Supporting Information

for

Temperature, light and solvent-induced spin transition in a 3D 2-fold interpenetrated PtS-type porous coordination polymer

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Experimental Section

All reagents were obtained from commercial sources and used as received. The ligand 4,4′,4″,4‴-tetrakis(4-pyridylethen-2-yl)tetraphenylmethane (tppm) was synthesized by a literature method.[1]

Power X-ray diffraction data were recorded on Panalytical X'pert PRO diffractometer at 298K. Magnetic measurements were carried out on a Quantum Design SQUID magnetometer working in the 2-300 K temperature range with 1.5 K min^{-1} sweeping rate under a magnetic field of 5000 Oe.

Nitrogen adsorption (Surface area, BET) was carried out on a Micromerities Tristar II Surface Area and Porosity Analyzer at 77 K.

Synthesis of $1{\cdot}5CH_3OH{\cdot}2CH_2Cl_2$: A CH_2Cl_2 solution (5 mL) of tppm (7.32 mg, 0.01 mmol) was placed in the bottom of a tube, upon which a 10 mL MeOH/CH_2Cl_2 solution (v/v = 1:15) was layered, then a MeOH solution (5 mL) of $Fe(SCN)_2$ (0.01 mmol in 5 mL) was carefully layered. The tube was sealed under nitrogen, and single crystals of $\mathbf{1}{\cdot}5CH_3OH{\cdot}2CH_2Cl_2$ suitable for X-ray diffraction analysis were obtained in 3 weeks. The amount of solvent molecules contained in the crystal was determined by elemental and thermogravimetric analysis results. Elemental analysis calcd (%) for $C_{62}H_{64}O_5N_6S_2Cl_4Fe$: C 60.30, H 5.223, N 6.805. Found: C 60.36, H 5.669, N 6.432. Elemental analysis calcd (%) for the solvent-free sample (under vacuum at 50 °C for 2 h, $C_{55}H_{40}N_6S_2Fe$): C 73.00, H 4.455, N 9.287. Found: C 72.54, H 4.469, N 9.211. IR (KBr pellet, cm^{-1}): 3418, 3026, 2046, 1598, 1506, 1419, 1199, 1016, 968, 820.

Crystallographic Data Collection and Structure Determination.

X-ray diffraction data were recorded on Agilent SuperNova diffractometer at 153 and 200 K, respectively. The structure was solved by direct method and refined by full-matrix least-squares techniques on F^2 with SHELXL-97.[2] Non-hydrogen atoms were refined anisotropically, hydrogen atoms were generated geometrically and refined isotropically. Attempts to define the highly disordered solvent molecules were unsuccessful, so the structure was refined with the PLATON[3] "SQUEEZE" procedure. Void channels were calculated by Mercury[4] "Void" command.

Squeeze details for **1** at 153K: Approximately 69.8% of the unit cell volume comprises a large region of disordered solvent which could not be modeled as discrete atomic sites. We employed PLATON SQUEEZE to calculate the contribution to the diffraction from the solvent region and thereby produced a set of solvent-free diffraction intensities. SQUEEZE estimated a total count of 1574.9 electrons per unit cell. According to the final formula which

was calculated from TGA combined with elemental analysis data, these electrons were assigned to be 40 methanol and 16 dichloromethane molecules per unit cell. The F(000) value with solvent is 5152, Mu (mm^{-1}) value with solvent is 2.348, and crystal density with solvent is 0.677. The final formula was calculated from TGA combined with elemental analysis data.

Squeeze details for **1** at 200K: Approximately 66.4% of the unit cell volume comprises a large region of disordered solvent which could not be modeled as discrete atomic sites. We employed PLATON SQUEEZE to calculate the contribution to the diffraction from the solvent region and thereby produced a set of solvent-free diffraction intensities. SQUEEZE estimated a total count of 748 electrons per unit cell. According to the final formula which was calculated from TGA combined with elemental analysis data, these electrons were assigned to be 20 methanol and 8 dichloromethane molecules per unit cell. The F(000) value with solvent is 2576, Mu (mm^{-1}) value with solvent is 2.231, and crystal density with solvent is 0.644. The final formula was calculated from TGA combined with elemental analysis data.

