

Supporting Information

**Enhanced stability and colorimetric detection on Ag(I) ion of a
methylthio-functionalized Zn(II) metal-organic framework**

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Table of Contents

Experimental details	3
MOF syntheses	5
Figures and Tables	6
Fig. S1 The synthetic procedure for H ₆ L1	6
Fig. S2 The ¹ H NMR spectrum of compound SM2 in CDCl ₃	6
Fig. S3 The ¹⁹ F NMR spectrum of compound SM2 in CDCl ₃	7
Fig. S4 The ¹³ C NMR spectrum of compound SM2 in CDCl ₃	7
Fig. S5 The ¹ H NMR spectrum of H ₆ L1 in DMSO- <i>d</i> ₆	8
Fig. S6 The ¹³ C NMR spectrum of H ₆ L1 in DMSO- <i>d</i> ₆	8
Fig. S7 Synthetic scheme for the NOTT-6SMe-Zn	9
Fig. S8 PXRD patterns of NOTT-6SMe-Zn	9
Fig. S9 Thermogravimetric (TG) plots of NOTT-6SMe-Zn	10
Fig. S10 The FT-IR spectra of NOTT-6SMe-Zn	11
Fig. S11 Synthetic scheme for the NOTT-Zn	11
Fig. S12 PXRD patterns of NOTT-Zn	12
Fig. S13 Emission spectra of NOTT-Zn	12
Fig. S14 Photographs of the NOTT-6SMe-Zn	13
Fig. S15 Emission spectra of NOTT-6SMe-Zn	13
Fig. S16 Photographs of the NOTT-6SMe-Zn	14
Fig. S17 XPS survey spectra of NOTT-6SMe-Zn	14
Fig. S18 Scanning electron microscopy (SEM) images of NOTT-6SMe-Zn	15
Fig. S19 An elemental mapping of NOTT-6SMe-Zn	15
Fig. S20 An elemental mapping of NOTT-Zn	16
Fig. S21 The FT-IR spectra of NOTT-Zn	16
Table S1 Crystallographic refinement parameters and results of NOTT-6SMe-Zn	17
References	18

Experimental details

General procedure. Starting materials, reagents, and solvents were purchased from commercial sources (J&K, Aldrich and Acros) and used without further purification. Elemental analysis was performed with a Vario Micro CUBE CHN elemental analyzer. FT-IR spectra were obtained using a Nicolet Avatar 360 FT-IR spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded at 298 K on a 400 MHz Bruker superconducting magnet high-field NMR spectrometer, with working frequencies of 400 MHz for ^1H and 100 MHz for ^{13}C nuclei. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents, with tetramethylsilane (TMS) as the internal standard. Thermogravimetric analyses (TG) were carried out in a nitrogen stream using PerkinElmer Thermal analysis equipment (STA 6000) with a heating rate of 10 °C/min. The ratios of the metal ions (between Ag^+ and Zn^{2+}) were determined by using a PerkinElmer Optima™ 2100 DV ICP optical emission spectrometer. Powder X-ray diffraction data were collected in reflection mode at room temperature on a Rigaku Smart Lab diffractometer with mixture of Cu-K α 1 ($\lambda = 1.54056$ Å) and Cu-K α 2 ($\lambda = 1.5418$ Å) radiation. The X-ray tube operated at a voltage of 30 kV and a current of 30 mA. Scanning electron microscopy (SEM) images were obtained from a field-emission scanning electron microscope (Hitachi, SU8220). Fluorescence emission spectra were obtained with a FluoroMax-4 fluorescence photometer. Fluorescence images were acquired with a Zeiss Observer Z1 Research Microscope.

Single crystal X-ray crystallography. Single crystal data for NOTT-6SMe-Zn were collected using a Bruker APEX-II CCD diffractometer with an I- μ -S micro-focus X-ray source using Cu K α radiation ($\lambda = 1.54178$ Å). Data were collected at 293 K. Data were collected, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX3 v2018. The space group was assigned and the structure was solved by direct methods using XPREP within the SHELXTL suite of programs¹ and refined by full matrix least squares against F^2 with all reflections using Shelxl2018² using the graphical interface Olex2³. As the solvent guests are disordered in the pores, all of them have been squeezed, which leads to several alerts (e.g., no acceptor was found for some O-H bonds from coordinated water molecules). Anisotropic temperature factors

were applied to all non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and refined by applying riding models. Additional details are given in Table S1. Complete crystallographic data for NOTT-6SMe-Zn, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre as CCDC 2056514. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of 2, 4, 6-tris (4-bromo-2, 6-difluorophenyl)-1, 3, 5-triazine (SM1).

SM1 was synthesized according to the previously reported work.⁴

Synthesis of hexamethyl 4',4''',4''''-(1,3,5-triazine-2,4,6-triyl)tris(3',5'-difluoro-[1,1'-biphenyl]-3,5-dicarboxylate) (SM2).

A two-neck round-bottomed flask (50 mL) was loaded with a magnetic stirring bar, powders of **SM1** (0.654 g, 1.0 mmol), (3,5-bis(methoxycarbonyl)phenyl)boronic acid (1.428 g, 6 mmol), Potassium phosphate tribasic (1.910 g, 6 mmol) and (triphenylphosphine) palladium (58.0 mg, 0.05 mmol), and then evacuated and refilled with N₂ thrice. Solvents of 1,4-dioxane (10 mL) was degassed and injected *via* cannula under N₂ into the flask. The flask was then connected to a condenser and the mixture was heated for 24 h under N₂ protection. After the reaction mixture was cooled to room temperature, the mixture was poured into water (50 mL) and extracted by ethyl acetate (3 × 50 mL). The combined organic layer was then washed by water (3 × 50 mL), dried over anhydrous MgSO₄, and the organic solvent was removed with a rotary evaporator. The residue was further purified by column chromatography (silica gel, with petroleum ether and ethyl acetate as the eluent) to afford a white solid (**SM2**, 834 mg, yield 84% based on **SM1**). ¹H NMR (400 MHz, CDCl₃) δ 8.75 (s, 3H), 8.48 (s, 6H), 7.41 (d, *J* = 8.7 Hz, 6H), 4.01 (s, 18H). ¹⁹F NMR (376 MHz, CDCl₃) δ -110.84 (d, *J* = 8.6 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 165.61 (s), 163.73 (dd, *J* = 261.9, 5.1 Hz), 147.22 (t, *J* = 9.7 Hz), 138.03 (t, *J* = 2.2 Hz), 132.25 (s), 132.19 (s), 131.80 (s), 111.06 (dd, *J* = 20.9, 3.4 Hz), 109.12 (s), 92.06 (t, *J* = 19.5 Hz), 52.94 (s). FT-IR (KBr pellet, v/cm⁻¹): 3432 (w), 3071 (w), 2949 (w), 2919 (w), 2848 (w), 1718 (s), 1634 (s), 1584 (m), 1560(s), 1510 (s), 1438 (s), 1397 (m), 1355 (s), 1280 (s), 1187 (m), 1108 (s), 1033 (s), 958 (w), 893 (m),858 (s), 827 (m), 771 (s), 723 (w), 697 (w), 584 (w), 555 (m).

