# Solution-Processable Benzothiazole-Substituted Formazanate Zinc(II) Complex Designed for Robust Resistive Memory Device

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**Table S1. Crystal data and structure refinement for 1 (CCDC 2356039).**

| Identification code | 1 |
|---|---|
| Empirical formula | $C_{54}H_{34}Cl_2N_{10}O_2S_2Zn$ |
| Formula weight | 1055.30 |
| Temperature/K | 100 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a (Å) | 11.2270(4) |
| b (Å) | 31.2653(9) |
| c (Å) | 14.0665(5) |
| α (°) | 90 |
| β (°) | 111.5770(10) |
| γ (°) | 90 |
| Volume (Å$^3$) | 4591.6(3) |
| Z | 4 |
| $\rho_{calc}$g.cm$^{-3}$ | 1.527 |
| μ, mm$^{-1}$ | 0.800 |
| F(000) | 2160.0 |
| Crystal size (mm$^3$) | 0.26 × 0.23 × 0.22 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection (°) | 4.114 to 56.582 |
| Index ranges | $-14 \le h \le 14$, $-38 \le k \le 41$, $-18 \le l \le 18$ |
| Reflections collected | 78484 |
| Independent reflections | 11378 [$R_{int}$ = 0.0434, $R_{sigma}$ = 0.0275] |
| Data/restraints/parameters | 11378/0/640 |
| Goodness-of-fit on $F^2$ | 1.050 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0373, $wR_2$ = 0.0887 |
| Final R indexes [all data] | $R_1$ = 0.0459, $wR_2$ = 0.0925 |
| Largest diff. peak/hole (e Å$^{-3}$) | 0.67/-0.46 |

