Supporting Information

Zn(II) and Cu(II) Complexes of Thiophene-Based Salphen-Type New Ligand: Solution-Processable High-Performance Field-Effect Transistor Materials

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Materials and Physical measurements:

All chemicals and solvents were received from Aldrich/Merck of reagent grade and used without any further purification. NMR spectra were recorded on a JEOL-FT NMR-AL 400 MHz or a Bruker AVANCE 500 FT-NMR spectrometer using $CDCl_3$/DMSO-d_6 as solvent and chemical shift values are reported in ppm (δ scale) relative to Me_4Si as internal standard. Infrared spectra were measured on KBr disc with a Perkin-Elmer spectrophotometer. UV-vis spectra were recorded on a Hitachi U4100 spectrophotometer, with a quartz cuvette. The mass spectra were recorded on a WATERS micromass Q-Tof micro^{TM} instrument. Elemental analyses were carried out on a Carlo-Erba model 1106 elemental analyzer. Cyclic voltammetry was performed with a computer-controlled Princeton Applied Research 263A electrochemical workstation using platinum (Pt) disk as a working electrode, Pt wire as the counter electrode and Ag/$AgNO_3$ (10 mM in acetonitrile) as the reference electrode. 0.1 M TBAPC was used as supporting electrolyte.

Synthesis of ligand and complexes:

2-Formyl-3-(methoxy/hydroxyl)thiophene were prepared by reported methods.[1]

1: A solution of 1,2-diaminobenzene (42 mg, 0.39 mmol) in 2 mL dry acetonitrile was added dropwise to the solution of 2-formyl-3-hydroxy thiophene (100 mg, 0.78 mmol) in 3 mL dry acetonitrile with vigorous stirring at room temperature under N_2 atmosphere, yellow precipitate appeared within 30 min. Reaction mixture was stirred for 4 h at ambient temperature; precipitate was filtered-off and washed with cold acetonitrile. Precipitate was dissolved in dry DCM and allowed to evaporate at room temperature to get the yellow crystals. Yield: 110 mg (86%). M. p.: 158 °C. Anal. Calc. for $C_{16}H_{12}N_2O_2S_2$: C, 58.52; H, 3.68; N, 8.53. Found: C, 58.65; H, 3.57; N, 7.53 %. ESI-MS: Calc. for $C_{16}H_{12}N_2O_2S_2$: m/z 328.0340. Found 329.0068 $[M + H]^+$. IR (cm^{-1}, KBr, selected): 3430 (O-H), 1622 (C=O), 1577 (C=C), 1352, 1226. ^{1}H NMR (500MHz, δ, ppm, DMSO-*d*$_6$): 11.85 (s, 2H); 8.73 (s, 2H); 7.98 (d, *J* = 5.50 Hz, 2H); 7.48 (dd, *J* = 6.00 Hz, *J* = 3.50 Hz, 2H); 7.18 (dd, *J* = 6.00 Hz, *J* = 3.50 Hz, 2H), 6.59 (d, *J* = 5.50 Hz, 2H). ^{13}C NMR (500MHz, δ, ppm, DMSO-*d*$_6$): 174.32, 145.65, 139.21, 136.37, 125.52, 121.96, 115.92, 111.52. UV-vis (DMF) λ_{max}/nm (ε/M^{-1} cm^{-1}): 310 (12665), 381 (28147), 436 (13792).

1·Cu: Ligand **1** (100 mg, 0.30 mmol) was suspended in 5 mL dry methanol and a solution of cupric chloride (41 mg, 0.30 mmol) in 2 mL methanol was added dropwise with constant stirring at room temperature under N_2 atmosphere. Colour of the reaction mixture immediately turned from yellow to brownish-red. The mixture was stirred at ambient temperature for 3 h and then precipitate was filtered, washed thoroughly with methanol and dried in vacuum; shiny brownish product was obtained. The product was dissolved in DMF and allowed to evaporate slowly. After a couple of weeks, red block crystals of complex **1·Cu** suitable for X-ray diffraction were obtained. Yield: 110 mg (93%). M. p.: 352 °C. Anal. Calc. for $C_{16}H_{10}N_2O_2S_2Cu$: C, 49.28; H, 2.58; N, 7.18. Found: C, 49.28; H, 2.43; N, 7.32 %. ESI-MS: Calc. for $C_{16}H_{12}N_2O_2S_2Cu$: m/z 388.9480. Found 389.8945 $[M + H]^+$. IR (cm^{-1}, KBr, selected): 1594 (C=N), 1569 (C=C), 1348, 1325. UV-vis (DMF) λ_{max}/nm (ε/M^{-1} cm^{-1}): 306 (21176), 390 (33529), 590 (~198, shoulder).

