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Electronic Supplementary Information

Synthesis and characterization of double helical dinuclear Zn-salen complex and its application in the detection of nitroaromatics

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1. General Information

3,5-ditert butylsalicylaldehyde, and 2,2'-diaminodiphenyl ether were purchased from Sigma Aldrich and used as received. $Zn(CH_3COO)_2{\cdot}2H_2O$ was purchased from Central Drug house (P) Ltd. and Et_3N was purchased from LobaChemie. 2,4,6-trinitrophenol (TNP) purchased from Spectrochem, 4-nitrobenzene and 4-nitrophenol from S. D. Fine Chem. Ltd. were used without any further purification. Toluene and THF were purchased from RANKEM, dried over sodium benzophenone and distilled fresh prior to use. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 500 MHz spectrometer. Chemical shifts for ^{1}H NMR spectra were referenced to residual solvent resonances and reported in parts per million (ppm). High resolution mass spectrophotometry (HRMS) of crystals was recorded on Q-ToF Micro Waters LCMS spectrophotometer. Separation Module used was UPLC Acquity H class series system, ionization mode was electro spray Positive ES^+ with injection volume 0.6 µL and flow rate 0.3 ml/min. Desolvation temperature and source temperature was 450 and 120 °C and gases used were N_2 and Ar. Mobile Phase used was 0.1% formic acid in water solvent A /0.1% formic acid in acetonitrile (CH_3CN) solvent B=20/80. UV-vis spectra were recorded on Agilent-8453 double beam absorption spectrophotometer using quartz cell of 1 cm path length. Emission spectra were recorded on PerkinElmer LS 55 luminescence spectrophotometers. CHNS analyses were measured on Euro EA 3000 analyzer. FTIR spectrum was recorded on a Perkin Elmer-Spectrum RX-FTIR in the scan range of 400–4000 cm^{-1}. Thermal gravimetric analysis (TGA) was performed using SDT 650 instrument at a heating rate of 10 °C/min under nitrogen atmosphere.

Single crystal X-ray diffraction

X-ray data was collected from Bruker AXS (Kappa Apex 2) CCD diffractometer equipped with graphite monochromatic Mo Kα (λ = 0.7107 Å) radiation source. The data was performed with 100% completeness for θ up to 25°. ω and φ scans were employed for data collection. The frame width for ω was set at 0.5° to collect the data. The frames were integrated and the data were reduced for Lorentz and polarization corrections using saintnt. To the data set, multi-scan absorption correction was applied. All structures were solved using sir-92 and refined using SHELXL-97. The non-hydrogen atoms were refined with anisotropic displacement parameter. All the hydrogen atoms could be located in the difference Fourier map. The hydrogen atoms bonded to carbon atoms were fixed at chemically meaningful positions and were allowed to ride with the parent atom during refinement.

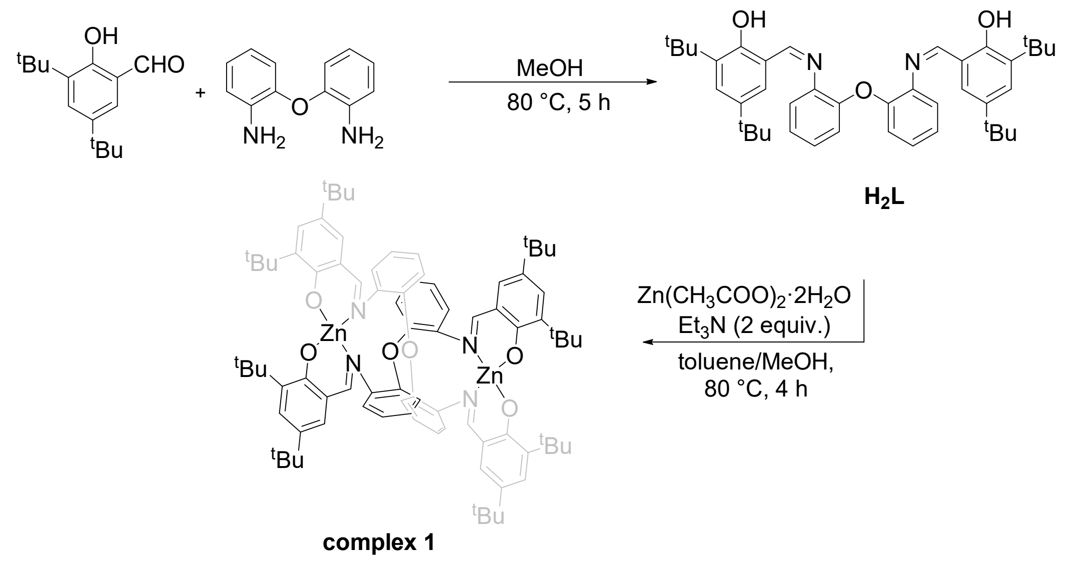
2. General Procedures

*2.1 Synthesis of **H_2L***

Ligand (H_2L) was synthesized using literature procedure.[1] To a methanol solution of 3,5-ditert-butyl salicylaldehyde (2 mmol), added formic acid (1 mol%) followed by addition of methanol solution of 2,2'-diaminodiphenyl ether (1.2 mmol), the reaction mixture was refluxed for 5 h at 80 °C. Yellow-orange precipitates were obtained, the contents were filtered and washed with methanol. Orange shinny crystals were obtained from diethyl ether by slow evaporation at room temperature.

*2.2 Synthesis of complex **1***

To a stirred toluene solution of H_2L (1 mmol) and Et_3N (2 mmol) added the methanol solution of $Zn(CH_3COO)_2.2H_2O$ (1 mmol). The colour of reaction mixture turns yellow, the reaction mixture was heated at 80 °C for 4 h to afford a yellow precipitate and solvent was removed under vacuum to obtain yellow solid. The yellow solid was dissolved in toluene and filtered; the filtrate was concentrated and put for crystallization. Yellow block like crystals were obtained at room temperature after 12 h.



Scheme S1. Schematic representation for the synthesis of complex **1**.

3 Characterization Data

H$_2$L^1: Orange solid; m.p.= 131.2-131.4 °C; Yield: 78%.
IR (KBr, cm^{-1}): 3459 (m), 2935 (s), 1610 (m), 1398 (m), 1204 (s), 1114 (s).
^{1}H NMR (500 MHz, CDCl$_3$) δ= 8.73 (s, 1H, -CH=N-), 7.39-7.27 (m, 1H, Ar), 7.26-7.25 (m, 1H, Ar), 7.18-7.12 (m, 3H, Ar), 7.12-6.97 (m, 1H, Ar), 1.40 (s, 9H, -C(CH$_3$)$_3$), 1.26 (s, 9H, -C(CH$_3$)$_3$);**^{13}C NMR (125 MHz, CDCl$_3$)** δ=165.04 (C-O), 158.63 (C-O), 149.84(-CH=N), 140.28 (-CH=N), 139.81 (Ar), 136.99 (Ar), 128.07 (Ar), 127.35 (Ar), 126.95 (Ar), 124.23 (Ar), 121.10 (Ar), 119.42 (Ar), 118.51 (Ar), 35.19 (C(CH$_3$)$_3$), 34.22 (C(CH$_3$)$_3$), 31.62 (-CH$_3$), 31.59 (-CH$_3$), 29.58 (-CH$_3$).

Complex 1: Yellow crystalline solid; Yield: 75%.
IR (KBr, cm^{-1}): 2946 (s), 1621 (m), 1416 (m), 1227 (s), 1154 (s), 733 (s).
^{1}H NMR (500 MHz, CDCl$_3$) δ= 7.89 (s, 1H, -CH=N-), 7.38-7.35 (m, 2H, Ar), 7.17-7.13 (m, 1H, Ar), 6.93-6.90 (t, 1H, Ar), 6.60 (d, 1H, Ar, *J*= 8.2 Hz), 6.43 (d, 1H, Ar, *J*= 2.5 Hz), 6.33-3.30 (m, 1H, Ar), 1.39 (s, 9H, -C(CH$_3$)$_3$), 1.19 (s, 9H, -C(CH$_3$)$_3$); **^{13}C NMR (125 MHz, CDCl$_3$)** δ= 171.16 (C-O), 167.48 (C-O), 147.89 (-CH=N), 140.91 (-CH=N), 140.29 (Ar), 138.02 (Ar), 134.01 (Ar), 130.49 (Ar), 130.45 (Ar), 129.19 (Ar), 128.38 (Ar), 126.03 (Ar), 125.45 (Ar), 124.10 (Ar), 120.23 (Ar), 119.87 (Ar), 118.16 (Ar), 35.35 (C(CH$_3$)$_3$), 33.88(C(CH$_3$)$_3$), 31.46 (-CH$_3$), 29.01 (-CH$_3$), 21.61 (CH$_3$-C$_6$H$_5$); **HRMS:** m/z 1393.6310 [$C_{98}H_{116}N_4O_6Zn_2$]$^+$ (calculated: 1393.5809); **Elemental analysis**: C 74.65, H 7.43, N 3.54; Found C 74.64, H 7.46, N 3.56%.