Crystal data of **1**·$5CH_3OH$·$2CH_2Cl_2$ at 153 K: $C_{55}H_{40}N_6S_2Fe$ (solvent-free formula), FW = 904.92 g mol^{-1}, orthorhombic, *Pnna* (no. 52), a = 16.9124(7) Å, b = 40.300(4) Å, c = 35.5336(13) Å, V = 24218(3) $Å^3$; Z = 8, D_c = 0.496 g cm^{-3}, final $R1$ = 0.0938 and $wR2$ = 0.2304 for $I > 2\sigma(I)$, 51639 reflections, 16637 unique reflections.

Crystal data of **1**·$5CH_3OH$·$2CH_2Cl_2$ at 200 K: $C_{55}H_{40}N_6S_2Fe$ (solvent-free formula), FW = 904.92 g mol^{-1}, orthorhombic, *Pban* (no. 50), a = 17.2737(11) Å, b = 35.4221(17) Å, c = 20.8250(17) Å, V = 12742.2(15) $Å^3$; Z = 4, D_c = 0.472 g cm^{-3}, final $R1$ = 0.1110 and $wR2$ = 0.2977 for $I > 2\sigma(I)$, 27965 reflections, 10446 unique reflections.

[1] A. M. W. C. Thompson, J. Hock, J. A. McCleverty and M. D. Ward, *Inorg. Chim. Acta*, 1997, **256**, 331-334.

[2] a) A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, b115-119; b) G. M. Sheldrick, *SHELXL-97*; Program for refinement of crystal structures. University of Göttingen, Göttingen, Germany, **1997**.

[3] A. L. Spek, Utrecht University: Utrecht, The Netherlands, **1998**; b) A. L. Spek, *Acta Cryst.* 2009, D65, 148-155.

[4] a) R. Taylor, C. F. Macrae, *Acta Cryst.*, 2001, B57, 815-827; b) I. J. Bruno, J. C. Cole, P. R. Edgington, M. K. Kessler, C. F. Macrae, P. McCabe, J. Pearson and R. Taylor, *Acta Cryst.*, 2002, B58, 389-397; c) C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Cryst.*, 2006, **39**, 453-457; d) C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Cryst.*, 2008, **41**, 466-470.

Guest Exchange: Samples **1**·CH_3OH, **1**·C_2H_5OH, **1**·CH_2Cl_2, **1**·$CHCl_3$, **1**·C_2H_5OH/CH_2Cl_2, **1**·$MeOH/CHCl_3$, **1**·$C_2H_5OH/CHCl_3$, **1**·CH_3CN, **1**·CH_3COCH_3, and **1**·C_6H_{12} were obtained

by guest exchange through immersion of the as-synthesized sample **1**·5CH_3OH·2CH_2Cl_2 (~ 10 mg) in respectively pure solvents (20 mL) for 3 times. As for the mixed solvent, the v/v ratio is 1:1. Elemental analysis results see Table S4, PXRD patterns see Figure S5.

Table S1. Crystal data and structural refinements for **1**·5CH_3OH·2CH_2Cl_2.

Temperature	153 K (solvent-free)	153 K	200 K (solvent-free)	200 K
Formula	$C_{55}H_{40}N_6S_2Fe$	$C_{62}H_{64}Cl_4FeN_6O_5S_2$	$C_{55}H_{40}N_6S_2Fe$	$C_{62}H_{64}Cl_4FeN_6O_5S_2$
M_r / g mol^{-1}	904.92	1234.96	904.92	1234.96
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pnna*	*Pnna*	*Pban*	*Pban*
a / Å	16.9124(7)	16.9124(7)	17.2737(11)	17.2737(11)
b / Å	40.300(4)	40.300(4)	35.4221(17)	35.4221(17)
c / Å	35.5336(13)	35.5336(13)	20.8250(17)	20.8250(17)
V / Å^3	24218(3)	24218	12742.2(15)	12742.2(15)
Z	8	8	4	4
D_c / g cm^{-1}	0.496	0.677	0.472	0.644
F(000)	3760	5152	1880	2576
GOF	0.976	0.976	0.975	0.975
Final R1	0.0938	0.0938	0.1110	0.1110
wR2 indices (all data)	0.2304	0.2304	0.2977	0.2977

Table S2. Selected bond lengths and angles at 153 K.

