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A Three-Dimensional Porous Supramolecular Architecture *via* π–π Assembly of Two-Dimensional Metal-Organic Frameworks (MOFs): Structure-versus-Luminescence Reversibility and Gas Adsorption Property

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Figure S4. The solid state absorption of **1** at RT (black), -120 °C (blue) and 120 °C (red). Note that all absorptions have been normalized.

Experimental Section

Materials and Physical Techniques. General: All chemicals were of reagent grade and were used as commercially obtained without further purification. Elementary analyses (carbon, hydrogen and nitrogen) were performed using a Perkin-Elmer 2400 elemental analyzer. IR spectra were recorded on a Nicolet Fourier Transform IR, MAGNA-IR 500 spectrometer in the range of 500 – 4000 cm^{-1} using the KBr disc technique. Thermogravimetric analysis (TGA) of compound **1** was performed on a computer-controlled Perkin-Elmer 7 Series/UNIX TGA7 analyzer. Single-phased powder samples were loaded into alumina pans and heated with a ramp rate of 5 °C/min from room temperature to 800 °C under a nitrogen atmosphere.

Synthesis of $\{[Zn(dpds)(bdc)]\cdot MeOH\cdot 2H_2O\}_n$ (1): A H_2O/MeOH solution (4 mL) of disodium terephthalate (Na_2bdc, 0.0021 g, 0.01 mmol) was added to a H_2O/MeOH solution (8 mL) of $Zn(ClO_4)\cdot 6H_2O$ (0.0010 g, 0.01 mmol) and 4,4'-dipyridyldisulfide (dpds, 0.0022g, 0.01 mmol) at room temperature to give a colorless solution. Colorless block-like crystals of **1** were obtained after several days in 41 % (0.0021 g) yield. Anal. Calc. for $C_{19}H_{20}ZnS_2N_2O_7$ (**1**): C 44.07, N 5.41, H 3.89. Found: C 44.27, N 5.33, H 4.21. IR (KBr pellet): ν = 3384 (m), 1597 (s), 1505 (m), 1486 (m), 1402 (s), 1382 (s), 1367 (s), 1319 (m), 1218 (m), 1064 (m), 827 (m), 749 (m), 719 (m) cm^{-1}.

Crystallographic Data Collections and Refinements of 1, de-solvated 1a and re-hydrated 1b. Single-crystal structural analysis of **1** was performed on a Siemens SMART diffractometer incorporating a CCD detector with Mo radiation (λ = 0.71073 Å) at −123 °C, where the structural analyses of compounds **1a** and **1b** were determined with the data collections of the crystal **1** being performed at 120 °C and de-solvated/re-hydrated crystal **1** being performed RT, respectively. A preliminary orientation matrix and unit cell parameters were determined from 3 runs of 15 frames each, and each frame corresponded to a 0.3° scan in 10 s, following by spot integration and least-squares refinement. Data collections were measured using ω scans of 0.3° per frame for 20 s until a complete hemisphere had been collected. Cell parameters were retrieved using SMART[1] software and refined with SAINT[24] on all observed reflections. Data reduction was performed with the SAINT[2] software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS.[3] Direct phase determination and subsequent difference Fourier map synthesis yielded the positions of all non-hydrogen atoms, which were subject to anisotropic refinements. All hydrogen atoms were generated geometrically with the exception of the hydrogen atoms attached to the oxygen atoms of the crystallized methanol and water molecules, which were located in the difference Fourier map with the corresponding positions and isotropic displacement parameters being refined. The occupancy of methanol O7 and C19 atoms in compound **1** and water O5 and O6 atoms in compound **1b** are refined. The final full-matrix and least-squares refinement on F^2 were applied for all observed reflections [$I > 2\sigma(I)$]. All calculations were performed using the SHELXTL-PC V 5.03 software package.[4] Crystallographic data, details of data collections at different temperatures and structure refinements of compound **1** are listed in Table S1. CCDC 1015113, CCDC 1015114 and CCDC 1015115 for the **1**, **1a** and **1b**, respectively, contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internet.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

1. *SMART V 4.043 Software for CCD Detector System*; Siemens Analytical Instruments Division: Madison, WI, **1995**.
2. *SAINT V 4.035 Software for CCD Detector System*; Siemens Analytical Instruments Division: Madison, WI, **1995**.
3. Sheldrick, G. M. *Program for the Refinement of Crystal Structures*; University of

Göttingen: Göttingen, Germany, **1993**.

