Electronic Supplementary Material (ESI) for Dalton Transactions.

Novel symmetric TTF-pyridyl thiolato zinc complex: Synthesis, characterization and crystal structure analysis

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Supplementary Material

General remarks. THF was freshly distilled under N_2 over sodium/benzophenone. Toluene was distilled under nitrogen atmosphere over calcium hydride. Other reagents were used as received. NMR spectra were obtained using JEOL JNM-400 400 MHz or ECP-500 500 MHz spectrometers. HRMS (FAB^+) were obtained using a JEOL JMS-700. Infrared spectra were recorded in KBr pellets with a JASCO FT/IR-4100 spectrometer. Cyclic voltammetry and differential pulse voltammetry data were collected with an ALS-512B electrochemical analyzer with a 0.1 M benzonitrile solution of $TBAClO_4$ as a supporting electrolyte at 25 °C. A Pt working electrode, a Pt counter electrode, and an Ag/AgCl reference electrode were used The system was internally calibrated with a ferrocene/ ferrocenium Fc/Fc^+ ($E^0_{(Fc/Fc+)}$ = 0.48 V vs Ag/AgCl).

Synthesis of 4. BMT-TTF (**2**) (1.00 g, 3.7 mmol) was dissolved in dry THF (30 mL) under N_2 atmosphere and this mixture was cooled to –78 °C. To this solution, *n*-BuLi (1.6 M hexane solution, 2.5 mL, 4.0 mmol) was added dropwise at −78 ℃ for 10 min. After stirring at –78 °C for 1 h, Me_3SnCl (0.81 g, 4.05 mmol) was added dropwise at −78 ℃ for 10 min and the reaction mixture was gradually warmed up to room temperature overnight. The mixture was extracted with dichloromethane, and the organic phase was washed with water, dried over Na_2SO_4 and concentrated in vacuo. The obtained orange oil was dried in vacuo, and then $Pd(PPh_3)_4$ (390 mg, 0.34 mmol), 2-bromopyridine (0.53 g, 3.37 mmol), and dry toluene (20 mL) were added. The mixture was degassed by N_2 bubbling for 30 min and then heated to reflux for 24 h under N_2 atmosphere. After cooled to room temperature, the reaction mixture was extracted with dichloromethane, and the organic phase was washed with water, dried over Na_2SO_4 and concentrated in vacuo. The resulting residue was purified by a column-chromatography on silica gel with CH_2Cl_2/*n*-hexane (1:1, v/v) as an eluent. Compound **4** (830 mg) was obtained as a dark red powder in 66% yield.

mp 127–129 ℃ (dec.). ^{1}H-NMR (500 MHz; $CDCl_3$; Me_4Si): δ 8.55 (dd, J = 6.2, 2.1 Hz, 1H, py), 7.67 (ddd, J = 8.2, 8.2, 2.1 Hz, 1H, py), 7.46 (d, J = 8.2 Hz, 1H, py), 7.19 (dd, J = 6.2, 8.2 Hz,1H, py), 6.97 (s, 1H, TTF), 2.43 (s, 6H, SMe). HRMS FAB^+ (Matrix = 3-Nitrobenzyl alcohol) ($C_{13}H_{11}NS_6$): Found 372.9209; Calcd. 372.9216. IR (KBr) ν_{max}/cm^{-1} 1430, 1636, 2337, 2912.

Synthesis of 5. A solution of freshly prepared 0.5 M LDA (1.3 mL, 0.64 mmol) in dry THF was added slowly to a solution of **4** (200 mg, 0.54 mmol) in dry THF (20 mL) at −78 ℃, and the resulting solution was stirred for additional 40 min at −78 ℃. Methyl 3-thiocyanatopropionate (93 mg, 0.64 mmol)[1] was added via a syringe to the solution, and the mixture was allowed to warm to −78 ℃ over a period of 1 h and finally quenched by an addition of water. This mixture was extracted with dichloromethane, and the organic phase was washed with water, dried over Na_2SO_4 and concentrated in vacuo. The resulting residue was purified by a column-chromatography on silica gel with CH_2Cl_2/*n*-hexane (4:1, v/v) as an eluent. After recrystallization from CH_2Cl_2/*n*-hexane, ligand **5** (240 mg) was obtained as a dark red oil in 90% yield.

