ESI

A low-dimensional molecular spin system with two steps of magnetic transitions and liquid crystal property

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Table S1: Crystallographic and refinement Data for the tapped phase at 293 K

Molecular formula	$C_{13}H_{19}N_6NiS_4$
Molecular mass	446.30
crystal system	monoclinic
Space group	P2(1)/m
a/Å	4.4980(3)
b/Å	20.5770(14)
c/Å	13.6962(9)
α/°	90
β/°	96.193(6)
γ/°	90
V/Å^3 / Z	1260.24(15) / 2
μ/mm^{-1}	4.263
F(000)	462
ρ/g cm^{-3}	1.176
R_1	0.1989
wR_2	0.5476
Goodness of fit on F^2	2.427

Table S2: Crystallographic and refinement Data for **1** at 293 K and 105 K

Complex	**1** at 293 K	**1** at 105 K
Molecular formula	$C_{19}H_{19}N_6NiS_4$	$C_{19}H_{19}N_6NiS_4$
Molecular mass	518.37	518.37
crystal system	Triclinic	Triclinic
Space group	P -1	P -1
a/Å	4.5025(6)	4.4540(5)
b/Å	13.6474(13)	13.6238(15)
c/Å	20.5060(19)	20.238(2)
α/o	84.901(8)	84.472(9)
β/o	85.132(9)	85.962(8)
γ/o	83.759(9)	82.683(9)
V/Å^3 / Z	1244.0(2) / 2	1210.3(2) / 2
μ/mm^{-1}	4.405	4.528
F(000)	534.0	532.0
ρ/g cm^{-3}	1.384	1.422
R_1	0.0472	0.0441
wR_2	0.1678	0.1397
Goodness of fit on F^2	1.127	1.227

Table S3: Selected Bond Lengths (Å) and Bond Angles (°) for 1 at 293 K and 105 K

		1 at 293 K	
Ni(1)-S(1)	2.134(1)	Ni(2)-S(3)	2.136(1)
Ni(1)-S(2)	2.147(1)	Ni(2)-S(4)	2.151(1)
S(1)-Ni(1)-S(1A)	180.00(1)	S(3)-Ni(2)-S(3A)	180.00(6)
S(1)-Ni(1)-S(2)	87.58(5)	S(3)-Ni(1)-S(4A)	92.56(5)
S(1A)-Ni(1)-S(2)	92.42(5)	S(3)-Ni(1)-S(4)	87.44(5)
		1 at 105 K	
Ni(1)-S(1)	2.138(1)	Ni(2)-S(3)	2.143(1)
Ni(1)-S(2)	2.152(1)	Ni(2)-S(4)	2.155(1)
S(1)-Ni(1)-S(1A)*	180.00(6)	S(3)-Ni(2)-S(3A)	180.00(5)
S(1)-Ni(1)-S(2)	87.23(5)	S(3)-Ni(1)-S(4A)	92.69(5)
S(1A)-Ni(1)-S(2)	92.77(5)	S(3)-Ni(1)-S(4)	87.31(5)