4. SHELXTL 5.03 (PC-Version), Program Liberary for Structure Solution and Molecular Graphics; Siemens Analytical Instruments Division: Madison, WI, **1995**.

***In situ* X-ray Powder diffraction of 1:** The powder X-ray diffraction pattern of **1** was recorded at the BL01C2 beamline of National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The ring of NSRRC was operated at energy 1.5 GeV with a typical current 300 mA with top-up injection mode. The wavelength of the incident X-rays was 1.0332 Å (12.0 KeV), delivered from the superconducting wavelength-shifting magnet and a Si(111) double-crystal monochromator. The diffraction pattern was recorded with a Mar345 imaging-plate detector approximately 300 mm from the sample and typical exposure duration of 5 min. The pixel size of Mar345 was 100 μm. The resolution is about 0.02° in 2θ. The one-dimensional powder diffraction profile was converted with program FIT2D and cake-type integration. The diffraction angles were calibrated according to Bragg positions of Ag-Benhenate and Si powder (NBS640b) standards. X-ray powder diffraction for **1** *in situ* was performed from 25 to 450 °C with approximately 4 °C/min heating rate. The powder sample was sealed in a quartz capillary (1.0 mm) and heated with a stream of hot air; each PXRD pattern *in situ* was exposed for about 3 min. The crystal structures of **1** at RT, 120, 150, and 180 °C were refined by Rietveld Method[5] of GSAS program.[6] (see Figure S1 in the supplementary materials)

5. Rietveld, H. M. *J. Appl. Cryst.* **1969**, *2,* 65.
6. Larson, A. C.; Von Dreele, R. B. General Structure Analysis System, Los Alamos National Laboratory, Los Alamos, NM, USA, **1994**.

Measurements of Gas Adsorption of 1a. The adsorption isotherm of N_2, H_2 (77 K) and CO_2

(195 K) was measured in the gaseous state by using BELSORP-max volumetric adsorption equipment from BEL, Osaka, Japan. In the sample cell (~1.8 cm^3) maintained at T ± 0.03 K was placed the adsorbent sample (~100 – 150 mg), which has been prepared at 200 °C for **1a** and 10^{-2} Pa for about 24 hours prior to measurement of the isotherm. The adsorbate was placed into the sample cell, and then the change of pressure was monitored and the degree of adsorption was determined by the decrease of pressure at equilibrium state. All operations were through automatically computer-controlled.

Spectral measurement of 1: UV–vis diffusive reflectance spectra of crystal **1** were obtained with a HITACHI U-3900H spectrophotometer equipped with an integrating sphere accessory (Al_2O_3 was used as a reference). In order to investigate the differences in photoluminescence of **1** under different temperatures dues to the variation of topologies, **1** was measured with a confocal mode of a MonoVista confocal Raman microscope system (Princeton Instruments/Acton) equipped with a Linkam THMS 600 hot stage (Linkam Scientific Instruments, United Kingdom), in which the optics have been specially made to allow both UV (up to 280 nm) excitation and emission. In this approach, a 325 nm laser line (He-Cd laser, KIMMON IK3301R-G) was used as an excitation source throughout the measurement. The photoluminescence was separated from the scattering light of excitation pulse by a edge filter with a cut-off wavelength of 325 nm (333AELP, Omega Optical) and sent by an optical fiber to the entrance slit of a polychromator (blazed at 500 nm) coupled with a sensitive charge coupled detector (CCD, Princeton Instruments, PI-MAX). The CCD was operated in shutter mode and the measurements were performed with 100 ms exposure time. All spectra were accumulated over an average of 10 scans.

