Supporting Information

I_2-induced SC-SC transformation within two-dimensional Zn(II)-triazole framework: an ideal detector of cyano-containing molecules

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Experimental Section

General remarks. All the reagents were commercially available and used without further purification. The elemental analysis of carbon, nitrogen, and hydrogen was performed on a PerkinElmer 240 elemental analyzer. Powder X-ray diffraction analysis was carried out on a D/Max-2500 X-ray diffractometer using $Cu_{K\alpha}$ radiation. ^1H NMR data were measured using a Bruker Avance 400 MHz spectrometer. Chemical shifts δ are reported in ppm relative to tetramethylsilane. The photoluminescence spectra were recorded by an MPF-4 fluorescence spectrophotometer with a xenon arc lamp as the light source. The TGA experiments were performed on a NETZSCH TG 209 instrument with a heating rate of 10 ^oC min^{-1}. SEM images were collected in the Nova Nano SEM 230.

Synthesis of bis(4-(4H-1,2,4-triazol-4-yl)phenyl)sulfane (BTPS)

4-(4-aminophenylthio)benzenamine (2.16 g, 10 mmol) and diformylhydrazine (1.91 g, 22 mmol) were mixed, heated slowly to 160 ^oC, and held at 160-170 ^oC for 0.5 h. The reaction mixture, which solidified on cooling to room temperature, was dissolved in 20 mL of hot ethanol with Norit, and filtered hot. Diethyl ether (100 mL) was added to the cooled solution. The solid which separated from this mixture after standing overnight in a cold box deposited 1.26 g. (39.6% of the theoretical amount) of bis(4-(4H-1,2,4-triazol-4-yl)phenyl)sulfane (BTPS). After a second recrystallization from alcohol-ether and a final recrystallization from toluene the product was obtained as water-soluble, light purple needles. Elemental analysis calcd (%) for $C_{16}H_{12}N_6S$: C 59.98, H 3.78, N 26.23; found: C 59.89, H 3.66, N 26.18.

Synthesis of $\{[Zn(BTPS)(TPA)]\cdot 1.5DMF\cdot H_2O\}_n$ (1)

A mixture of BTPS (0.064 g, 0.2 mmol), $Zn(NO_3)_2$ (0.0605 g, 0.2 mmol), TPA (0.0332 g, 0.2 mmol), H_2O (2 mL), and DMF (6 mL) were put in a 20 mL acid-digestion bomb and heated at 90 °C for 3 days. The light purple crystal products suitable for single-crsytal X-ray diffraction studies were collected after washing with H_2O (2 × 5 mL) and diethyl ether (2 × 5 mL). Yield: 80%. Elemental analysis calcd (%) for $C_{28.5}H_{30}N_{7.5}O_{6.5}SZn$: C 50.41, H 4.45, N 15.47; found: C 50.33, H 4.49, N 15.56.

Synthesis of $\{[Zn_2I(BTPS)_2(TPA)_{1.5}]\cdot 1.5H_2O\}_n$ (1')

100 mg proper size crystals of **1** were soaked in a 10 mL of cyclohexane solution containing 254 mg of iodine. After the insertion of iodine, the resulting dark purple crystals suitable for single-crsytal X-ray diffraction studies were separated from the excess iodine solution and were thoroughly washed with cyclohexane, and then dried in air. Yield: 65%. Elemental analysis calcd (%) for $C_{44}H_{33}IN_{12}O_{7.5}S_2Zn_2$: C 45.11, H 2.84, N 14.35; found: C 45.06, H 2.90, N 14.43.

Table 1. Crystallographic data and details of refinements for BTPS, **1** and **1'**.