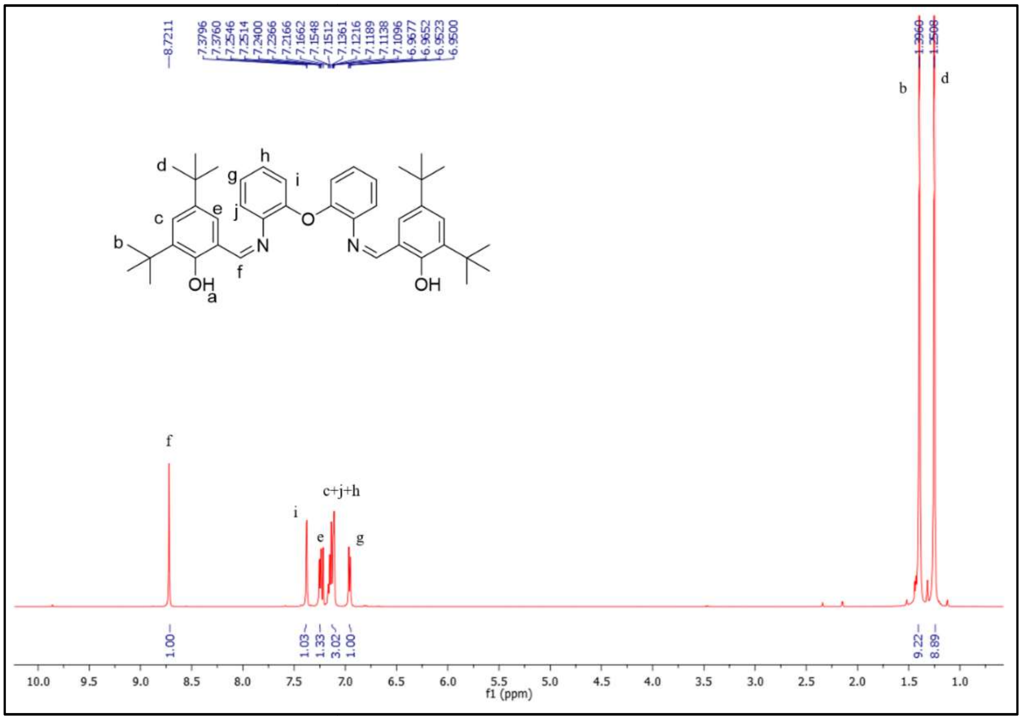


Figure S1 ^{1}H NMR spectrum of **H_2L** in $CDCl_3$ at room temperature (500 MHz).

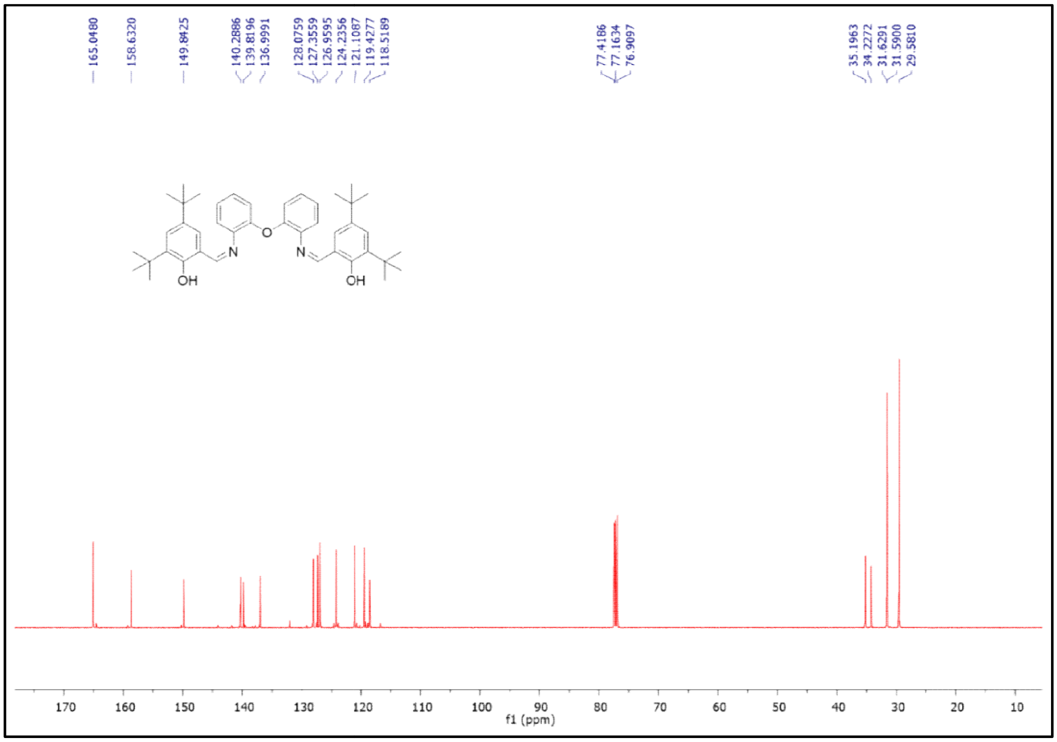


Figure S2 ^{13}C NMR spectrum of **H_2L** in $CDCl_3$ at room temperature (125 MHz).

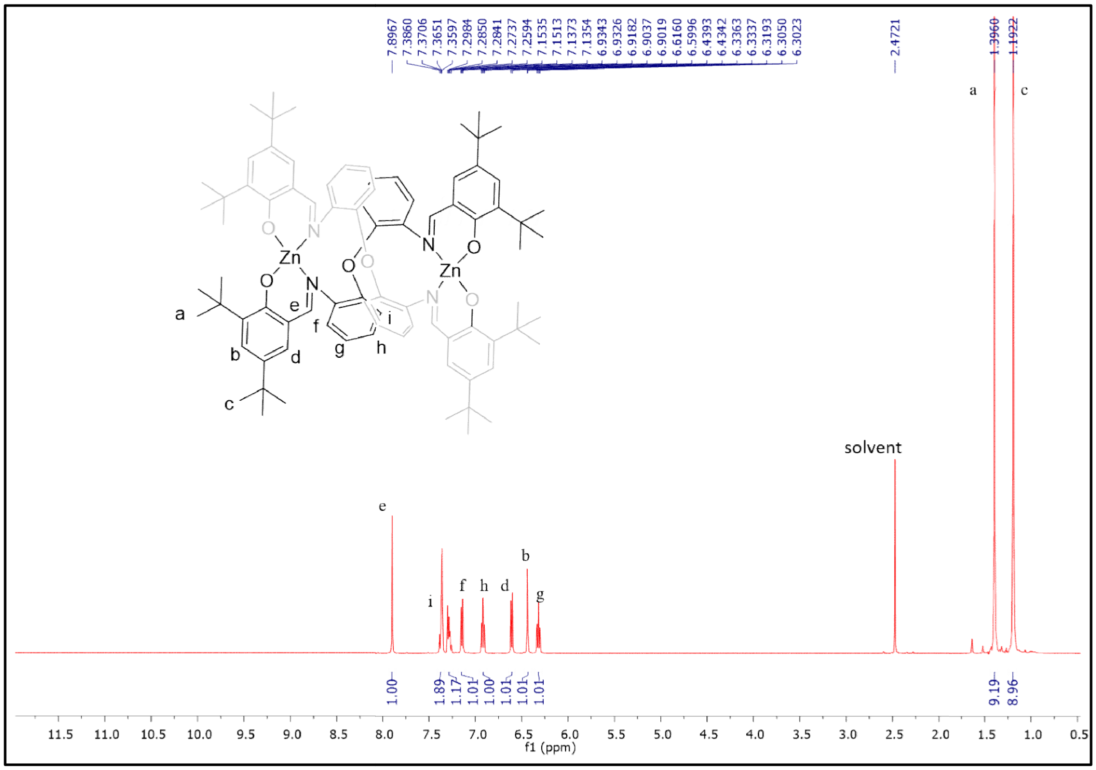


Figure S3 ^{1}H NMR spectrum of **1** in $CDCl_3$ at room temperature (500 MHz).

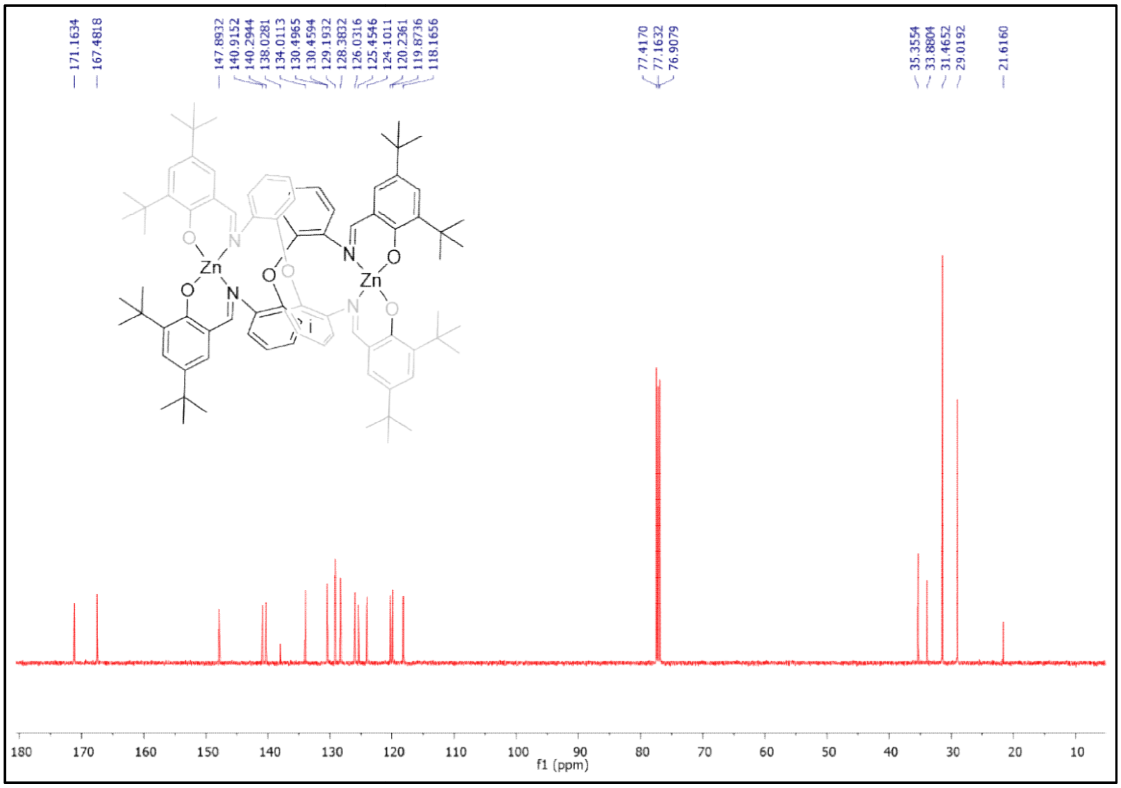


Figure S4 ^{13}C NMR spectrum of **1** in $CDCl_3$ at room temperature (125 MHz).