1·Zn·MeOH: A solution of zinc acetate (56 mg, 0.30 mmol) in 2 mL dry methanol was added dropwise to the suspension of ligand **1** (100 mg, 0.30 mmol) in 5 mL methanol under vigorous stirring at room temperature under N_2 atmosphere. The mixture was stirred overnight and then precipitate was filtered, washed thoroughly with methanol and dried in vacuum to get the yellow complex. Yield: 107 mg (83%). M.P.: 140 °C (dec.). Anal. Calc. for $C_{17}H_{14}N_2O_3S_2Zn$: C, 48.17; H, 3.33; N, 6.61. Found: C, 48.37; H, 3.13; N, 6.71 %. ESI-MS:

Calc. for $C_{17}H_{14}N_2O_3S_2Zn$: m/z 421.9737. Found 390.9215 [(**1**.Zn + H]$^+$, 412.8495 [**1**.Zn + Na]$^+$. IR (cm^{-1}, KBr, selected): 3422 (O-H), 1598 (C=N), 1578 (C=C), 1497 (s), 1431 (s), 1345 (s). ^{1}H NMR (400MHz, δ, ppm, DMSO-d_6): 8.90 (s, 2H); 7.82 (d, J = 5.32 Hz, 2H); 7.74 (dd, J = 6.10 Hz, J = 3.04 Hz, 2H); 7.16 (dd, J = 6.10 Hz, J = 3.84 Hz, 2H), 6.59 (d, J = 6.12 Hz, 2H), 4.11 (q, J = 4.56 Hz, 1H), 3.16 (d, J = 4.56 Hz, 3H) . ^{13}C NMR (500MHz, δ, ppm, DMSO-d_6): 177.1, 151.9, 138.6, 136.0, 125.2, 125.0, 115.3, 108.6, 48.60. UV-vis (DMF) λ_{max}/nm (ε/M^{-1} cm^{-1}): 383 (26125), 443 (11030).

Device Fabrication:

Al metal is coated as the gate electrode by physical vapor deposition (10^{-6} mbar, 40 nm thick) on pre-cleaned RCA treated glass substrate. Spin-on-glass dielectric layer was spin coated at 1000 rpm for 1 min and annealed at 140 °C for 15 mins. Typical dielectric thickness is estimated to be around 100 nm as measured using Filmetrics (F20 – EXR) thickness measurement set up. Capacitance of the dielectric layer was measured to be ~ 4 nF/cm^2 using the inbuilt C-V meter of Keithley 4200 semiconductor parameter analyzer. The surface of the dielectric layer was coated (1500 rpm for 30 s) with a thin monolayer of hexamethyldisilazane (HMDS) and then annealed at 110°°C for 2 h. The MOCs were dissolved in a mixed solvent of (DMF + DMSO) in the ratio 1:1 at a concentration of 15 mg/ml. Films were then spin coated at 300 rpm to obtain thickness ~ 80 nm. No annealing was performed on the optimized devices. However, to remove the high boiling solvents the MOC coated devices were left in vacuum for 1 hr. Devices were then completed by coating Au source-drain (S-D) electrodes at (10^{-6} mbar, 40 nm thick). Electrical characterization of the devices were obtained with two identical Keithley 2400 and high impedance electrometer 6514 and cross-checked with measurements from Keithley 4200 Semiconductor characterization system. Mobility for the samples were obtained using the equation: $I_{ds} = (\mu_{FET}\ WC/2L)\ (V_g - V_{th})^2$,where I_{ds} is the drain current, W and L are, respectively, the channel width and length, C is the capacitance per unit area of the gate insulator layer, V_{gs} and V_{th} are the gate voltage and the threshold voltage respectively. Mobility values obtained are the mean values from 10 devices fabricated for each of the molecule.

