw cap vial (20 mL), and 4 mL of dye solution was added. The cap was screwed on tightly, and the vial was shaken on an orbital shaker (HZQ-50H by Shanghai Yiheng) with a speed of 180 rpm in the dark. The mixture was centrifuged at 11000 rpm for 2 min and the supernatant was subjected to analyzing the equilibrium concentration of dye.

The concentration of dye before or after the adsorption was estimated by UV-vis spectra, and the absorbance maximum was monitored: CV 590 nm, MB 665 nm, RB 555 nm, MG 425 or 618 nm, MO 465 nm, CR 498 nm.

The adsorption capacity of dye was calculated by the following equation:

$$q_e = \frac{C_0 - C_e}{m} V \qquad \text{eq. 1}$$

Where q_e is the equilibrium adsorption capacity of dye (μmol·g^{-1} or mg·g^{-1}), C_0 the initial concentration of dye (mol·L^{-1} or mg·L^{-1}), C_e the equilibrium concentration of dye (mol·L^{-1} or mg·L^{-1}), V (L) the volume of dye solution, and m (g) the weight of adsorbent.

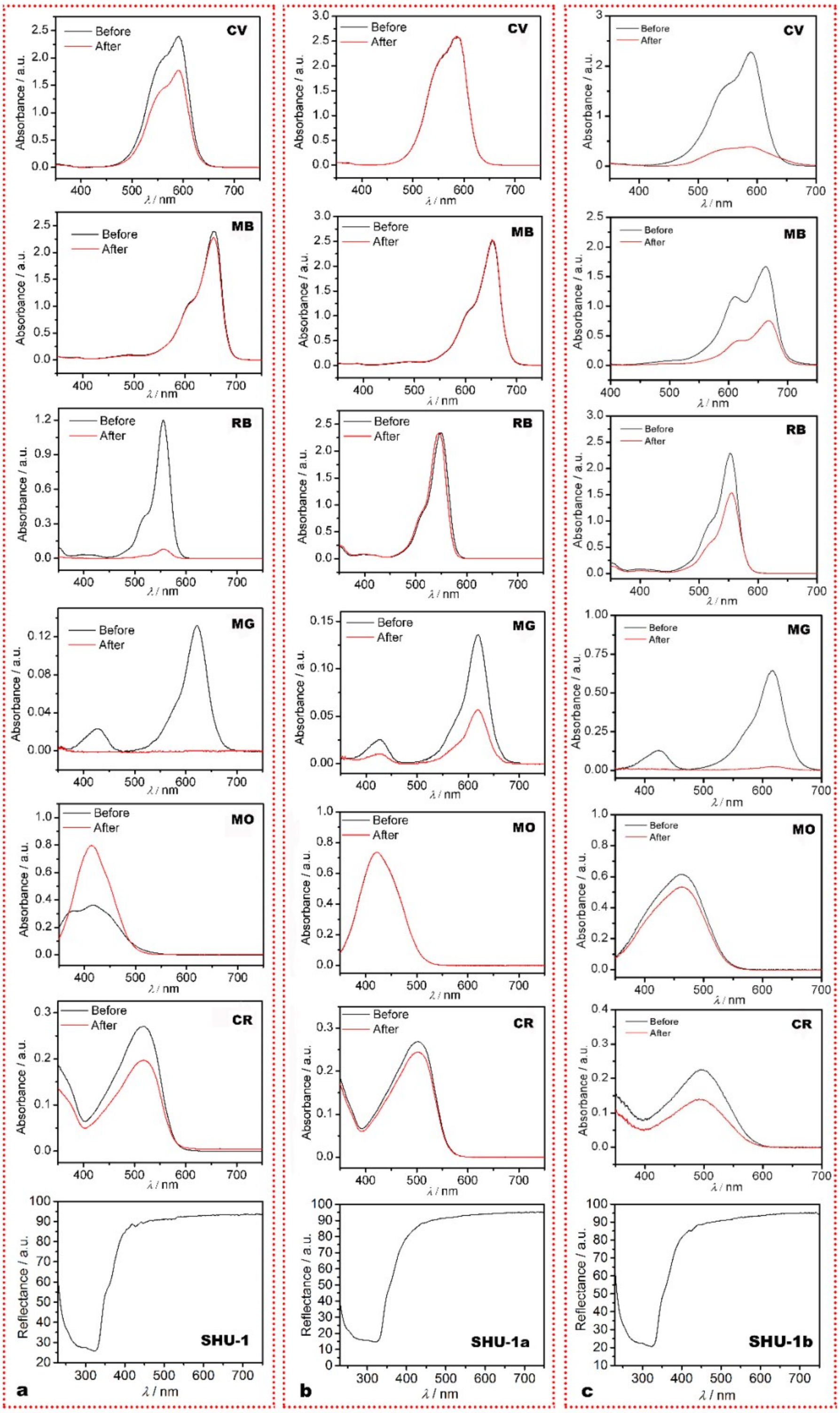


Figure S11. UV-vis absorption spectra before and after dye adsorption, (a) **SHU-1**, (b) **SHU-1a**, (c) **SHU-1b**. At the bottom of each column, UV-vis diffuse reflectance spectra were given.

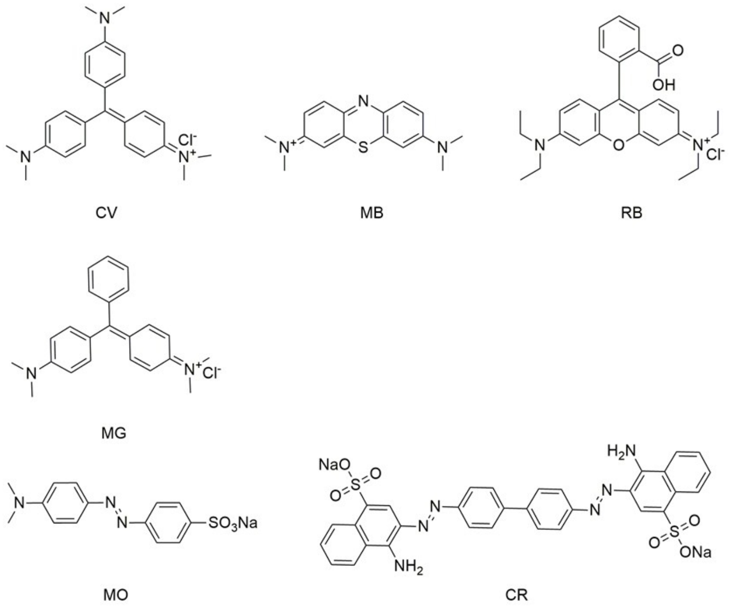


Figure S12. Structures and abbreviations of organic dyes.

Table S2. Dye adsorption capacities for **SHU-1**, **SHU-1a** and **SHU-1b**.

Compound	q_e / μmol·g^{-1}							Solvent and Adsorption Time
	CV	MB	RB	MO	CR	MG-1	MG-2	
SHU-1	1.73	0.47	6.20	0	1.85	6.67	51.50	Acetone, 48 h
SHU-1a	0.01	0.11	0	0.02	0.68	4.33	40.58	Methanol, 4 h
SHU-1b	5.44	3.73	2.13	0.88	2.56	6.33	94.40	Water, 1 h

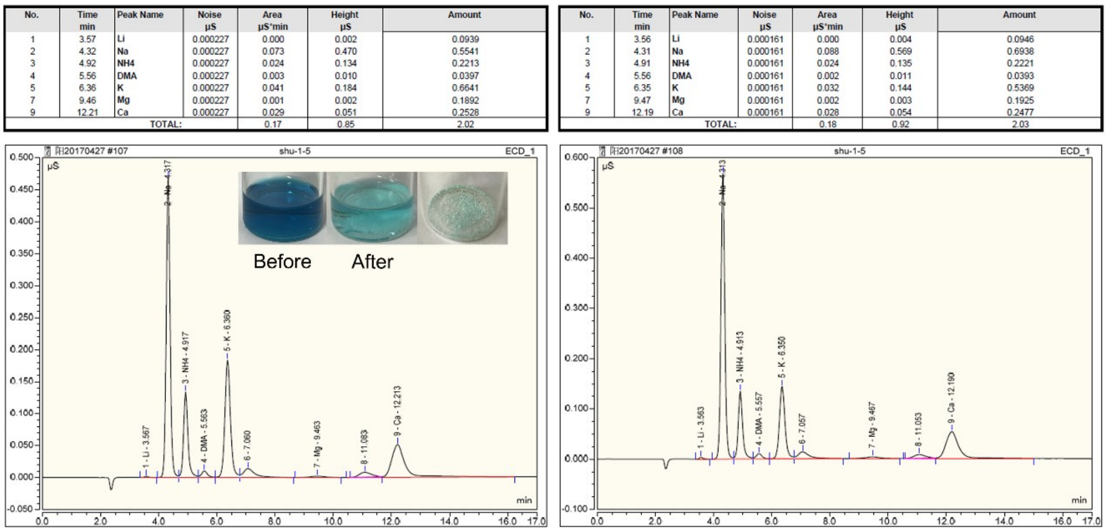
The initial concentration: CV, MB, RB, MO, CR, MG-1, 5.00×10^{-5} mol·L^{-1}; MG-2 4.00×10^{-4} mol·L^{-1} for **SHU-1** and **SHU-1a**, 8.00×10^{-4} mol·L^{-1} for **SHU-1b**.

