Electronic Supplementary Information

for

# Switchable On-Off Spin-Crossover Properties of Iron(II) Compounds by Trimming Intermolecular Hydrogen Bonds

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## Materials and Methods

$FeCl_2 \cdot 6H_2O$, 2-(9-anthracenyl)-1*H*-imidazole[4,5-f][1,10]phenanthroline (L), KSCN, ascorbic acid, pyridine, and MeOH were purchased from commercial sources and used without further purification.

Single-crystal X-ray diffraction data were obtained on Rigaku Oxford XtaLAB PRO diffractometer with graphite-monochromated Mo *Kα* radiation ($\lambda$ = 0.71073 Å). Elemental analyses of C, H, and N were performed on an EUROVECTER EA3000 analyzer. The infrared spectra were measured on a Bruker ALPHA FT-IR spectrometer in the range of 4000–400 $cm^{-1}$. The powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 Advance diffractometer with Cu *Kα* radiation ($\lambda$ = 1.54056 Å) at room temperature. Thermogravimetric (TG) analyses were conducted on a TG-DTA 6200 instrument under $N_2$ atmosphere in the range of 20–800 ℃. Differential scanning calorimetry (DSC) data were measured on a PerkinElmer DSC 8000 instrument. The measurements of variable-temperature magnetic susceptibilities were performed on a Quantum Design MPMS XL7 magnetometer in the range of 10–395 K under the 5000 Oe magnetic field.

## Synthesis

**Synthesis of $[Fe(py)_4(NCS)_2]$.** A mixture of $FeCl_2 \cdot 6H_2O$ (0.7 g, 3 mmol) and KSCN (0.6 g, 6 mmol) was dissolved in MeOH (100 mL) with enough ascorbic acid. Then the solution was filtered and pyridine (40 mL) was added into the filtrate with stirring. Yellow precipitate was collected by filtration. The powder product was put into glove box for preventing form oxidation and for further use.

**Synthesis of $[FeL_2(NCS)_2] \cdot 3MeOH$ (1·3MeOH).** A mixture of $[Fe(py)_4(NCS)_2]$ (0.075 g, 0.15 mmol), L (0.06 g, 0.15 mmol) and MeOH (12 mL) was sealed in a 25 mL Teflon-lined stainless autoclave and heated to 160 ℃ for 24 hours, and then the autoclave was cooled to room temperature over 5 hours. Because of impurities were present, the mixture was scoured with methanol to obtain pure crystals, then reddish black block crystals were collected (32 mg, ~38% based on Fe). Elemental analysis cald. (%): C, 66.788; H, 4.180; N, 13.201. Found: C, 66.861; H, 3.954; N, 13.329. IR (RT, KBr pellet): 3632(m), 3415(w), 3045(w), 2367(w), 2059(s), 1605(w), 1543(w), 1501(w), 1438(w), 1403(m), 1354(m), 1312(w), 1173(w), 1137(w), 1075(m), 1019(m), 900(w), 795(m), 739(s), 635(w), 593(w), 536(w), 467(w), 418(w).

**Synthesis of $[FeL_2(NCS)_2]$ (1).** Crystals of **1·3MeOH** were put into a dynamic vacuum and heated to 160 ℃. Because sample **1** was extremely easy to absorb water molecules in air

moisture, its elemental analysis, IR and TG data were not able to be measured. Single crystal for structural determination was prepared by sealing a crystal of **1** (quick picked up from vacuum) in capillary in groove box.

**Synthesis of 1·3MeOH from 1.** In situ prepared sample **1** was quickly put in methanol solution and kept for 4 hours. Yield: 100%.

**Synthesis of $[FeL_2(NCS)_2]\cdot 2H_2O$ ($1\cdot 2H_2O$)**. Crystals of **1·3MeOH** were put into dynamic vacuum and heated to 160 ℃. After 2 hours, the sample was taken out and put into air. The reddish black block crystals of **$1\cdot 2H_2O$** were obtained in 100% yield. Elemental analysis cald. (%): C, 67.198; H, 3.625; N, 13.994. Found: C, 67.085; H, 3.514; N, 13.865. IR (RT, KBr pellet): 3632(w), 3059(m), 2360(s), 2053(s), 1599(w), 1550(w), 1515(w), 1431(w), 1403(w), 1354 (w), 1305(w), 1179(w), 1137(w), 1075(w), 1112(w), 893(w), 802(w), 733(m), 663(w), 607(w), 544(w), 474(w), 418(w).

CCDC: 1965898-1965904.

## Tables

**Table S1.** Crystallographic data for **1·3MeOH** at different temperatures.

| Temperature | 150 K | 300 K |
|---|---|---|
| Empirical formula | $C_{59}H_{44}FeN_{10}O_3S_2$ | $C_{59}H_{44}FeN_{10}O_3S_2$ |
| Formula weight | 1061.01 | 1061.01 |
| Crystal system | Orthorhombic | Orthorhombic |
| Space group | *Pccn* | *Pccn* |
| *a* / Å | 11.9880(3) | 12.1817(8) |
| *b* / Å | 24.7721(7) | 25.0030(17) |
| *c* / Å | 16.8246(5) | 17.0415(13) |
| $\alpha$/° | 90 | 90 |
| $\beta$/° | 90 | 90 |
| $\gamma$/° | 90 | 90 |
| Volume / Å$^3$ | 4996.4(2) | 5190.5(6) |
| *Z* | 4 | 4 |
| $\rho_{calc}$ g/cm$^3$ | 1.411 | 1.358 |
| $\mu$ / mm$^{-1}$ | 0.445 | 0.428 |
| *F*(000) | 2200 | 2200 |
| *R*1 [$I >= 2\sigma(I)$] | 0.0299 | 0.0517 |
| *wR*2 [all data] | 0.0816 | 0.1399 |
| $R_{int}$ | 0.0242 | 0.0389 |