^{1}H-NMR (400 MHz; $CDCl_3$; Me_4Si): δ 8.59 (d, J = 5.0 Hz, 1H, py), 8.21 (d, J = 8.0 Hz, 1H, py), 7.70 (ddd, J = 8.0, 8.0, 1.7 Hz, 1H, py), 7.22 (dd, J = 5.0, 8.0 Hz 1H, py), 3.63 (s, 3H, COOMe), 3.14 (t, 2H, J = 7.1 Hz, CH_2COO), 2.69 (t, 2H, J = 7.1 Hz, SCH_2), 2.44 (s, 3H, SMe), 2.42 (s, 3H, SMe). HRMS FAB$^+$ (Matrix = 3-Nitrobenzyl alcohol) ($C_{17}H_{17}N_2O_2S_7$): Found 490.9325; Calcd. 490.9304. IR (KBr) ν_{max}/cm^{-1} 1225, 1364, 1436, 1580, 1737, 2343, 3447.

Synthesis of zinc complex 1. To a degassed dry DMF solution (10 mL) of **5** (70 mg, 0.14 mmol) was added $CsOH \cdot H_2O$ (24 mg, 0.14 mmol) in methanol (2.0 mL) over a period of 5 min at room temperature. After the mixture was further stirred for 0.5 h, $ZnCl_2$ (55 mg, 0.40 mmol) was added in one portion, and the mixture was stirred for additional 2 h. This mixture was extracted with dichloromethane, and the organic phase was washed with water, dried over Na_2SO_4 and concentrated in vacuo. After recrystallization from CH_2Cl_2/MeOH, **1** (45 mg) was obtained as red powder in 74% yield.

mp > 300 ℃. ^{1}H-NMR (500 MHz; $CDCl_3$; Me_4Si): δ 8.56 (d, J = 5.6 Hz, 1H, py), 7.86 (ddd, J = 8.2, 8.2, 2.1 Hz, 1H, py), 7.57 (d, J = 8.2 Hz, 1H, py), 7.35 (dd, J = 8.2, 5.6 Hz 1H, py), 2.45 (s, 3H, SMe), 2.44 (s, 3H, SMe). HRMS FAB$^+$ (Matrix = 3-Nitrobenzyl alcohol) ($C_{26}H_{20}N_2S_{14}Zn$): Found 871.7007; Calcd. 871.7008. IR (KBr) ν_{max}/cm^{-1} 1406, 2326, 2915, 3629.