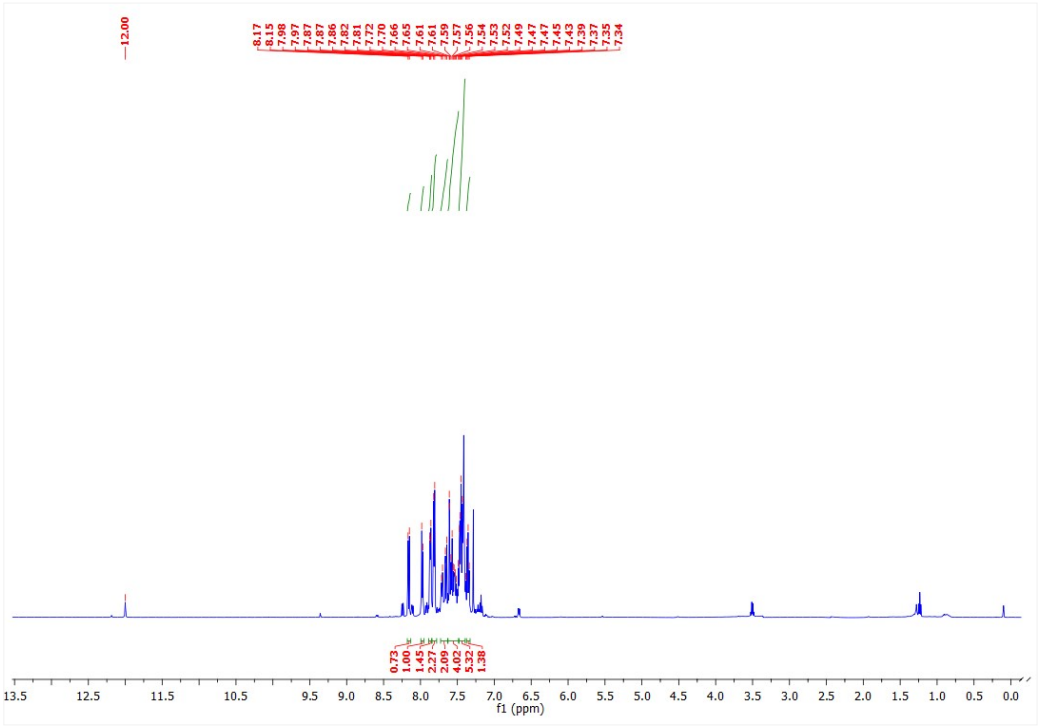



**Figure S1.** $^{1}H$ NMR of **LH** in $CDCl_3$.

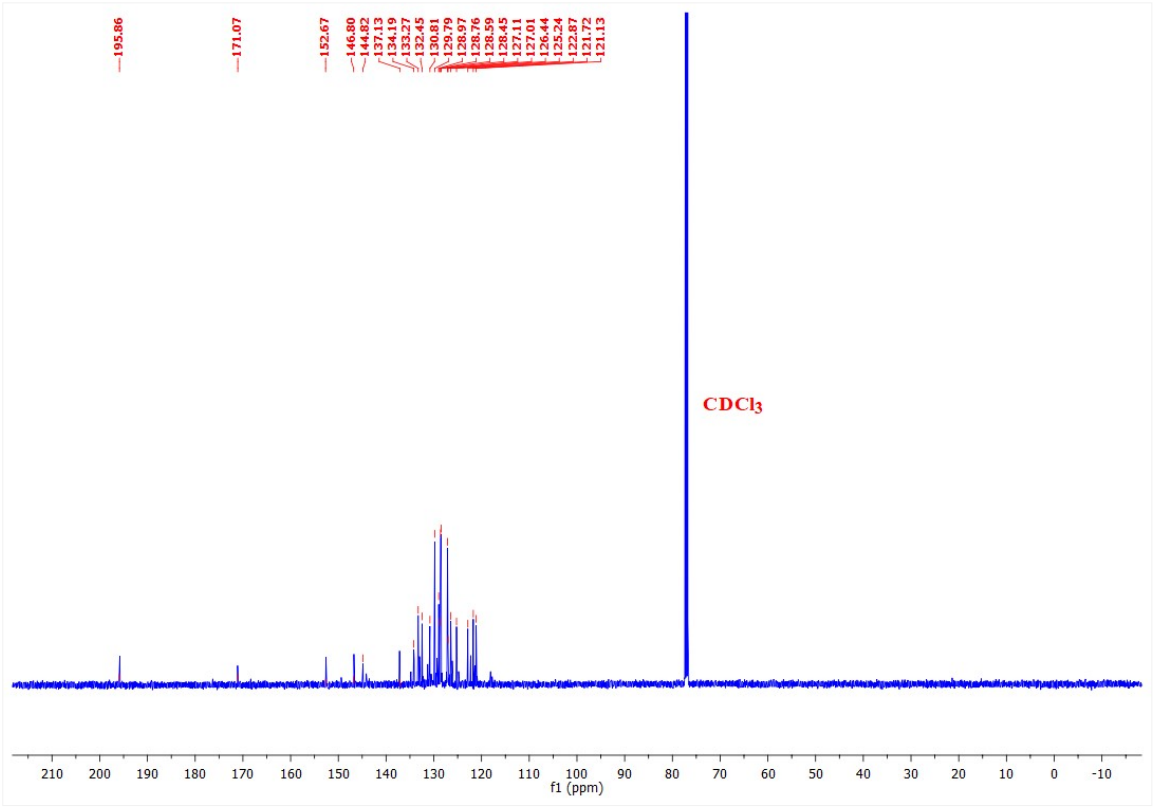



**Figure S2.** $^{13}C\{^{1}H\}$ NMR of **LH** in $CDCl_3$.

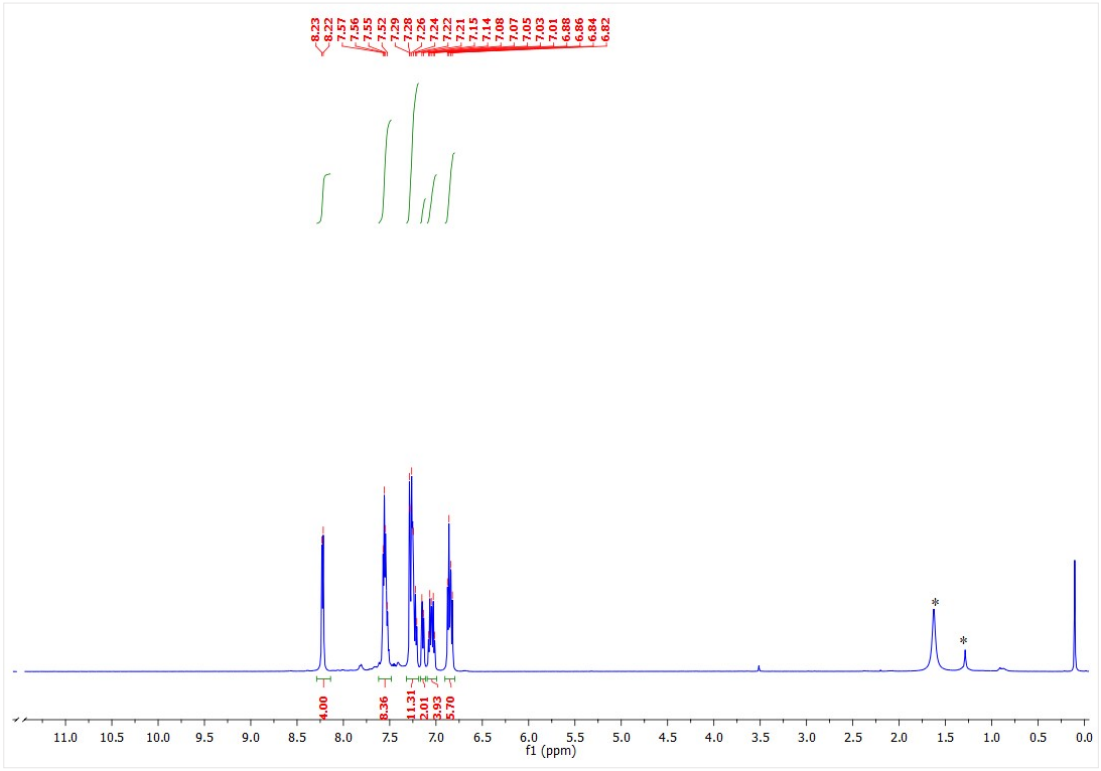



**Figure S3.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of complex **1**.