	BTPS	**1**	**1'**
formula	$C_{16}H_{12}N_6S$	$C_{28.5}H_{30}N_{7.5}O_{6.5}SZn$	$C_{44}H_{33}IN_{12}O_{7.5}S_2Zn_2$
M (g mol^{-1})	320.38	679.03	1171.58
crystal system	Orthorhombic	Triclinic	Triclinic
space group	*Pccn*	*P*-1	*P*-1
temperature	173(2)	173(2)	296(2)
a (Å)	12.0045(11)	9.0152(5)	8.940(2)
b (Å)	10.8025(9)	12.4589(6)	15.624(4)
c (Å)	11.0878(10)	13.9479(7)	18.684(6)
α (º)	90	105.4220(10)	65.286(3)
β (º)	90	91.7560(10)	84.924(5)
γ (º)	90	94.9000(10)	74.295(4)
V (Å^3)	1437.9(2)	1502.37(13)	2281.3(11)
Z	4	2	2
F (000)	664	703	1172
ρ_{calc} (Mg m^{-3})	1.480	1.501	1.706
μ (mm^{-1})	0.234	0.945	1.887
data/restraints/params	1785 / 0 / 105	7457 / 97 / 457	10602 / 0 / 617
GOF on F^2	1.045	1.047	1.081
R_1[a] (I=2σ(I))	0.0395	0.0399	0.1091
ωR_2[a] (all data)	0.1080	0.1054	0.4389

[a] $R_1 = \Sigma||F_o| - |F_c||/|F_o|$. [b] $\omega R_2 = [\Sigma w(|F_o|^2-|F_c^2|^2/w|F_o^2|^2]^{1/2}$.

Table 2. Selected bond lengths [Å] and angles [°] for BTPS, **1** and **1'**.

BTPS					
S(1)-C(1)	1.7747(14)	N(1)-C(7)	1.3644(17)	N(1)-C(8)	1.3657(19)
N(1)-C(4)	1.4313(17)	N(2)-C(7)	1.3047(19)	N(2)-N(3)	1.3952(17)
N(3)-C(8)	1.3091(19)	C(1)-C(2)	1.3972(19)	C(1)-C(6)	1.398(2)
C(2)-C(3)	1.3917(19)	C(3)-C(4)	1.3889(19)	C(4)-C(5)	1.3879(19)
C(5)-C(6)	1.388(2)	C(1)-S(1)-C(1)#1	103.24(9)	C(7)-N(1)-C(8)	104.37(12)
C(7)-N(1)-C(4)	127.73(12)	C(8)-N(1)-C(4)	127.85(12)	C(7)-N(2)-N(3)	107.27(12)
C(8)-N(3)-N(2)	106.61(12)	C(2)-C(1)-C(6)	119.88(12)	C(2)-C(1)-S(1)	117.84(11)
C(6)-C(1)-S(1)	122.14(11)	C(3)-C(2)-C(1)	120.23(13)	C(4)-C(3)-C(2)	119.22(12)
C(5)-C(6)-C(1)	119.81(13)	N(3)-C(8)-N(1)	110.95(13)		
1					
Zn(1)-O(1)	1.9259(14)	Zn(1)-O(3)	1.9549(15)	Zn(1)-N(1)	2.0196(17)
Zn(1)-N(5)#1	2.0202(18)	O(1)-Zn(1)-O(3)	98.66(6)	O(1)-Zn(1)-N(1)	116.61(7)
O(3)-Zn(1)-N(1)	118.27(7)	O(1)-Zn(1)-N(5)#1	116.74(7)	O(3)-Zn(1)-N(5)#1	105.39(7)
N(1)-Zn(1)-N(5)#1	101.47(7)				
1'					
Zn(1)-O(3)	1.953(5)	Zn(1)-O(1)	1.964(6)	Zn(1)-N(1)	2.035(6)
Zn(1)-N(4)#1	2.059(6)	Zn(2)-O(5)	1.947(7)	Zn(2)-N(10)#2	2.032(7)
Zn(2)-N(7)	2.040(7)	Zn(2)-I(1)	2.5415(13)	O(3)-Zn(1)-O(1)	107.5(3)
O(3)-Zn(1)-N(1)	103.3(3)	O(1)-Zn(1)-N(1)	117.1(3)	O(3)-Zn(1)-N(4)#1	103.2(3)
O(1)-Zn(1)-N(4)#1	119.1(3)	N(1)-Zn(1)-N(4)#1	104.7(3)	O(5)-Zn(2)-N(10)#2	110.2(3)
O(5)-Zn(2)-N(7)	105.6(3)	N(10)#2-Zn(2)-N(7)	99.6(3)	O(5)-Zn(2)-I(1)	116.4(2)
N(10)#2-Zn(2)-I(1)	118.3(2)	N(7)-Zn(2)-I(1)	104.28(19)		