**Table S2.** Crystallographic data for **1·2H$_2$O** at different temperatures.

| Temperature | 150 K | 293 K |
|---|---|---|
| Empirical formula | $C_{56}H_{36}FeN_{10}O_2S_2$ | $C_{56}H_{36}FeN_{10}O_2S_2$ |
| Formula weight | 1000.92 | 1000.92 |
| Crystal system | Orthorhombic | Orthorhombic |
| Space group | *Pccn* | *Pccn* |
| *a* / Å | 12.3848(11) | 12.5057(19) |
| *b* / Å | 23.950(3) | 24.082(4) |
| *c* / Å | 16.0358(17) | 16.140(2) |
| $\alpha$/° | 90 | 90 |
| $\beta$/° | 90 | 90 |
| $\gamma$ /° | 90 | 90 |
| Volume / Å$^3$ | 4756.4(8) | 4860.6(13) |
| *Z* | 4 | 4 |
| $\rho_{calc}$ g/cm$^3$ | 1.398 | 1.368 |
| $\mu$ / mm$^{-1}$ | 0.461 | 0.451 |
| *F*(000) | 2064 | 2064 |
| *R*1 [$I >= 2\sigma(I)$] | 0.0876 | 0.1377 |
| *wR*2 [all data] | 0.2108 | 0.2870 |
| $R_{int}$ | 0.1391 | 0.1996 |

**Table S3**. Crystallographic data for **1** at 150 K.

| Temperature | 150 K |
|---|---|
| Empirical formula | $C_{56}H_{32}FeN_{10}S_2$ |
| Formula weight | 964.89 |
| Crystal system | Orthorhombic |
| Space group | *Pccn* |
| *a* / Å | 12.0479(17) |
| *b* / Å | 25.4757(15) |
| *c* / Å | 14.6834(15) |
| $\alpha$/° | 90 |
| $\beta$/° | 90 |
| $\gamma$ /° | 90 |
| Volume / Å$^3$ | 4506.8(8) |
| *Z* | 4 |
| $\rho_{calc}$ g/cm$^3$ | 1.422 |
| $\mu$ / mm$^{-1}$ | 0.481 |
| *F*(000) | 1984 |
| *R*1 [$I >= 2\sigma(I)$] | 0.1308 |
| *wR*2 [all data] | 0.2924 |
| $R_{int}$ | 0.2275 |

**Table S4.** Crystallographic data for **1·3MeOH** obtained from **1** at different temperatures.

| Temperature | 150 K | 293 K |
|---|---|---|
| Empirical formula | $C_{59}H_{44}FeN_{10}O_3S_2$ | $C_{59}H_{44}FeN_{10}O_3S_2$ |
| Formula weight | 1061.01 | 1061.01 |
| Crystal system | Orthorhombic | Orthorhombic |
| Space group | *Pccn* | *Pccn* |
| *a* / Å | 11.9693(13) | 12.1381(13) |
| *b* / Å | 24.7798(13) | 24.950(3) |
| *c* / Å | 16.7667(9) | 16.8691(16) |
| $\alpha$/° | 90 | 90 |
| $\beta$/° | 90 | 90 |
| $\gamma$/° | 90 | 90 |
| Volume / Å$^3$ | 4973.0(7) | 5108.7(9) |
| *Z* | 4 | 4 |
| $\rho_{calc}$ g/cm$^3$ | 1.417 | 1.379 |
| $\mu$ / mm$^{-1}$ | 0.447 | 0.435 |
| *F*(000) | 2200 | 2200 |
| *R*1 [$I >= 2\sigma(I)$] | 0.1401 | 0.1429 |
| *wR*2 [all data] | 0.3159 | 0.3116 |
| $R_{int}$ | 0.1090 | 0.1737 |

**Table S5.** Selected bound lengths (Å) for all compounds at different temperature.

| Compounds | **1·3MeOH** | | **1·2H$_2$O** | | **1** |
|---|---|---|---|---|---|
| Temperatur | 150 K | 300 K | 150 K | 293 K | 150K |
| Fe1-N1 | 1.949(1) | 2.059(1) | 1.955(5) | 2.037(10) | 2.094(6) |
| Fe1-N2 | 1.971(1) | 2.172(2) | 1.981(4) | 2.163(7) | 2.213(5) |
| Fe1-N3 | 1.976(1) | 2.140(2) | 1.980(4) | 2.149(7) | 2.210(5) |