Synthesis of hexamethyl 4',4''',4''''-(1,3,5-triazine-2,4,6-triyl)tris(3',5'-difluoro-[1,1'-biphenyl]-3,5-dicarboxylate) (H₆L1).

Powders of **SM2** (497 mg, 0.5 mmol) and CH₃SNa (1.051 g, 15 mmol) and a magnetic stirrer were loaded into a 25 mL two-neck round-bottom flask under N₂ protection. The flask was connected to a Schlenk line, and 10 mL degassed DMF was then transferred into the flask via cannula. After being stirred at room temperature for 24 h, the mixture was poured into the water (100 mL) and HCl (10%) was then added slowly with vigorous stirring. After the pH value of the mixture became lower than 2, the precipitate was collected by suction filtration and washed with water extensively. Yield: 474 mg (88%, based on **SM2**). The obtained product was pure as indicated by NMR spectrum and was used for crystal growth without further purification. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.50 (s, 3H), 8.43 (s, 6H), 7.53 (s, 6H), 2.51 (s, 18H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 173.70, 167.07, 143.3, 141.08, 139.08, 134.72, 130.32, 129.92, 127.45, 122.24, 16.36. FT-IR (KBr pellet, v/cm⁻¹): 3406 (s), 3076 (s), 2982 (s), 2916 (s), 2622 (m), 2531 (m), 1701 (s), 1606 (m), 1580 (m), 1515 (s), 1435 (s), 1413 (s), 1347 (m), 1315 (m), 1246 (s), 1210 (s), 1141 (m), 1100 (m), 965 (m), 918 (w), 828 (m), 800 (m), 755 (s), 729 (w), 659 (w).

MOF syntheses

Preparation of single crystals of NOTT-6SMe-Zn. H₆L1 (5.0 mg, 4.6 μmol) and Zn(NO₂)₂·6H₂O (5 mg, 16.8 μmol) were loaded into a heavy-wall glass tube (10 mm OD, 6 mm ID), and then a solution of DMF (0.6 mL) was added. The tube was then flame-sealed and heated at 130 °C in a programmable oven for 48 h, followed by slow cooling (1.0 °C/min) to room temperature, during which single crystals suitable for single-crystal X-ray diffraction were formed (yield 60% based on H₆L1). FT-IR (KBr pellet, v/cm⁻¹): 3372 (s), 3072 (w), 2922 (w), 1621 (s), 1574 (s), 1542 (s), 1408 (s), 1435 (s), 1351 (s), 1100 (w), 1019 (w), 967 (w), 777 (s), 723 (s). X-ray powder diffraction of the bulk sample indicated a pure phase consistent with the single-crystal structure. After solvent exchange and drying, elemental analysis (EA) found [C (42.21%), H (3.55%), N (3.47%), S (13.00%)]; a fitting formula can be determined to be

$\text{Zn}_3(\text{H}_2\text{O})_3(\text{C}_{51}\text{H}_{33}\text{N}_3\text{O}_{12}\text{S}_6) \cdot (\text{DMF})_{0.7} \cdot (\text{H}_2\text{O})_7$ (mw 1499), which gives a calculated profile as [C (42.53%), H (3.89%), N (3.46%), S (12.83%)].

Preparation of single crystals of NOTT-Zn. NOTT-Zn was prepared similarly with the synthetic procedure of NOTT-6SMe-Zn using $\text{H}_6\text{L2}$ instead of $\text{H}_6\text{L1}$.

Figures and Tables

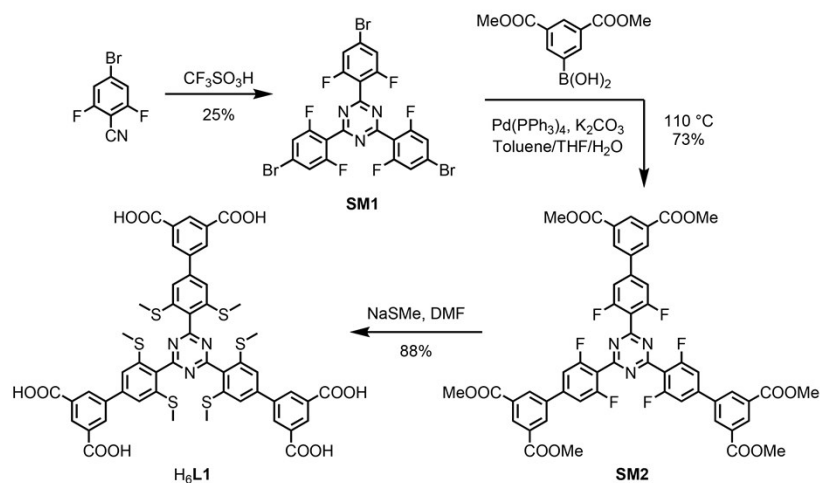


Fig. S1 The synthetic procedure for $\text{H}_6\text{L1}$.

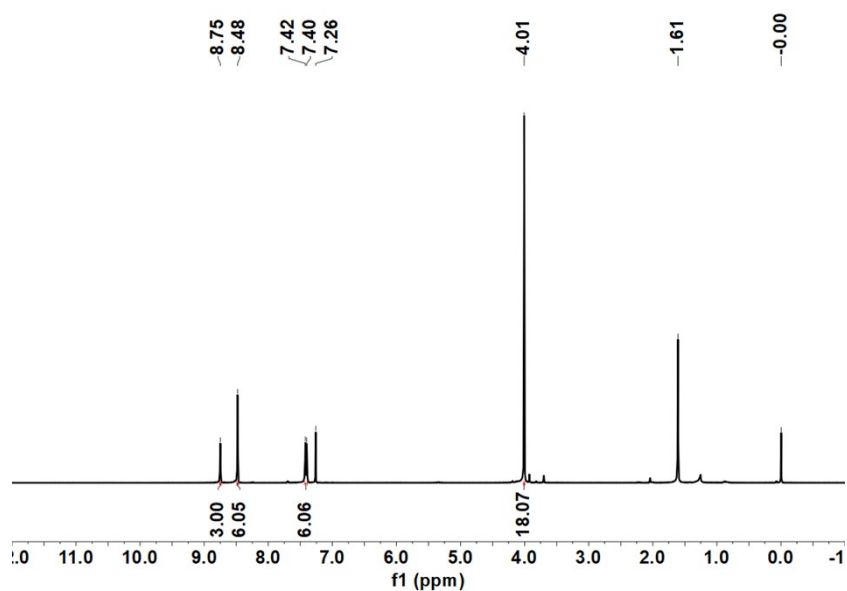


Fig. S2 The ^1H NMR spectrum of compound **SM2** in CDCl_3 .