Fe(1)-N(1)	2.000(4)	N(1)-Fe(1)-N(1)$^{\#1}$	90.2(2)	N(2)$^{\#5}$-Fe(2)-N(2)$^{\#6}$	90.1(4)
Fe(1)-N(1)$^{\#1}$	2.000(4)	N(3)$^{\#2}$-Fe(1)-N(1)	178.91(19)	N(4)$^{\#4}$-Fe(2)-N(2)$^{\#5}$	89.6(3)
Fe(1)-N(3)$^{\#2}$	1.981(4)	N(3)$^{\#2}$-Fe(1)-N(1)$^{\#1}$	88.82(15)	N(4)$^{\#4}$-Fe(2)-N(2)$^{\#6}$	179.6(4)
Fe(1)-N(3)$^{\#3}$	1.981(4)	N(3)$^{\#2}$-Fe(1)-N(3)$^{\#3}$	92.2(2)	N(4)$^{\#4}$-Fe(2)-N(4)	90.7(4)
Fe(1)-N(5)	1.899(14)	N(3)$^{\#3}$-Fe(1)-N(1)	88.82(15)	N(6)$^{\#4}$-Fe(2)-N(2)$^{\#5}$	89.3(4)
Fe(1)-N(5)$^{\#1}$	1.899(14)	N(3)$^{\#3}$-Fe(1)-N(1)$^{\#1}$	178.91(19)	N(6)$^{\#4}$-Fe(2)-N(2)$^{\#6}$	90.2(5)
Fe(2)-N(2)$^{\#5}$	2.173(4)	N(5)$^{\#1}$-Fe(1)-N(1)	91.2(3)	N(6)$^{\#4}$-Fe(2)-N(4)	90.4(4)
Fe(2)-N(2)$^{\#6}$	2.173(4)	N(5)$^{\#1}$-Fe(1)-N(1)$^{\#1}$	92.7(3)	N(6)$^{\#4}$-Fe(2)-N(4)$^{\#4}$	89.9(5)
Fe(2)-N(4)	2.153(6)	N(5)$^{\#1}$-Fe(1)-N(3)$^{\#2}$	88.5(3)	N(6)-Fe(2)-N(2)$^{\#5}$	90.2(5)
Fe(2)-N(4)$^{\#4}$	2.153(6)	N(5)$^{\#1}$-Fe(1)-N(3)$^{\#3}$	87.7(3)	N(6)-Fe(2)-N(2)$^{\#6}$	89.3(4)
Fe(2)-N(6)	1.870(11)	N(5)$^{\#1}$-Fe(1)-N(5)	174.5(5)	N(6)-Fe(2)-N(4)	89.9(5)
Fe(2)-N(6)$^{\#4}$	1.870(11)	N(5)-Fe(1)-N(1)	92.7(3)	N(6)-Fe(2)-N(4)$^{\#4}$	90.4(4)
		N(5)-Fe(1)-N(1)$^{\#1}$	91.2(3)	N(6)-Fe(2)-N(6)$^{\#4}$	179.3(6)
		N(5)-Fe(1)-N(3)$^{\#2}$	87.3(3)		
		N(5)-Fe(1)-N(3)$^{\#3}$	88.5(3)		

Symmetry codes: #1) $x, -y + 1/2, -z + 1/2$; #2) $x - 1, -y + 1/2, -z + 1/2$; #3) $x - 1, y, z$; #4) $-x + 3/2, -y, z$; #5) $-x + 3/2, y - 1/2, -z + 3/2$; #6) $x, -y + 1/2, -z + 3/2$.