Table S1. Crystal Data and Refinement Details of **1**, **1a** and **1b**.

	1	**1a**	**1b**
empirical formula	$C_{18.62}H_{18.47}N_2O_{6.62}S_2Zn_1$	$C_{18}H_{12}N_2O_4S_2Zn_1$	$C_{18}H_{14.2}N_2O_{5.1}S_2Zn_1$
formula mass (g mol^{-1})	505.67	449.79	469.60
Temperature (°C)	-123(2)	120(2)	22(2)
crystal system	Triclinic	Triclinic	Triclinic
space group	P-1	P-1	P-1
a, (Å)	9.4960(11)	9.6705(5)	9.5666(4)
b (Å)	11.5347(13)	11.6246(6)	11.5400(5)
c (Å)	11.8048(13)	11.7082(6)	11.8627(5)
α (deg)	67.494(2)	66.363(1)	67.610(1)
β (deg)	81.395(2)	82.283(1)	80.961(1)
γ (deg)	69.474(2)	68.217(1)	68.932(1)
V (Å^3)	1118.5(2)	1119.5(1)	1129.64(8)
Z	2	2	2
D_{calcd} (g cm^{-3})	1.501	1.334	1.381
μ (mm^{-1})	1.324	1.306	1.300
θ range (deg)	2.29–25.00	1.90–27.50	1.86–27.50
total no. of data collected	13798	12281	12869
no.of unique data	5117	4988	5106
no. of obsd data (I > 2σ(I))	4088	4209	4655
R_{int}	0.0538	0.0276	0.0213
refine params	270	245	255
R_1, wR_2[a] (I > 2σ(I))	0.0713, 0.1923	0.0383, 0.1070	0.0463, 0.1579
R_1, wR_2[a] (all data)	0.0873, 0.2036	0.0444, 0.1135	0.0491, 0.1604
GOF[b]	1.038	1.083	1.088

[a] $R_1 = \Sigma||F_o - F_c||/\Sigma|F_o|$; $wR_2(F^2) = [\Sigma w|F_o^2 - F_c^2|^2/\Sigma w(F_o^4)]^{1/2}$.

[b] $\mathrm{GOF} = \{\Sigma[w|F_o^2 - F_c^2|^2]/(n-p)\}^{1/2}$

Table S2. The O–H···O hydrogen bonds for **1** and **1b**, respectively.[a]

Compound 1

D–H···A (°)	D–H (Å)	H···A (Å)	D···A (Å)	∠ D–H···A (°)
O(5)–H(5A)···O(4)$_i$	0.87	1.97	2.788(5)	158
O(5)–H(5B)···O(2)$_{ii}$	0.86	1.93	2.758(5)	160
O(6)–H(6A)···O(5)	0.88	1.87	2.690(5)	154
O(6)–H(6B)···O(4)	0.91	2.22	3.056(5)	153

[a] Symmetry operations used to generate equivalent atoms: (i) −x−2, −y+3, −z+2 (ii) −x−1, −y+3, −z+2.

Compound 1b

D–H···A (°)	D–H (Å)	H···A (Å)	D···A (Å)	∠ D–H···A (°)
O(5)–H(5A)···O(4)$_i$	0.87	1.97	2.806(6)	159.2
O(5)–H(5B)···O(2)$_{ii}$	0.87	2.01	2.844(6)	160.4

[a] Symmetry operations used to generate equivalent atoms: (i) −x−2, −y+3, −z+2 (ii) −x−1, −y+3, −z+2.

Table S3. Crystal data of single crystal and powder sample for **1** at different temperatures.