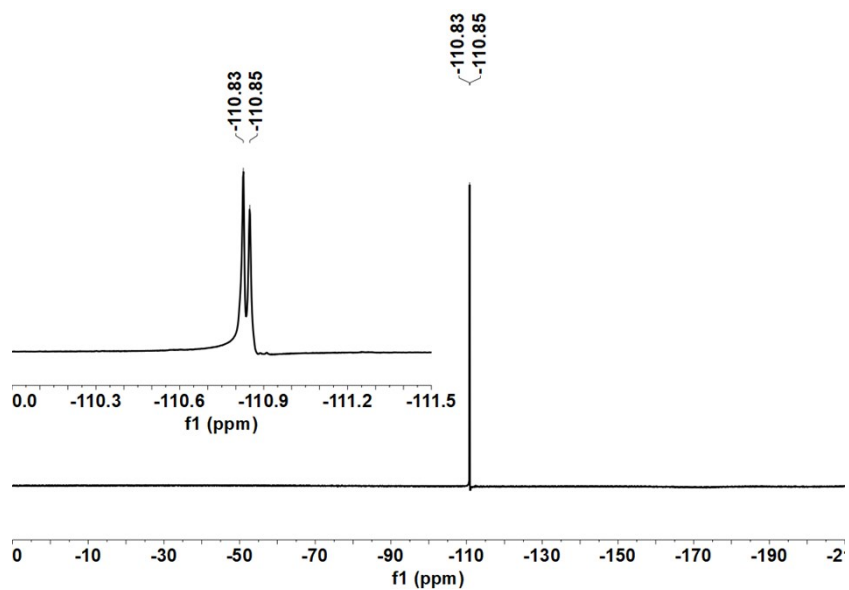


Fig. S3 The ^{19}F NMR spectrum of compound **SM2** in CDCl_3 .

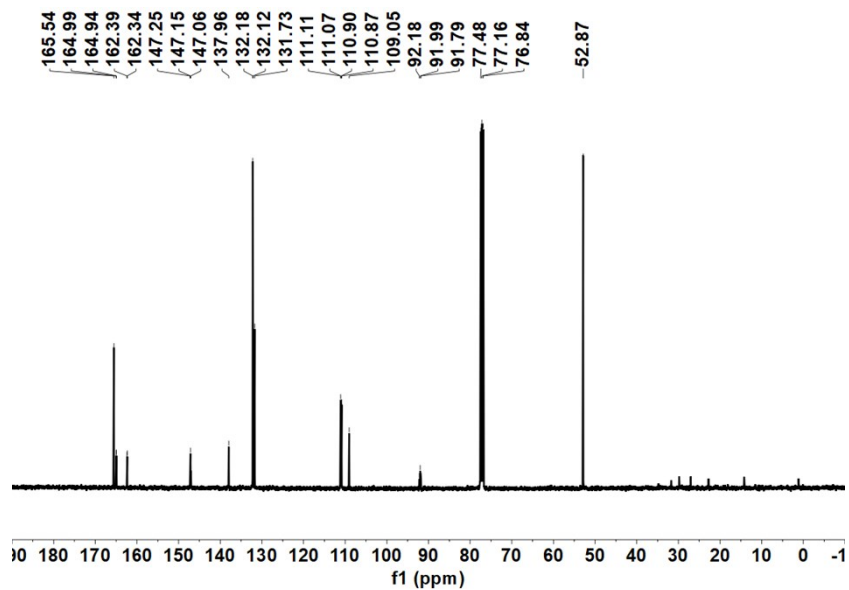


Fig. S4 The ^{13}C NMR spectrum of compound **SM2** in CDCl_3 .

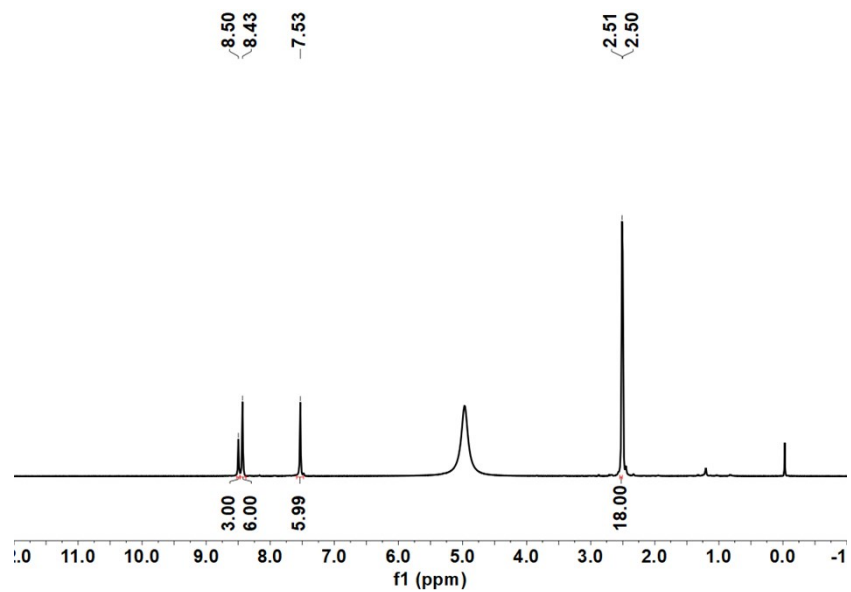


Fig. S5 The ^1H NMR spectrum of $\text{H}_6\text{L1}$ in $\text{DMSO-}d_6$.