**Table S6.** Selected bound angles (°) for all compounds at different temperature.

| Compounds | **1·3MeOH** | | **1·2H$_2$O** | | **1** |
|---|---|---|---|---|---|
| Temperatur e | 150 K | 300 K | 150 K | 293 K | 150K |
| N1-Fe1-N1a | 89.37(8) | 94.33(13) | 90.5(3) | 96.2(5) | 92.7(3) |
| N1-Fe1-N2 | 92.29(5) | 92.99(8) | 92.10(17) | 166.4(3) | 164.3(2) |
| N1a -Fe1-N2 | 174.39(5) | 167.78(8) | 173.63(18) | 92.6(3) | 95.0(2) |
| N1-Fe1-N2a | 174.39(5) | 167.78(8) | 173.63(18) | 92.6(3) | 95.0(2) |
| N1a-Fe1-N2a | 92.29(5) | 92.99(8) | 92.10(17) | 166.4(3) | 164.3(2) |
| N1-Fe1-N3a | 91.95(5) | 92.81(8) | 91.85(18) | 95.5(3) | 97.9(2) |
| N1a-Fe1-N3 | 91.95(5) | 92.81(8) | 91.85(18) | 95.5(3) | 97.9(2) |
| N1-Fe1-N3 | 91.76(5) | 96.95(8) | 90.75(18) | 93.0(3) | 90.9(2) |
| N1a-Fe1-N3a | 91.76(5) | 96.95(8) | 90.75(18) | 93.0(3) | 90.9(2) |
| N2-Fe1-N2a | 86.57(7) | 81.58(9) | 86.0(2) | 80.7(3) | 80.9(2) |
| N2a-Fe1-N3 | 93.54(5) | 92.44(7) | 95.00(17) | 94.4(3) | 95.64(19) |
| N2-Fe1-N3 | 82.64(5) | 76.58(6) | 82.29(17) | 75.8(3) | 74.52(19) |
| N2-Fe1-N3a | 93.54(5) | 92.44(7) | 95.00(17) | 94.4(3) | 95.64(19) |
| N2a-Fe1-N3a | 82.64(5) | 76.58(6) | 82.29(17) | 75.8(3) | 74.52(19) |
| N3a-Fe1-N3 | 174.77(7) | 165.62(9) | 176.3(2) | 167.3(4) | 167.3(3) |

**Table S7.** The distortion of octahedral coordination geometry.

| Complex | Σ (deg) |
|---|---|
| **1·3MeOH** at 150 K | 37.93 |
| **1·2H$_2$O** at 150 K | 39.16 |
| **1·3MeOH** at 300 K | 70.03 |
| **1·2H$_2$O** at 293 K | 74.79 |
| **1** at 150 K | 81.71 |

**Table S8.** The distances (Å) and angles (dge) of intermolecular interactions.

| Complex | **1·3MeOH** | | **1·2H$_2$O** | | **1** |
|---|---|---|---|---|---|
| Temperature | 150 K | 300 K | 150 K | 293 K | 150 K |
| $C_{phen}$–H···S | 3.597 | 3.918 | 3.755 | 3.744 | 3.931 |
| $C_{phen}$–H···S | 3.941 | 3.946 | 3.761 | 3.835 | 3.689 |
| $C_{anth}$–H···S | 3.811 | 3.948 | 3.638 | 3.619 | 3.769 |
| O2–H···S | 3.349 | 3.341 | — | — | — |
| $C_{MeOH}$–H···S | 4.006 | 3.569 | — | — | — |
| O1–H···N4 | 2.673 | 2.705 | 2.764 | 2.771 | — |
| N5–H···O | 2.726 | 2.771 | 2.830 | 2.859 | — |
| $\pi \cdots \pi_{phen \cdots anth}$ | 4.047 | 4.128 | 3.716 | 3.783 | 3.732 |
| | 3.687 | 3.735 | 3.657 | 3.672 | 3.554 |
| plane ··· centroid | 3.790 | 3.889 | 3.489 | 3.575 | 3.571 |
| | 3.429 | 3.508 | 3.421 | 3.470 | 3.422 |
| Offset angle | 13.917 | 14.702 | 5.471 | 7.710 | 12.798 |
| | 8.279 | 10.184 | 4.026 | 6.664 | 8.918 |
| $\pi \cdots \pi_{anth \cdots anth}$ | 3.769 | 3.801 | 3.601 | 3.612 | 3.823 |
| plane ··· centroid | 3.432 | 3.515 | 3.412 | 3.462 | 3.689 |
| Offset angle | 1.584 | 1.485 | 2.188 | 1.519 | 4.285 |