Crystal data collection and refinement:

Crystals of ligands and complexes were individually mounted on a glass pip. Intensity data were collected on a Brukar's KAPPA APEX II CCD Duo system. Mostly, data were collected at 100 K(few collected at 298 K) with graphite-monochromatic Mo Kα radiation (λ = 0.71073 Å). Data reduction was performed using Bruker SAINT software.[2] Crystal structures were solved by direct methods using SHELXL-97 and refined by full-matrix least-squares refinement on F^2 with anisotropic displacement parameters for non-H atoms using SHELXL-97.[3] Hydrogen atoms associated with carbon atoms were refined in geometrically constrained riding positions. Hydrogen atoms associated with oxygen and nitrogen atoms were included in the located positions. Structure graphics shown in the Figures were created using the XSeed software package version 2.0.[4] Selected bond lengths and bond angles for complex **1·Cu** are mentioned in Table S1. Details of the crystal parameters, data collections and refinements are listed in Table S2.

Table S1. Selected bond lengths (Å) and bond angles (˚) for complex **1·Cu**

	Bond length		Bond length
Cu1-O2	1.9099(16)	O2-C16	1.291(3)
Cu1-O1	1.9225(16)	N1-C12	1.314(3)
Cu1-N1	1.9562(18)	N1-C1	1.412(3)
Cu1-N2	1.9563(19)	N2-C3	1.310(3)
O1-C7	1.290(3)	N2-C2	1.409(3)
	Bond angle		Bond angle
O2-Cu1-O1	86.77(7)	O2-Cu1-N2	173.34(7)
O2-Cu1-N1	95.80(7)	O1-Cu1-N2	95.11(7)
O1-Cu1-N1	171.38(8)	N1-Cu1-N2	83.26(8)

Table S2. Crystallographic data for 1 and 1·Cu

	1	**1·Cu**
Chemical Formula	$C_{16}H_{12}N_2O_2S_2$	$C_{16}H_{10}N_2O_2S_2Cu_1$
Formula weight	345.00	391.94
Cryst system	Orthorhombic	Monoclinic
Space group	*Pbca*	*C2/c*
a (Å)	9.8208(10)	21.422(4)
b (Å)	17.0040(18)	7.3343(13)
c (Å)	17.852(2)	18.884(4)
α (°)	90	90
β (°)	90	109.604(8)
γ (°)	90	90
Vol ($Å^3$)	2981.1(6)	2795.0(9)
D_{calcd} (g/cm^3)	1.345	1.863
μ (mm^{-1})	0.323	1.872
θ range (°)	2.28-27	2.02-27
Z	7	8
range *h*	–10 to +12	–27 to +26
range *k*	–21 to +19	–9 to +7
range *l*	–22 to +21	–24 to +24
Reflns collected	14572	19788
Independent reflns	3255	3062
Obsd reflns	2697	2519
T (K)	100	100
*R*1	0.0323	0.0279
*wR*2	0.0816	0.0639
GOF	1.048	1.043

Characterization of Ligand 1

^{1}H NMR spectrum of ligand **1** in DMSO-d_6 exhibited the signals for six different types of proton indicating the presence of symmetric bis(enol-imine) tautomeric form. ^{13}C NMR spectrum of ligand **1** showed eight peaks which is consistent with the structure suggested by

^{1}H NMR spectrum. However, the single crystal X-ray diffraction (SCXRD) study displayed mix tautomeric structure (enol-imine form at one end and keto-enamine at the other end) for **1** (*vide infra*). Thus, solid state structure of **1** did not retain in solution phase. The varying feature of the absorption spectrum for **1** in different solvents (Figure S1) can be ascribed to the presence of variable proportions of the tautomers (Chart S1) in solvents of different polarity.[5]