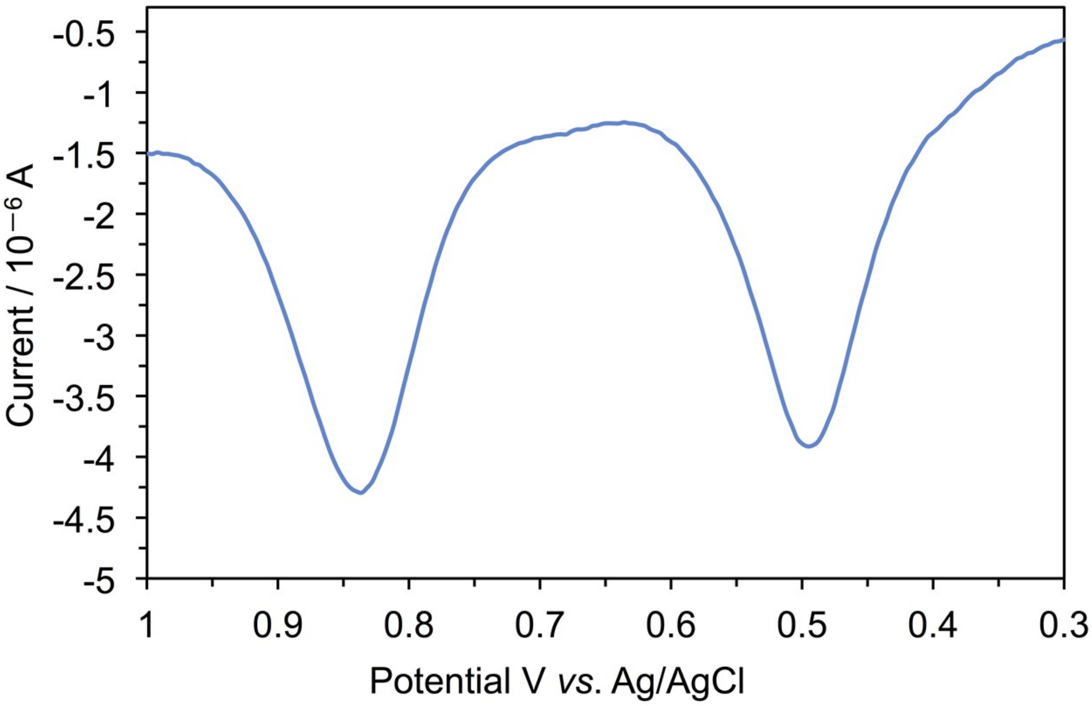


Figure S1. Differential pulse voltammogram of zinc complex **1** in benzonitrile using measurement parameters; step: 4.0 mV, pulse width: 50 ms, pulse period: 0.20 s, scan rate: 20 mV s^{-1}.

Table S1. Absorption maximum wavelength (λ_{max}) and molar extinction coefficients (ε) of the UV-Vis spectra of compounds **1**, **4**, **5** and BMT-TTF (**2**) in their 10^{-5} $CHCl_3$ solutions.

Molecule	λ_{max} (nm) (logε)
1	267 (4.64), 337 (4.64), 473 (4.09)
4	241 (4.27), 306 (4.14), 332 (4.06), 425 (3.55)
5	241 (4.44), 287 (4.30), 331 (4.24), 420 (3.59)
BMT-TTF(2)	334 (3.90), 423 (3.57)