## Figures

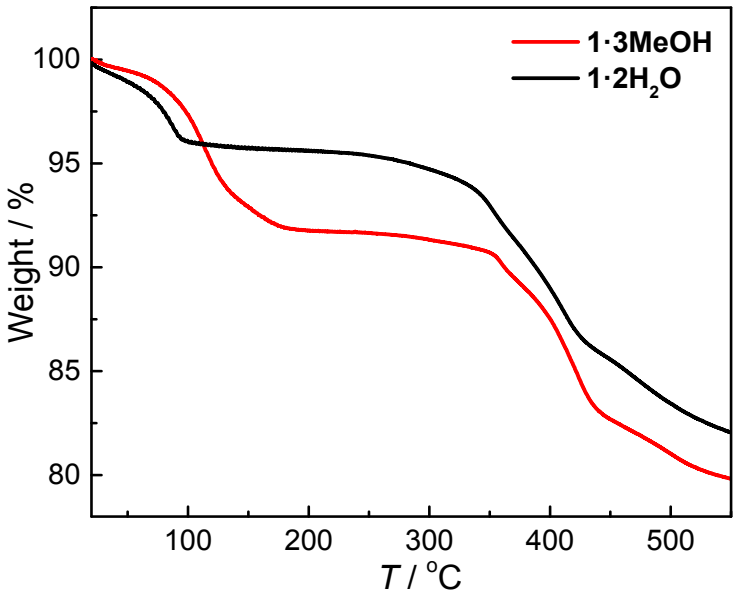


**Fig. S1** Thermogravimetric data of **1·3MeOH** and **1·2H$_2$O**.

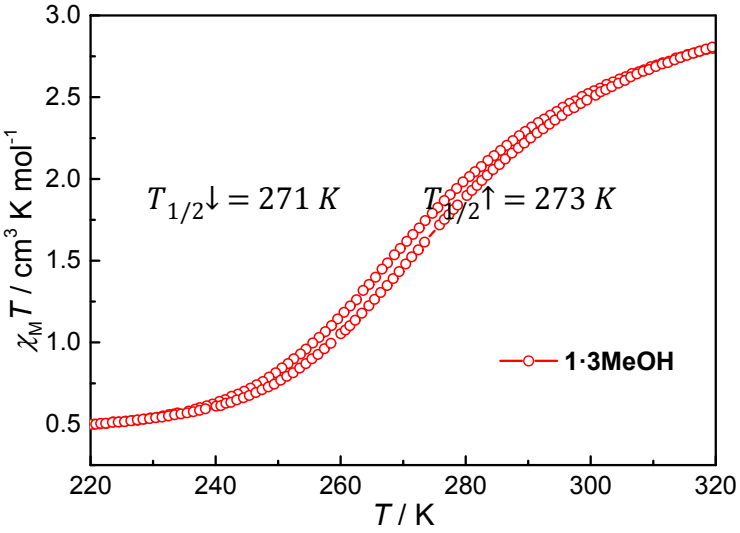


**Fig. S2** $\chi_M T$ versus *T* plot of **1·3MeOH** in the temperature range of 220–320 K showing a 2 K-wide hysteresis.

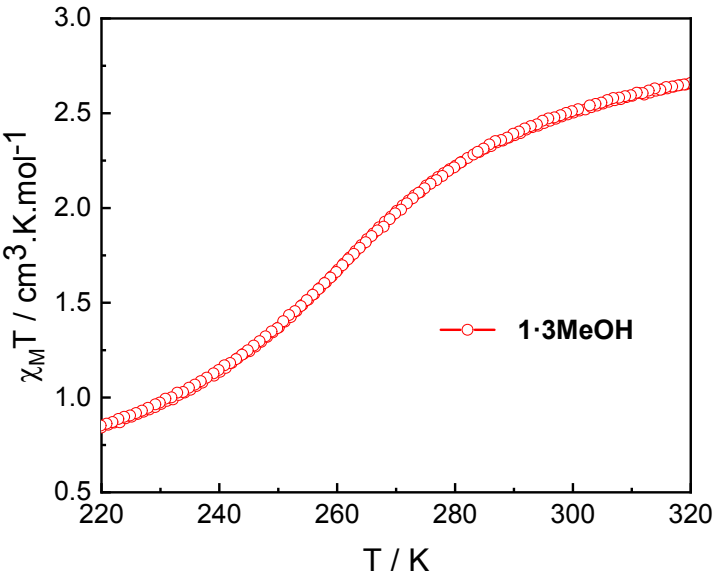


**Fig. S3** $\chi_M T$ versus *T* plot of **1·3MeOH** in the temperature range of 220–320 K with settle mode showing no hysteresis.