[a] Symmetry transformations used to generate equivalent atoms: For BTPS: #1 -*x* + 3/2, -*y* + 1/2, *z*; for **1**: #1 -*x* + 1, -*y* + 1, -*z* #2 -*x* + 1, -*y* + 3, -*z* #3 -*x* + 2, -*y* + 2, -*z* - 1 #4 -*x*, -*y* +1, -*z* + 1; for **1'**: #1 *x*, *y* - 1, *z* #2 *x*, *y* + 1, *z* #3 -*x* - 1, -*y*, -*z* + 1 #4 -*x*, -*y*, -*z* #5 -*x* + 2, -*y* + 1, -*z* + 1.

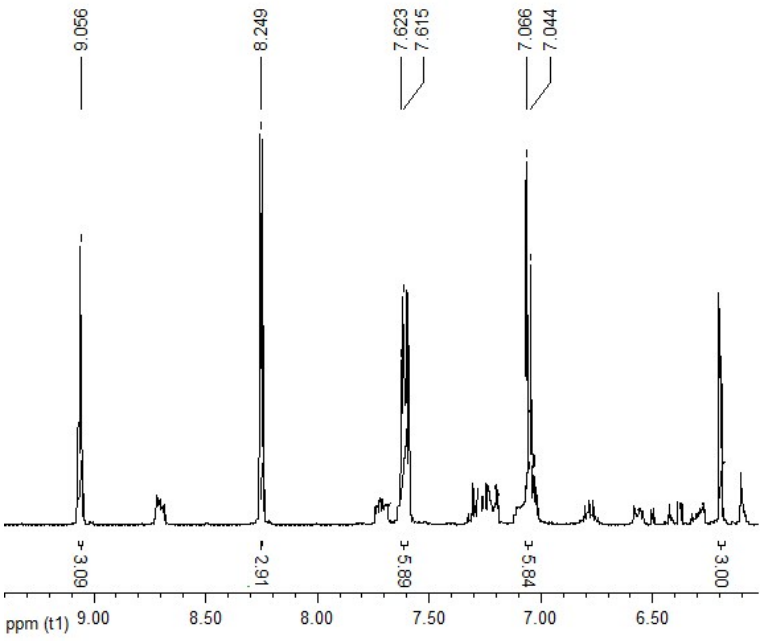

Fig. S1. ^{1}H NMR data of BTPS.

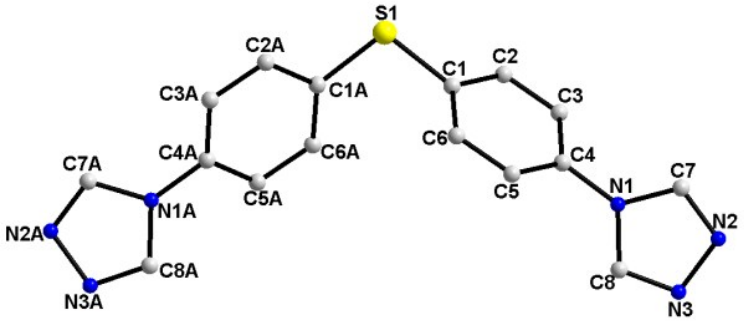

Fig. S2. The fundamental structural unit of BTPS. C gray, blue N, yellow, S.