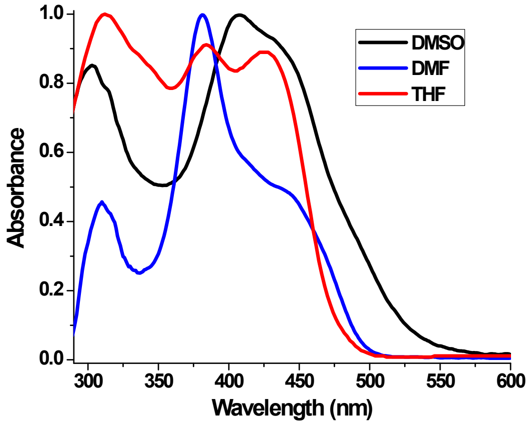
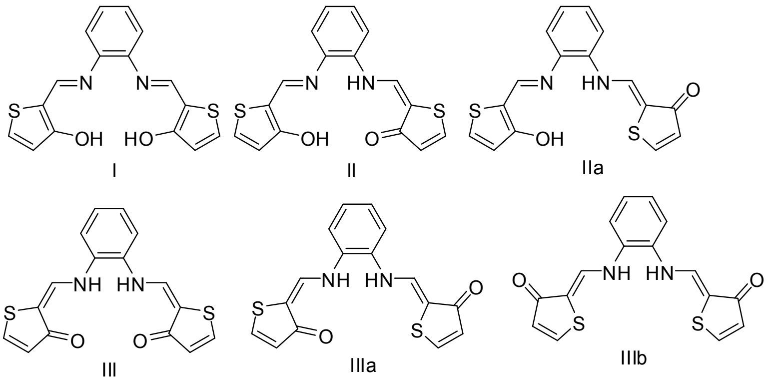


Figure S1. Absorption spectra of **1** in different solvents

Chart S1. Various possible tautomers of ligand **1**



The ORTEP diagram (Figure 1) clearly indicates the non-symmetric nature of **1** in the solid state. Both intramolecular [N1-H2**…**O2; 2.074 Å and 137.77°] and intermolecular [O1-H1**…**O2; 1.815 Å and 165.26°] H-bonding interactions are present in the crystal packing. Intermolecular H-bonding construct the 1D chain along *a*-axis, while several intermolecular nonbonding interactions present in the crystal packing led to the formation of 3D supramolecular assembly.

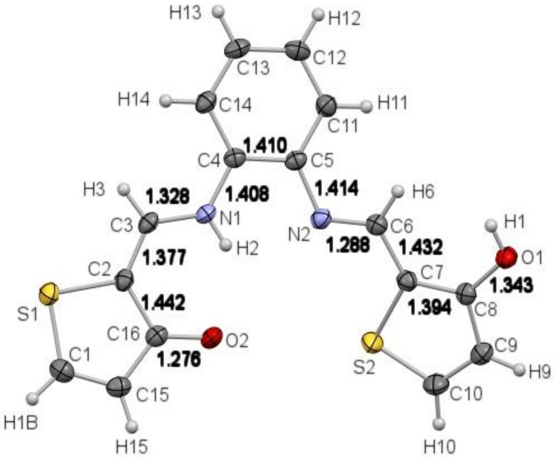


Figure S2. Crystal structure of **1**

Characterization of complexes

The absorption spectra of **1·Cu** and **1·Zn·MeOH** showed intense peaks at 392 and 382 nm (with shoulder at 444 nm), respectively, corresponding to the ligand based π–π^* transitions (Figure S2).[6] Additionally, absorption spectrum of the complex **1·Cu** showed a shoulder at 590 nm which is indicative of d-d transition for square planar geometry around Cu(II) ion.[7]

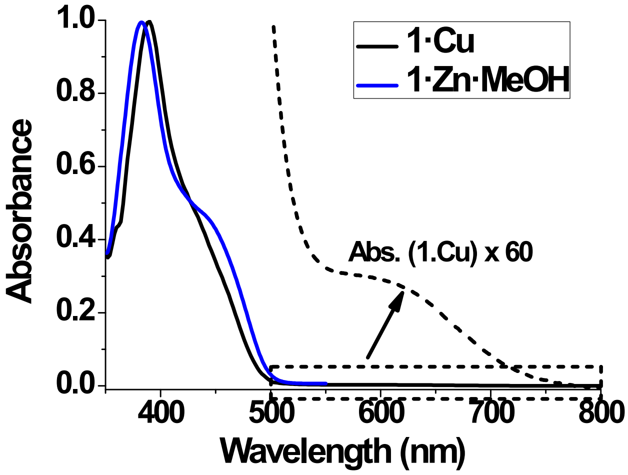


Figure S3. Absorption spectra of **1·Cu** and **1·Zn·MeOH** in DMF

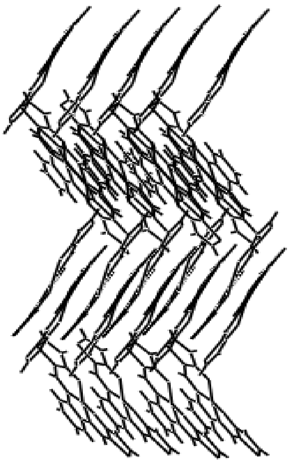


Figure S4. Packing diagram of complex **1·Cu**.