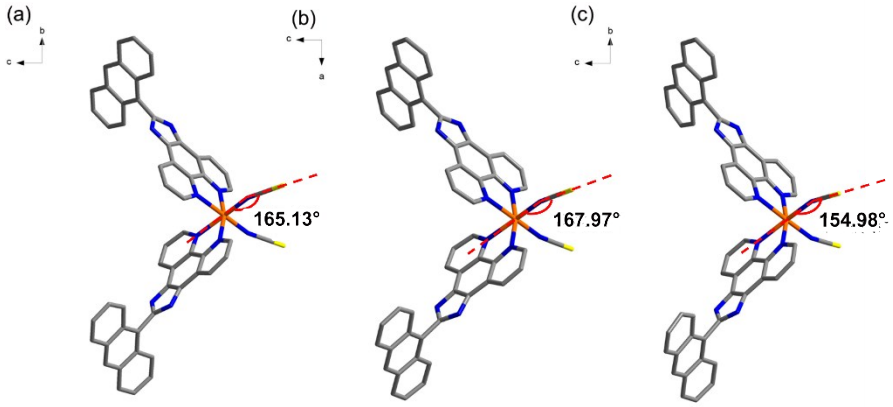


**Fig. S4** The angles of $C_{SCN}$–N–Fe for compounds **1·3MeOH** (a), **1·2H$_2$O** (b) and **1** (c).

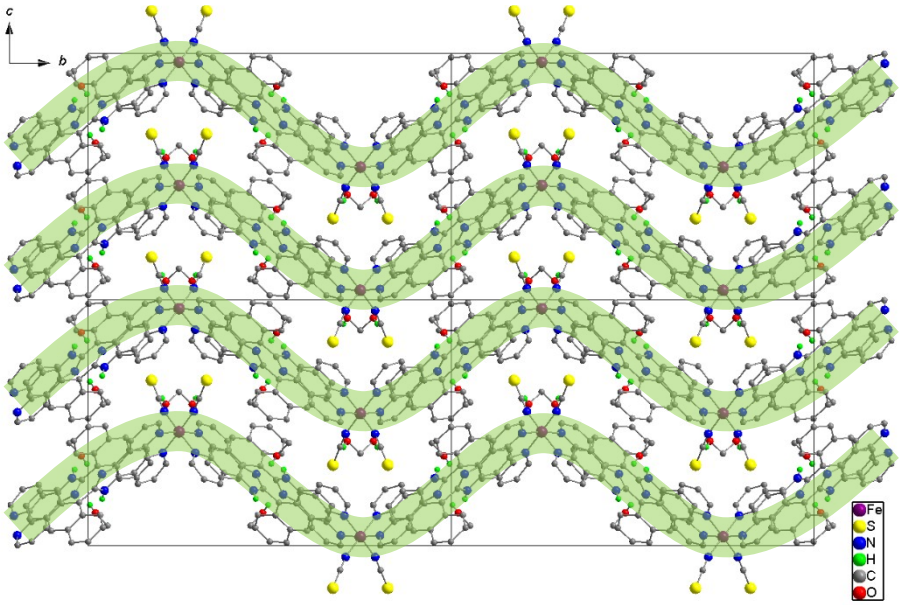


**Fig. S5** Three-dimensional structure of **1·3MeOH** showing corrugate layers.

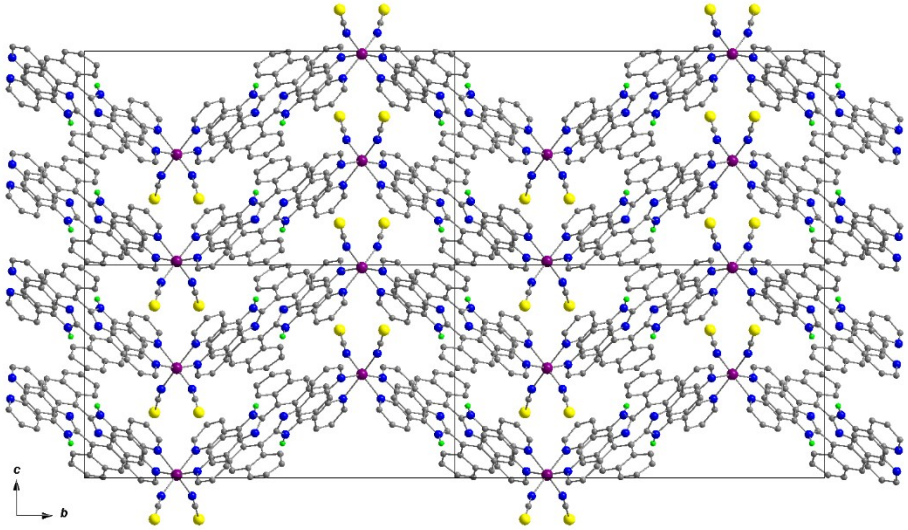


**Fig. S6** Three-dimensional structure of **1**.

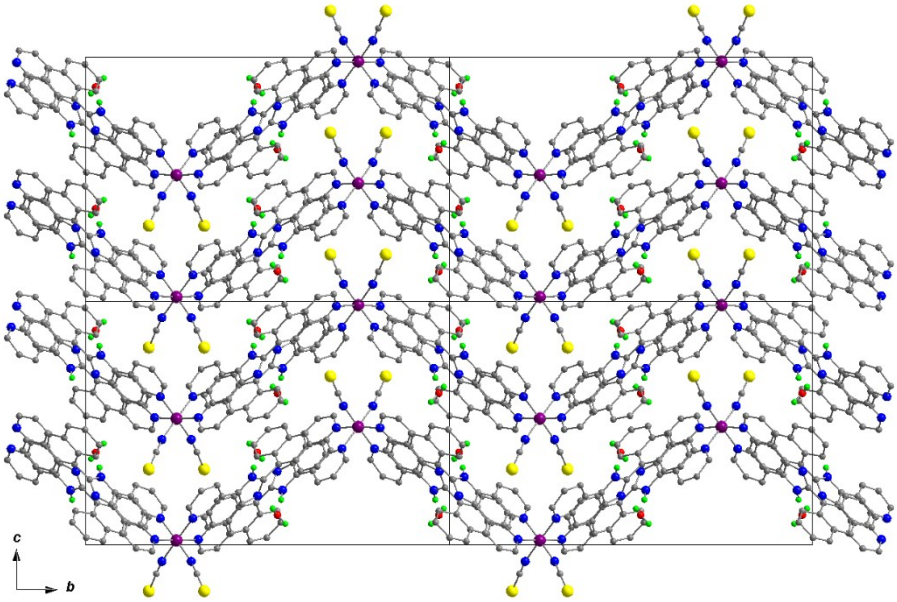


**Fig. S7** Three-dimensional structure of **1·2H$_2$O**.

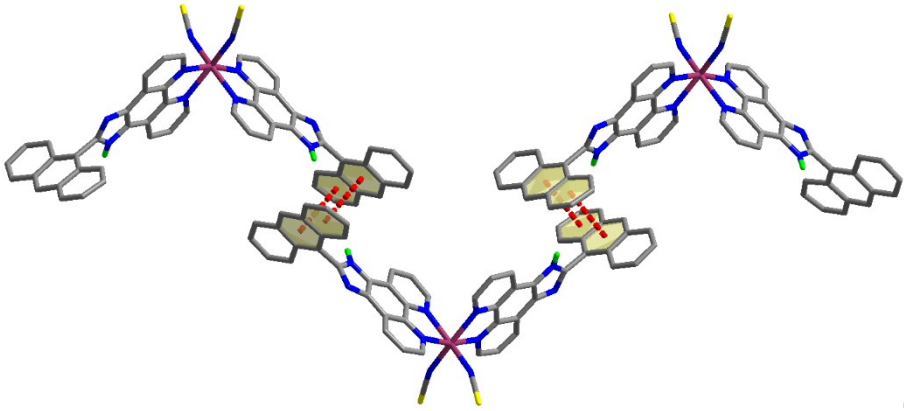