Symmetric code: A = 1-x, 1-y, 1-z

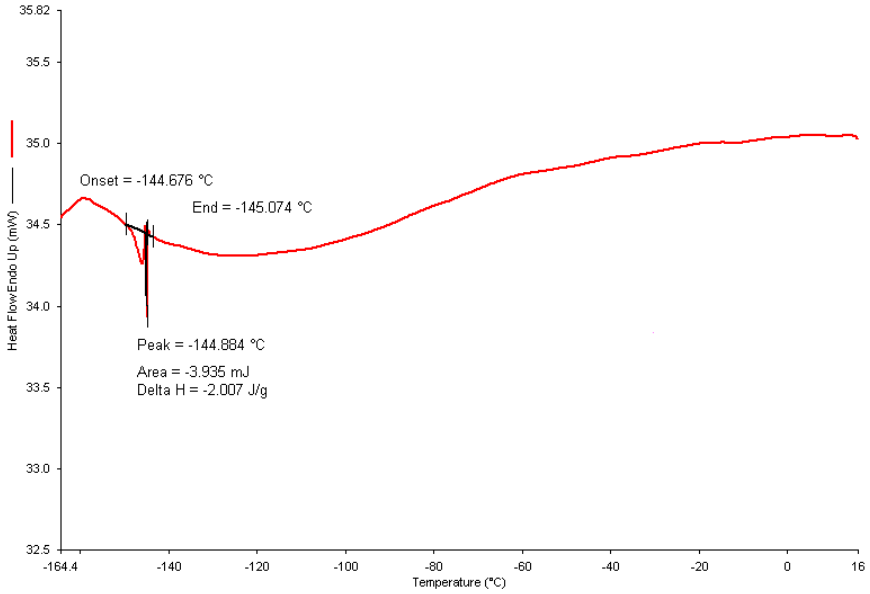


Figure S1 DSC plot of as-prepared sample of **1** measured from -164 to 16 °C shows an enthalpy change corresponding to the magnetic transition in low-temperature region (T_C ≈ 128.5 K).

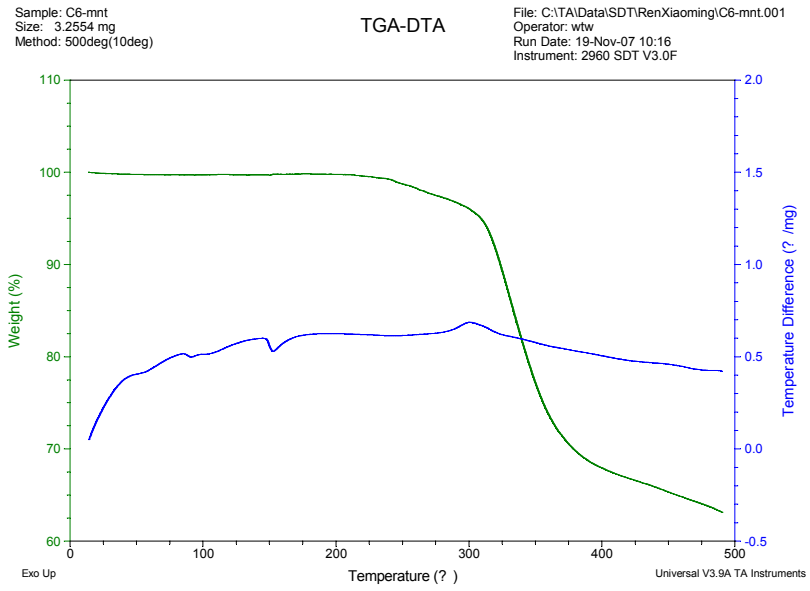


Figure S2 TGA and DTA curves for as-prepared sample of **1** (the measurements were performed under N_2 atmosphere) in 20-500 °C range disclosed that **1** is thermally stable below 237 °C; the weight losing is about 5% in 237-307 °C and 32% in 307-500 °C ranges.

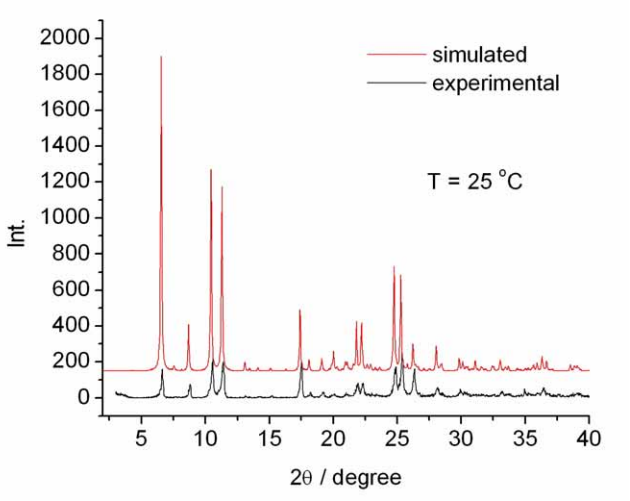


Figure S3 Powder X-ray diffraction patterns at 25 °C (experimental and simulated profiles) for as-prepared sample of **1** which confirms the phase purity of the as-prepared sample.