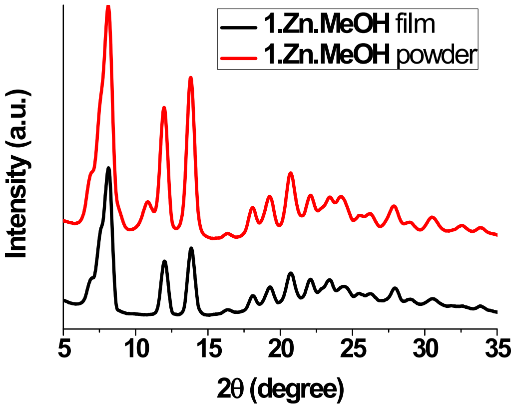


Figure S5. Thin film and powder XRD patterns for **1·Zn.MeOH**

TGA was recorded for the ligand as well as the complexes to check their thermal stability (Figure S4). Compound **1** showed a temperature of 5% weight loss (T_d) 182 ºC. Complex **1·Cu** exhibited a good thermal stability with a T_d of 316 ºC. Complex **1·Zn·MeOH** displayed a typical two-step thermal degradation. Loss of ~4% of the initial mass at 170 ºC (first step) is attributed to the removal of MeOH, whereas the thermal stability of the resulting species with a T_d of 301 ºC is comparable with that of the **1·Cu** complex. So, thermal stability of the complexes is better than that of the ligand if their application in devices is considered.

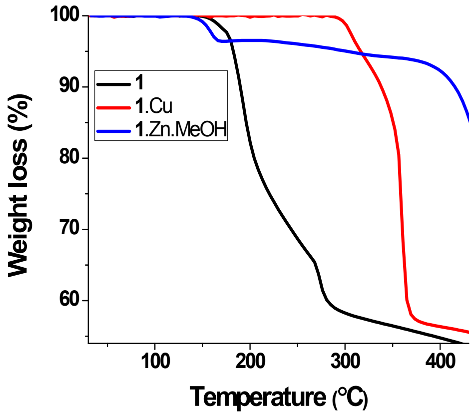


Figure S6. TGA of **1**, **1·Cu** and **1·Zn·MeOH**

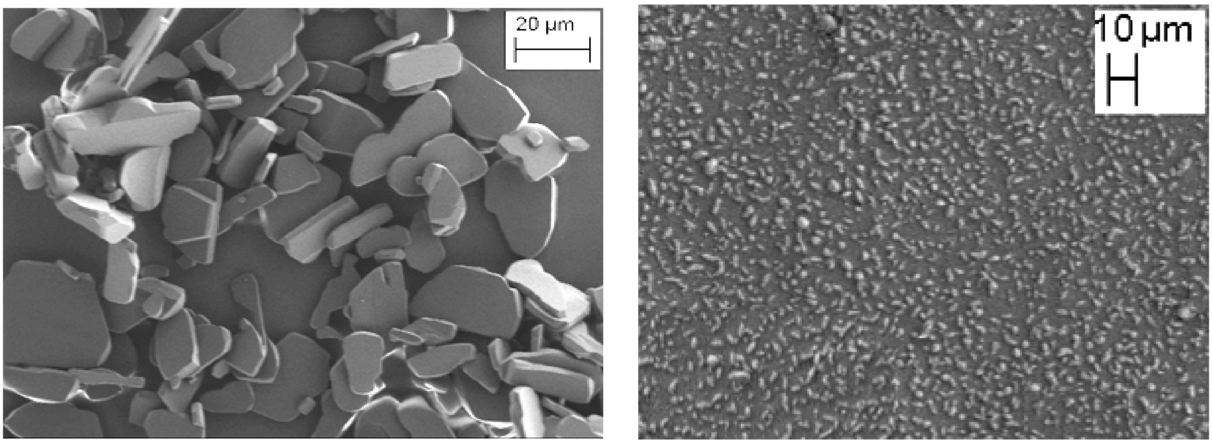


Figure S7. SEM images of **1·Cu** (left) and **1·Zn·MeOH** (right)