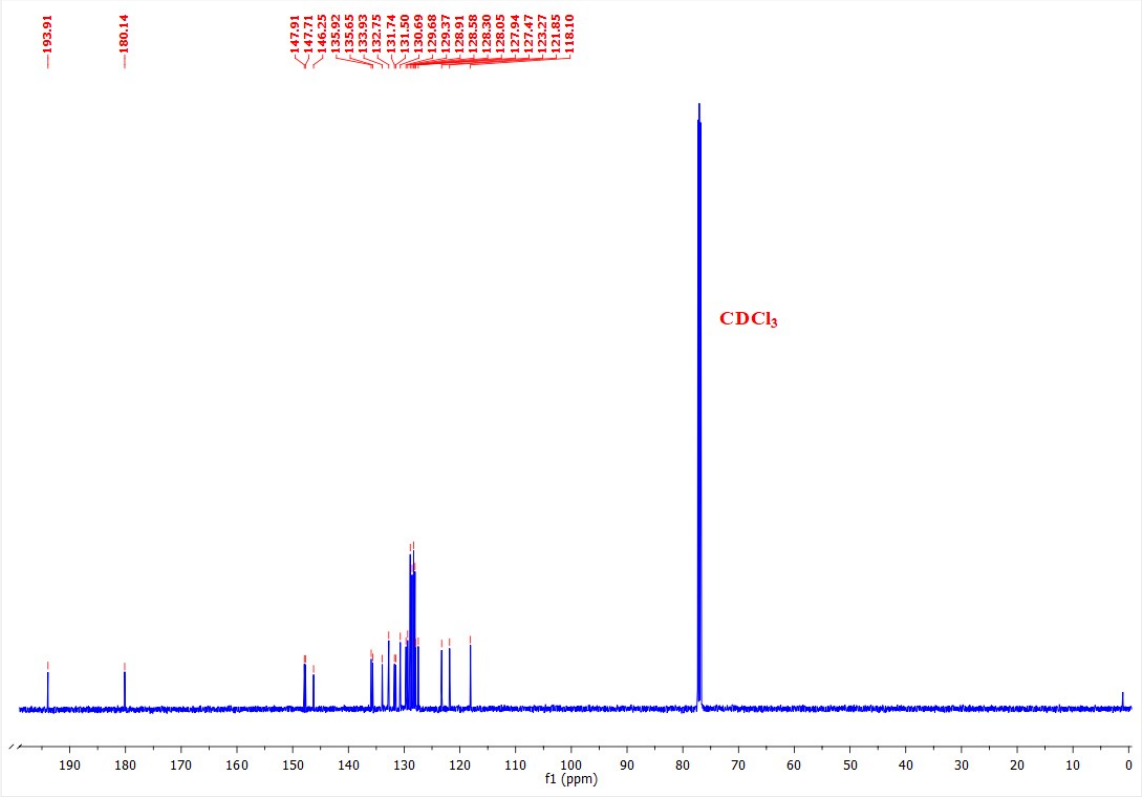



**Figure S4.** $^{13}C$ NMR (126 MHz, $CDCl_3$) of complex **1**.

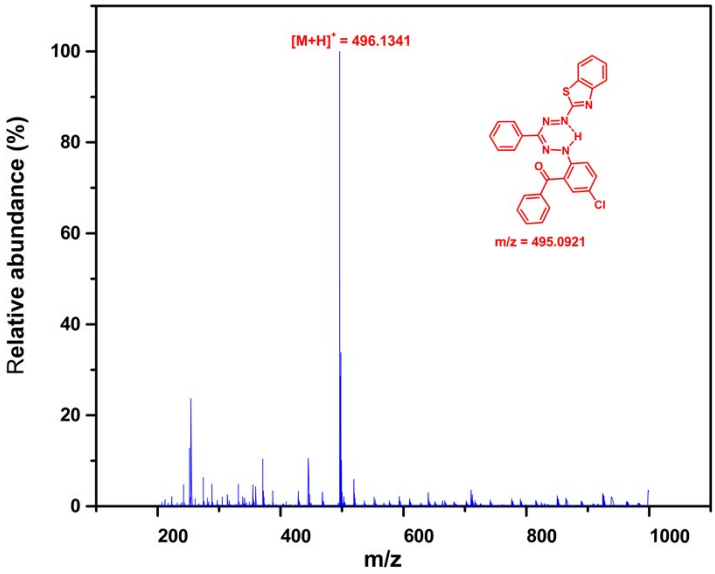



**Figure S5.** HRMS analysis for **LH**: Anal. Calcd. for $[M+H]^+$ peak, m/z = 496.0921. Found $[M+H]^+$ peak, m/z = 496.1341.