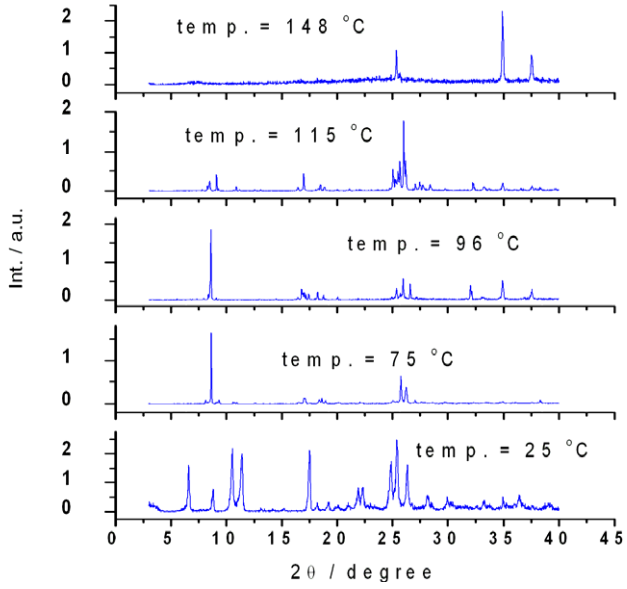


Figure S4 PXRD patterns were measured from 25 (crystal) to 148 °C (mesophase) in the 2θ range of 3-40° for **1**.

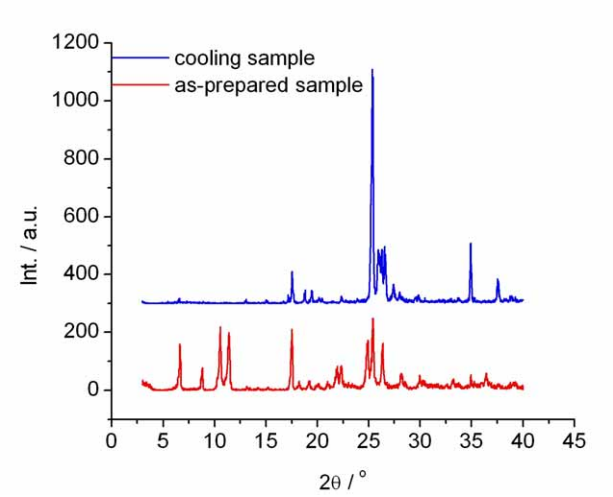


Figure S5 PXRD profiles measured for the as-prepared sample and the cooling sample after melted at 25 °C in the 2θ range of 3-40° for **1**, which show different patters.

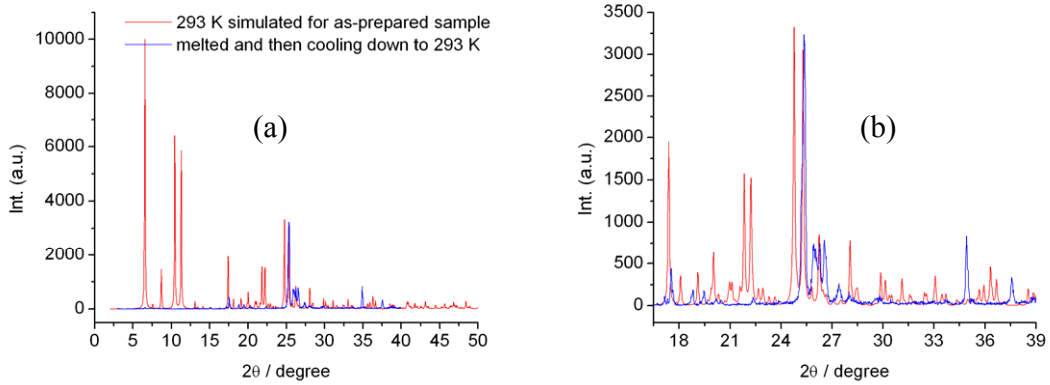


Figure S6 PXRD profiles (Figure b is an enlarged one of Figure a), in which the red line represents the simulated PXRD pattern for the as-prepared sample of **1** from the single crystal data at 293 K and the blue line is the experimental PXRD pattern for the sample that is melted and then cooling down to 25 °C for **1**. From Figure b, the somewhat difference are observed between two patterns although they are similar to each other.