**Fig. S8** Interlayer π···π interactions in all compounds.

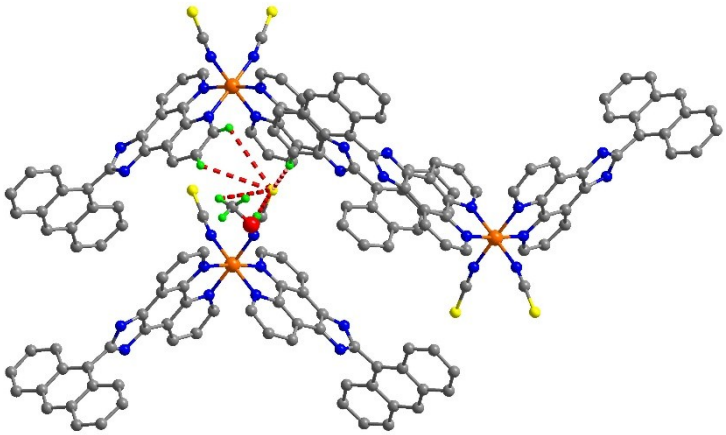

**Fig. S9** S···H contacts in **1·3MeOH**.

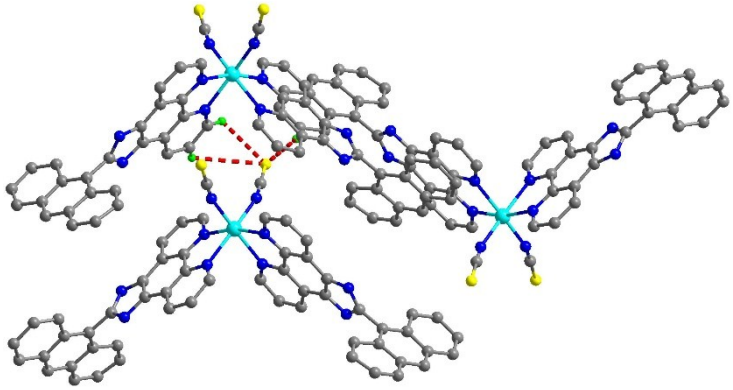

**Fig. S10** S···H contacts in **1**.

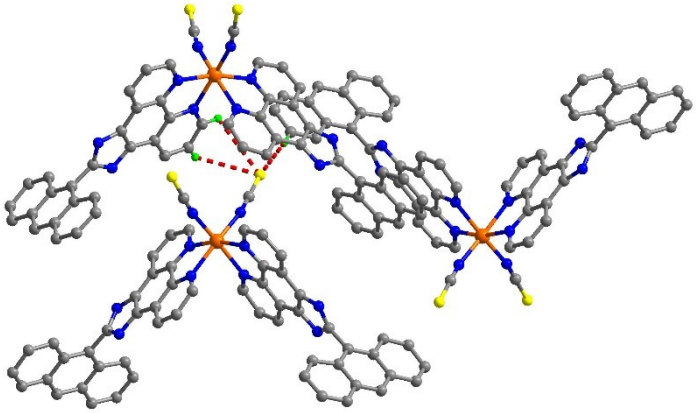

**Fig. S11** S···H contacts in **1·2H$_2$O**.

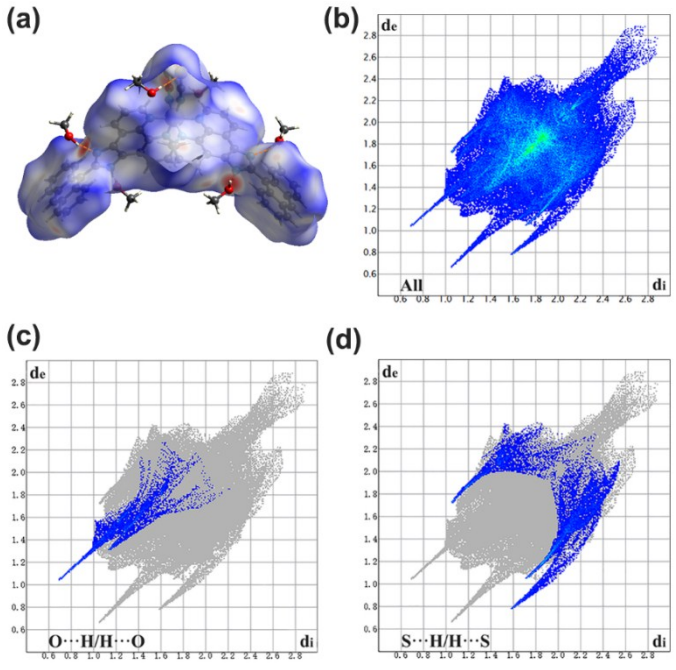


**Fig. S12** Hirshfield Surface analysis for **1·3MeOH** at LS (a), the Hirshfield Surface with $d_{norm}$ (b), 2D fingerprint plots of O···H/H···O contacts (c), and 2D fingerprint plots of S···H/H···S contacts (d).