Table S3. Selected bond lengths and angles at 200 K.

Fe(1)-N(1)	2.127(3)	$N(1)^{\#2}$-Fe(1)-N(1)	90.88(18)	$N(2)^{\#4}$-Fe(2)-$N(2)^{\#6}$	177.8(9)
Fe(1)-$N(1)^{\#1}$	2.127(3)	$N(1)^{\#2}$-Fe(1)-$N(1)^{\#1}$	179.1(3)	$N(2)^{\#5}$-Fe(2)-N(2)	177.8(9)
Fe(1)-$N(1)^{\#2}$	2.127(3)	$N(1)^{\#2}$-Fe(1)-$N(1)^{\#3}$	89.12(18)	$N(2)^{\#5}$-Fe(2)-$N(2)^{\#4}$	90.5(8)
Fe(1)-$N(1)^{\#3}$	2.127(3)	$N(1)^{\#3}$-Fe(1)-$N(1)^{\#1}$	90.88(18)	$N(2)^{\#5}$-Fe(2)-$N(2)^{\#6}$	89.5(8)
Fe(1)-N(3)	2.004(16)	N(1)-Fe(1)-$N(1)^{\#1}$	89.12(18)	N(2)-Fe(2)-$N(2)^{\#4}$	89.5(4)
Fe(1)-$N(3)^{\#1}$	2.004(16)	N(1)-Fe(1)-$N(1)^{\#3}$	179.1(3)	N(2)-Fe(2)-$N(2)^{\#6}$	90.5(4)
Fe(2)-N(2)	2.220(4)	$N(3)^{\#1}$-Fe(1)-N(1)	90.46(13)	$N(4)^{\#4}$-Fe(2)-N(2)	91.0(2)
Fe(2)-$N(2)^{\#4}$	2.220(8)	$N(3)^{\#1}$-Fe(1)-$N(1)^{\#1}$	89.55(13)	$N(4)^{\#4}$-Fe(2)-$N(2)^{\#4}$	88.9 (5)
Fe(2)-$N(2)^{\#5}$	2.220(4)	$N(3)^{\#1}$-Fe(1)-$N(1)^{\#2}$	89.55(13)	$N(4)^{\#4}$-Fe(2)-$N(2)^{\#5}$	91.0(7)
Fe(2)-$N(2)^{\#6}$	2.220(4)	$N(3)^{\#1}$-Fe(1)-$N(1)^{\#3}$	90.46(13)	$N(4)^{\#4}$-Fe(2)-$N(2)^{\#6}$	88.9 (5)
Fe(2)-N(4)	1.972(14)	N(3)-Fe(1)-N(1)	89.55(13)	N(4)-Fe(2)-N(2)	88.9(2)
Fe(2)-$N(4)^{\#4}$	1.972(14)	N(3)-Fe(1)-$N(1)^{\#1}$	90.46(13)	N(4)-Fe(2)-$N(2)^{\#4}$	91.0(5)
		N(3)-Fe(1)-$N(1)^{\#2}$	90.46(13)	N(4)-Fe(2)-$N(2)^{\#5}$	88.9(7)
		N(3)-Fe(1)-$N(1)^{\#3}$	89.55(13)	N(4)-Fe(2)-$N(2)^{\#6}$	91.0(5)
		N(3)-Fe(1)-$N(3)^{\#1}$	180.0	N(4)-Fe(2)-$N(4)^{\#4}$	180.0

Symmetry codes: #1) $x, -y + 1/2, -z + 1$; #2) $-x + 1/2, y, -z + 1$; #3) $-x + 1/2, -y + 1/2, z$; #4) $-x + 3/2, -y + 3/2, z$; #5) $x, -y + 3/2, -z + 2$; #6) $-x + 3/2, y, -z + 2$.

Table S4. Elemental analysis of **1** encapsulating various guest molecules.