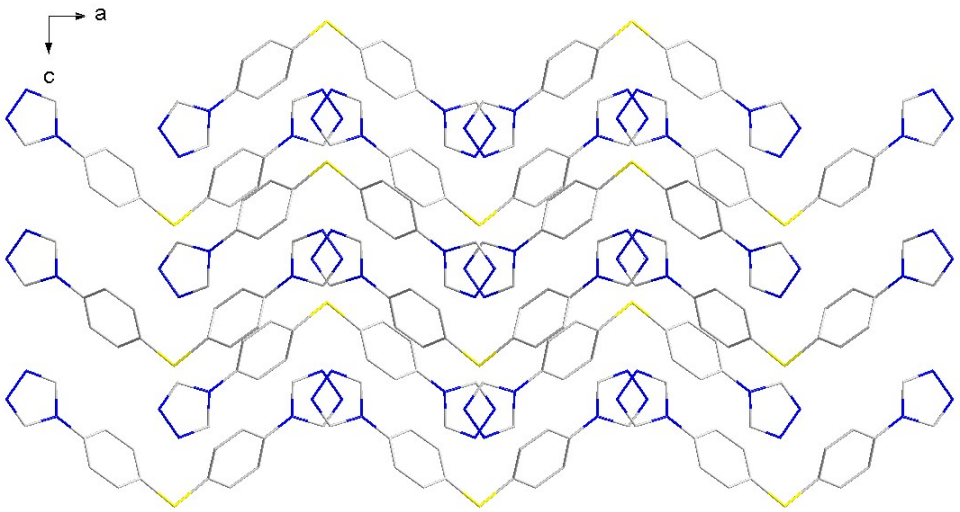

Fig. S3. The stacking diagram of the BTPS ligands along *b* axis. C gray, O red, S yellow, N blue.

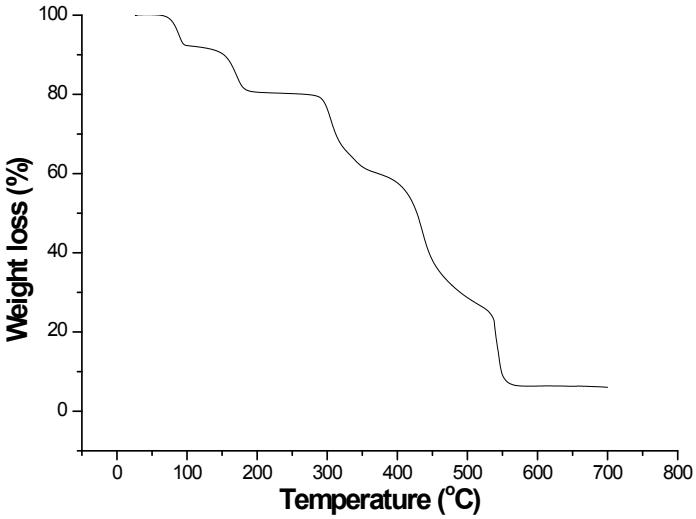

Fig. S4. TGA plot of **1**. A slight weight decrease corresponds to the loss of one and a half DMF (observed:16.13%; calcd: 16.40%).

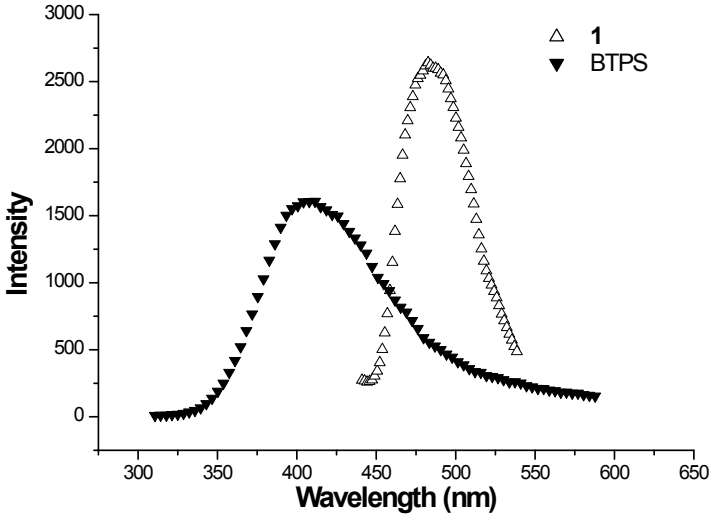

Fig. S5. Emission spectra of solutions of BTPS and **1** in DMF at room temperature (1×10^{-4} mol L^{-1})