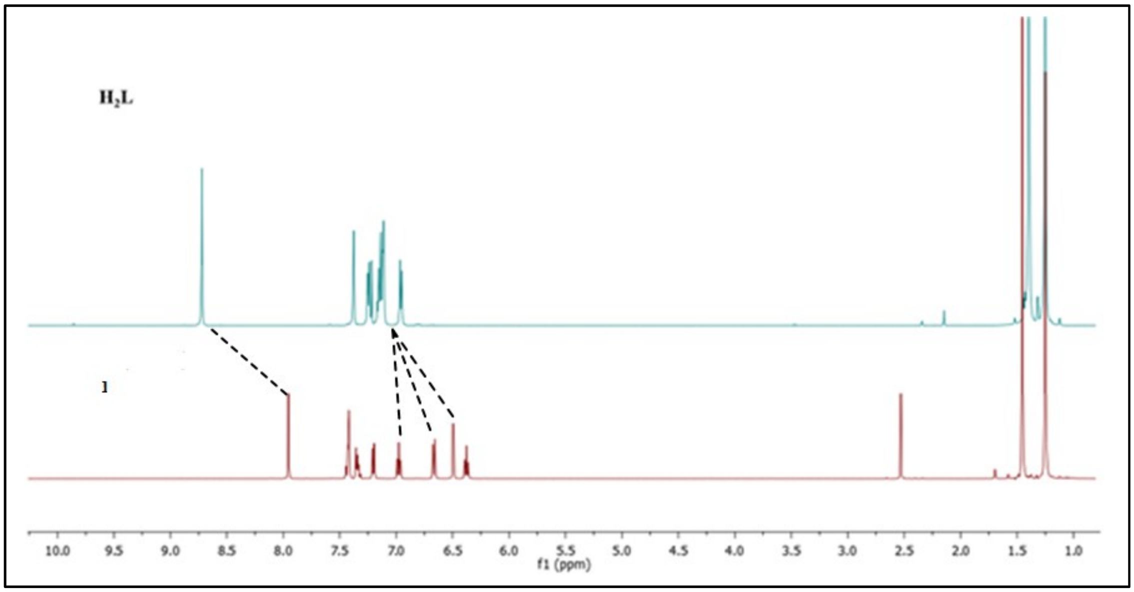
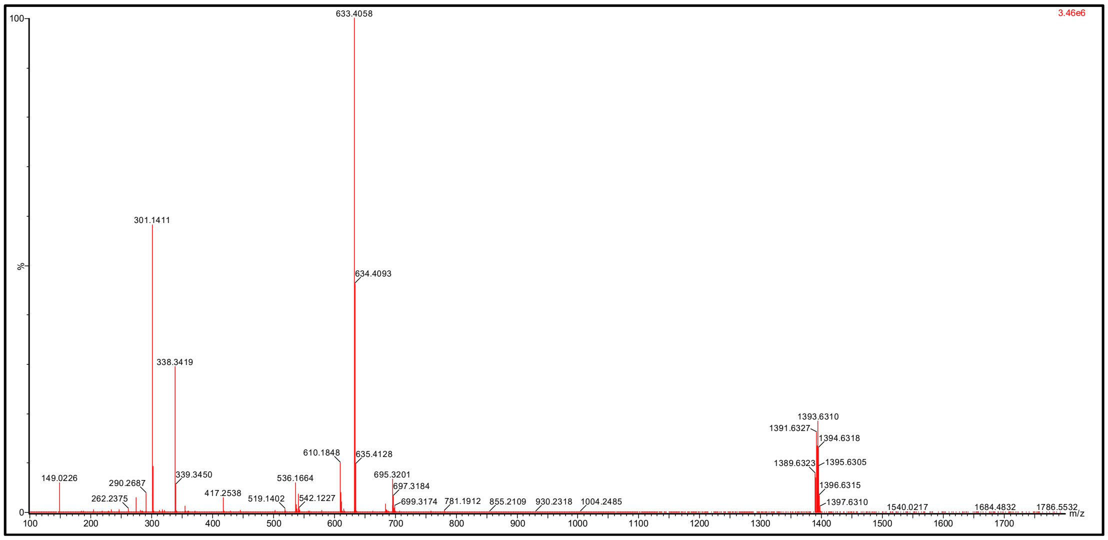


Figure S5 ^{1}H NMR spectra of **H_2L** and **1** in $CDCl_3$ at room temperature (500 MHz).

a)



b)

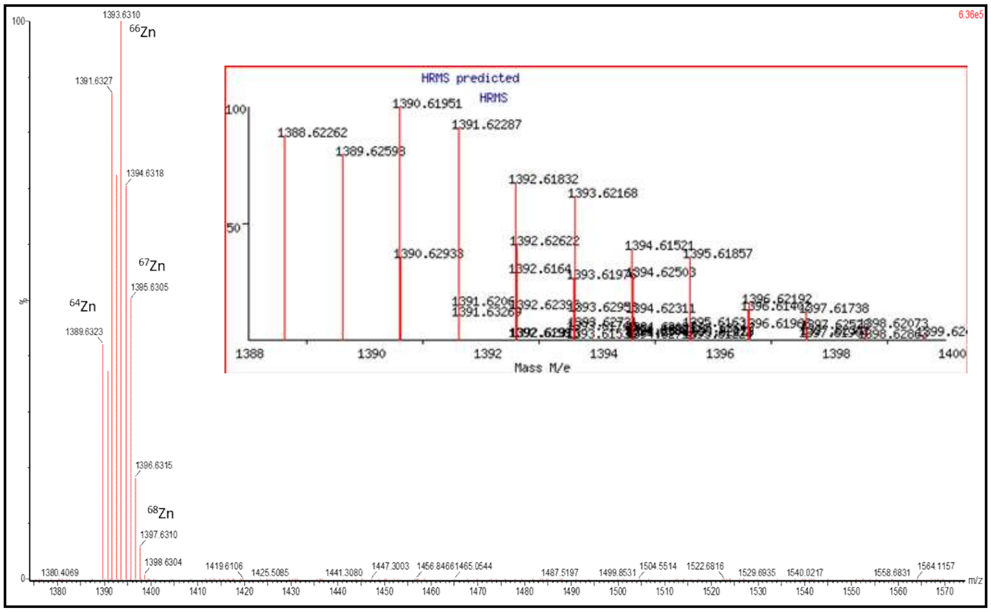


Figure S6 a) HRMS spectrum of **1** (in acetonitrile); **b)** Experimental and predicted HRMS spectrum of **1**.

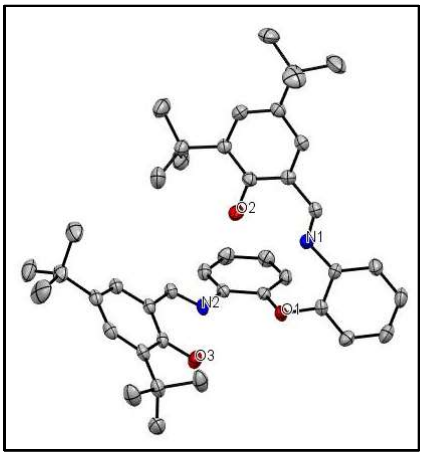
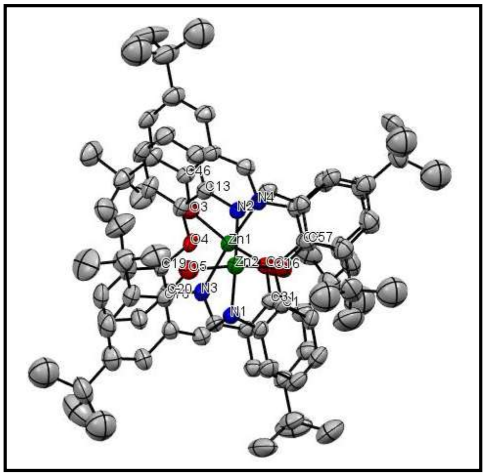


Figure S7 ORTEP representation of $\mathbf{H_2L}$. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity. Colour code: O (red), N (blue), C (grey).

a)



b)

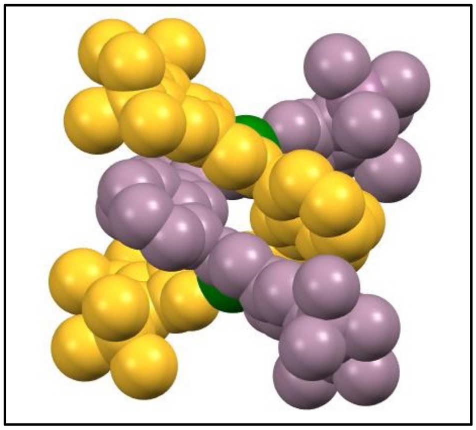


Figure S8 a) ORTEP representation of **1** (thermal ellipsoids are drawn at 50 % probability) toluene molecule and hydrogen atoms are omitted for clarity, Colour code: Zn (green), O (red), N (blue), C (grey); **b)** Space filling representation of **1** along b axis.