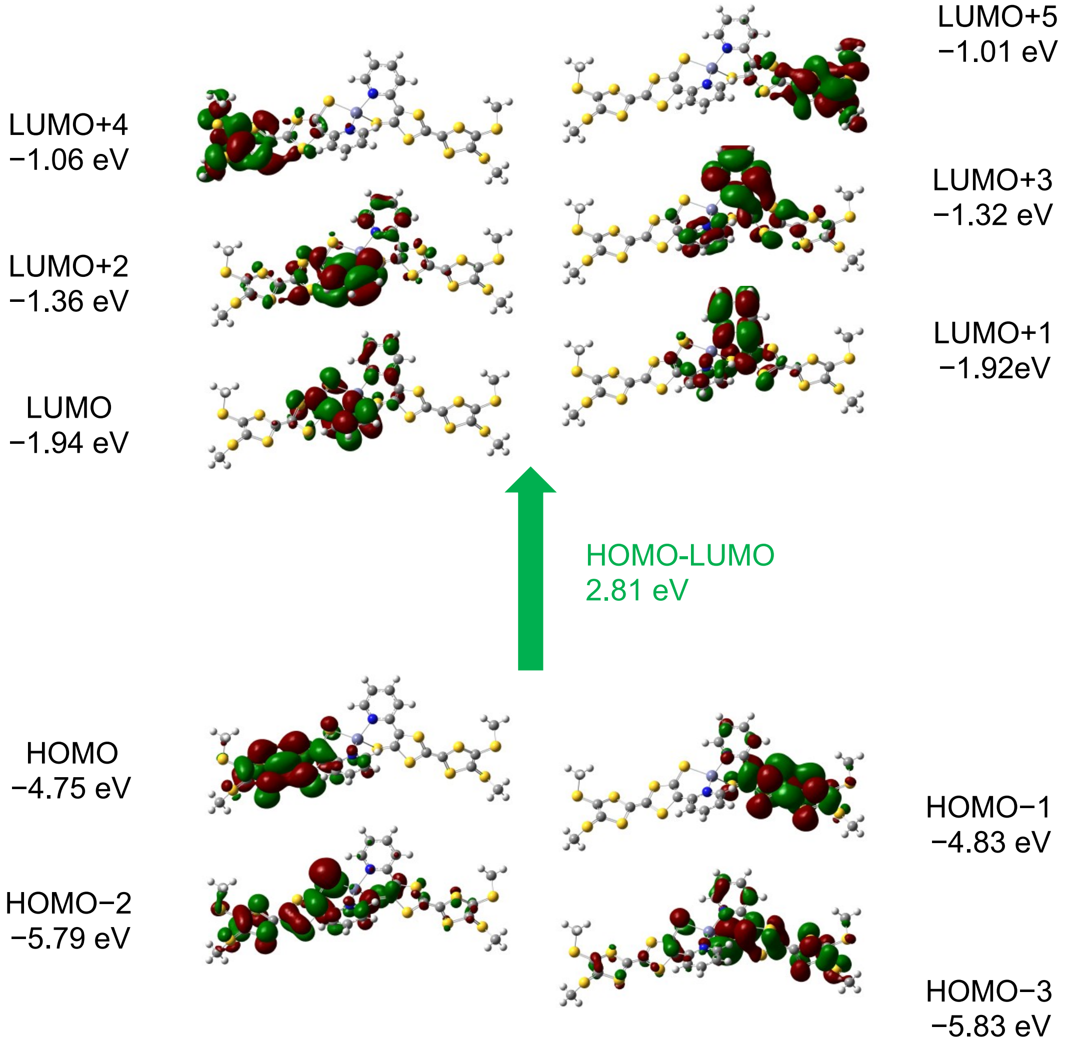


Figure S2. Molecular orbitals of zinc complex **1** calculated on the basis of a DFT method [B3LYP level using the LANL2DZ basis set for the central zinc atom and the 6-31G(d, p) basis set for the other atoms (GAUSSIAN 09 package)]

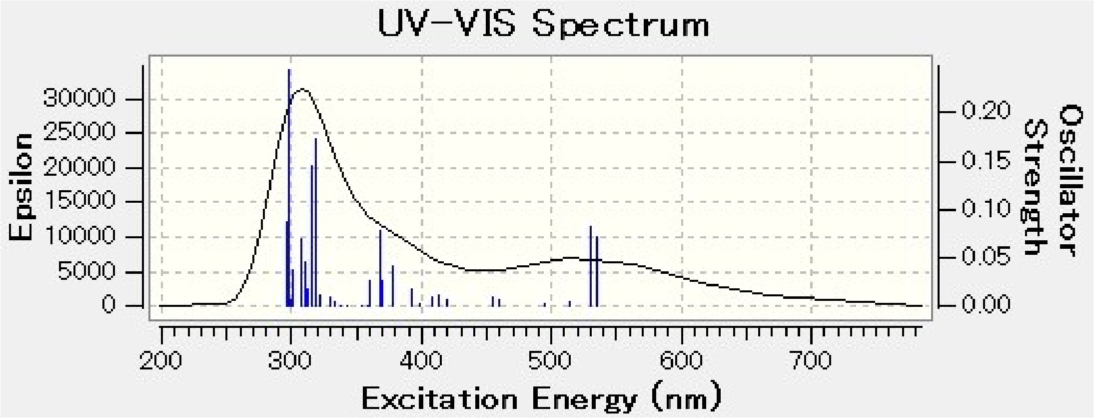


Figure S3. UV-Vis simulated spectrum of **1** calculated on the basis of a TD-DFT method [B3LYP level using the LANL2DZ basis set for the central zinc atom and the 6-31G(d, p) basis set for the other atoms (GAUSSIAN 09 package)]. The details of primal singlet-singlet excitations are summarized in Table S2.

Table S2. The details of primal singlet-singlet excitations; Calculated exited energies (*E*), wavelength (λ_{max}), oscillator strengths (*f*), and major composition in terms of molecular orbital contributions.

E (eV)	λ_{max} (nm)	*f*	Major composition[a]
2.32	535	0.07	H → L (41%), H → L+1 (57%)
2.34	529	0.08	H–1 → L (69%)
3.28	378	0.04	H–2 → L (66%)
3.36	369	0.08	H–3 → L (38%), H–2 → L+1 (54%)
3.89	319	0.17	H–2 → L+2 (46%), H–5 → L (24%)
3.94	315	0.15	H–3 → L+2 (45%), H–3 → L+5 (23%)
4.18	297	0.24	H–1 → L+8 (41%), H–3 → L+5 (34%)