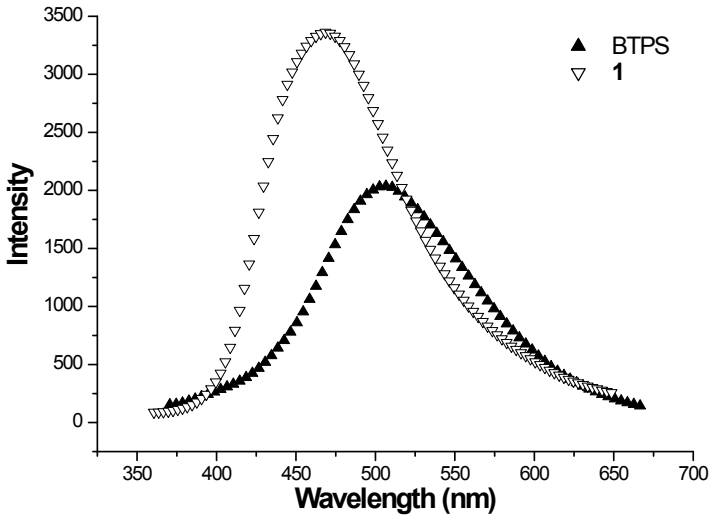

Fig. S6. Emission spectra of BTPS and **1** in the solid state at room temperature.

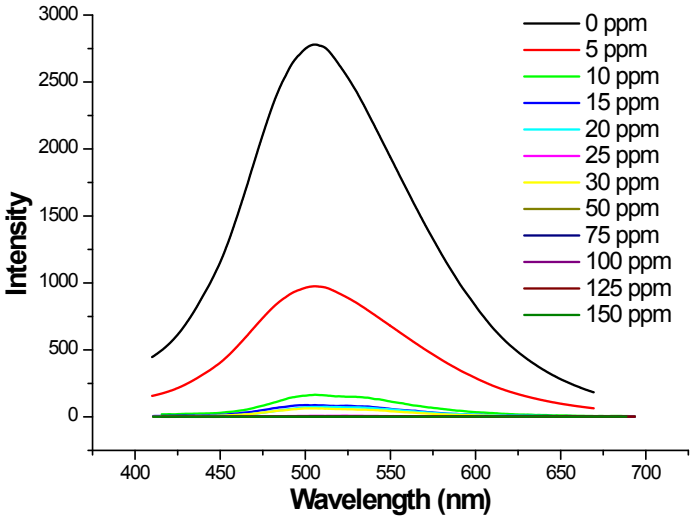

Fig. S7. Fluorescence titration of complex **1** dispersed in DMF with the addition of different concentrations of $[NBu_3][Mo(CN)_8]$.

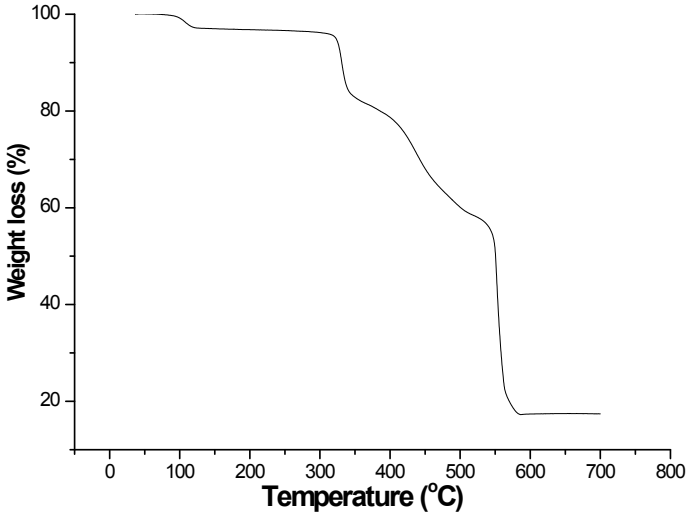

Fig. S8. TGA plot of **1'**. A slight weight decrease corresponds to the loss of one and a half H_2O molecules (obvserved:4.55%; calcd: 4.61%).

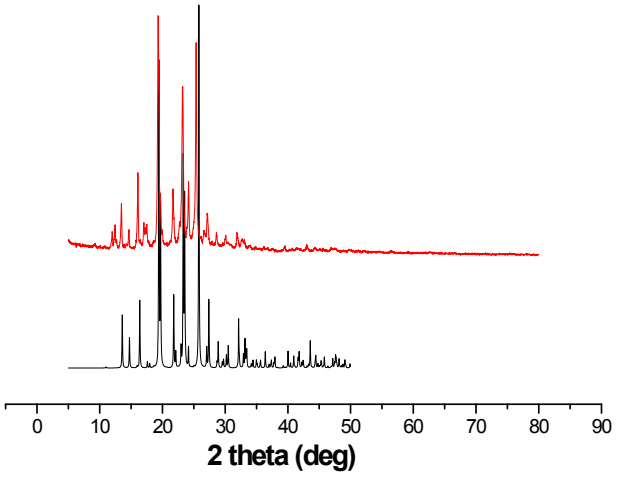

Fig. S9. PXRD patterns of **BTPS**. Black, simulated; red, as-synthesized.