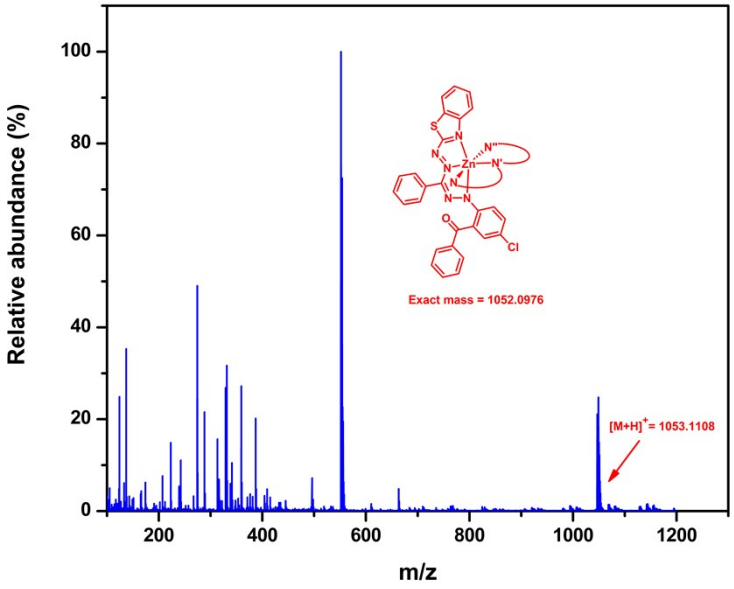



**Figure S6.** HRMS analysis for **1**: Anal. Calcd. for $[M+H]^+$ peak, m/z =1053.1048. Found $[M+H]^+$ peak, m/z = 1053.1108.

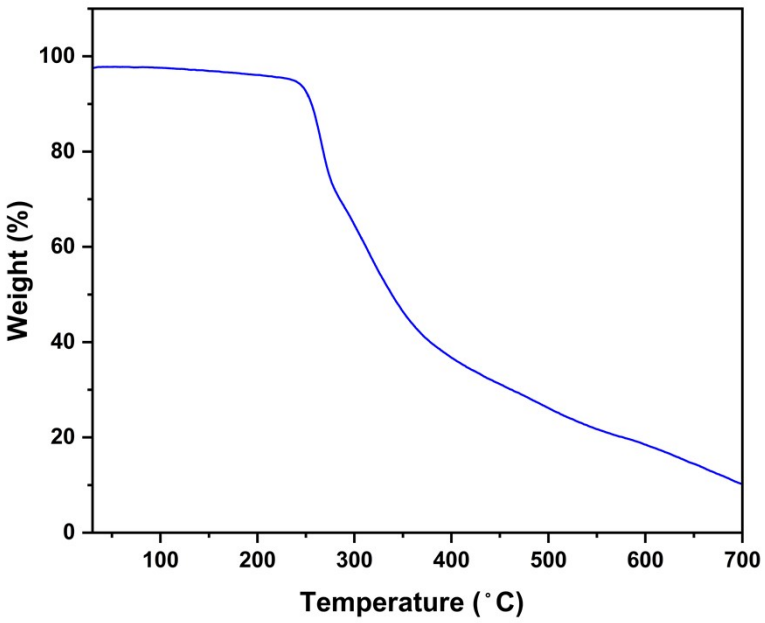
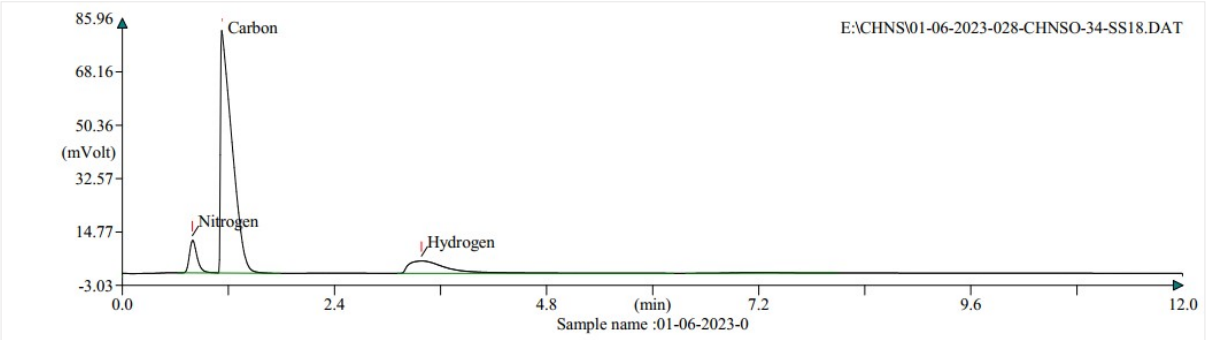