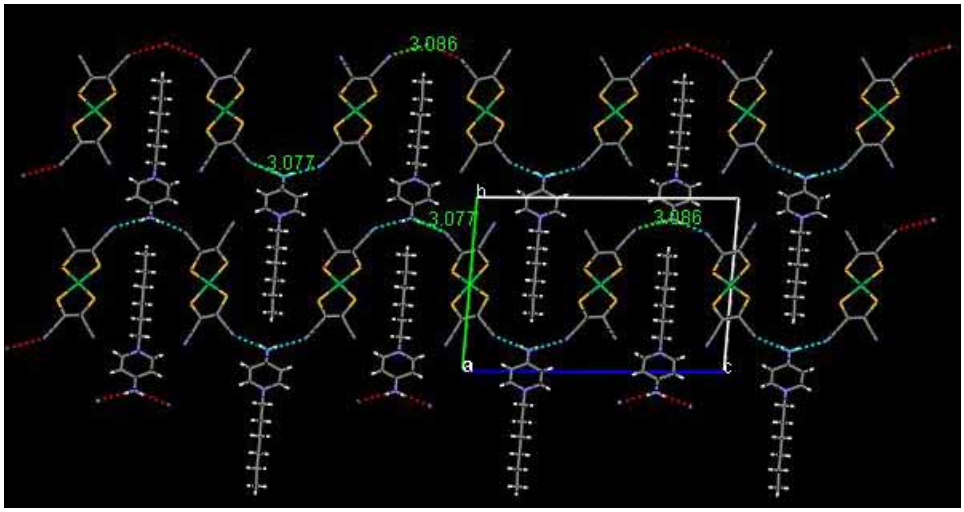


Figure S7 H-bonding sheet which is parallel to bc-plane (projected along a-axis) at 25 °C for as-prepared sample.