Table S3. Dye adsorption capacities for **SHU-1b** and other adsorbents.

Adsorbents	q_e / mg·g^{-1}	Temperature / ˚C	Reference
SHU-1b	34.5	25	This work
activated carbons (ACC)	8.3	25	S6
natural zeolite	24.5	25	S7
MIL-53	34.9	30	S8
MIL-100(Fe)	266	30	S8
chitosan bead	93.6	30	S9

6. Ion Chromatography Measurements

SHU-1 (34.2 mg) was added into a Teflon lined screw cap vial (20 mL), and 4 mL of acetone solution of MG (4.00×10^{-4} mol·L^{-1}) was added. The cap was screwed on tightly, and the vial was shaken on an orbital shaker (HZQ-50H by Shanghai Yiheng) with a speed of 180 rpm in the dark for 48 h. The solution was filtered by a syringe membrane filter with a pore size of 0.22 μm, and then the filtrate was diluted 5 times by water. The diluted solution was pretreated by RP column to removed residual MG, and subjected to ion chromatography for further analysis.



No.	Time min	Peak Name	Noise µS	Area µS*min	Height µS	Amount
1	3.57	Li	0.000227	0.000	0.002	0.0939
2	4.32	Na	0.000227	0.073	0.470	0.5541
3	4.92	NH4	0.000227	0.024	0.134	0.2213
4	5.56	DMA	0.000227	0.003	0.010	0.0397
5	6.36	K	0.000227	0.041	0.184	0.6641
7	9.46	Mg	0.000227	0.001	0.002	0.1892
9	12.21	Ca	0.000227	0.029	0.051	0.2528
TOTAL:				0.17	0.85	2.02

No.	Time min	Peak Name	Noise µS	Area µS*min	Height µS	Amount
1	3.56	Li	0.000161	0.000	0.004	0.0946
2	4.31	Na	0.000161	0.088	0.569	0.6938
3	4.91	NH4	0.000161	0.024	0.135	0.2221
4	5.56	DMA	0.000161	0.002	0.011	0.0393
5	6.35	K	0.000161	0.032	0.144	0.5369
7	9.47	Mg	0.000161	0.002	0.003	0.1925
9	12.19	Ca	0.000161	0.028	0.054	0.2477
TOTAL:				0.18	0.92	2.03

Figure S13. The results for parallel tests of ion chromatography after MG adsorption, and the insets shows the color changes of solution and samples.

The blank and specificity experiments of $(CH_3)_2NH_2^+$ (DMA) have been conducted, and the calibration curves showed a good linearity of the analysis system. Parallel tests have been carried out for the analysis of the exchanged amount of DMA (**Fig. S13**). The results showed the retention time of DMA was ca. 5.56 min, and the content of DMA was ca. 0.0395 mg/kg in eluent. The exchanged amount of DMA was 2.31×10^{-5} mg per mg of **SHU-1**.

7. Vapor Induced Structural Transformations

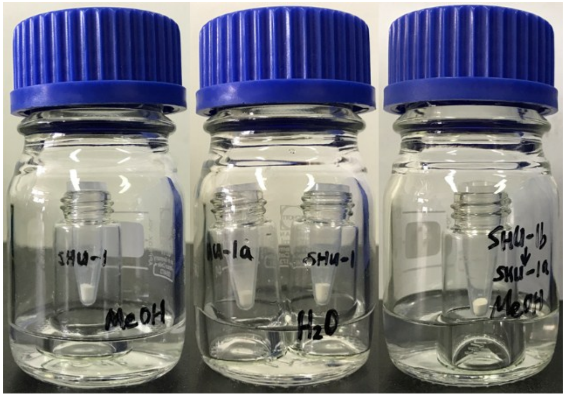


Figure S14. The setup for vapor induced structural transformations.