**Figure S7.** Thermogravimetric analysis of **1**.




| Peak Number (#) | Retention Time (min) | Area (.1*uV*sec) | Element % | Component Name |
|---|---|---|---|---|
| 1 | 0.792 | 660180 | 12.895 | Nitrogen |
| 2 | 1.125 | 7313276 | 61.724 | Carbon |
| 3 | 3.383 | 1241559 | 3.311 | Hydrogen |

**Figure S8.** Elemental analysis of **1.** Anal. Calcd. (%) for $C_{54}H_{34}Cl_2N_{10}O_2S_2Zn$: C, 61.46; H, 3.25; N, 13.27. Found: C, 61.72; H, 3.31; N, 12.89.

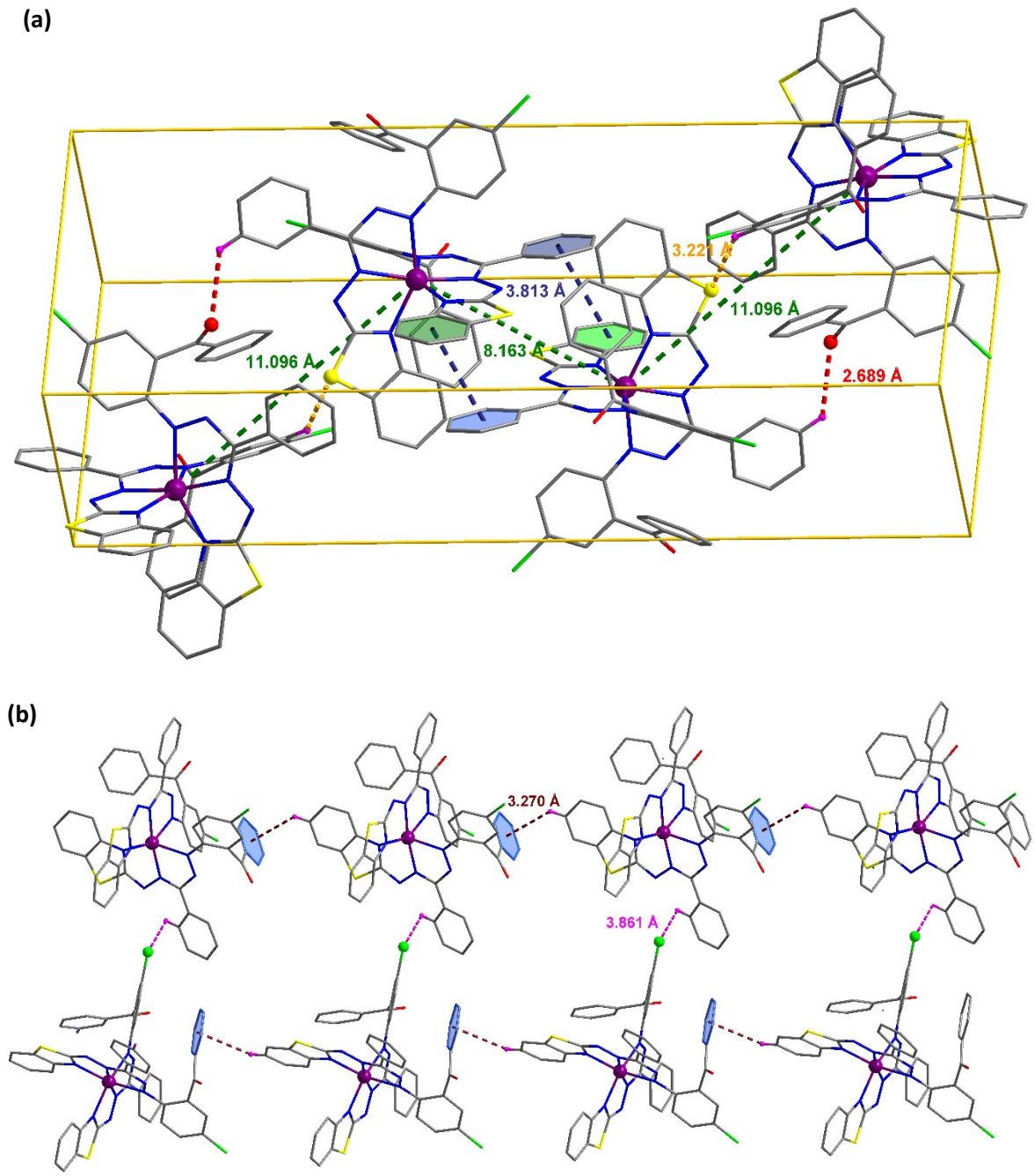



**Figure S9.** (a) Unit cell of complex **1** displaying CH--O, CH--S, and π--π interactions**.** (b) Crystal packing mode in 1 displaying CH--π and CH--Cl interactions.