Formula	$C_{18.62}H_{18.47}N_2O_{6.62}S_2Zn$ (crystal)	$C_{20}H_{24}N_2O_8Zn$ (crystal)	$C_{18}H_{14.2}N_2O_{5.1}S_2Zn$ (crystal)	$C_{20}H_{24}N_2O_8Zn$ (powder)	$C_{20}H_{20}N_2O_6Zn$ (powder)	$C_{20}H_{20}N_2O_6Zn$ (powder)
Wavelength / Å	0.7107	0.7107	0.7107	1.0332	1.0332	1.0332
Temperature / °C	−120	120	25	25	120	180
Space group	P −1	P −1	P −1	P −1	P −1	P −1
Cell parameters / Å	a = 9.4960(11), b = 11.5347(13), c = 11.8048(13), α = 67.494(2) β = 81.395(2) γ = 69.474(2)	a = 9.6705(5), b = 11.6246(6), c = 11.7082(6), α = 66.363(1) β = 82.283(1) γ = 68.217(1)	a = 9.5666(4), b = 11.5400(5), c = 11.8627(5), α = 67.610(1) β = 80.961(1) γ = 68.932(1)	a = 9.5690(4), b = 11.5318(4), c = 11.8784(4), α = 68.1815(34) β = 80.9362(33) γ = 69.2454(30)	a = 9.6568(4), b = 11.5798(5), c = 11.7351(5), α = 66.904(4) β = 81.739(5) γ = 68.369(4)	a = 9.6709(4), b = 11.6131(5), c = 11.7216(5), α = 66.281(4) β = 82.185(4) γ = 67.906(4)
Cell volume / Å^3	1118.5(2)	1119.50(10)	1129.64(8)	1137.39(4)	1122.09(4)	1116.57(4)
Z	2	2	2	2	2	2
R_1 / %	7.13	3.83	4.43			
R_1 / %	8.73	4.44	4.70			
GOF	1.038	1.083	1.131			
R_p / %				2.61	2.03	2.10
R_{wp} / %				3.78	3.13	2.84
χ^2				2.645	1.128	0.805