Table S1. Crystal data of **H_2L** and **1**

	H_2L	**Complex 1**
Empirical formula	$C_{42}H_{52}$ N_2O_3	$C_{98}H_{116}N_4O_6Zn_2$
Formula weight	632.85	1576.68
Temperature	190(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	P-1
Unit cell dimensions	a = 13.5134(11) Å; α= 90° b = 24.709(2) Å;β=112.292(3)° c = 12.1453(10) Å; γ= 90°	a = 17.642(6) Å; α=100.238(15)° b = 19.539(7) Å; β= 98.553(14)° c = 26.908(9) Å; γ= 91.101(16)°
Volume	3752.2(5) Å^3	9016(6) Å^3
Z	4	4
Density (calculated)	1.120 Mg/m^3	1.162 Mg/m^3
Absorption coefficient	0.070 mm^{-1}	0.585 mm^{-1}
F(000)	1368	3360
Crystal size	0.250 x 0.200 x 0.150 mm^3	0.250 x 0.200 x 0.150 mm^3
Theta range for data collection	2.962 to 26.072°	3.051 to 25.000°
Index ranges	-16<=h<=15, -30<=k<=30, -14<=l<=14	-20<=h<=20, -23<=k<=23, -31<=l<=31
Reflections collected	63919	156878
Independent reflections	7391 [R(int) = 0.0806]	31532 [R(int) = 0.0697]
Completeness to theta = 25.242°	99.7 %	99.3 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7453 and 0.6940	0.7452 and 0.6220
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	7391 / 0 / 432	31532 / 2665 / 2237

Goodness-of-fit on F^2	1.057	1.058
Final R indices [I>2sigma(I)]	R1 = 0.0614, wR2 = 0.1434	R1 = 0.0789, wR2 = 0.1632
R indices (all data)	R1 = 0.0944, wR2 = 0.1598	R1 = 0.1321, wR2 = 0.1975
Extinction coefficient	n/a	n/a
Largest diff. peak and hole	0.219 and -0.258 e.Å^{-3}	1.518 and -0.622 e.Å^{-3}
CCDC number	**2093188**	**2091095**

R[F2 >2s(F2)], wR(F2), S

Table S2. Selected bond lengths [Å] and angles [°] for **H_2L**

C(1)-O(1)	1.396(3)
C(6)-N(1)	1.418(3)
C(27)-N(2)	1.416(3)
C(28)-N(2)	1.279(3)
C(34)-O(3)	1.363(3)
C(2)-C(1)-O(1)	118.78(19)
O(1)-C(1)-C(6)	119.59(19)
N(1)-C(7)-C(8)	122.3(2)
N(1)-C(7)-H(7)	118.9
N(1)-C(7)-H(7)	118.9
O(2)-C(13)-C(8)	120.0(2)
O(2)-C(13)-C(12)	119.5(2)
C(23)-C(22)-O(1)	123.26(19)
O(1)-C(22)-C(27)	116.05(18)
C(26)-C(27)-N(2)	123.48(19)
C(22)-C(27)-N(2)	118.49(19)
N(2)-C(28)-C(29)	122.0(2)
N(2)-C(28)-H(28)	119.0
O(3)-C(34)-C(33)	120.0(2)
O(3)-C(34)-C(29)	119.70(19)
C(7)-N(1)-C(6)	121.05(19)
C(28)-N(2)-C(27)	120.10(19)
C(22)-O(1)-C(1)	115.95(16)

TableS3. Selected bond lengths [Å] and angles [°] for **1**

Zn(1)-O(3)	1.932(3)
Zn(1)-O(2)	1.939(3)
Zn(1)-N(3)	2.008(4)
Zn(1)-N(4)	2.009(4)
Zn(2)-O(6)	1.920(4)
Zn(2)-O(5)	1.929(4)
Zn(2)-N(2)	1.998(4)
Zn(2)-N(1)	1.999(4)
C(1)-O(1)	1.395(5)
C(6)-N(1)	1.421(6)
C(7)-O(1)	1.396(5)
C(12)-N(4)	1.427(6)
C(13)-N(2)	1.435(6)
C(18)-O(4)	1.401(6)
C(19)-O(4)	1.391(6)
C(20)-N(3)	1.441(6)
C(25)-N(3)	1.306(6)
C(31)-O(2)	1.298(6)
C(40)-N(4)	1.302(6)
C(46)-O(3)	1.299(6)
C(55)-N(2)	1.295(6)
C(57)-O(6)	1.305(6)

C(70)-N(1)	1.304(6)
C(76)-O(5)	1.292(6)
Zn(3)-O(12)	1.920(4)
Zn(3)-O(11)	1.922(3)
Zn(3)-N(6)	2.003(4)
Zn(3)-N(5)	2.003(4)
Zn(4)-O(9)	1.933(3)
Zn(4)-O(10)	1.939(3)
Zn(4)-N(8)	2.005(4)
Zn(4)-N(7)	2.007(4)
C(85)-N(5)	1.417(6)
C(86)-O(7)	1.399(5)
C(91)-O(7)	1.400(5)
C(96)-N(7)	1.435(6)
C(97)-N(6)	1.428(6)
C(102)-O(8)	1.389(6)
C(103)-O(8)	1.390(6)
C(104)-N(8)	1.431(6)
C(109)-N(7)	1.297(6)
C(115)-O(9)	1.304(6)
C(124)-N(8)	1.297(6)
C(130)-O(10)	1.293(6)
C(139)-N(5)	1.304(6)
C(145)-O(11)	1.300(6)
C(154)-N(6)	1.301(6)
C(156)-O(12)	1.298(6)
O(3)-Zn(1)-O(2)	120.24(16)
O(3)-Zn(1)-N(3)	103.77(15)
O(2)-Zn(1)-N(3)	94.67(15)
O(3)-Zn(1)-N(4)	95.38(15)
O(2)-Zn(1)-N(4)	102.55(15)
N(3)-Zn(1)-N(4)	143.10(16)
O(6)-Zn(2)-O(5)	119.32(17)
O(6)-Zn(2)-N(2)	95.42(16)
O(5)-Zn(2)-N(2)	101.72(16)
O(6)-Zn(2)-N(1)	105.33(17)
O(5)-Zn(2)-N(1)	95.72(16)
N(2)-Zn(2)-N(1)	141.69(16)
C(2)-C(1)-O(1)	121.8(4)
C(5)-C(6)-N(1)	122.6(4)
C(1)-C(6)-N(1)	119.7(4)
C(8)-C(7)-O(1)	121.8(4)
C(12)-C(7)-O(1)	117.4(4)
C(11)-C(12)-N(4)	122.0(4)
C(7)-C(12)-N(4)	120.0(4)
C(18)-C(13)-N(2)	120.7(4)
C(14)-C(13)-N(2)	121.8(5)
C(13)-C(18)-O(4)	117.5(4)
C(17)-C(18)-O(4)	121.8(5)
C(20)-C(19)-O(4)	118.2(4)
C(21)-C(20)-N(3)	122.2(5)
N(4)-C(40)-H(40)	115.4
N(2)-C(55)-C(56)	128.5(5)
N(2)-C(55)-H(55)	115.8
C(70)-N(1)-Zn(2)	119.3(3)
C(6)-N(1)-Zn(2)	122.4(3)
C(55)-N(2)-C(13)	118.7(4)
C(55)-N(2)-Zn(2)	120.2(3)
C(13)-N(2)-Zn(2)	120.9(3)
C(25)-N(3)-C(20)	117.0(4)
C(25)-N(3)-Zn(1)	120.5(3)
C(20)-N(3)-Zn(1)	122.4(3)
C(40)-N(4)-C(12)	118.5(4)