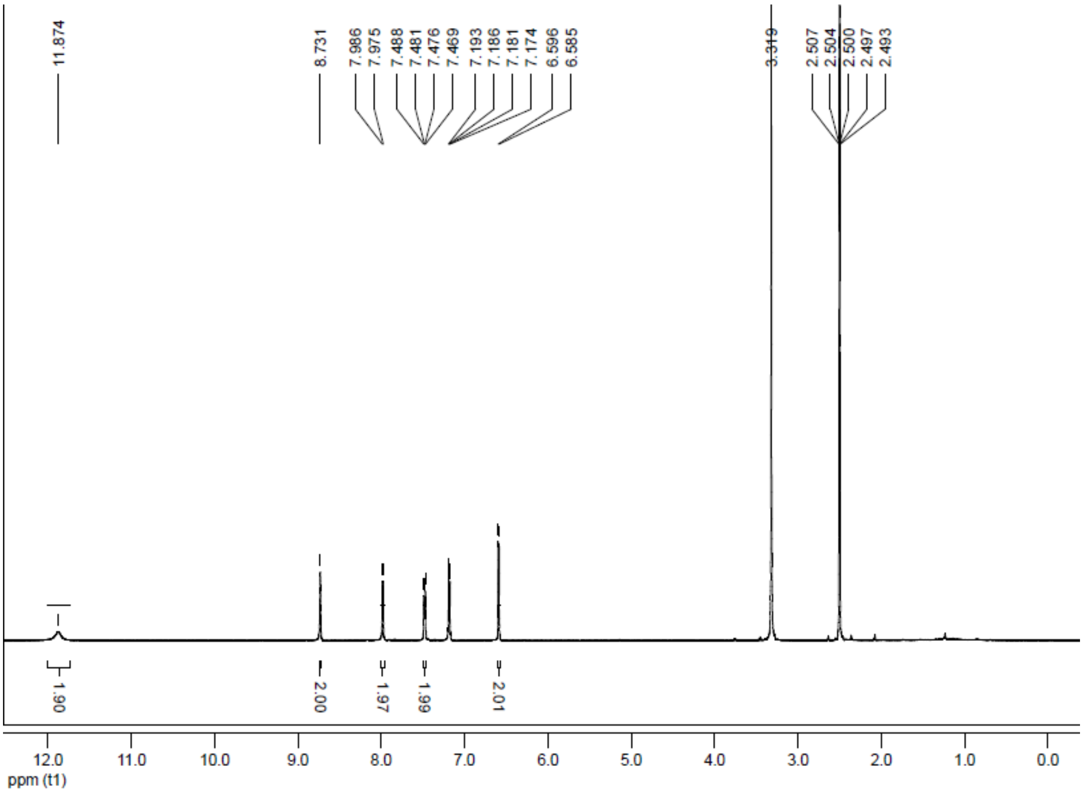


Figure S8. ^{1}H NMR spectrum of **1.**

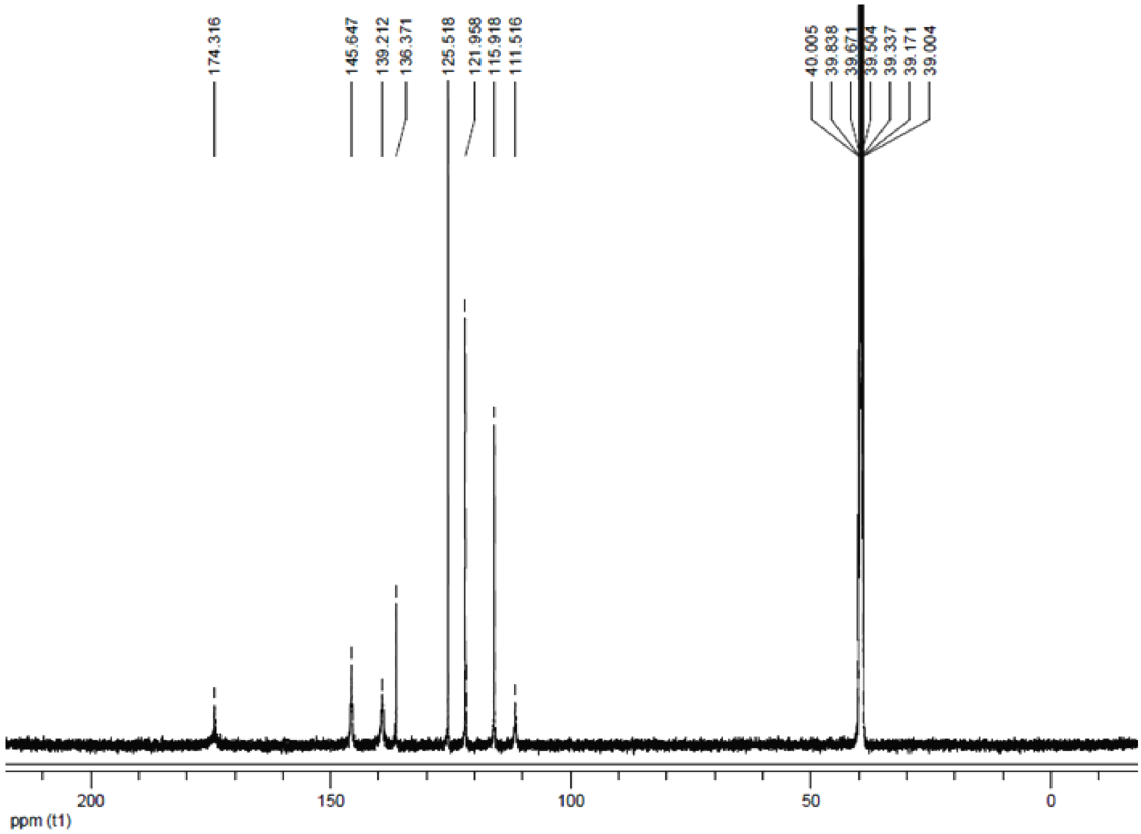