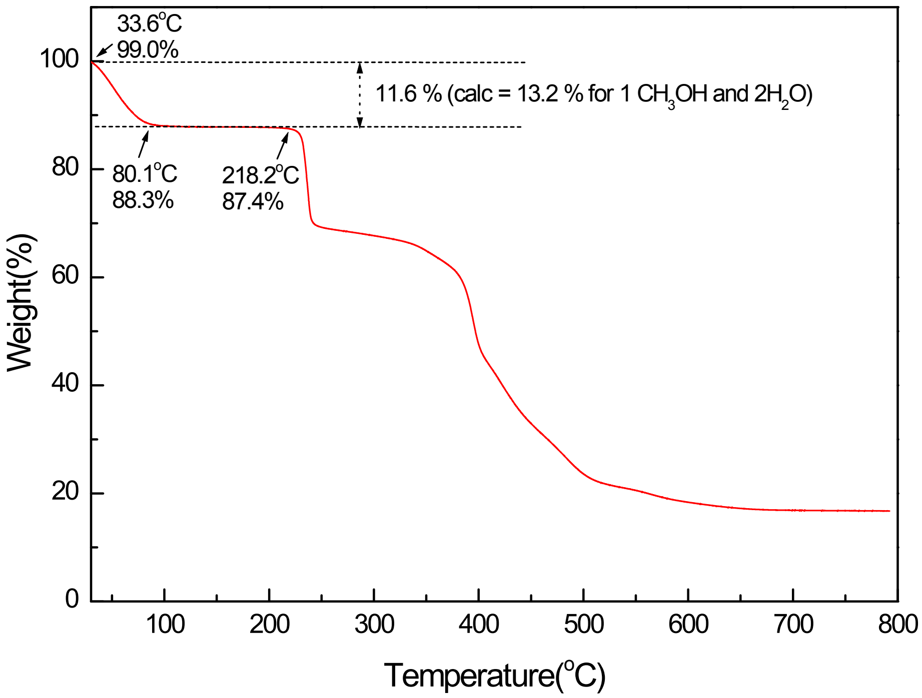
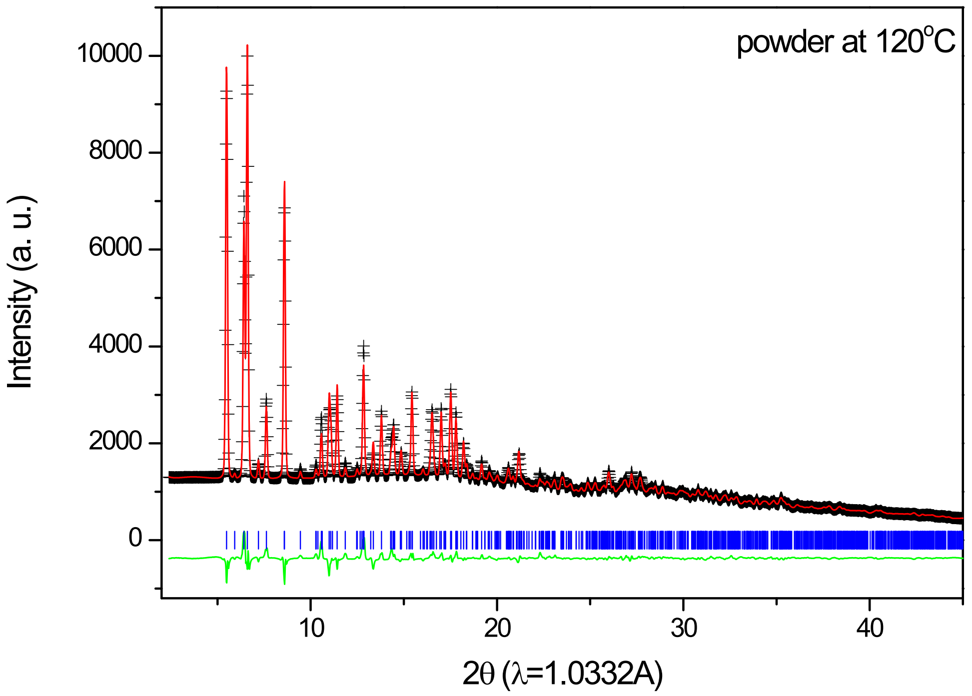
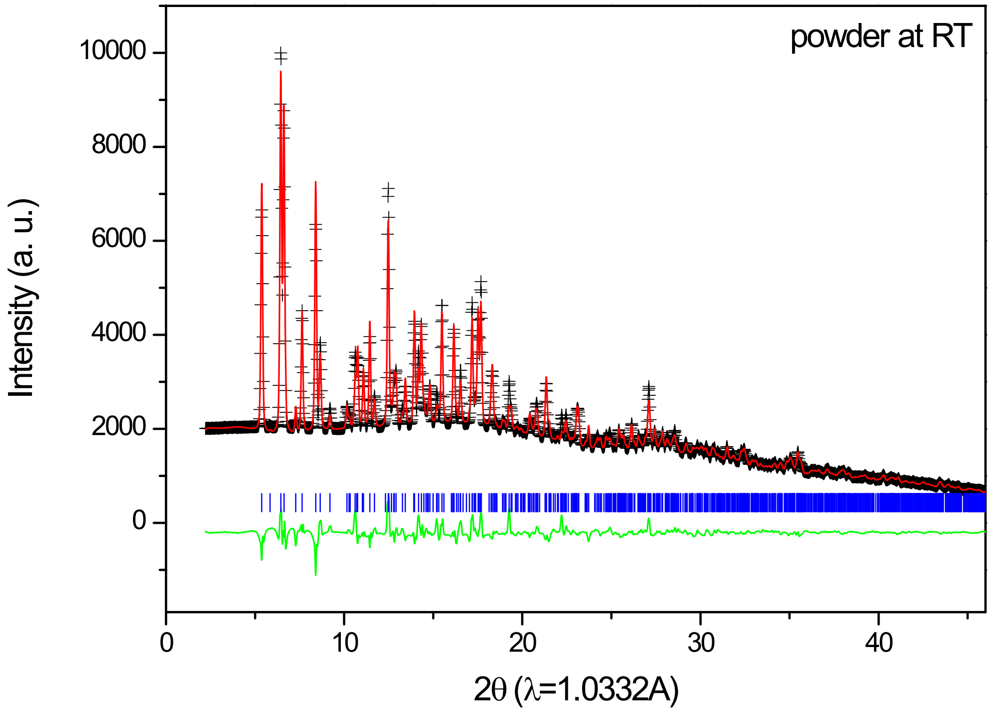