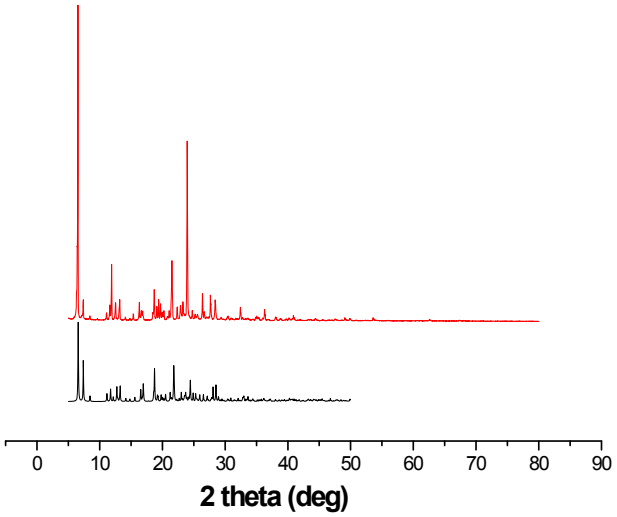

Fig. S10. PXRD patterns of **1**. Black, simulated; red, as-synthesized.

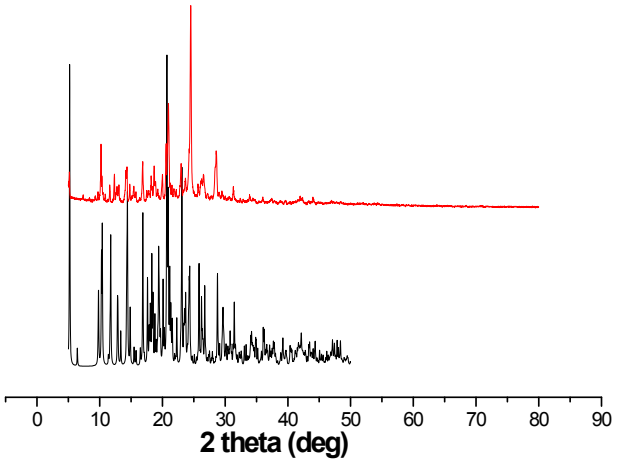

Fig. S11. PXRD patterns of **1'**. Black, simulated; red, as-synthesized.