C(40)-N(4)-Zn(1)	119.5(3)
C(12)-N(4)-Zn(1)	121.6(3)
C(1)-O(1)-C(7)	117.5(3)
C(31)-O(2)-Zn(1)	128.2(3)
C(46)-O(3)-Zn(1)	127.9(3)
C(19)-O(4)-C(18)	118.1(3)
C(76)-O(5)-Zn(2)	127.4(3)
C(57)-O(6)-Zn(2)	127.6(3)
O(12)-Zn(3)-O(11)	119.08(17)
O(12)-Zn(3)-N(6)	94.99(15)
O(11)-Zn(3)-N(6)	102.40(15)
O(12)-Zn(3)-N(5)	104.21(16)
O(11)-Zn(3)-N(5)	95.68(15)
N(6)-Zn(3)-N(5)	142.82(16)
O(9)-Zn(4)-O(10)	121.98(16)
O(9)-Zn(4)-N(8)	104.62(16)
O(10)-Zn(4)-N(8)	94.76(15)
O(9)-Zn(4)-N(7)	95.08(15)
O(10)-Zn(4)-N(7)	102.82(16)
N(8)-Zn(4)-N(7)	141.08(16)
C(86)-C(85)-N(5)	120.3(4)
C(90)-C(85)-N(5)	122.4(4)
C(87)-C(86)-O(7)	121.8(4)
C(92)-C(91)-O(7)	121.1(4)
C(91)-C(96)-N(7)	120.7(4)
C(95)-C(96)-N(7)	120.6(4)
C(98)-C(97)-N(6)	122.2(5)
C(102)-C(97)-N(6)	119.5(4)
C(105)-C(104)-N(8)	121.5(5)
C(103)-C(104)-N(8)	120.1(4)
N(6)-C(154)-C(155)	128.8(5)
N(6)-C(154)-H(154)	115.6
O(12)-C(156)-C(155)	121.6(4)
O(12)-C(156)-C(157)	119.5(4)
C(139)-N(5)-C(85)	118.4(4)
C(139)-N(5)-Zn(3)	119.6(3)
C(85)-N(5)-Zn(3)	121.8(3)
C(154)-N(6)-C(97)	119.1(4)
C(154)-N(6)-Zn(3)	119.9(3)
C(97)-N(6)-Zn(3)	120.6(3)
C(109)-N(7)-C(96)	117.8(4)
C(109)-N(7)-Zn(4)	120.3(3)
C(96)-N(7)-Zn(4)	121.8(3)
C(124)-N(8)-C(104)	117.5(4)
C(124)-N(8)-Zn(4)	120.2(3)
C(104)-N(8)-Zn(4)	122.2(3)
C(86)-O(7)-C(91)	118.4(3)
C(102)-O(8)-C(103)	118.4(4)
C(115)-O(9)-Zn(4)	127.5(3)
C(130)-O(10)-Zn(4)	128.3(3)
C(145)-O(11)-Zn(3)	127.9(3)
C(156)-O(12)-Zn(3)	128.0(3)

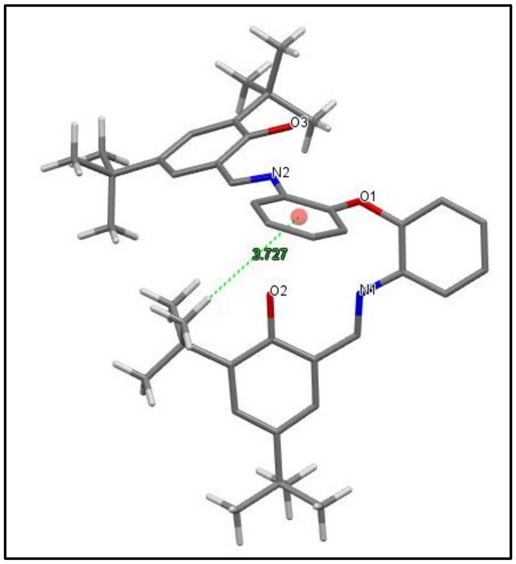
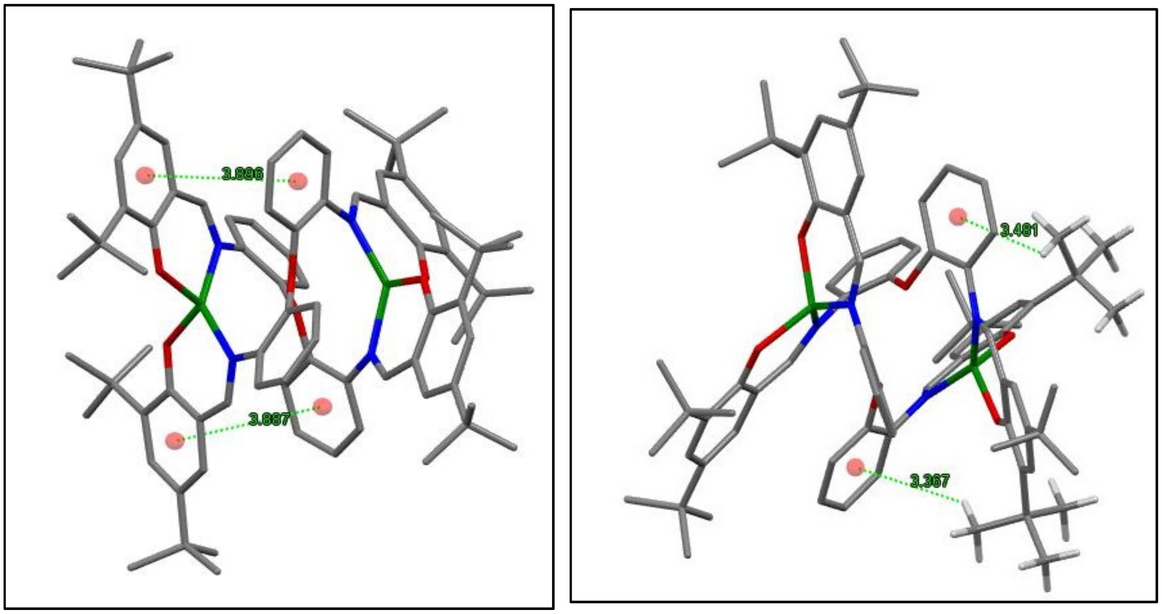


Figure S9 Depiction of intramolecular CH···π interactions in **H$_2$L**.



a)

b)

Figure S10 a) Intermolecular π···π interactions in aromatic rings of **1**; **b)** Intermolecular CH···π interactions in **1**.

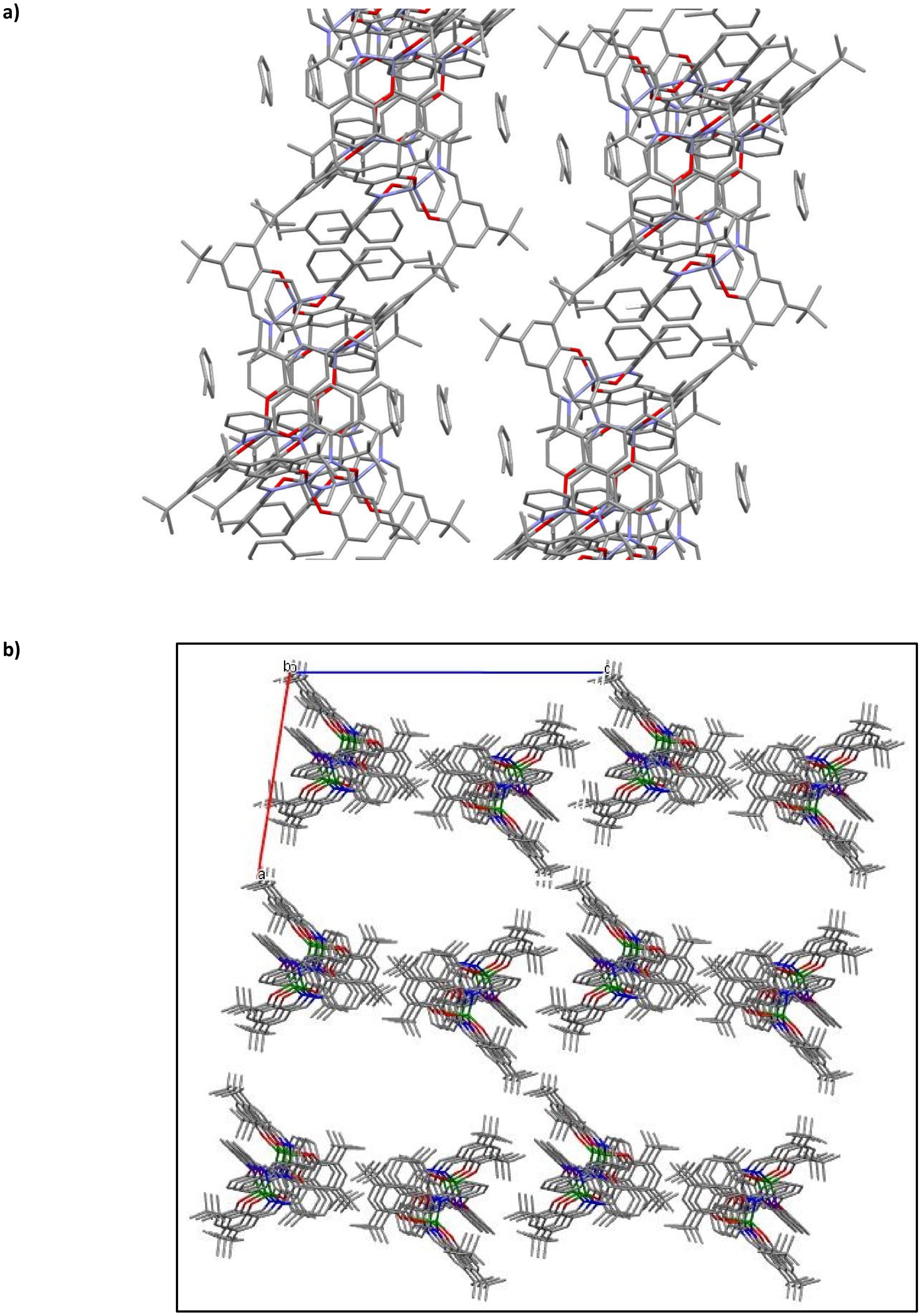


Figure S11 a) Packing diagram of **1** viewed along a axis; **b)** Capped stick diagram of 2D network of **1** along b axis.