33.6°C
99.0%
11.6 % (calc = 13.2 % for 1 CH3OH and 2H2O)
80.1°C
88.3%
218.2°C
87.4%
Weight(%)
0
20
40
60
80
100
100
200
300
400
500
600
700
800
Temperature(°C)

Figure S1


powder at 120°C
Intensity (a. u.)
10000
8000
6000
4000
2000
0
10
20
30
40
2θ (λ=1.0332A)

(a)


powder at RT
Intensity (a. u.)
10000
8000
6000
4000
2000
0
0
10
20
30
40
2θ (λ=1.0332A)

(b)

Figure S2

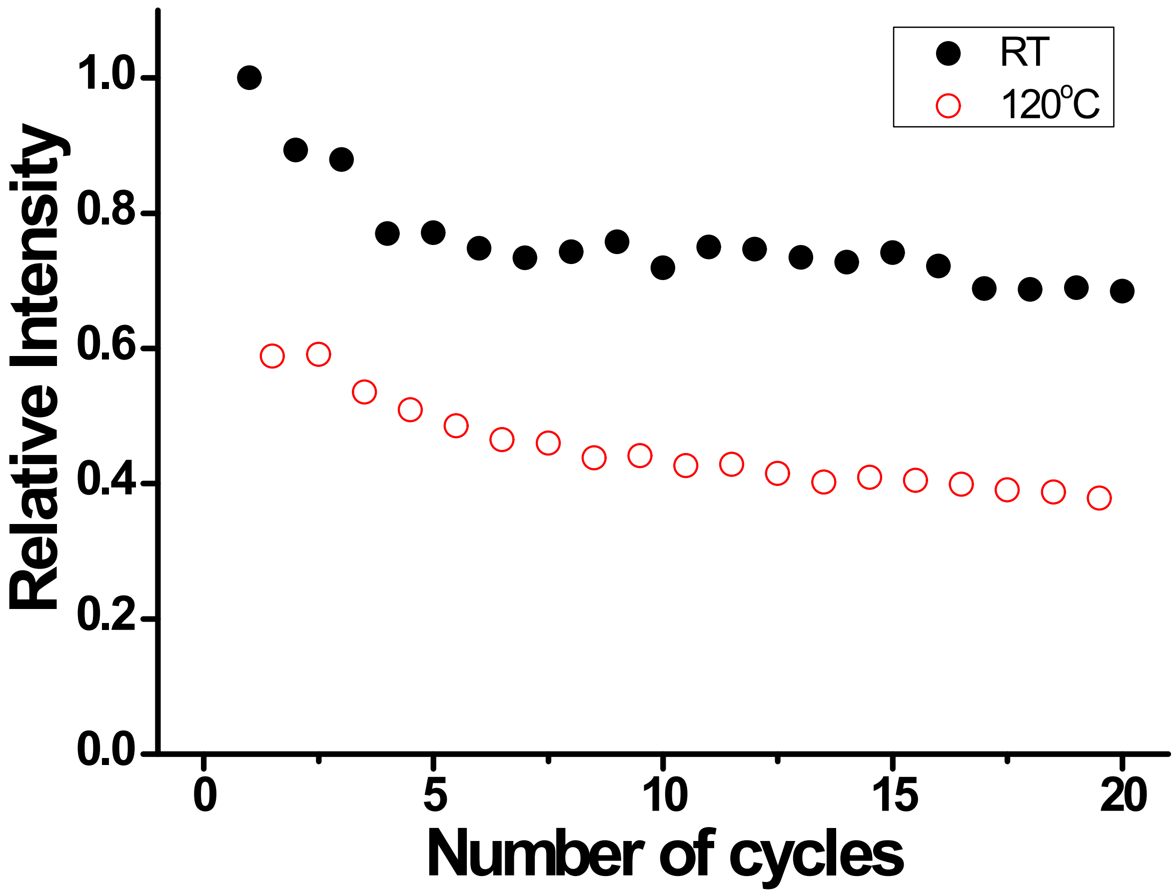