[a] H = HOMO, L = LUMO

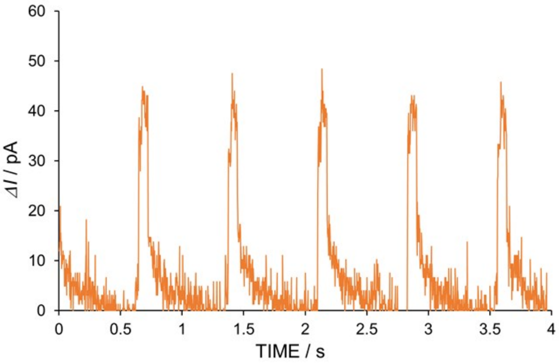
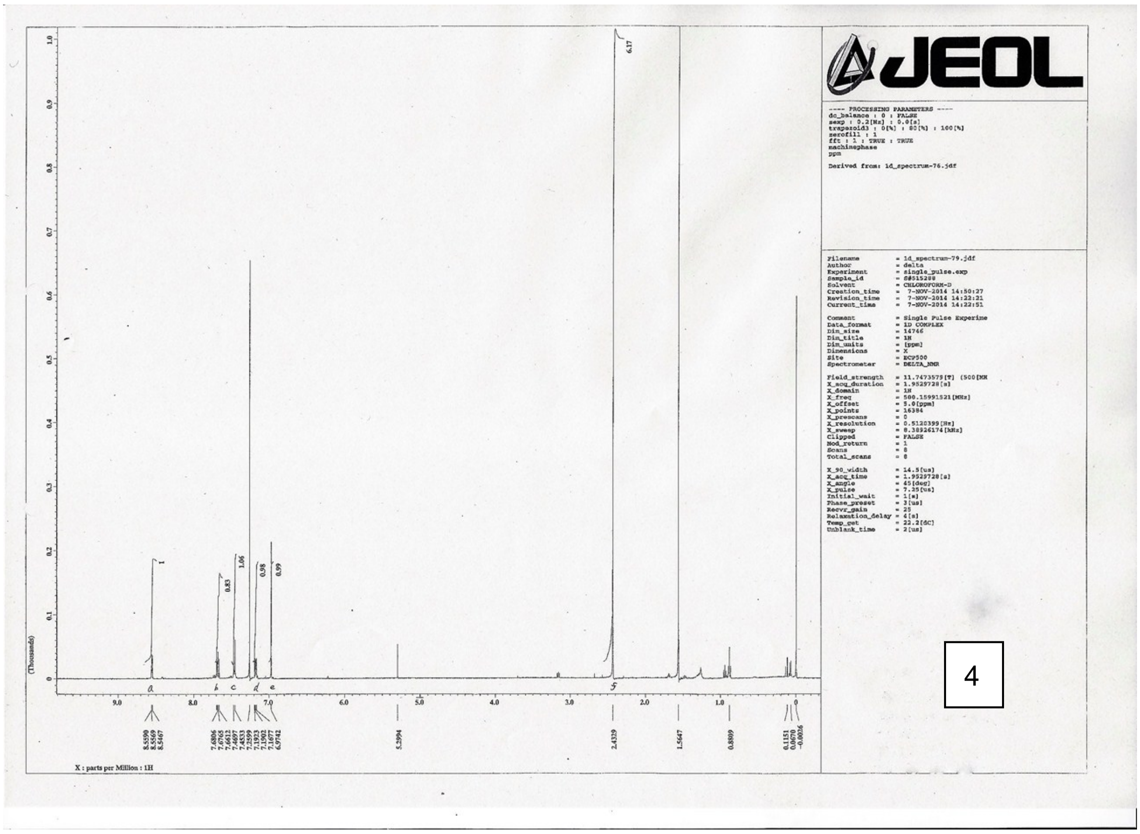


Figure S4. Photocurrent changes upon irradiation of the chopped white light (300-600 nm) to the single crystal of **1** measured along the *b*-axis.