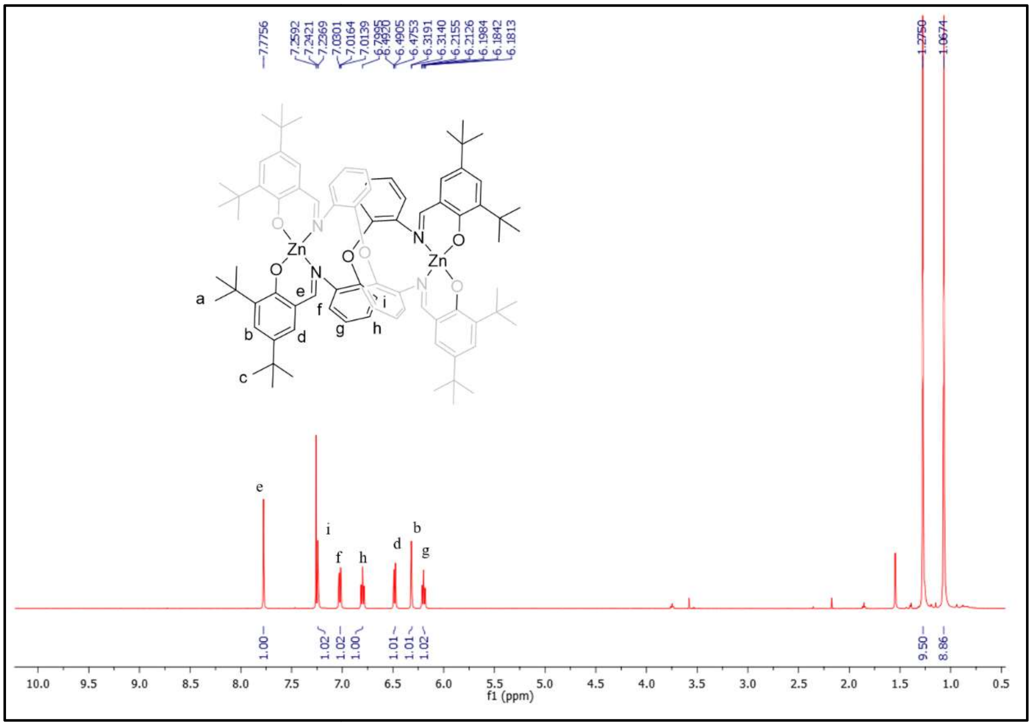


Figure S12 ^{1}H NMR spectrum of **1**(reaction was performed in THF) in $CDCl_3$ at room temperature (500 MHz).

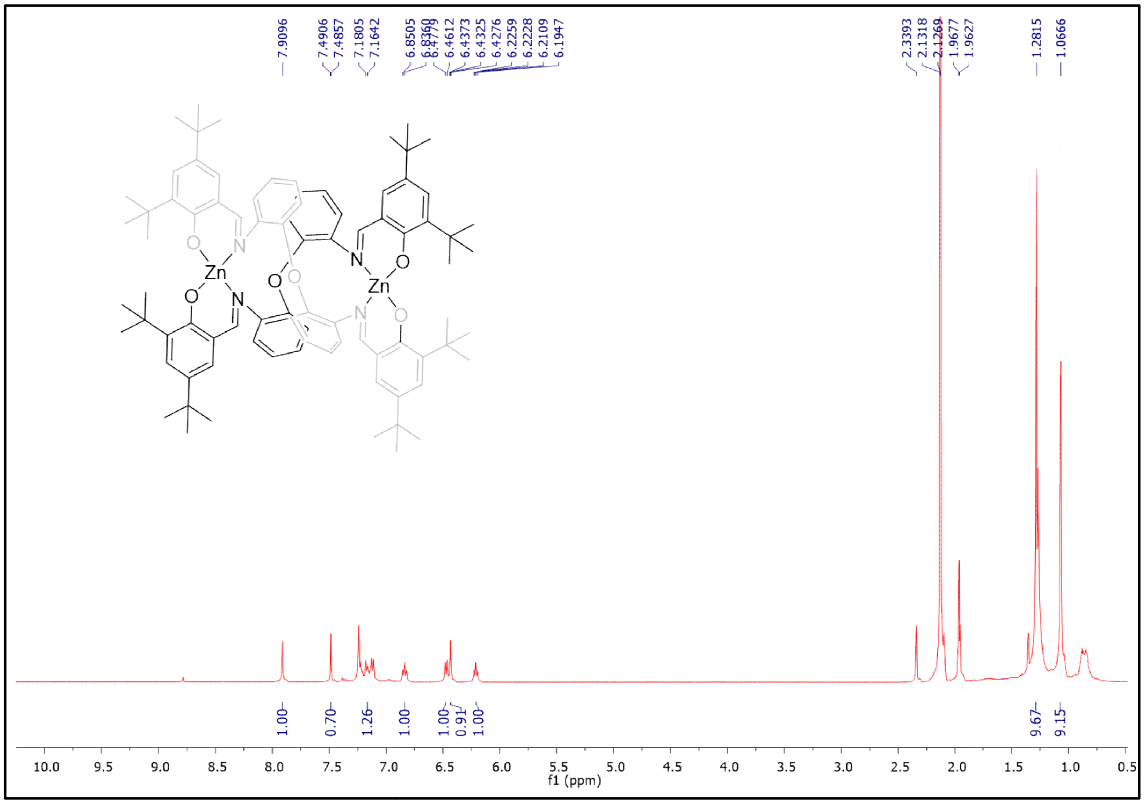


Figure S13 ^{1}H NMR spectrum of **1** in CD_3CN at room temperature (500 MHz).

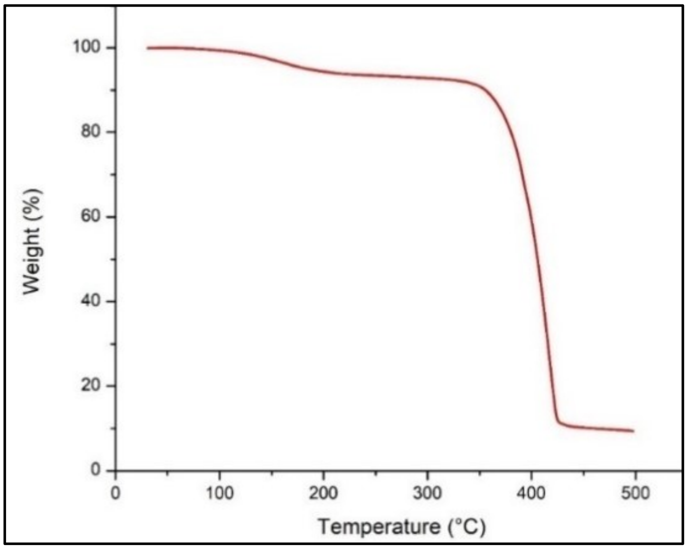


Figure S14 TGA thermogram of **1**.

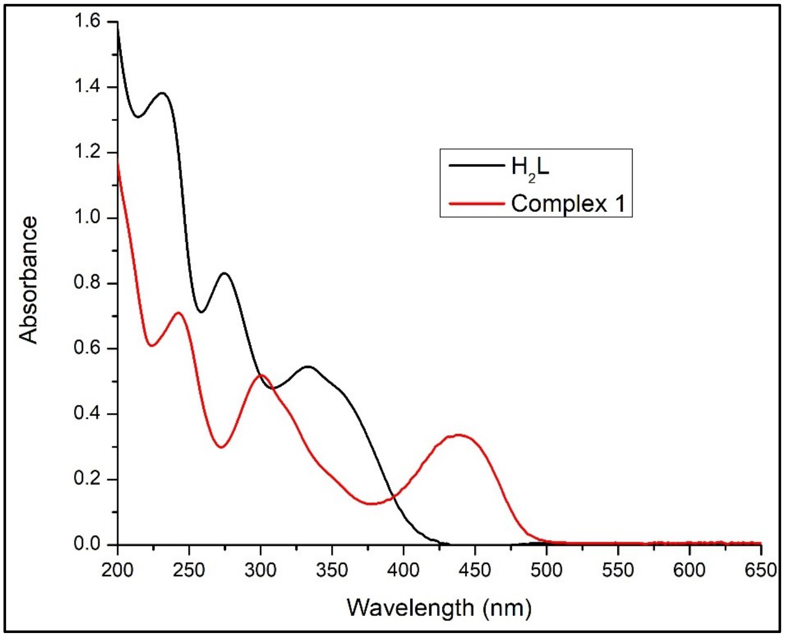


Figure S15 UV-vis spectra of **H_2L** and **1** in CH_3CN (1×10^{-5} M).

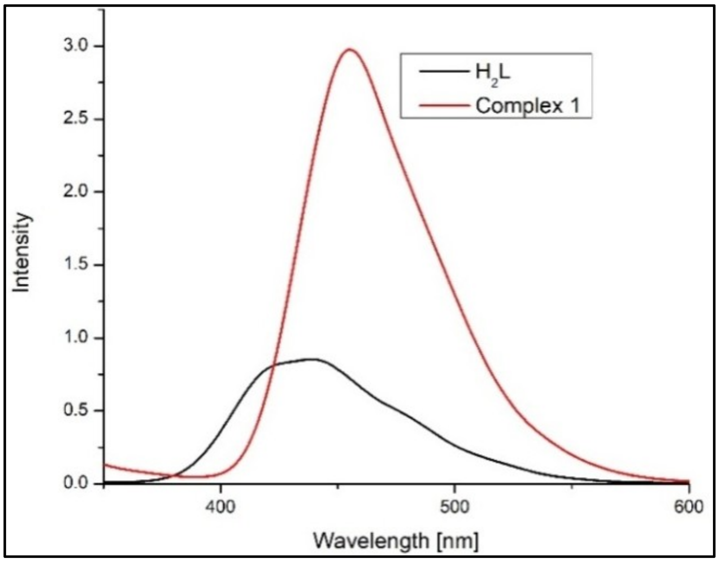


Figure S16 Emission spectra of $\mathbf{H_2L}$ and **1** in CH_3CN (1×10^{-5} M); λ_{ex}= 263 nm.