Solvent	Content [%]		Fitting Formula	calc. [%]	Solvent	Content [%]		Fitting Formula	calc. [%]
MeOH	N:	6.935	$[Fe(NCS)_2(tppm)]$	6.684	$MeOH/CH_2Cl_2$	N:	6.432	$[Fe(NCS)_2(tppm)]$	6.80
	C:	62.91	$\cdot 11CH_3OH$	63.04		C:	60.36	$\cdot 5MeOH\cdot 2CH_2Cl_2$	60.30
	H:	6.857		6.734		H:	5.669		5.223
EtOH	N:	6.524	$[Fe(NCS)_2(tppm)]$	6.599	$EtOH/CH_2Cl_2$	N:	6.763	$[Fe(NCS)_2(tppm)]$	6.675
	C:	66.86	$\cdot 8C_2H_5OH$	66.96		C:	61.65	$\cdot 4EtOH\cdot 2CH_2Cl_2$	62.01
	H:	6.864		6.965		H:	5.96		5.444
CH_2Cl_2	N:	7.351	$[Fe(NCS)_2(tppm)]$	6.991	$MeOH/CHCl_3$	N:	6.847	$[Fe(NCS)_2(tppm)]$	6.562
	C:	58.24	$\cdot 3.5CH_2Cl_2$	58.45		C:	59.66	$\cdot 8CH_3OH\cdot 3CHCl_3$	60.03
	H:	4.334		3.941		H:	5.528		5.746
$CHCl_3$	N:	6.424	$[Fe(NCS)_2(tppm)]$	6.65	$EtOH/CHCl_3$	N:	6.187	$[Fe(NCS)_2(tppm)]$	6.451
	C:	55.46	$\cdot 3CHCl_3$	55.52		C:	62.71	$\cdot 6C_2H_5OH\cdot 3CHCl_3$	62.79
	H:	3.856		3.432		H:	6.064		5.967
CH_3CN	N:	16.94	$[Fe(NCS)_2(tppm)$	17.04	cyclohexane	N:	6.985	$[Fe(NCS)_2(tppm)$	7.261
	C:	68.17	$\cdot 10CH_3CN$	68.48		C:	75.55	$\cdot 3C_6H_{12}$	75.75
	H:	5.721		5.364		H:	6.456		6.619
acetone	N:	7.360	$[Fe(NCS)_2(tppm)$	7.031					
	C:	70.30	$\cdot 5CH_3COCH_3$	70.34					
	H:	6.007		5.903					