NMR chart of **4** (JEOL ECP-500, 500MHz, $CDCl_3$)



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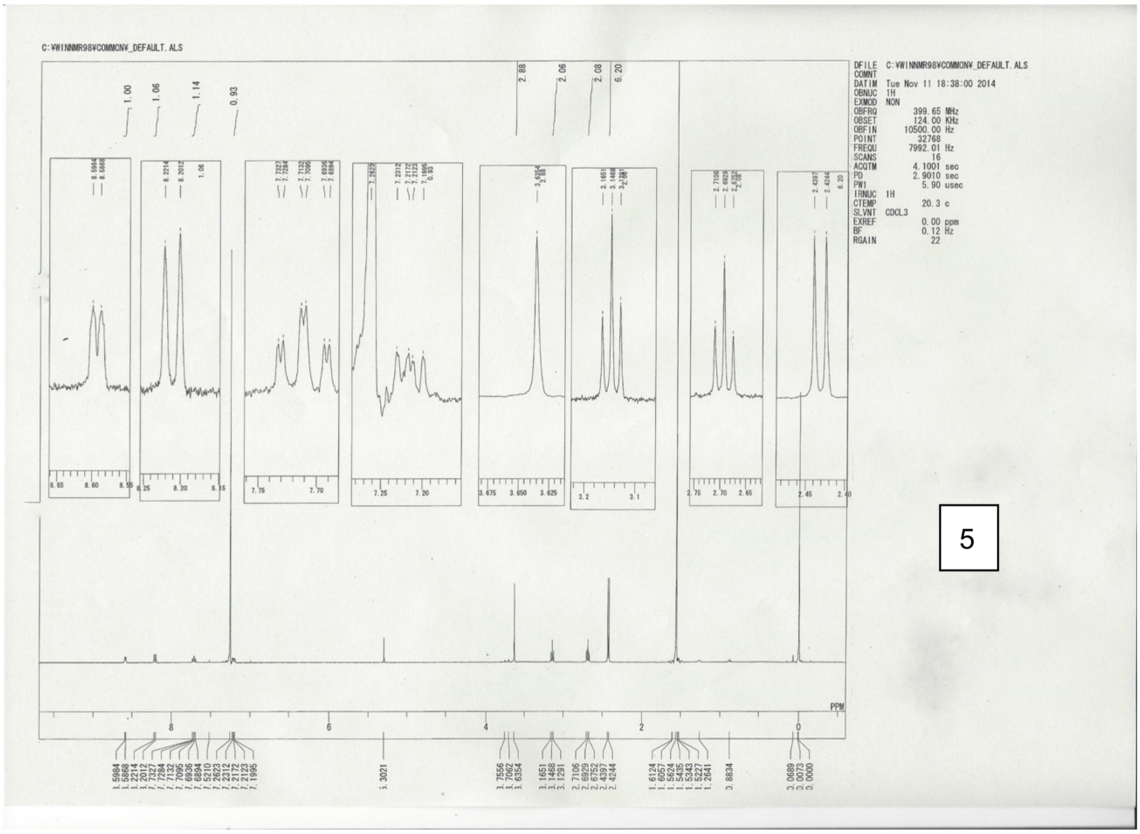
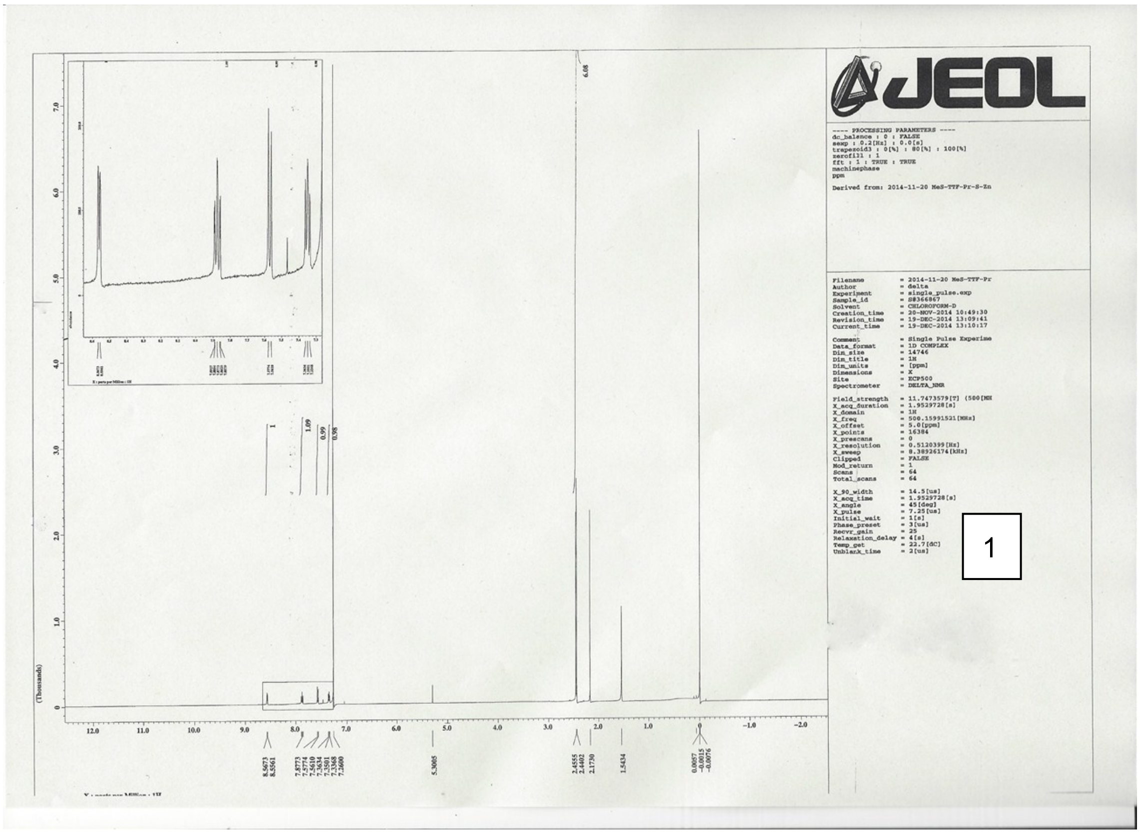
4