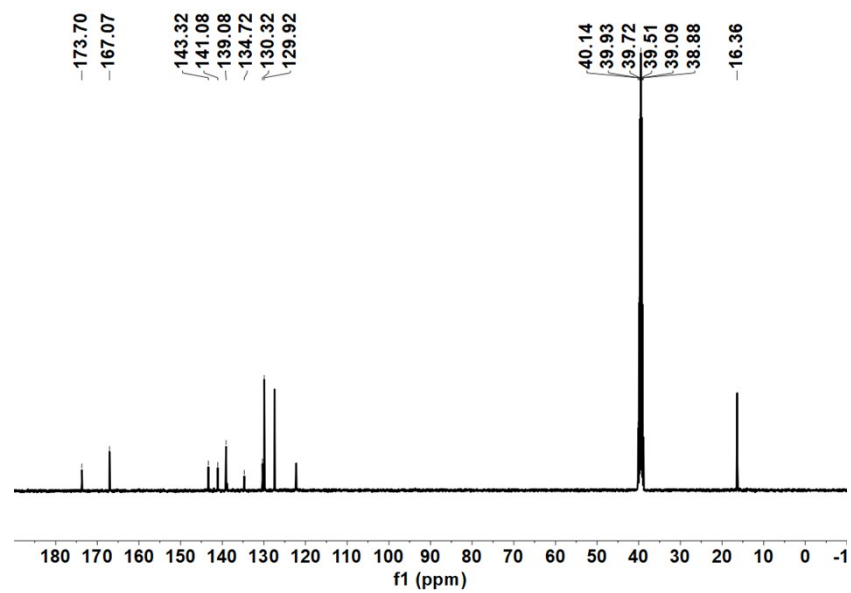


Fig. S6 The ^{13}C NMR spectrum of $\text{H}_6\text{L1}$ in $\text{DMSO-}d_6$.

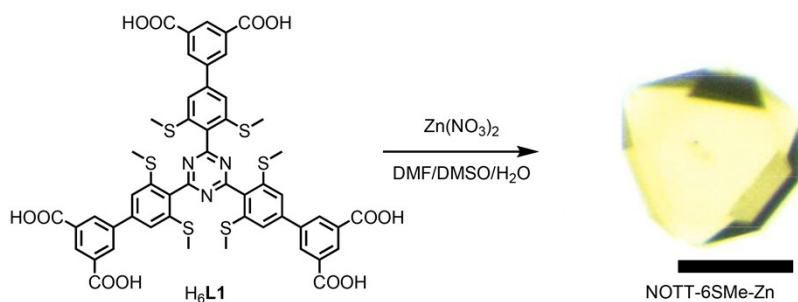


Fig. S7 Synthetic scheme for the NOTT-6SMe-Zn. (photograph of a single crystal was shown in the right. Scale bar: 100 μm).

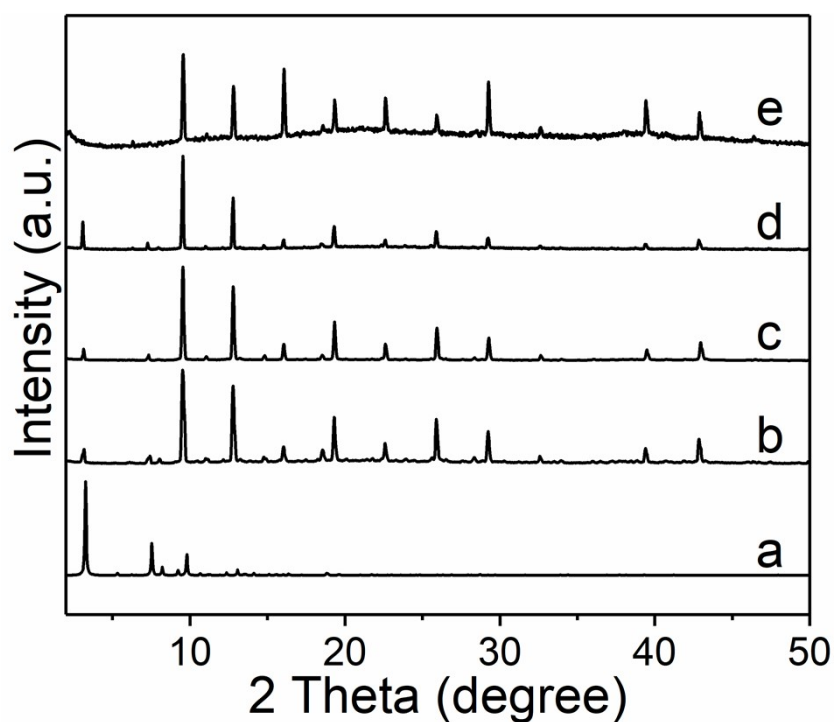


Fig. S8 PXRD patterns of NOTT-6SMe-Zn: (a) simulated, (b) as-synthesized, after immersing in (c) 100 ppm, (d) 500 ppm and (e) saturated AgNO_3 solution for 2 h at 80 $^\circ\text{C}$.

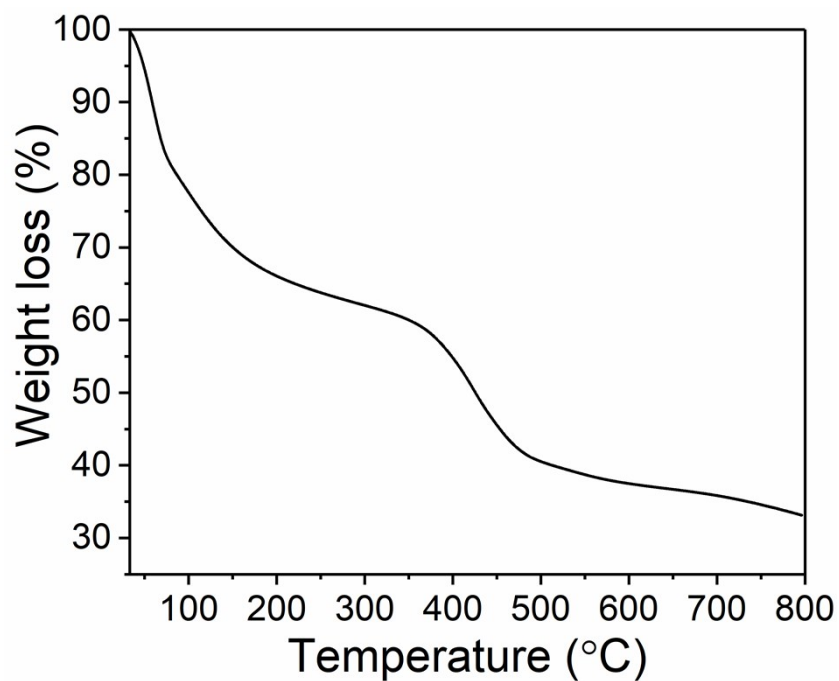


Fig. S9 Thermogravimetric (TG) plots of an as-made sample of NOTT-6SMe-Zn.

The initial weight loss (e.g., under 350 °C) of about 36.5% can be ascribed to the departure of the DMF and water molecules (According to EA analysis, 24.7% should correspond to adsorbed solvent molecules and 11.8% correspond to crystallized solvent molecules, respectively). The ensuing weight loss of 29.2% from 350 °C to 800 °C, which could be due to the decomposition of the organic ligands.