Figure S9. ^{13}C NMR spectrum of **1**

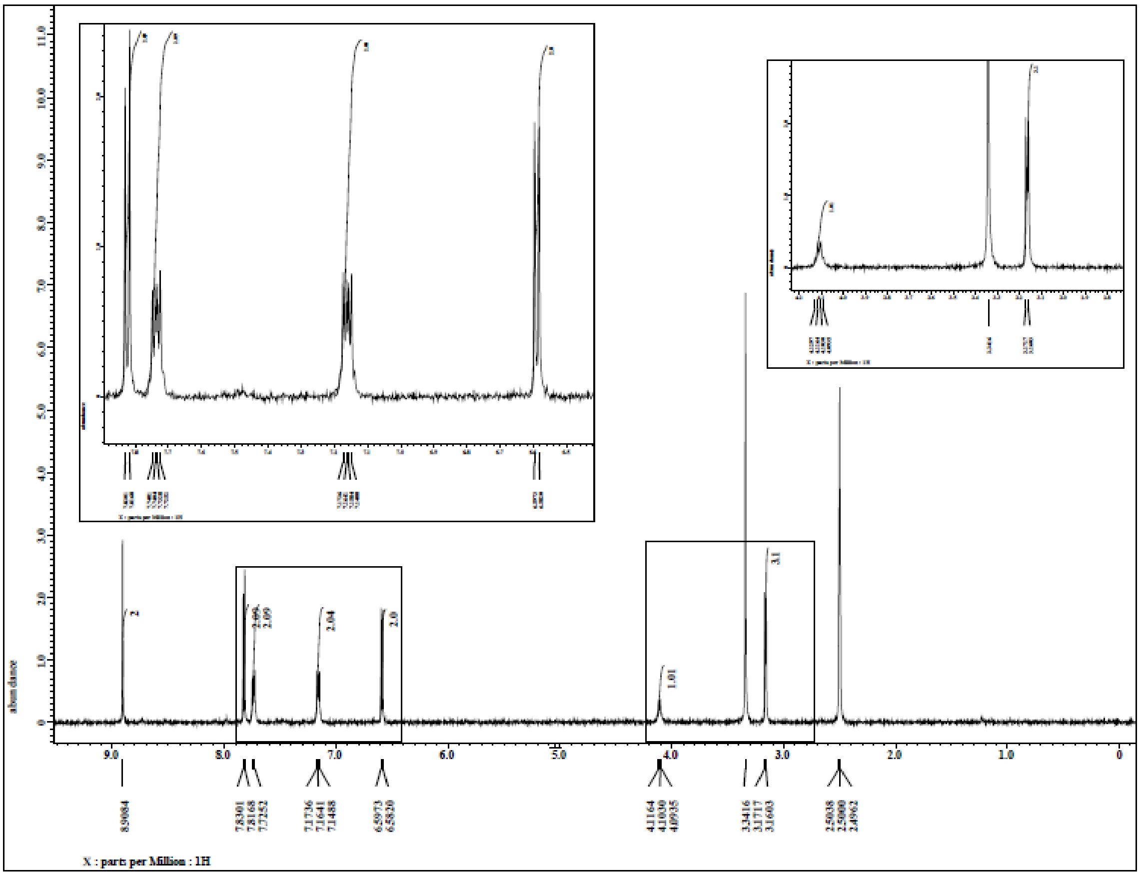


Figure S10. ^{1}H NMR spectrum of **1·Zn·MeOH**