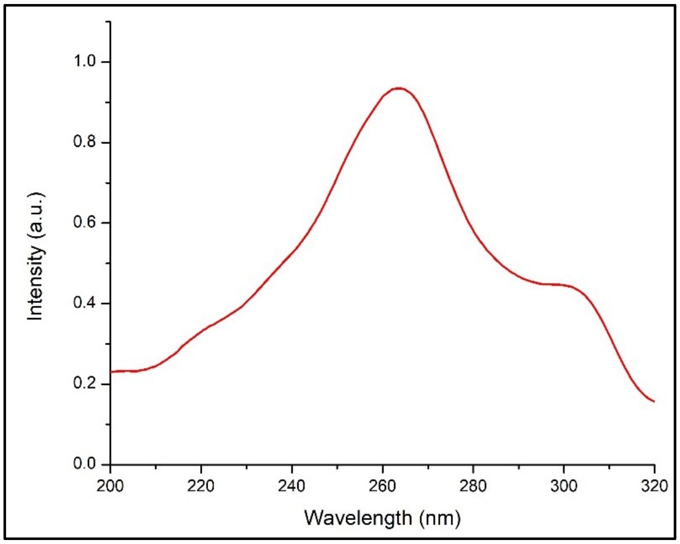


Figure S17 Excitation spectrum of **1**.

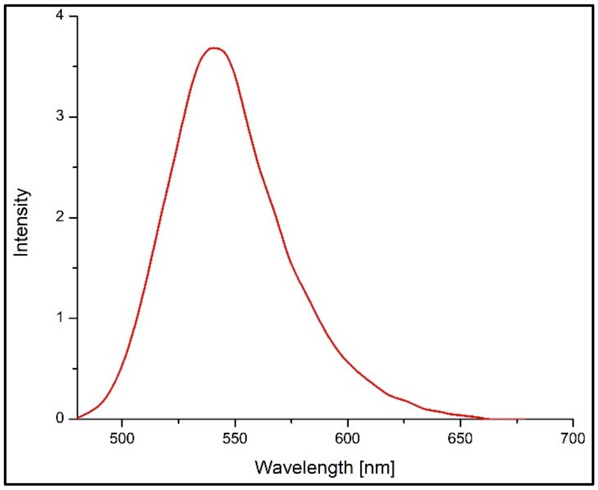


Figure S18 Solid state fluorescence spectrum of **1** upon excitation at 263 nm.

Mechanistic studies

Quantum yield[2]: Quantum yield is calculated using formula

$$q_u = q_r.m_u/m_r.\eta^2_u/\ \eta^2_r$$

where, q_r is quantum yield of reference.
q_u is quantum yield of sample.
m_u is slope of plot of integrated intensity/s area for sample.
m_r is slope of plot of integrated intensity/s area for reference.
η^2_u is refractive index of sample solution.
η^2_r is refractive index of reference solution.

Quinine sulphate was taken as reference. $q_r = 0.546$.

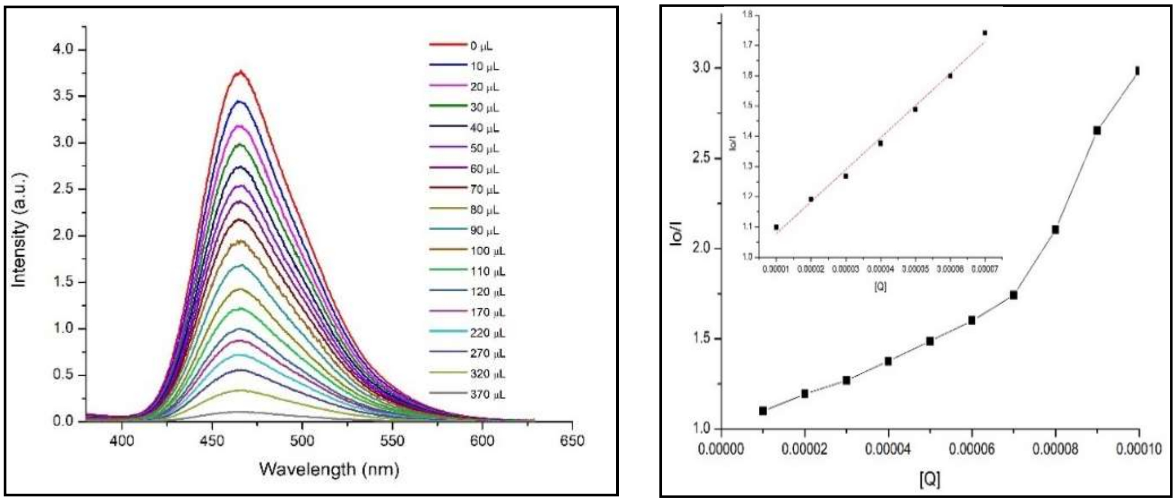
Quenching efficiency[2,3]: Stern-Volmer equation was used to determine the quenching efficiency of nitro aromatics $I_o/I = 1 + K_{sv}[Q]$

Where, I_o and I are the luminescence intensities before and after adding quencher, [Q] is the molar concentration of quencher and K_{sv} is quenching constant. The slope of linearly fitted curve gives the value of K_{sv}.

Slope of the florescence intensity[2,3]. Slope of the florescence intensity was calculated using linear fit of the fluorescence intensity against the concentration of the nitro compound plot.

Sr. No	Nitroaromatics	Slope of fluorescence intensity (R^2)
1	Trinitrophenol	-2.097×10^3 (0.99)
2	Nitrophenol	-1.812×10^3 (0.99)
3	Nitrobenzene	-1.053×10^3 (0.99)

Detection limit[2]: Detection limit was calculated using the following formula: Detection limit = $-3\sigma/m$, where σ = standard deviation of blank readings and m = slope of fluorescence intensity *vs.* concentration of the TNP plot.



(a) **(b)**

Figure 19a) Quenching of emission intensity of **1** on gradual addition of TNP (1×10^{-5} M solution in CH_3CN) (λ_{ex}= 263 nm); **b**) Stren-Volmer plot for **1** titrated with TNP in CH_3CN.

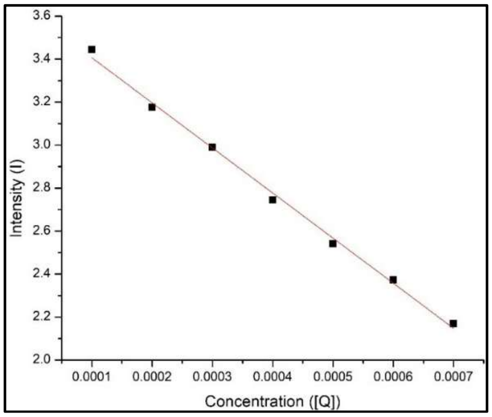
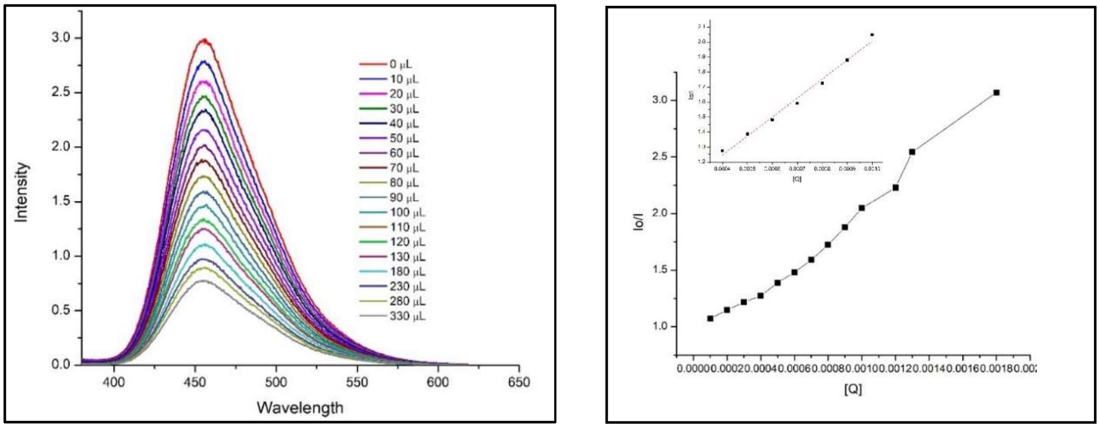
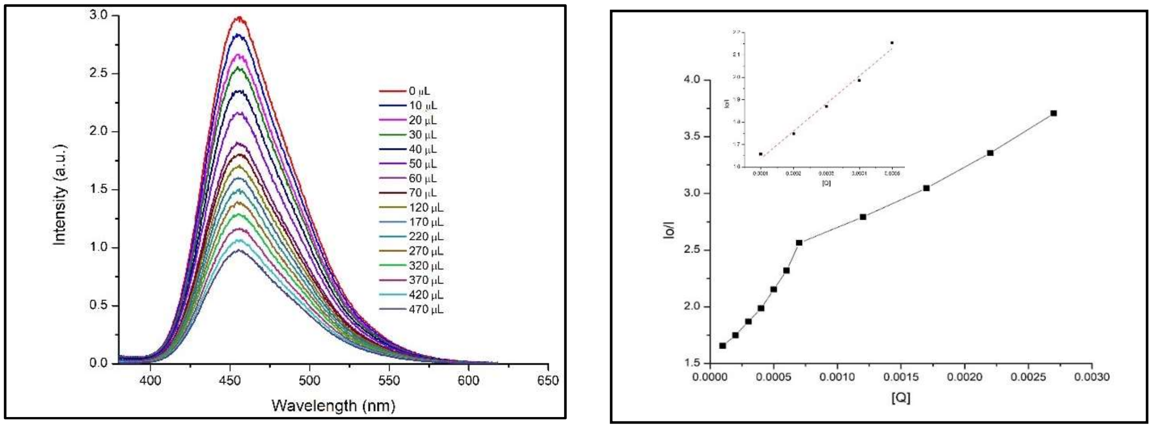