As shown in **Fig. S14**, ground sample of **SHU-1**, **SHU-1a** or **SHU-1b** in 1.5 mL PCR strip tube was placed in 50 mL DURAN® laboratory glass bottle containing excess solvent. The bottle was sealed tightly and standing undisturbed, and PXRD measurements were conducted at fixed intervals. During the whole process, no dissolution of samples was observed.

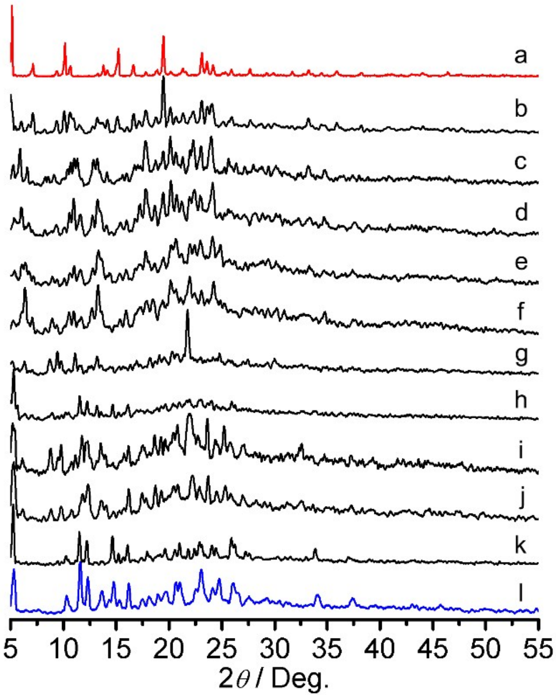


Figure S15. Vapor (methanol) induced structural transformations from **SHU-1** to **SHU-1a**. (a) As synthesized **SHU-1**, 0 h; (b) 32 h; (c) 56 h; (d) 94 h; (e) 142 h; (f) 190 h; (g) 238 h; (h) 286 h; (i) 334 h; (j) 382 h; (k) 670 h; (l) As synthesized **SHU-1a**.

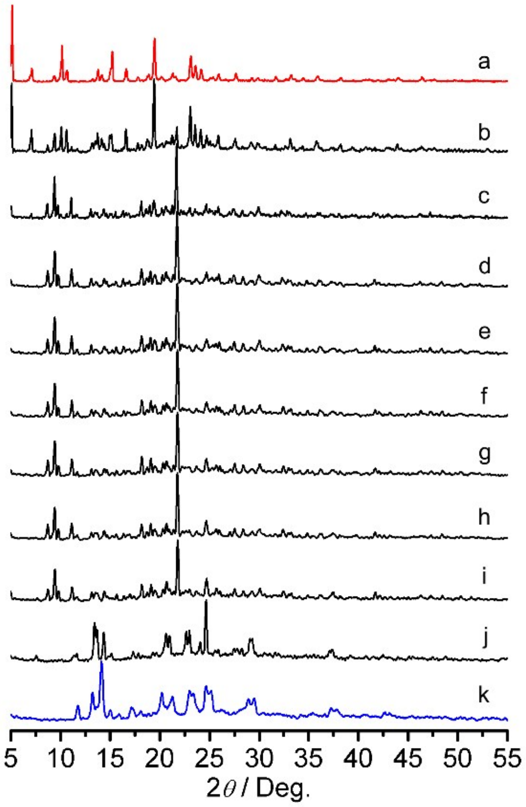


Figure S16. Vapor (water) induced structural transformations from **SHU-1** to **SHU-1b**. (a) As synthesized **SHU-1**, 0 h; (b) 32 h; (c) 56 h; (d) 94 h; (e) 142 h; (f) 190 h; (g) 238 h; (h) 286 h; (i) 334 h; (j) phase i soaked in water for 27 h; (k) As synthesized **SHU-1b**.

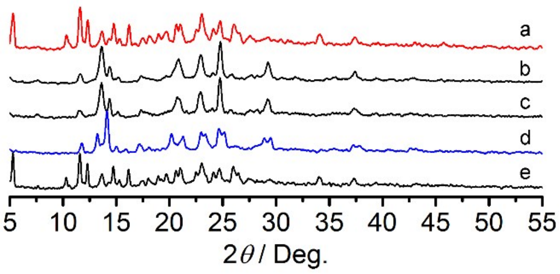


Figure S17. Vapor induced structural transformations between **SHU-1a** and **SHU-1b**. (a) As synthesized **SHU-1a**, 0 h; (b) in water vapor for 32 h; (c) in water vapor for 56 h; (d) As synthesized **SHU-1b**; (e) phase c in methanol vapor for 45 h.

8. Reference

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