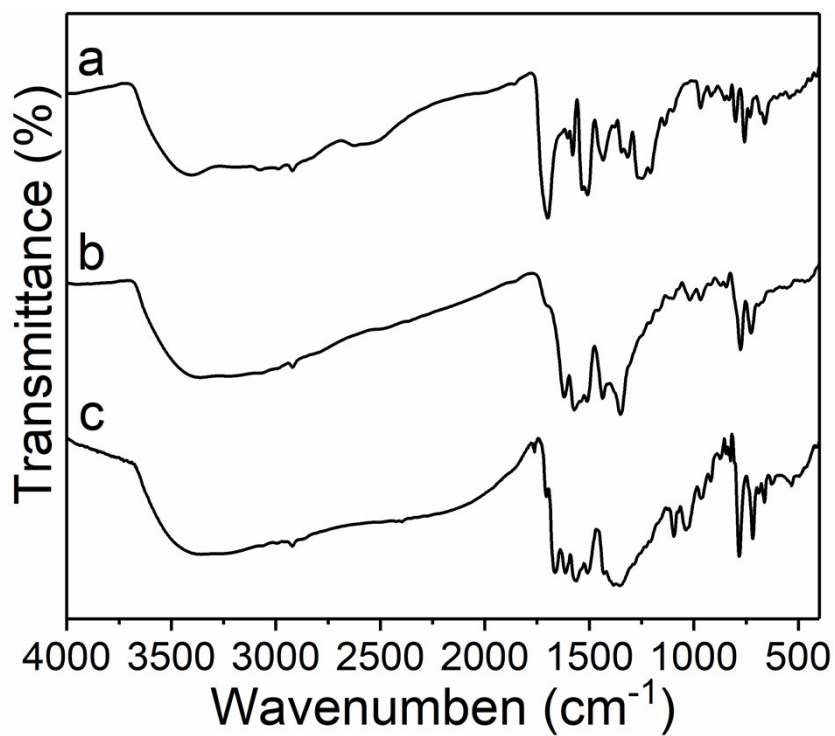


Fig. S10 The FT-IR spectra of (a) the ligand H₆L1, (b) as-made NOTT-6SMe-Zn and (c) after immersion in saturated AgNO₃ solution in DMF for 2 h at 80 °C.

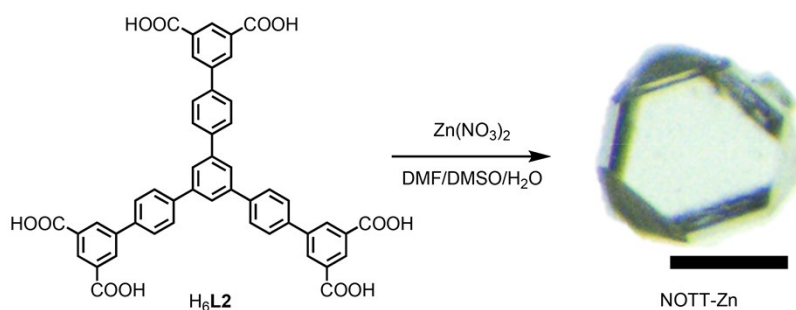


Fig. S11 Synthetic scheme for the NOTT-Zn. (photograph of a single crystal was shown in the right. Scale bar: 100 μm).

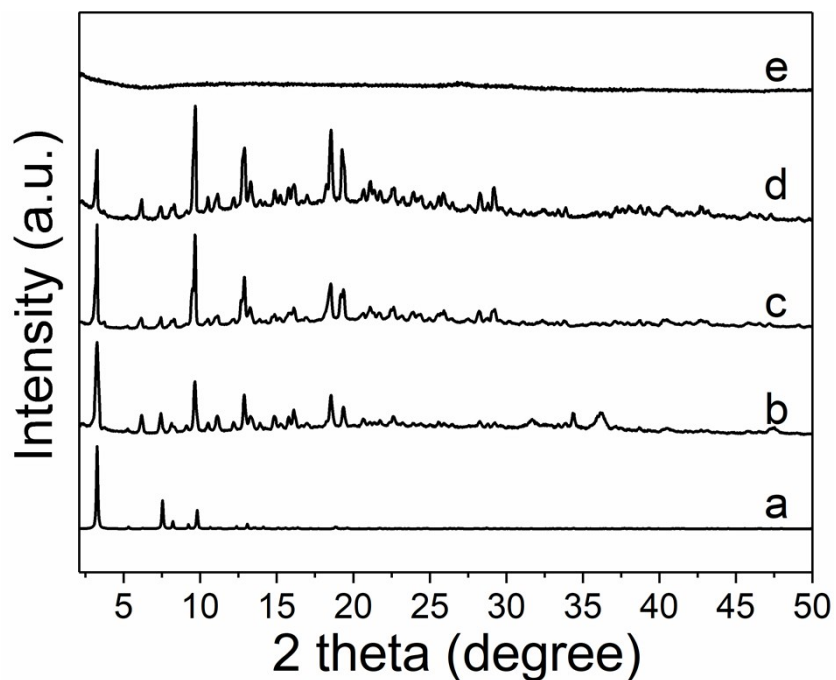


Fig. S12 PXR D patterns of NOTT-Zn: (a) simulated, (b) as-synthesized, after immersion in (c) 100 ppm, (d) 500 ppm and (e) saturated AgNO₃ solution in DMF for 2 h at 80 °C.

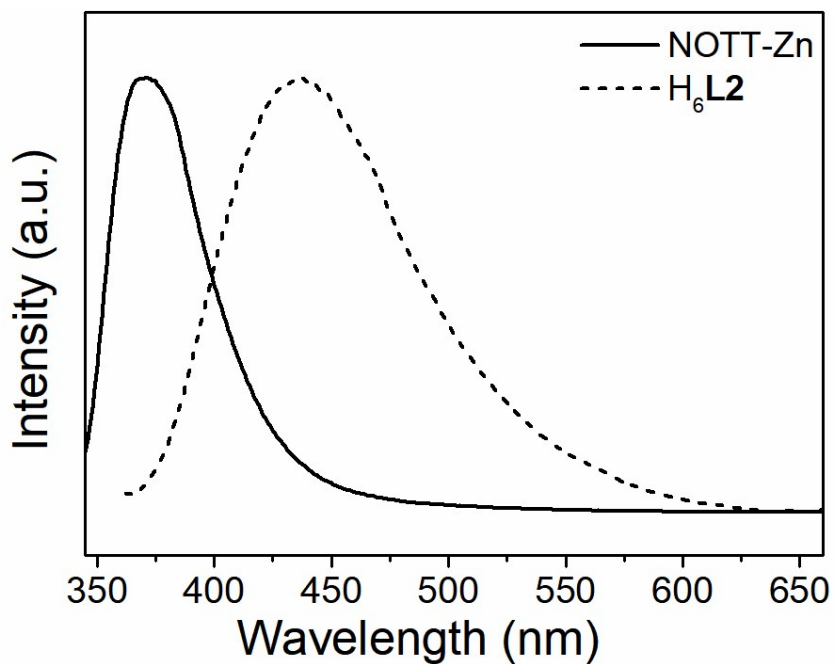


Fig. S13 Emission spectra of (dash) H₆L2 and (solid) NOTT-Zn when excited at $\lambda = 350$ nm.