Additional Figures

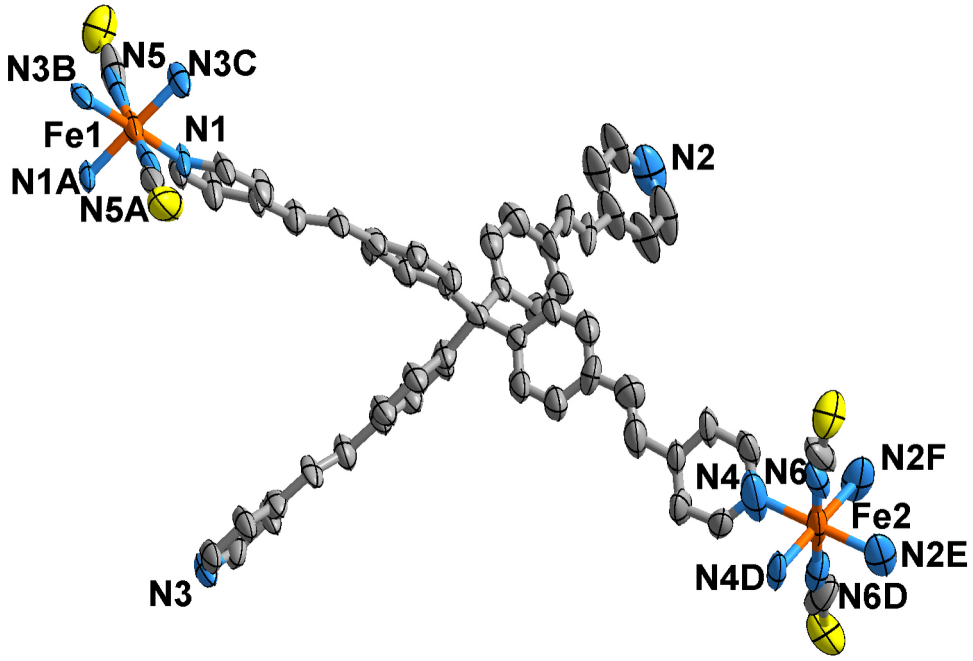

Figure S1. Coordination environment of the Fe^{II} atoms in **1** at 153 K.

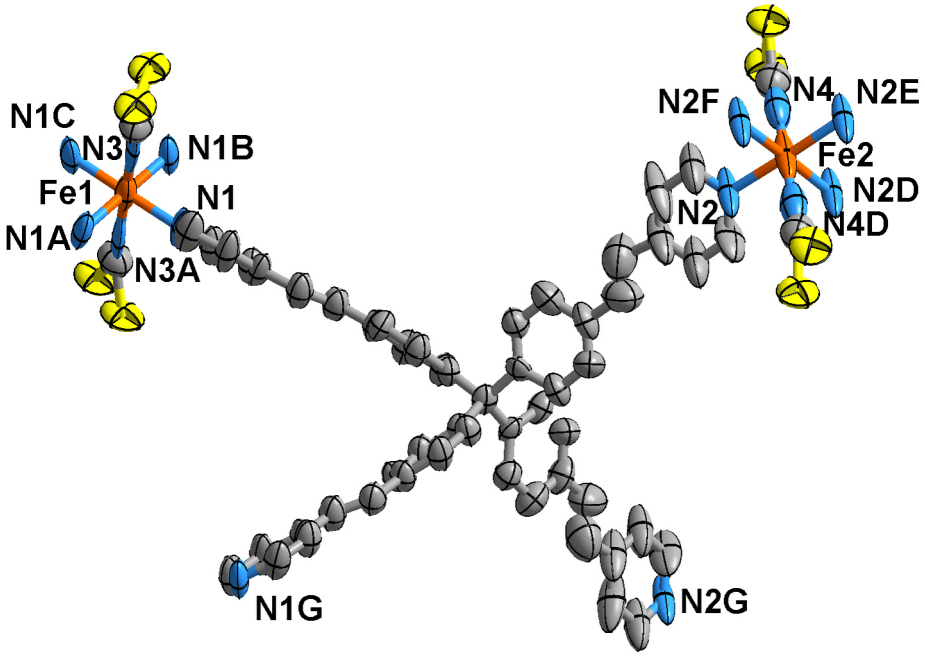

Figure S2. Coordination environment of the Fe^{II} atoms in **1** at 200 K.