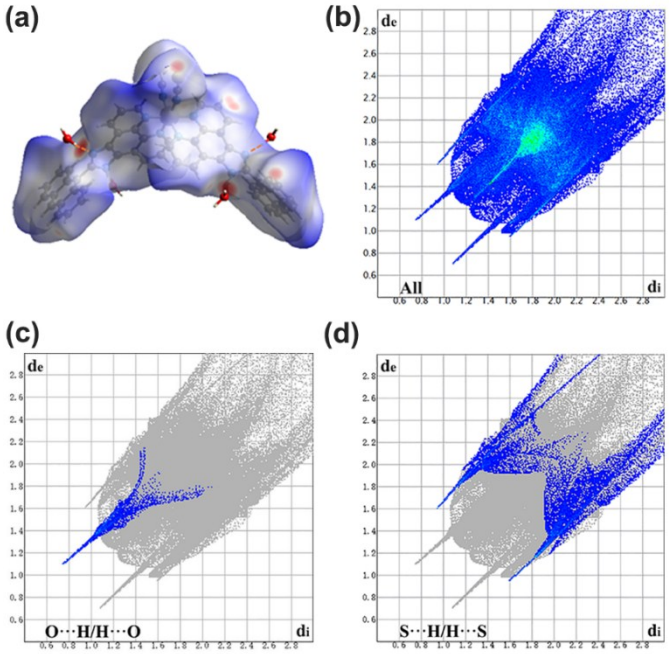


**Fig. S13** Hirshfield Surface analysis for **1·2H$_2$O** at LS (a), the Hirshfield Surface with $d_{norm}$ (b), 2D fingerprint plots of O···H/H···O contacts (c), and 2D fingerprint plots of S···H/H···S contacts (d).

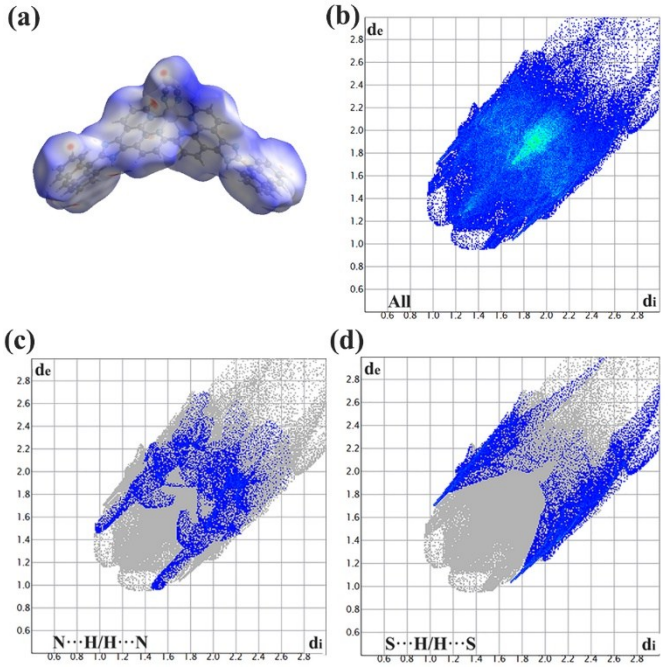


**Fig. S14** Hirshfield Surface analysis for **1** (a), the Hirshfield Surface with $d_{norm}$ (b), 2D fingerprint plots of N···H/H···N contacts (c), and 2D fingerprint plots of S···H/H···S contacts (d).