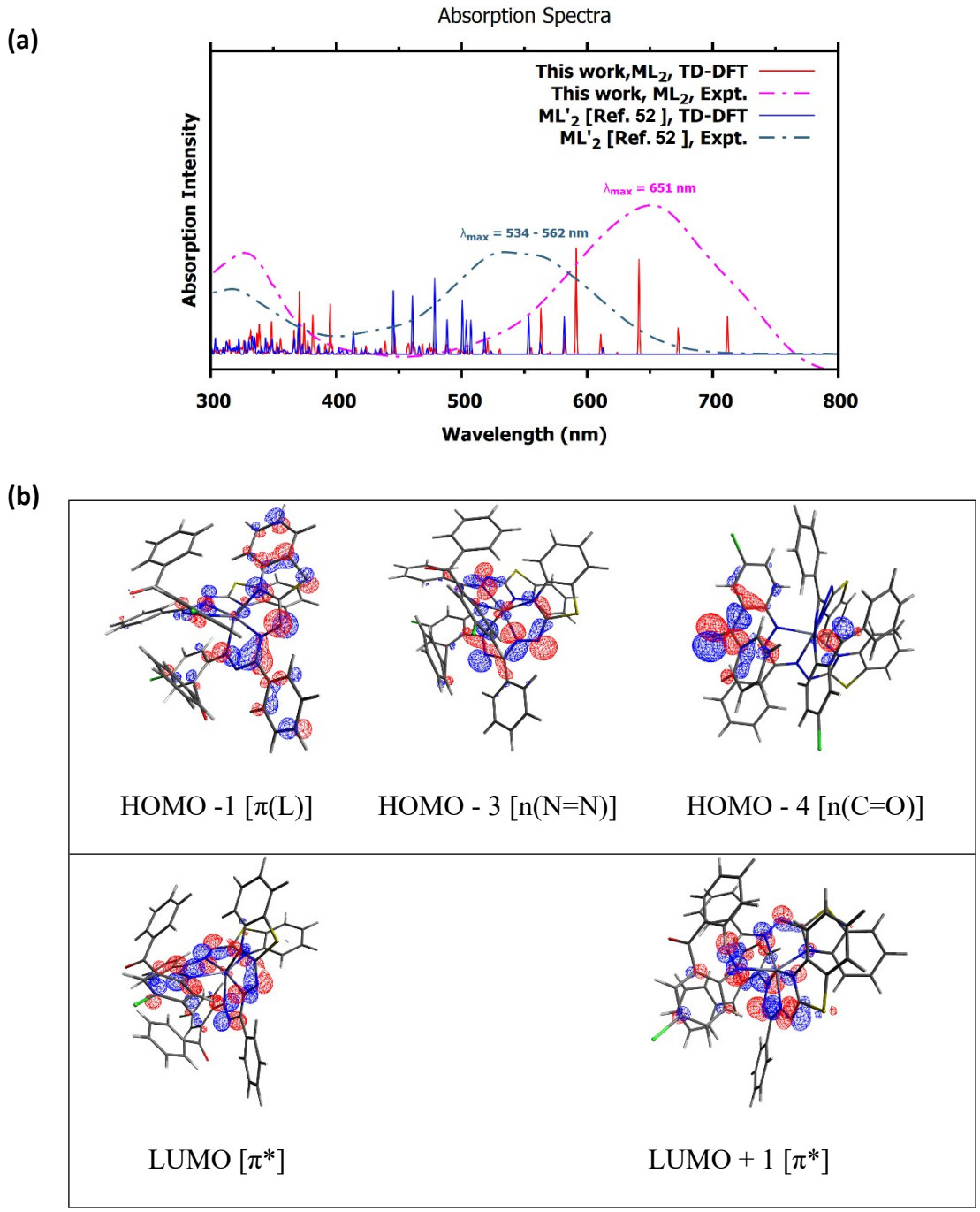



**Figure S10.** (a) Experimental and Computed absorption spectra of [$ML_2$], complex **1** (This work), and [$ML'_2$] complex [Ref. 52 in main manuscript] (Previous work) in $CHCl_3$ solution where M = Zn. (b) The molecular orbital representations of electronic transition that appear at the wavelength range from 590–650 nm (oscillator strength = 0.37-0.42) of TD-DFT computed absorption spectrum of complex **1** in $CHCl_3$ solvent. A contour value of 0.04 au is used to generate the plots.