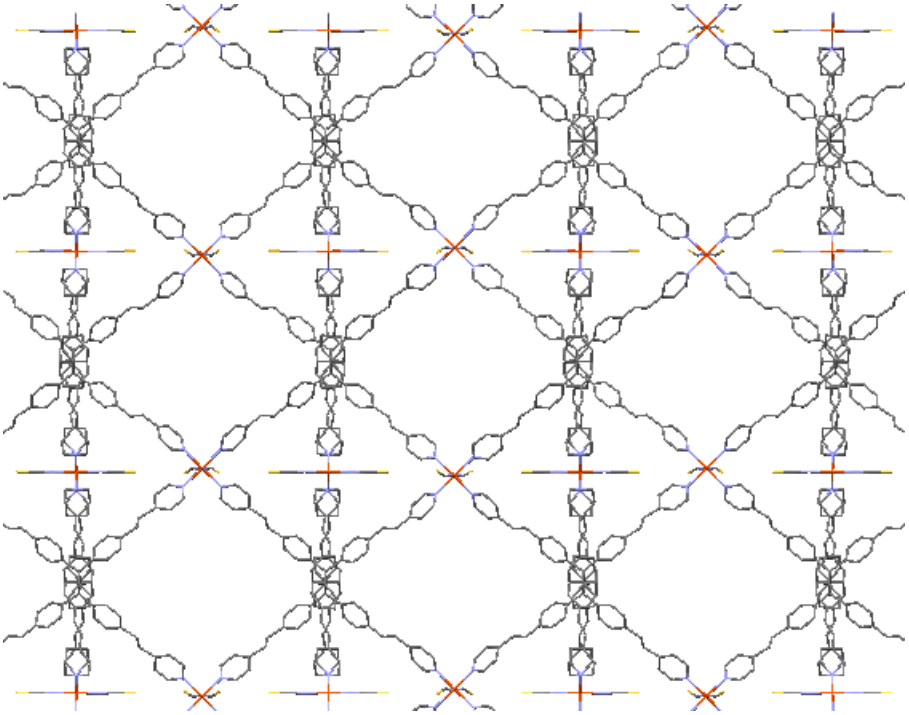

Figure S3. 2-fold interpenetrated 3D structure of **1** along the *a* axis.

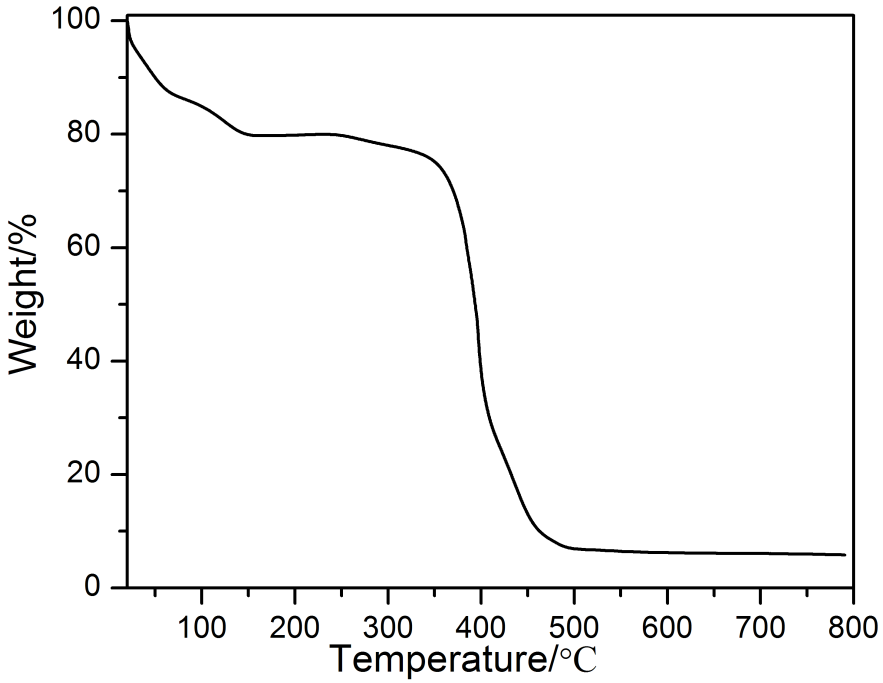

Figure S4. Thermogravimetric analysis of **1**·5CH_3OH·2CH_2Cl_2.