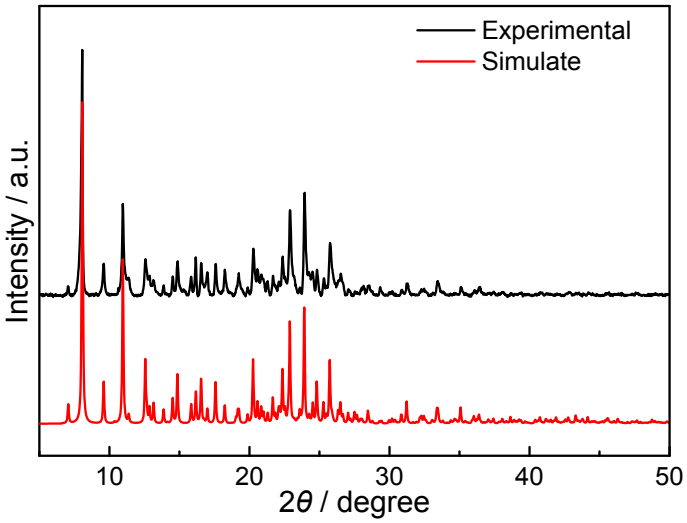


**Fig. S15** The PXRD pattern of **1·3MeOH** at room temperature.

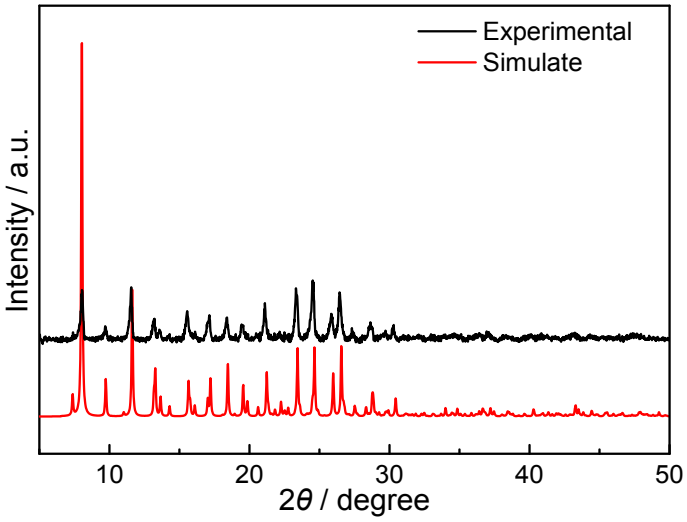


**Fig. S16** The PXRD pattern of **1·2H$_2$O** at room temperature.

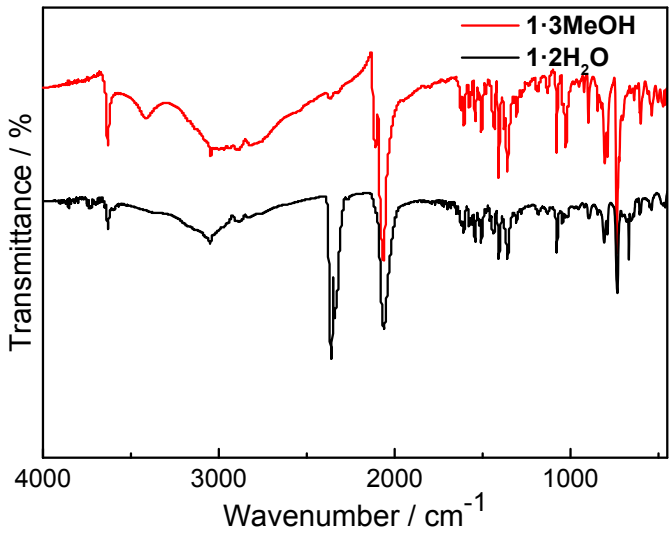


**Fig. S17** IR spectra of **1·3MeOH** and **1·2H$_2$O**.

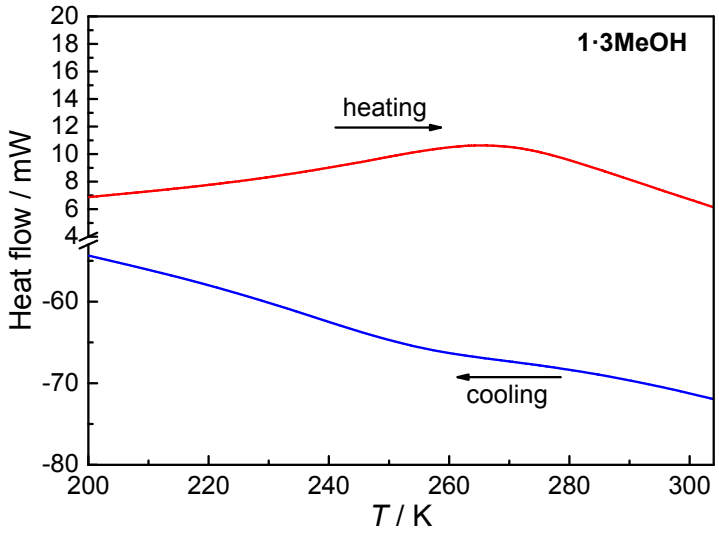


**Fig. S18** DSC data of **1·3MeOH**.

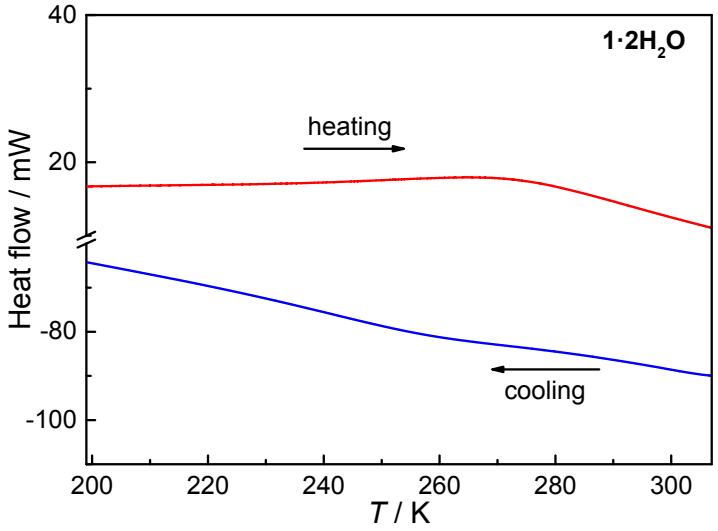


**Fig. S19** DSC data of **1·2H$_2$O**.