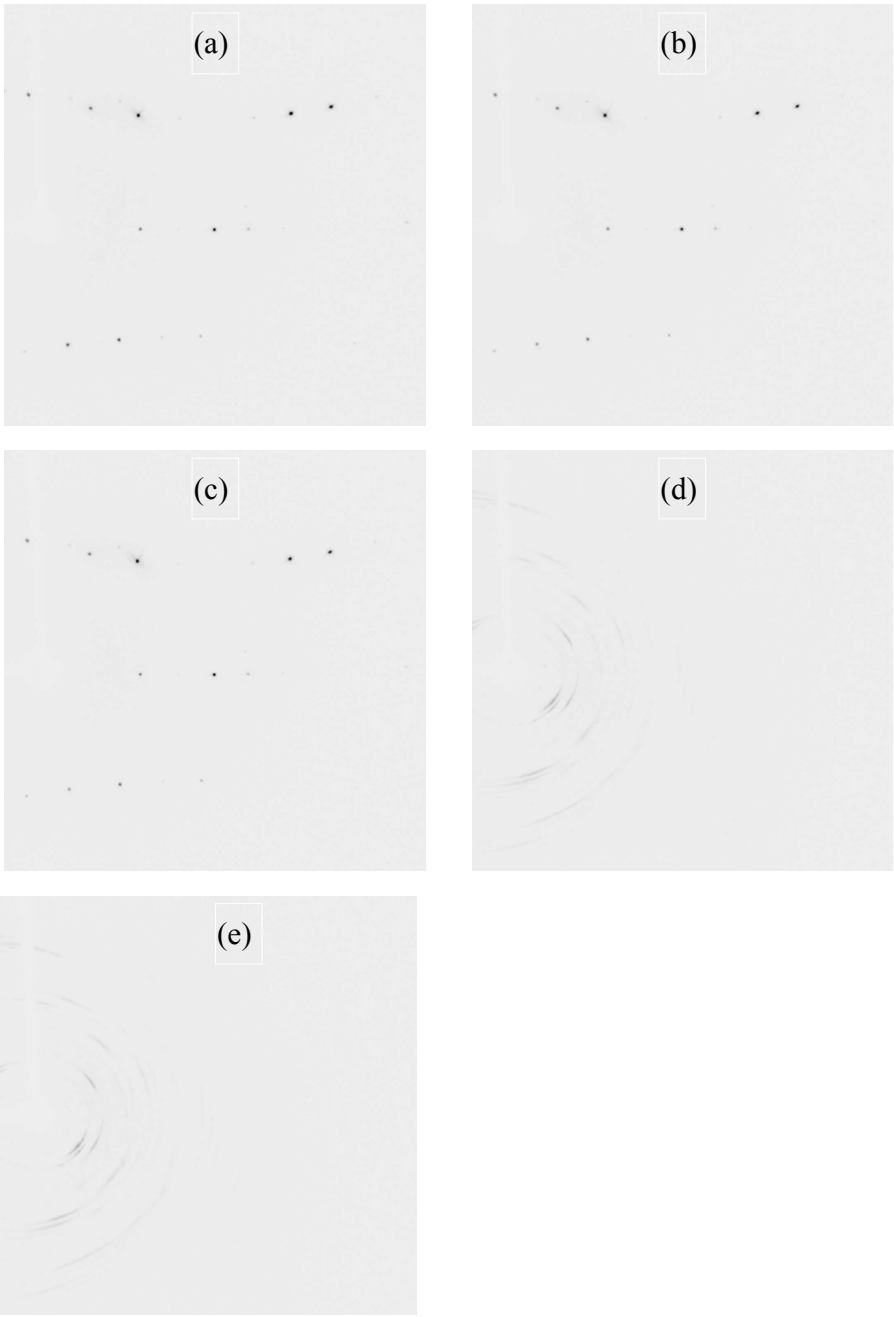


Figure S8 Diffractions change with temperature measured at (a) 320 K (b) 330 K (c) 345 K (d) 355 K and (e) 320 K after cooling.