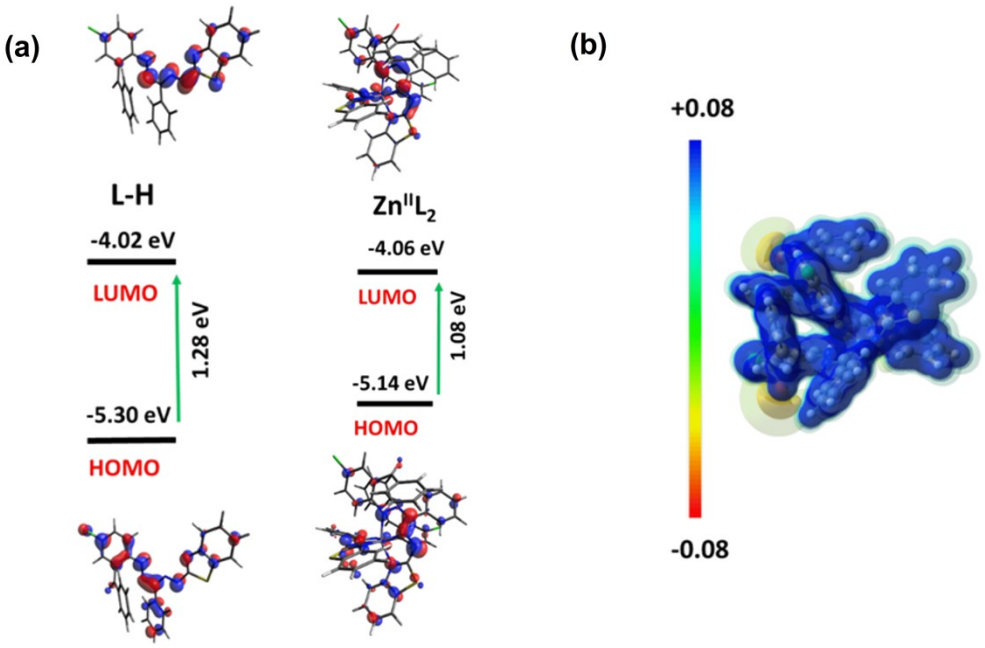



**Figure S11.** (a) BP86 computed frontier molecular orbitals of the Zn-metal complex **1** and uncoordinated benzothiazole-substituted formazan ligand (LH) are plotted with an isosurface value of 0.04 au. (b) The molecular electrostatic potential surface (isovalue: 0.025, 0.05, 0.08) of complex 1, the positive and negative ESP regions are represented by blue and red colors, respectively.

**Calculation of molecular orbital energy levels using electrochemical studies of complex 1:**

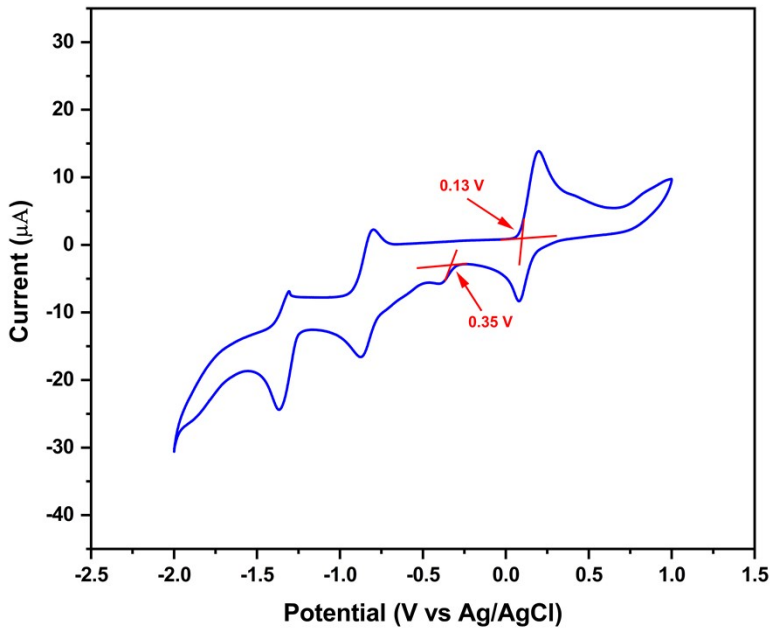



**Figure S13**. CV of the complex **1** at a scan rate of 10 mV/s acquired using a Pt-wire counter electrode, glassy carbon working electrode, and Ag/AgCl (3.0 M KCl) reference electrode.