Figure S20 Plot of limit of detection of **1** towards TNP.



a) **b)**

Figure S21 a) Quenching of fluorescence intensity of **1** on gradual addition of NP (1×10^{-5} M solution in CH_3CN) (λ_{ex}= 263 nm); **b**) Stren-Volmer plot for **1** titrated with NP in CH_3CN.



a) **b)**

Figure S22 a) Quenching of fluorescence intensity of **1** on gradual addition of NB (1×10^{-5} M solution in CH_3CN) (λ_{ex}= 263 nm); **b**) Stren-Volmer plot for **1** titrated with NB in CH_3CN.

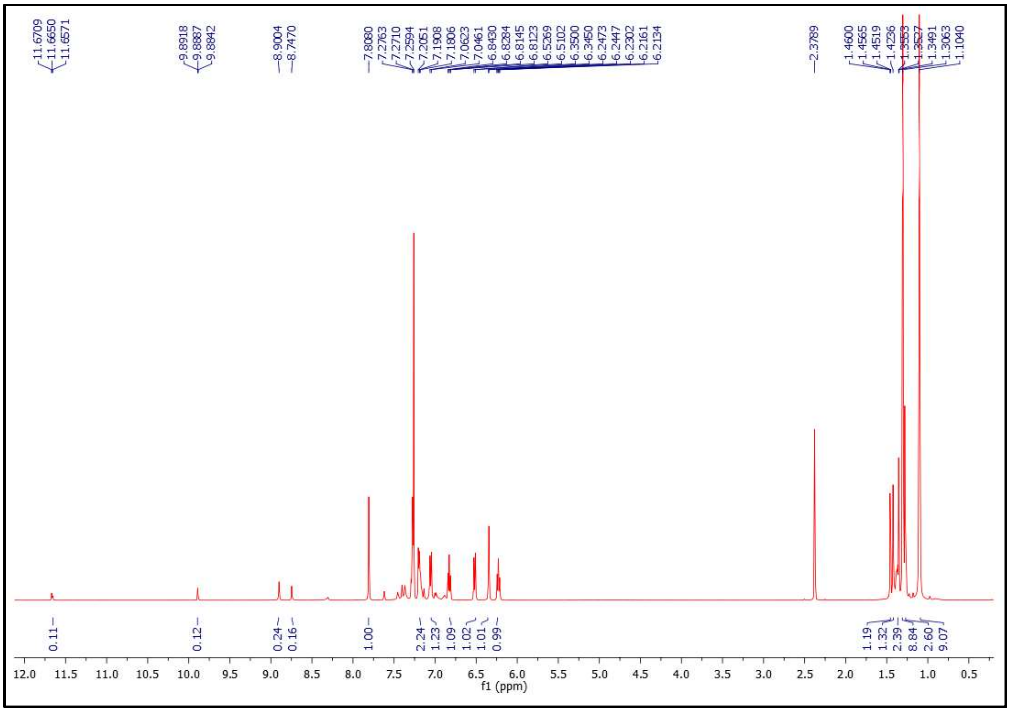


Figure S23 ^{1}H NMR spectrum of **1** (1 equiv.) and TNP (1 equiv.) in $CDCl_3$ at room temperature (500 MHz).

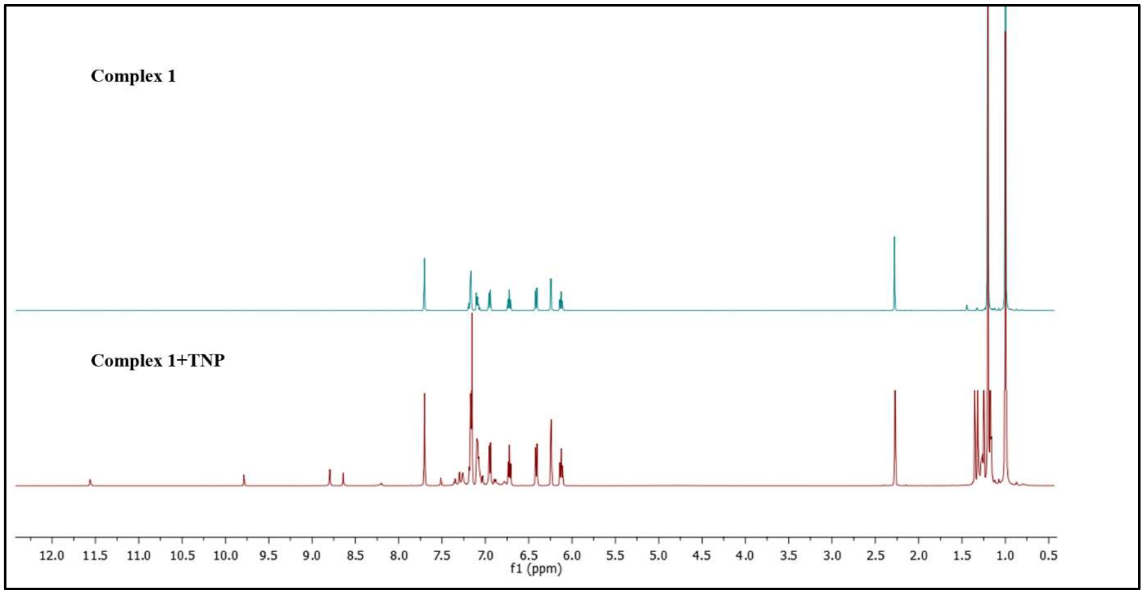


Figure S24 ^{1}H NMR of a mixture of **1** (1 equiv.) and TNP (1 equiv.) in $CDCl_3$ at room temperature (500 MHz)

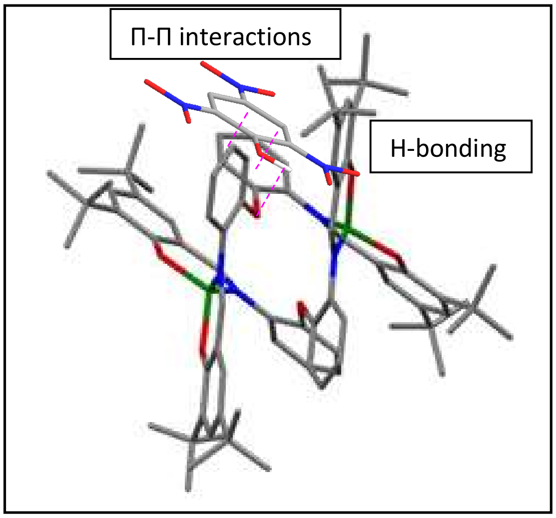


Figure S25 Interactions involved in the formation of ground-state charge-transfer complex of **1** with TNP.

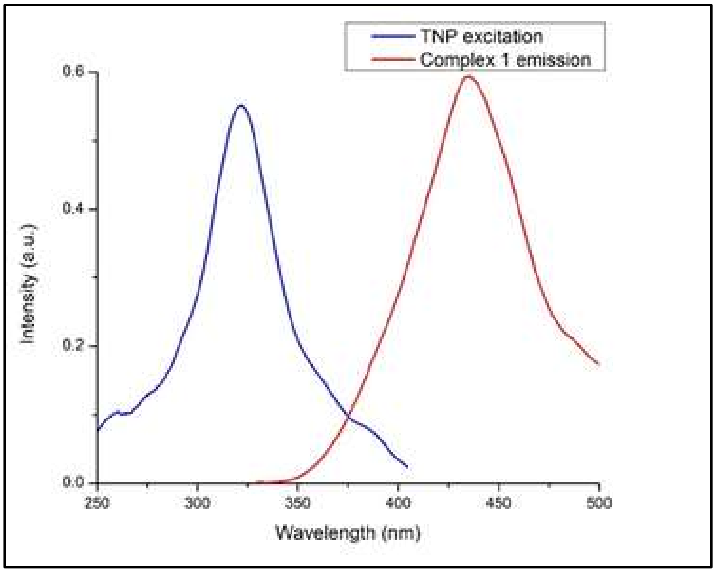


Figure S26 Spectral overlap between absorption and emission spectrum of TNP and **1** respectively.

References

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3 M. Karmakar, S. Roy and S. Chattopadhyay, *New J. Chem*., 2019, **43**, 10093-10102.