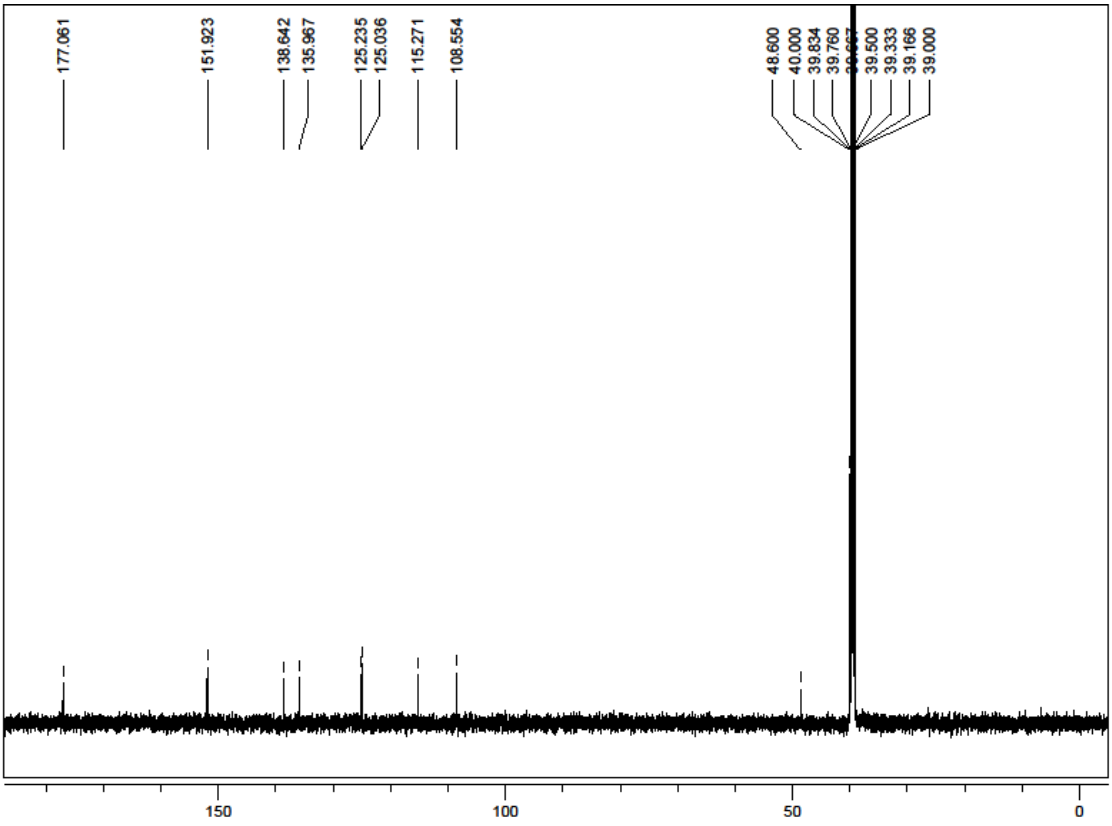


Figure S11. ^{13}C NMR spectrum of **1·Zn·MeOH**

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