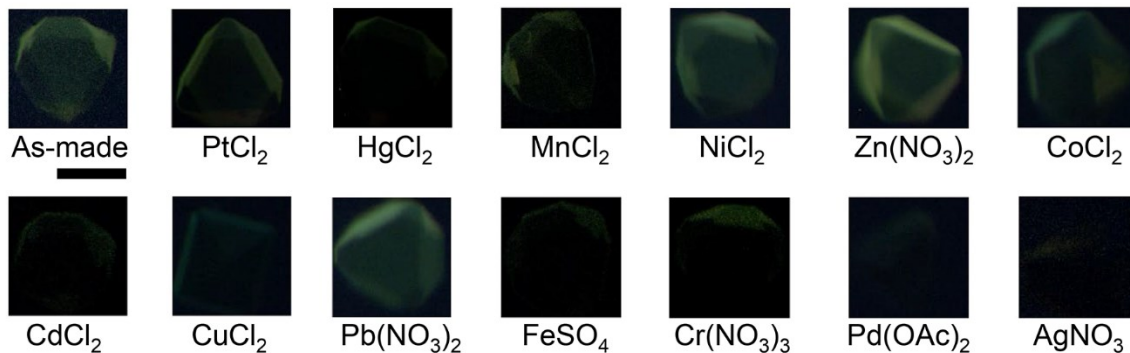


Fig. S14 Photographs of the NOTT-6SMe-Zn crystals under 365 nm UV light before and after immersion (for 2 h at 80 °C) in DMF solutions of various metal salts (1.0 ml each, 300 ppm for each metal ion). The scale bar is 100 μm.

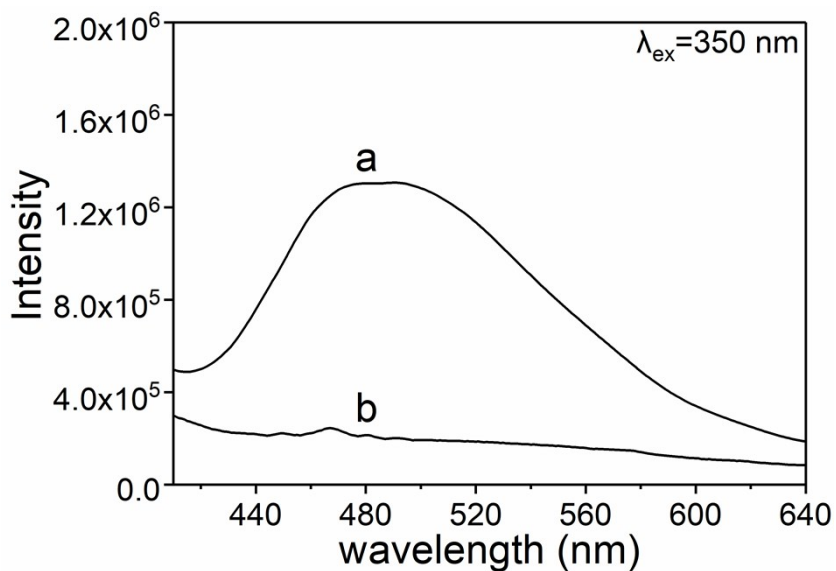


Fig. S15 Emission spectra of NOTT-6SMe-Zn: (a) as-synthesized and (b) after immersion (for 2 h at 80 °C) in 300 ppm Ag(I) in DMF at room temperature (λ_{ex} = 350 nm).

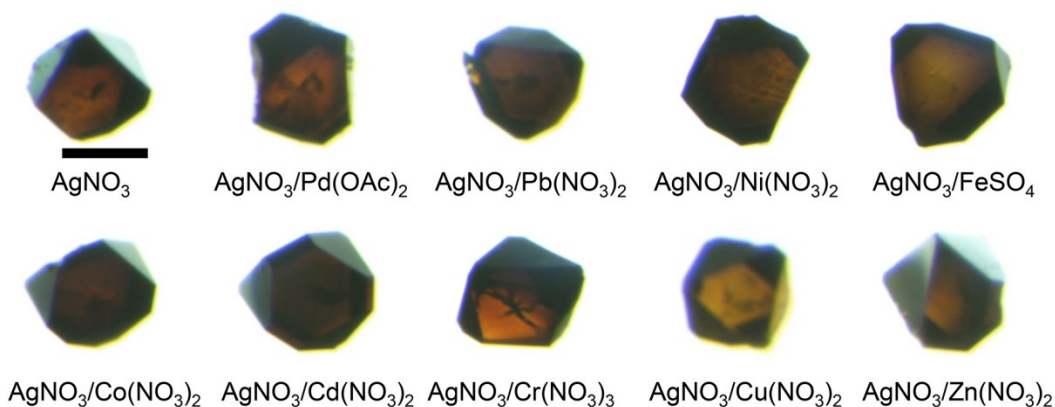


Fig. S16 Photographs of the NOTT-6SMe-Zn crystals (under natural light) after immersion (for 2.5 h at 85 °C) in DMF solutions of AgNO₃ and mixed metal salts (1.0 mL each, 100 ppm for each metal ion). The scale bar is 100 μm.