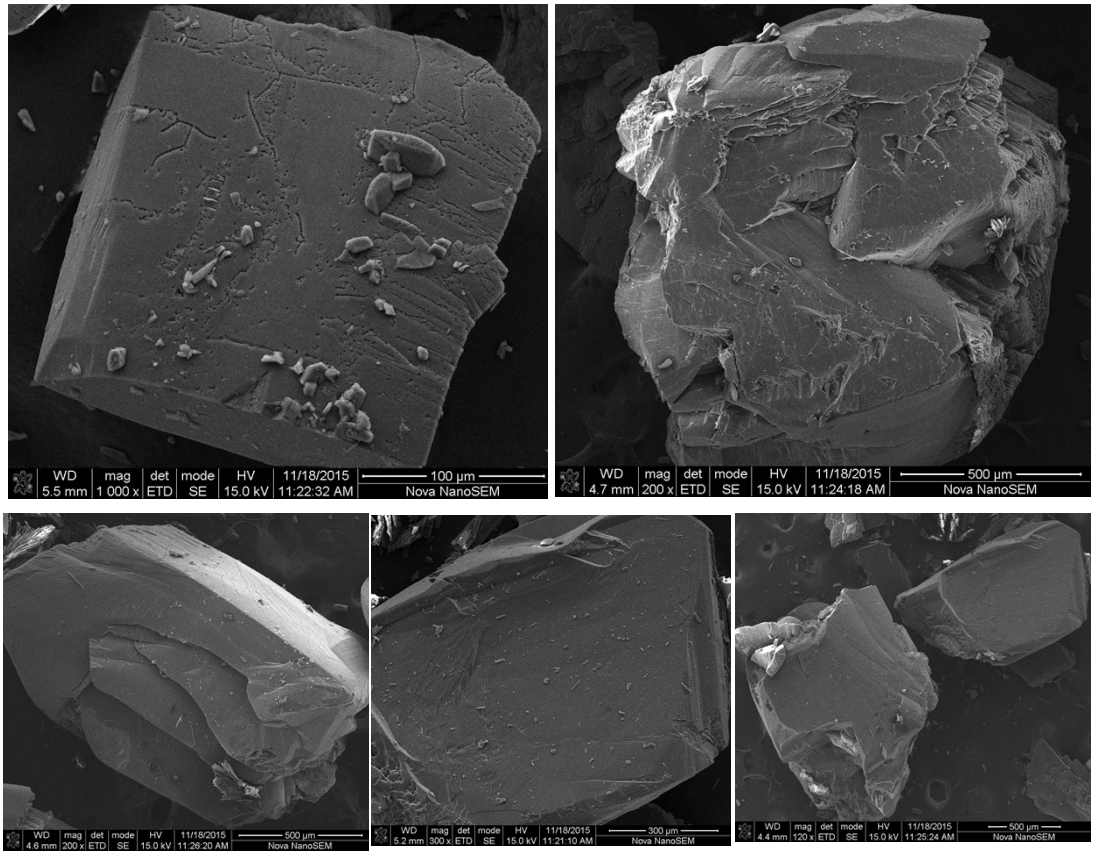

Fig. S12 SEM images of complex **1**.

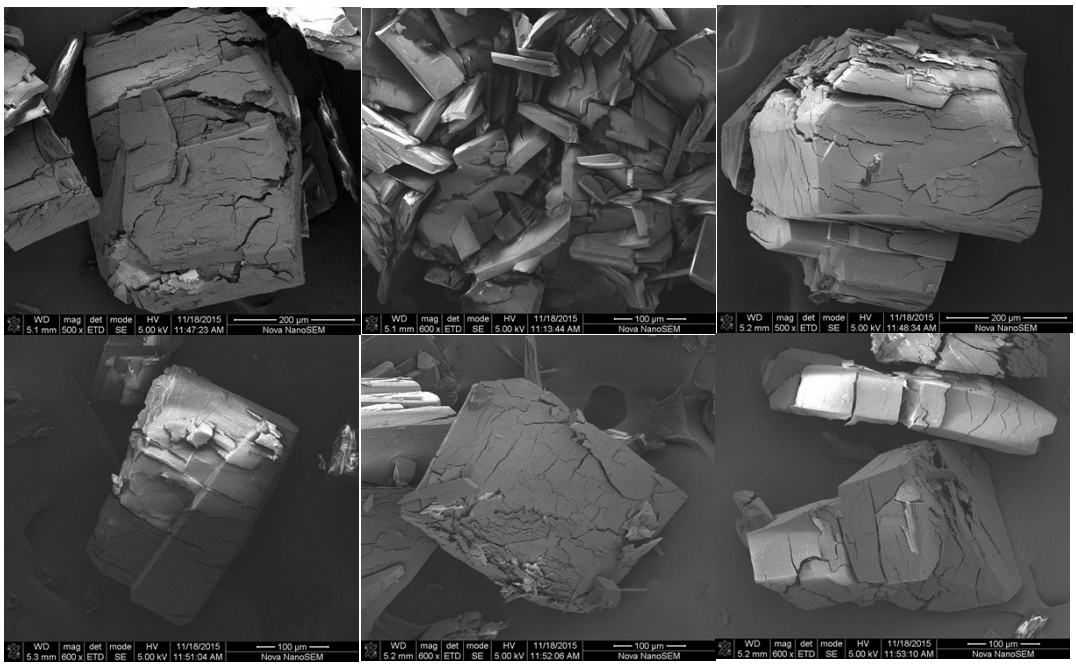

Fig. S13 SEM images of complex **1'**.