Figure S3. Relative emission changes of **1** induced by alternating RT to 120 °C heating–cooling cycle. Relative emission intensity represents the integrated fluorescence response. Excitation was provided at 325 nm, and the emission was integrated over 400 to 800 nm.

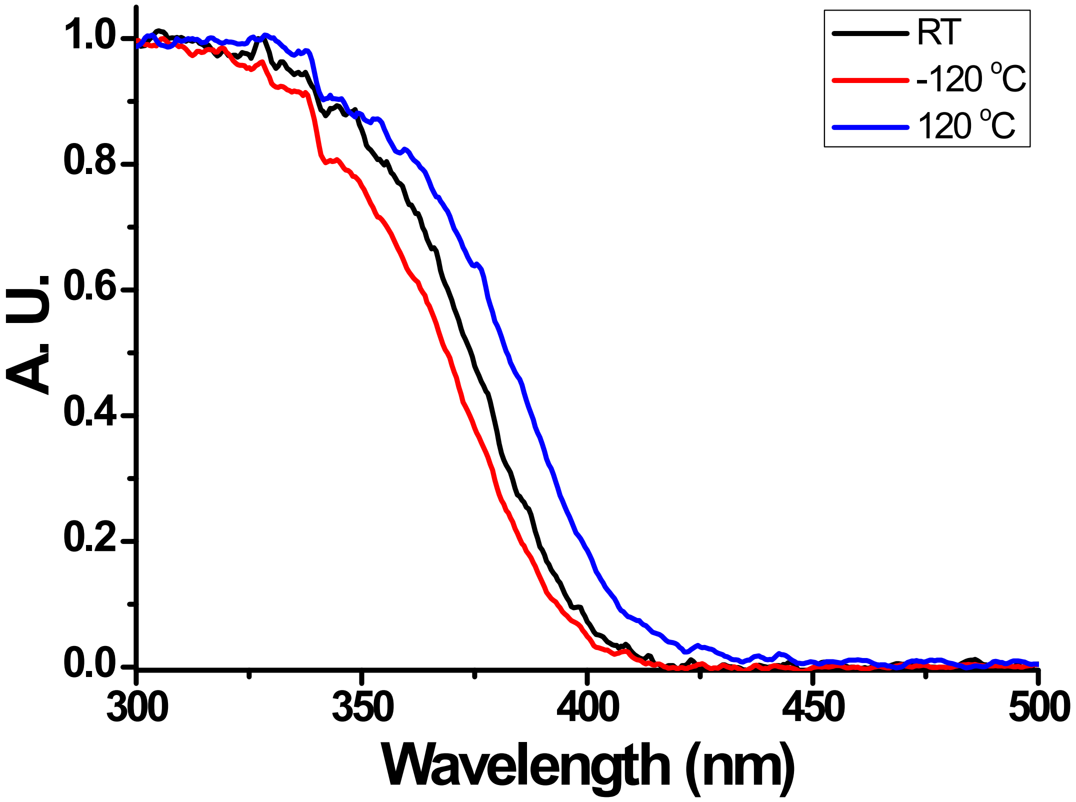


Figure S4. The solid state absorption of **1** at RT (black), 120 °C (blue) and -120 °C (red). Note that all absorptions have been normalized.