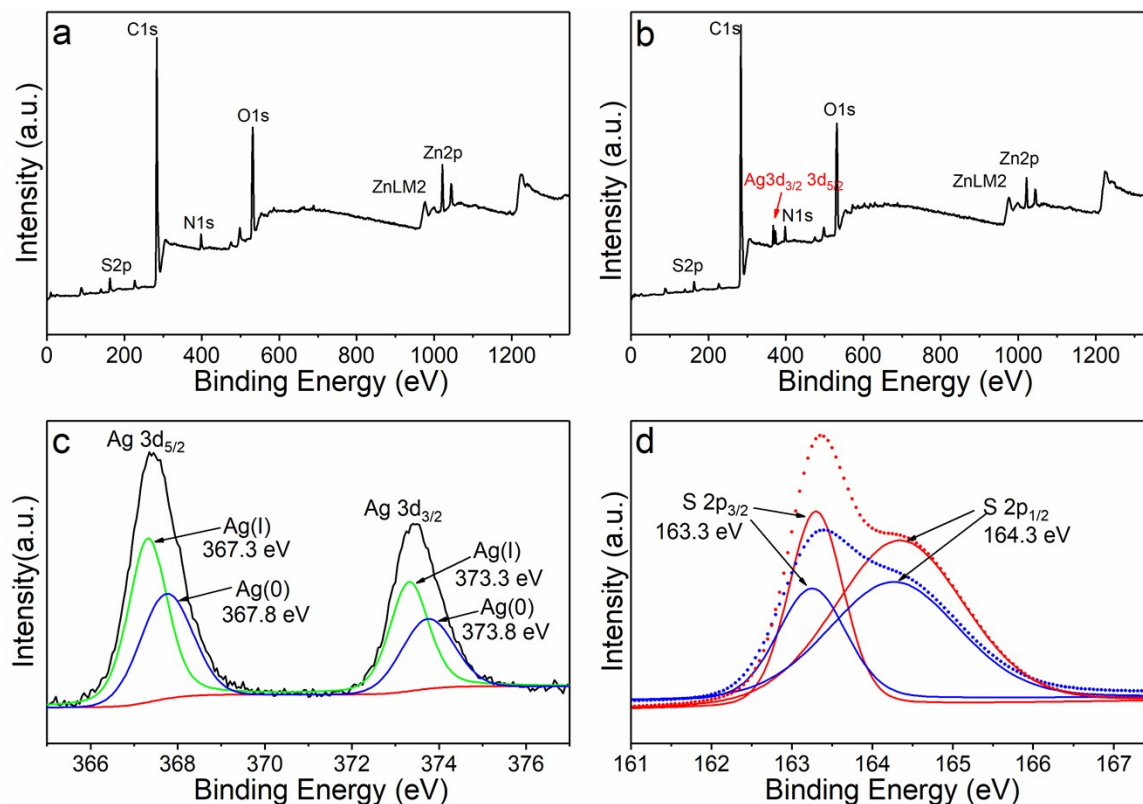


Fig. S17 XPS survey spectra of NOTT-6SMe-Zn (a) before and (b) after immersion in 1500 ppm AgNO₃/DMF solution. (c) Ag 3d spectrum of NOTT-6SMe-Zn after immersion in 1500 ppm AgNO₃/DMF solution. (d) S 2p spectrum of NOTT-6SMe-Zn before (red line) and after (blue line) immersion in 1500 ppm AgNO₃/DMF solution.

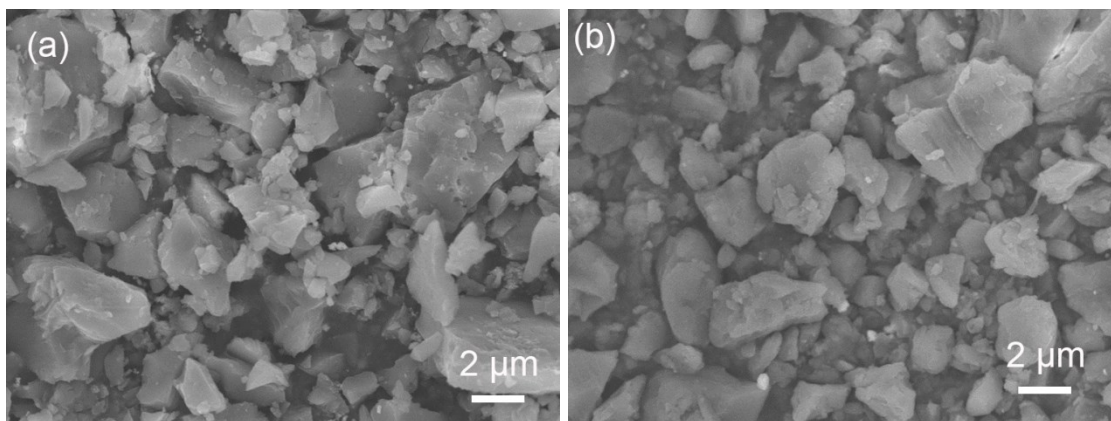


Fig. S18 Scanning electron microscopy (SEM) images (a) NOTT-6SMe-Zn of and (b) NOTT-Zn after immersion in 100 ppm AgNO₃/DMF solution at 85 °C for 2.5 h.

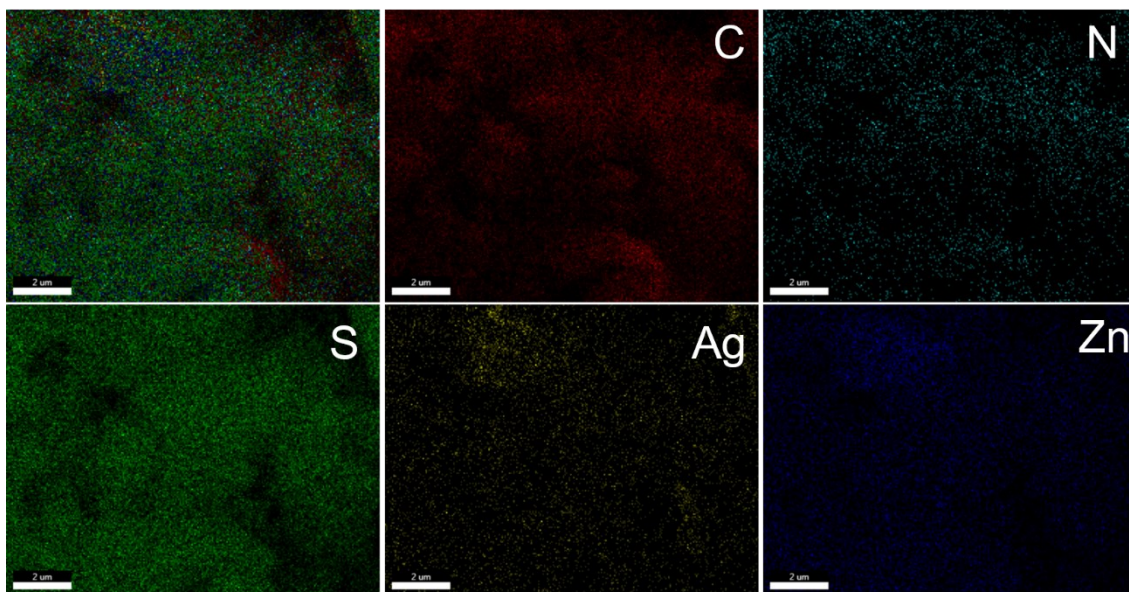


Fig. S19 An elemental mapping (showing the uniform distribution of elements) of NOTT-6SMe-Zn after immersion in 100 ppm AgNO₃/DMF solution at 85 °C for 2.5 h.