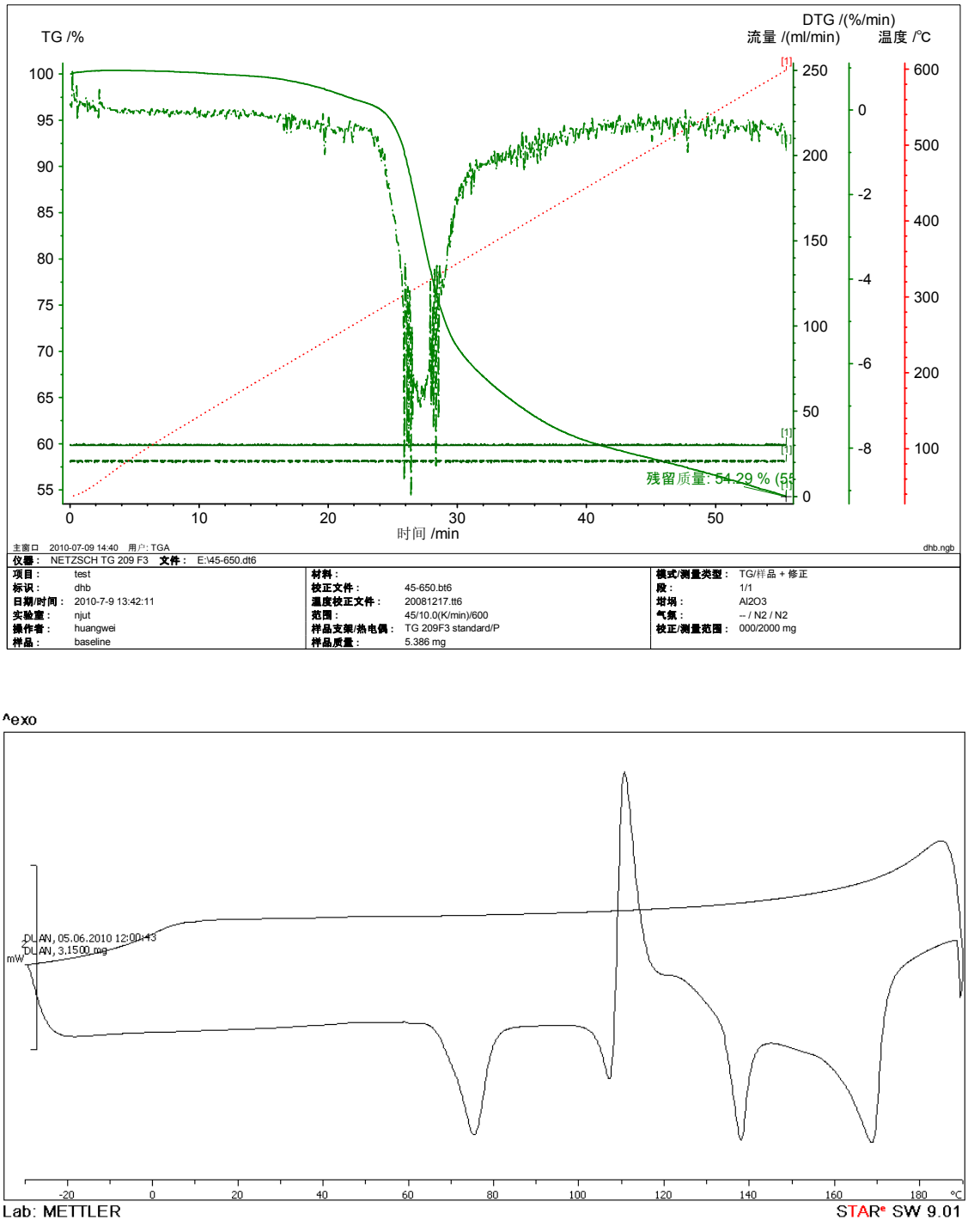


Figure S9 TG and DSC profile of $[C_6\text{-APy}][Cu(mnt)_2]$.