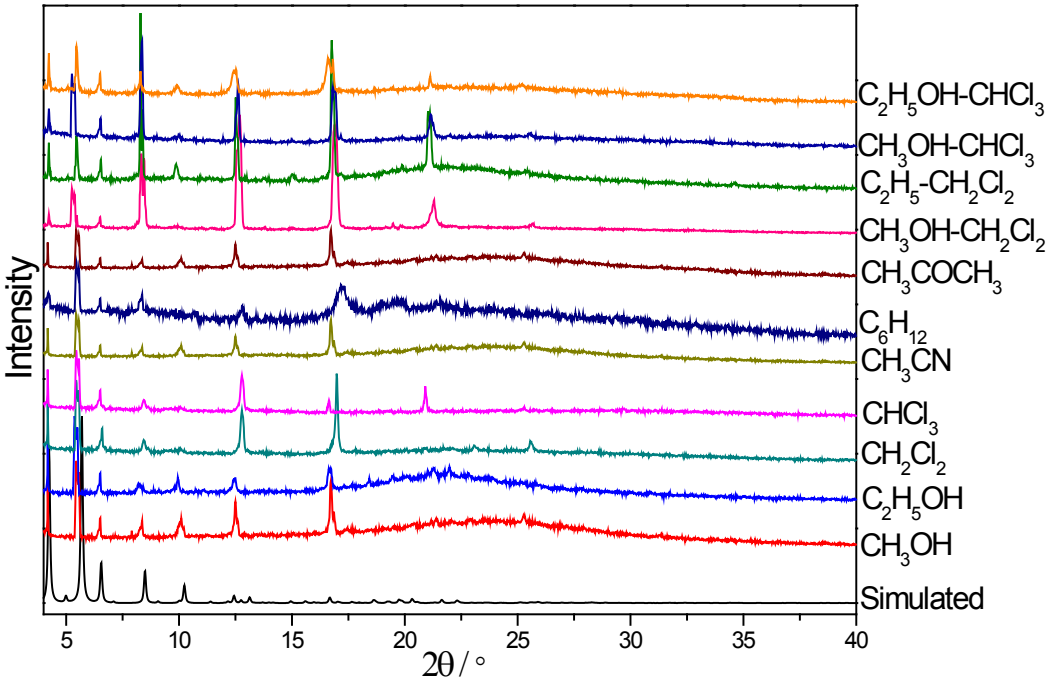

Figure S5. PXRD pattern of **1** encapsulating various solvent molecules at 298 K.

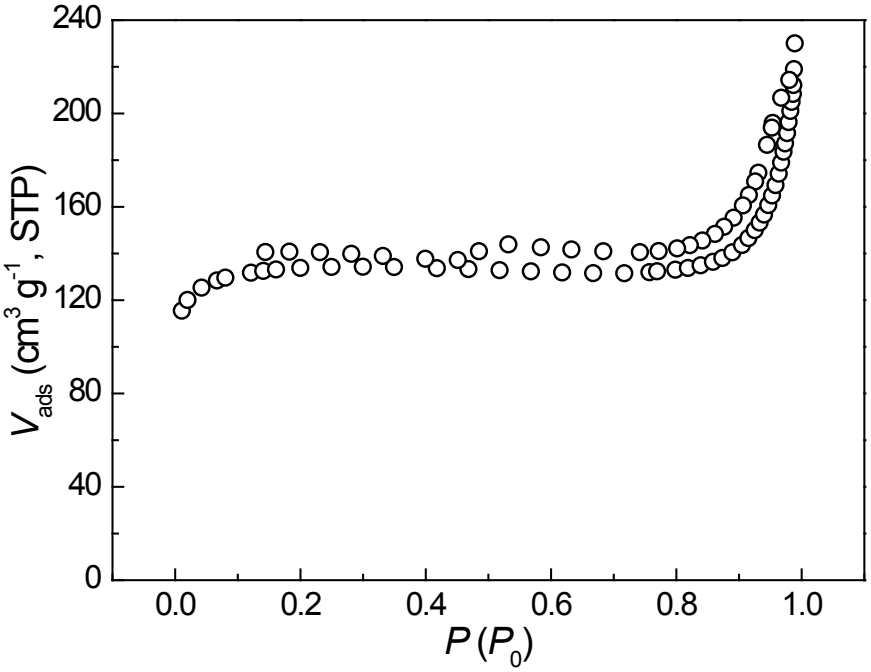

Figure S6. N_2 Adsorption-desorption isotherms of the activated sample **1** at 77 K. Brunauer−Emmett−Teller (BET) surface area is found to be 451.84 m^2 g^{-1} at 77 K.