NMR chart of **5** (JEOL JNM-400, 400MHz, CDCl$_3$)



5

NMR chart of **1** (JEOL ECP-500, 500MHz, $CDCl_3$)



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Details of X-ray Data Collection and Reduction for the single crystalline sample of complex 1.

The X-ray diffraction data were collected for a needle-like red crystal of zinc complex **1** ($C_{26}H_{20}N_2S_{14}Zn$) having approximate dimensions of 0.10 x 0.02 x 0.02 mm^3 at room temperature on a Rigaku AFC-8 Mercury CCD diffractometer with confocal X-ray mirror system [Mo-Kα□radiation (λ□= 0.71075 Å)] and a rotating anode generator (0.8 kW). Lorentz and polarization corrections were applied. The structure was solved by a direct method (SIR92)[2], expanded (DIRDIF94)[3] and refined on F with full-matrix least-squares analysis. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All the calculations were performed using the CrystalStructure crystallographic software package of the Molecular Structure Corporation.[4] The final cycle of full-matrix least-squares refinement on F was based on 2577 observed reflections ($I > 3.00\sigma(I)$) and 207 variable parameters and converged. Crystal data are given below. All data (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-1530870. Copies of the data can be obtained free of charge by application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for zinc complex **1**, chemical formula: $C_{26}H_{20}N_2S_{14}Zn$, Fw = 874.68, monoclinic, $C2/c$, a = 44.097(7), b = , 5.1503(7), c = 14.964(2) Å, β = 98.192(5)°, V = 3363.9(9) Å^3, Z = 4, $D_{\text{calcd.}}$ = 1.727 g/cm^3, μ (Mo Kα) = 16.240 cm^{-1}, F (000) = 1776, 4217 unique reflections (R_{int} = 0.0615), the final R and R_w were 0.0412 and 0.0366 (2577 reflections [$I > 3.0\sigma(I)$]), GOF = 1.109.

References

1. K. Takimiya, Y. Kataoka, N. Niihara, Y. Aso and T. Otsubo, *The Journal of Organic Chemistry*, 2003, **68**, 5217-5224.
2. A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J Appl Crystallogr*, 1994, **27**, 435.
3. P. T. A. Beurskens, G.; Beurskens, G.; Bosman, W. P.; de Gelder, D.; Israel, R.; Smith, J. M. M., *Technical Report of the Crystallography Laboratory*, University of Nijmegen: Nijmegen, The Netherlands, 1994.
4. CrystalStructure 3.8: Crystal Structure Analysis Package, Rigaku and Rigaku Americas, 9009 New Trails Dr. The Woodlands TX 77381 USA, 2002-2007.