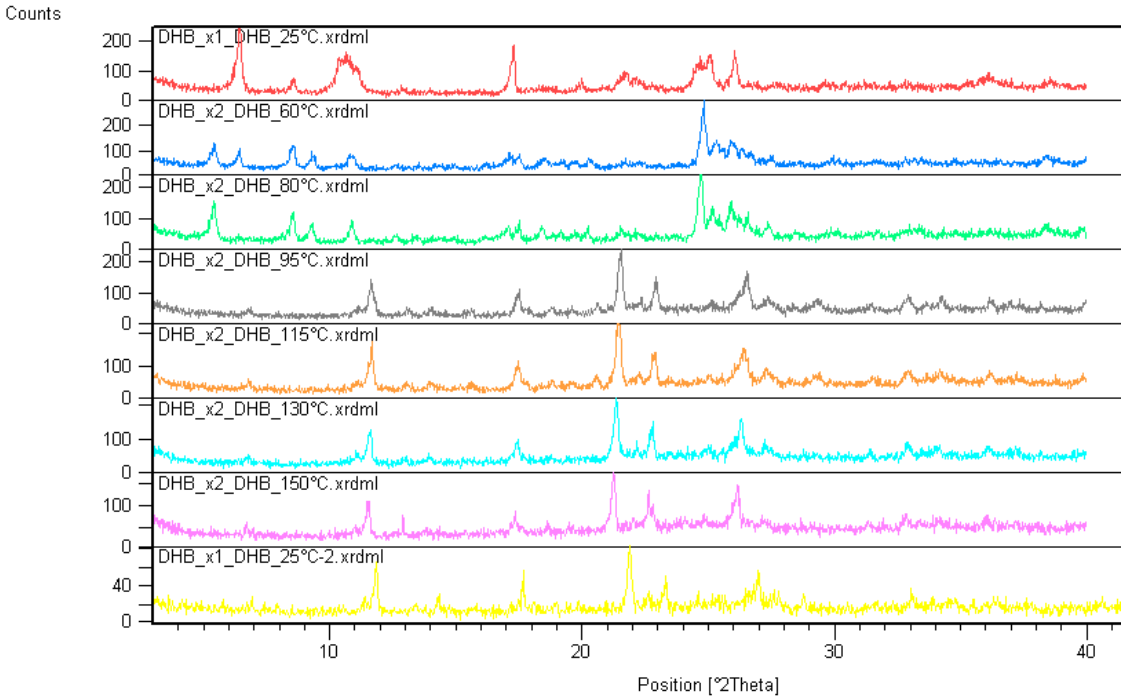
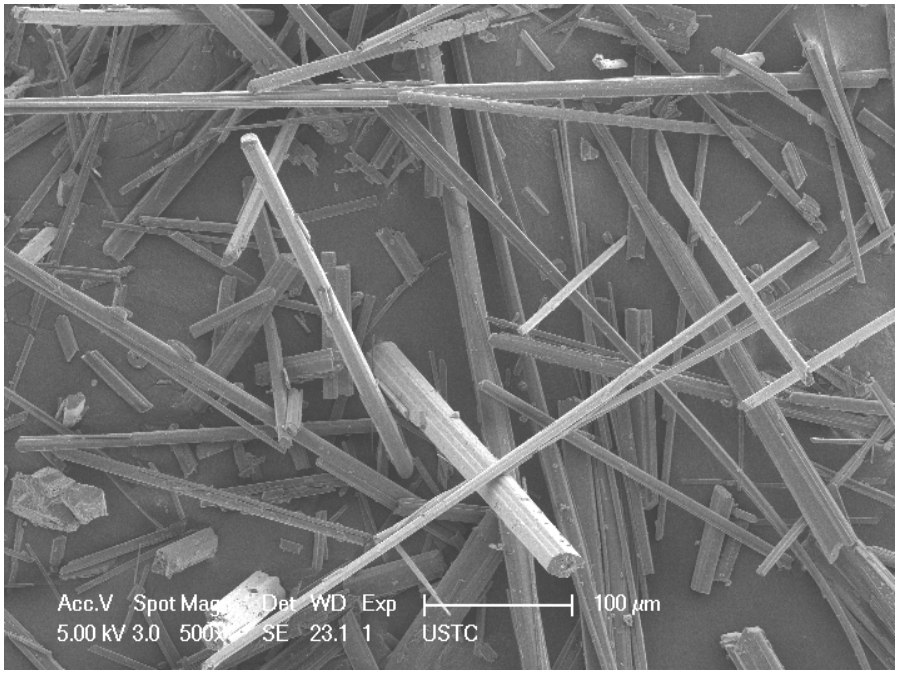
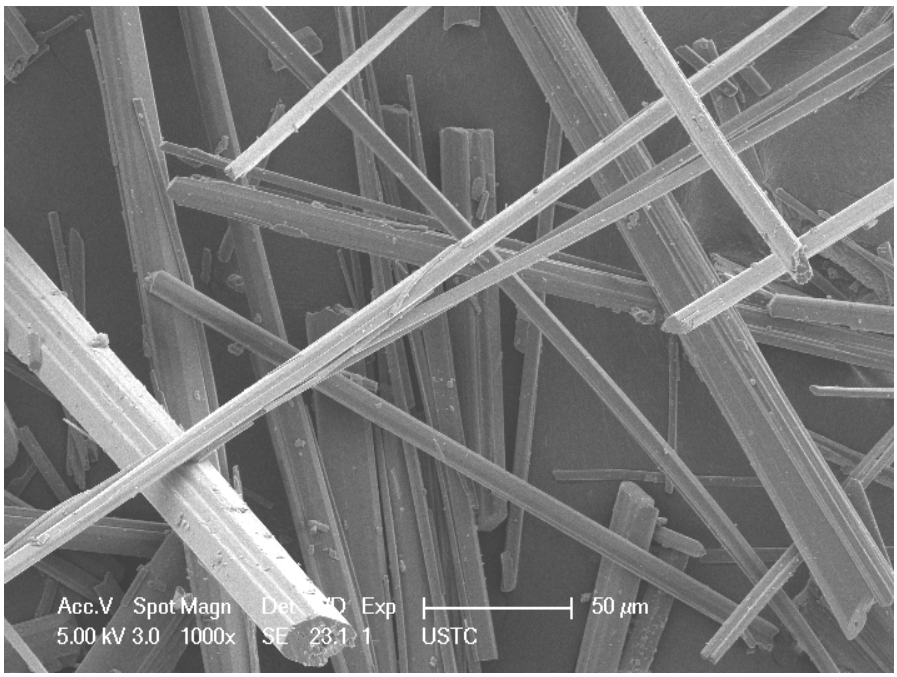
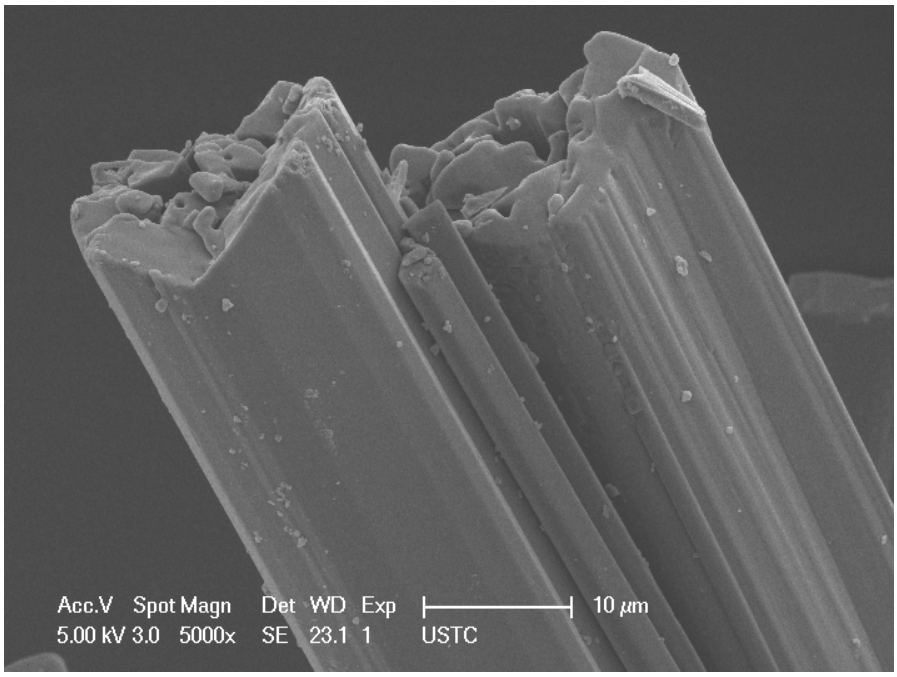