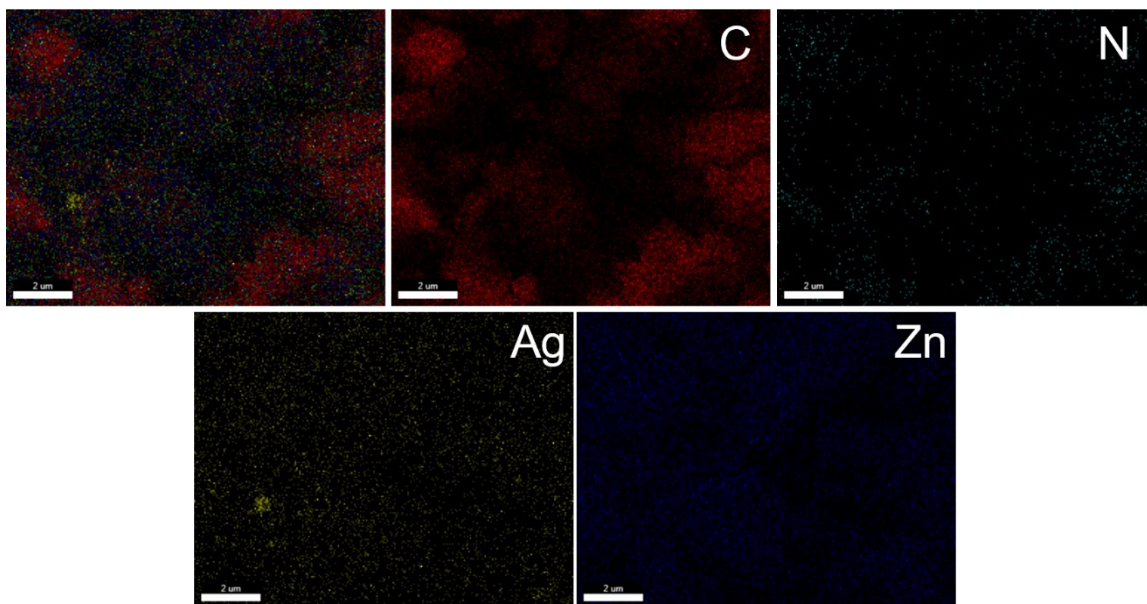


Fig. S20 An elemental mapping (showing the uniform distribution of elements) of NOTT-Zn after immersion in 100 ppm AgNO_3/DMF solution at $85\text{ }^\circ\text{C}$ for 2.5 h.

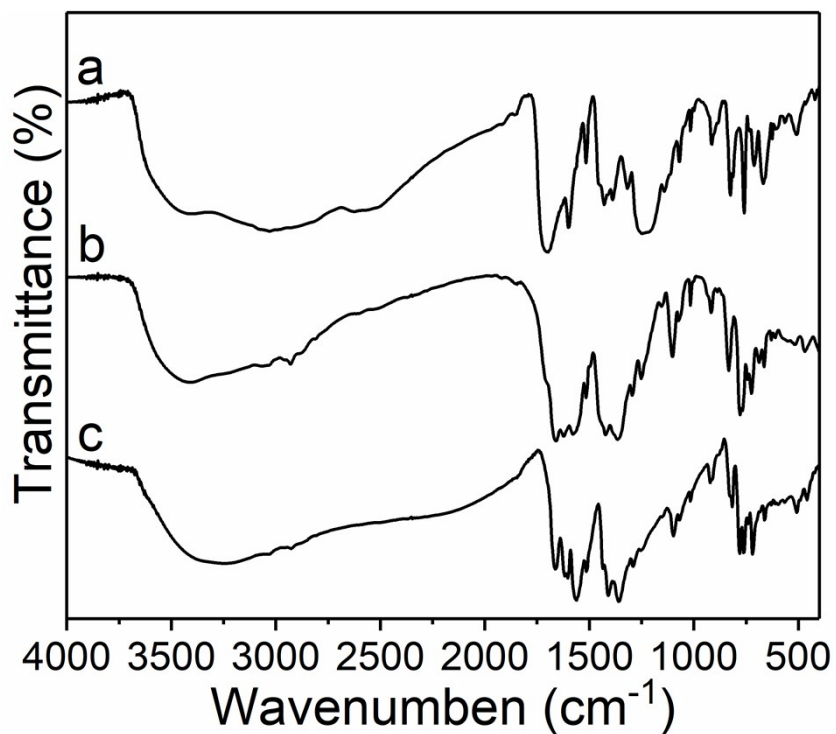


Fig. S21 The FT-IR spectra of (a) the ligand H_6L_2 , (b) as-made NOTT-Zn and (c) after immersion in saturated AgNO_3 solution in DMF for 2 h at $80\text{ }^\circ\text{C}$.

Table S1 Crystallographic refinement parameters and results of NOTT-6SMe-Zn after squeezing the crystallized guests.

Compound	NOTT-6SMe-Zn
Empirical formula	C ₅₁ H ₃₉ N ₃ O ₁₅ S ₆ Zn ₃ [+solvent]
Formula weight	1322.32
Temperature/K	293(2)
Wavelength/Å	1.54184
Crystal system	cubic
Space group	<i>Fm</i> $\bar{3}$ <i>m</i>
a/Å	46.8653
b/Å	46.8653
c/Å	46.8653
α /°	90.00
β /°	90.00
γ /°	90.00
V/Å ³	102933(5)
Z	32
Dc/g.cm ⁻³	0.683
μ /mm ⁻¹	1.815
F(000)	21504.0
R ₁ ^a [I>2 σ (I)]	0.1169
wR ₂ ^b (all data)	0.2573
GOF	1.024

$$^a R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|; \quad ^b wR_2 = (\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2)^{1/2}$$

References

- (1) Sheldrick, G. M. *Acta Crystallogr A* **2008**, *64*, 112.
- (2) Sheldrick, G. M. *Acta Crystallogr C Struct Chem* **2015**, *71*, 3.
- (3) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339.
- (4) He, Y.; Huang, M.; Deng, X.; Shengxian, C.; Wong, Y. L.; Hou, Y. L.; He, J.; Zeller, M.; Xu, Z. *Chem. Commun.* **2019**, *55*, 5091.