$$E_{HOMO} = -[E_{onset}(oxidation) + 4.8 – E_{FOC}] \quad \textbf{S2}$$

$$E_{LUMO} = -[E_{onset}(reduction) + 4.8 – E_{FOC}] \quad \textbf{S3}$$

$E_{HOMO}$ and $E_{LUMO}$ are the HOMO and LUMO energy levels, $E_{onset}$(oxidation) is the onset oxidation potential of complex **1**, 4.8 is the reference energy level of ferrocene (FOC, 4.8 eV below the vacuum level), and $E_{FOC}$ is the potential of FOC/FOC$^+$ vs. Ag/AgCl (0.33 eV, as measured by cyclic voltammetry).

$$E_{HOMO} = -[0.13 + 4.8 – 0.33]$$

$$= -4.6 \text{ eV}$$

$$E_{LUMO} = -[-0.35+4.8-0.33]$$

$$= -4.12 \text{ eV}$$

**Table S2.** Second-order perturbation energy $E_2$ (eV), off-diagonal Fock matrix elements *F(i,j)* and acceptor – donor energy values $(E_j - E_i)$ (a.u.) of selected donor-acceptor NBO-NBO* interactions in metal-complex **1**, as computed at BP86+D3/TZVPP+SDD method. $E_2$ > 1.0 kcal/mol are tabulated here

| Donor NBO (i) | Acceptor NBO(j) | $E_2$ (kcal/mol) | $E_j$ - $E_i$ (au) | F(i,j) |
|---|---|---|---|---|
| **Ligand-to-Metal** | | | | |
| LP(1)N | LP*(1)Zn | 29.57 - 34.77 | 0.36 - 0.39 | 0.094 - 0.101 |
| **Ligand-to-Ligand** | | | | |
| LP(2)S | π*(N-C) | 29.02 | 0.17 | 0.062 |
| LP(2)S | π*(C-C) | 17.26 | 0.20 | 0.053 |
| LP(3)Cl | π*(C-C) | 14.35 | 0.25 | 0.054 |
| LP(1)N | π*(N-N) | 1.64 | 0.24 | 0.018 |
| LP(1)N | π*(C-C) | 1.43 | 0.33 | 0.019 |
| LP(1)N | π*(O-C) | 5.39 | 0.30 | 0.036 |
| LP(1)N | π*(N-C) | 1.38 | 0.24 | 0.016 |
| π(O-C) | π*(C-C) | 4.76 | 0.33 | 0.035 |
| π(N-N) | C(LP*) | 41.10, 28.03 | 0.19, 0.22 | 0.079,0.069 |
| π(N-N) | π*(N-N) | 1.36, 19.95 | 0.23, 0.26 | 0.016, 0.064 |
| π(N-N) | π*(C-C) | 10.28 | 0.33 | 0.052 |
| π(N-C) | π*(N-N) | 8.72 | 0.22 | 0.039 |
| π(N-C) | π*(C-C) | 17.98 | 0.28 | 0.063 |
| π(C-C) | π*(O-C) | 17.12,4.09 | 0.21 | 0.053 |
| π(C-C) | π*(N-N) | 16.49 | 0.15 | 0.010 |
| π(C-C) | π*(C-C) | 11.51 – 19.07 | 0.24 – 0.21 | 0.047-0.056 |
| π(C-C) | π*(N-C) | 9.57 | 0.19 | 0.038 |
| π(C-C) | LP*C18 | 65.90 | 0.09 | 0.069 |
| | | | | |

**Table S3:** Calculated TD-DFT electronic transition wavelength (nm), oscillator strength ($f_{osc}$), major compositions in terms MO contributions, and electronic transition character for complex **1** ($Zn^{II}L_2$)

| S. no. | Wavelength (nm) | $f_{osc}$ | Major composition | Transition Character |
|---|---|---|---|---|
| **Complex 1** | | | | |
| 1. | 712 | 0.15 | (HOMO-2) → LUMO | n → π* |
| 2. | 673 | 0.10 | (HOMO-2) → LUMO | n → π* |
| 3. | 641 | 0.37 | (HOMO-1) + (HOMO-3) → LUMO | n + π (L) → π* |
| 4. | 611 | 0.08 | (HOMO-2) → LUMO+1 | n → π* |

| | | | | |
|---|---|---|---|---|
| 5. | 591 | 0.42 | (HOMO-1) + (HOMO-3) → LUMO | n + π (L) → π* |
| | | | (HOMO-1) + (HOMO-4) → LUMO+1 | n → π* |
| 6. | 582 | 0.18 | (HOMO-3) → (LUMO+1) | n → π* |
| 7. | 555 | 0.03 | (HOMO-7) → LUMO + (LUMO+1) | S(LP)+π → π* |
| 8. | 530 | 0.02 | (HOMO-6) → LUMO + (LUMO+1) | S(LP)+π → π* |