Figure S10 Temperature dependent PXRD for $[C_6\text{-APy}][Cu(mnt)_2]$ (the measurements in sequence of 25 °C→60→80→95→115→130→150→25 °C).


Acc.V Spot Magn Det WD Exp
5.00 kV 3.0 500x SE 23.1 1
100 µm
USTC


Acc.V Spot Magn Det WD Exp
5.00 kV 3.0 1000x SE 23.1 1
50 µm
USTC



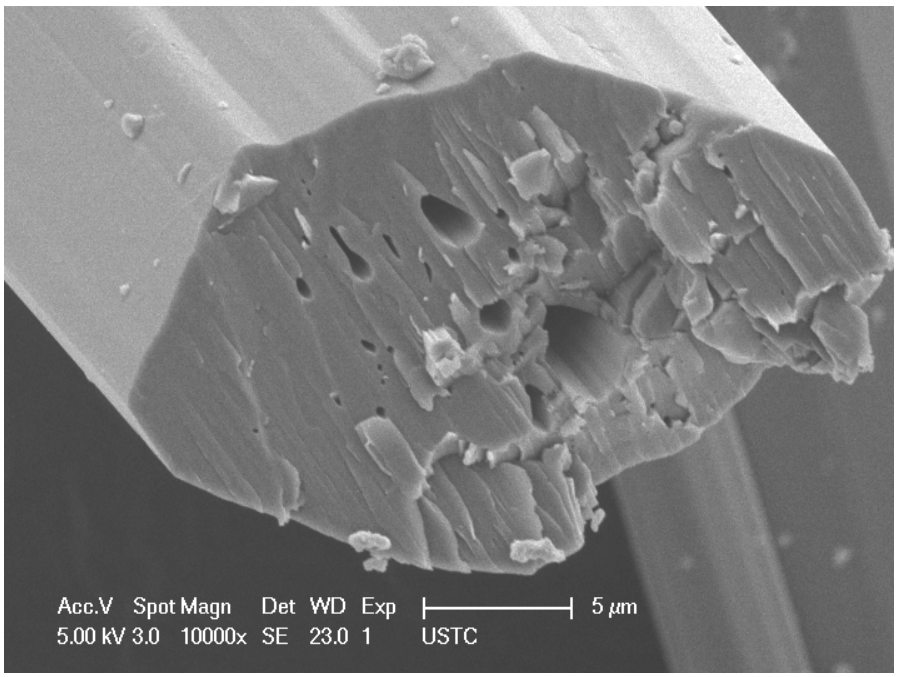


Figure S11 SEM micrographs of $[C_6\text{-APy}][Cu(mnt)_2]$.