Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Mesomorphic Properties, Polarized Photoluminescence and Computational Studies in Highly Luminescent Columnar Self-Assembled Room Temperature Metallomesogens based on Zn(II) Coordination Complexes

Massimo La Deda[1], Giuseppe Di Maio[1], Angela Candreva[1], Benoît Heinrich[2], Adelina-Antonia Andelescu[3], Evelyn Popa[3], Emilie Voirin[2], Valentin Badea[4], Mario Amati[5], Otilia Costişor[3], Bertrand Donnio[2]* and Elisabeta I. Szerb[3]*

[1]Department of Chemistry and Chemical Technologies, University of Calabria, 87036 Rende - CS (Italy)

[2]Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR7504, CNRS-Université de Strasbourg, 67034 Strasbourg (France)

[3]"Coriolan Drăgulescu" Institute of Chemistry, Romanian Academy, 24 Mihai Viteazu Bvd., 300223 Timisoara (Romania)

[4]Department of Applied Chemistry and Organic and Natural Compounds Engineering, Politehnica University Timisoara, Carol Telbisz 6, RO-300001 Timisoara, Romania

[5]Dipartimento di Scienze, Università degli Studi della Basilicata, Campus di Macchia Romana, 85100 Potenza, Italy

Corresponding authors: E-mail: eszerb@acad-icht.tm.edu.ro; bdonnio@ipcms.unistra.fr

9. Photophysical data for complexes **Zn_1-3**

10. Computational studies

1. Experimental section.

Materials and methods. All commercially available starting materials were used as received without further purification. Ligands 4-(4-methoxyphenyl)-2,6-di(pyridine-2-yl)pyridine (***tpy*_1**) [1,2], 4-(4-*N,N*-diethylbenzenamine)-2,6-di(pyridine-2-yl)pyridine (***tpy*_2**) [3], 4-(4-(3,4,5-tris(dodecyloxy)benzyloxy)phenyl)-2,6-di(pyridine-2-yl)pyridine (***tpy*_3**) [4] and the silver(I) salt of 3,4,5-tridodecyloxybenzoate [5] were obtained as previously reported. ^{1}H and ^{13}C NMR experiments were recorded on Bruker Avance III HD – 500 MHz spectrometer in $CDCl_3$ or DMSO-d_6, using tetramethylsilane (TMS) as internal standard. Elemental analyses (CHN) were performed with a Flash 2000 microanalyzer from ThermoFisher Scientific. MS experiments were performed on a hybrid electrospray quadrupole time-of-flight mass spectrometer MS (Synapt G2 HDMS, Waters, Manchester, U.K.) coupled to an automated chip-based nanoelectrospray device (Triversa Nanomate, Advion Biosciences, Ithaca, U.S.A.) operating in the positive ion mode. The MS analysis was performed on the Synapt G2 HDMS instrument with external calibration using the the singly charged ions produced by an ES-TOF tuning mix (G1969-85000, Agilent, U.S.A.). The nanoelectrospray device (Triversa Nanomate) was set at 1.5 kV on capillary and the pressure of the nebulizer gas was 0.55 psi. Optical textures of mesophases were observed with an Olympus BX53M polarizing microscope (POM) equipped with Linkam hot-stage. Images of the various phases were recorded using an Olympus UC90 camera. Transition temperatures and enthalpies were recorded using a Q1000 apparatus from TA Instruments, calibrated with indium. Three heating/cooling cycles were performed on each sample, with a heating and cooling rate of 5°C/min. Thermal Gravimetric Analysis (TGA) was carried out with a Q50 apparatus from TA Instruments, at a scanning rate of 5°C/min and with air as purge gas.

X-ray scattering: The SWAXS patterns were obtained with a transmission Guinier-like geometry. A linear focalized monochromatic Cu Kα1 beam (λ = 1.5405 Å) was obtained using a sealed-tube generator (600 W) equipped with a bent quartz monochromator. In all cases, samples were filled in home-made sealed cells of 1 mm path. The patterns were recorded with a curved

Inel CPS120 counter gas-filled detector linked to a data acquisition computer (periodicities up to 90 Å) and on image plates scanned by Amersham Typhoon IP with 25 μm resolution (periodicities up to 120 Å). The sample temperature was controlled within ±0.01 °C, and exposure times were varied from 2 to 6 h.

GIWAXS measurements were conducted at PLS-II 9A U-SAXS beamline of Pohang Accelerator Laboratory (PAL) in Korea. Sample was a thin film deposited by spin-coating on Si wafer substrate. The X-rays coming from the vacuum undulator (IVU) were monochromated using Si(111) double crystals and focused on the detector using K-B type mirrors. Patterns were recorded with a 2D CCD detector (Rayonix SX165). The sample-to-detector distance was about 222 mm for energy of 11.07 keV (1.120 Å).

Photophysical studies: Spectrofluorimetric grade solvents were used for the photophysical investigations in solution. A PerkinElmer Lambda 900 spectrophotometer was used to obtain the UV/vis absorption spectra; emission and excitation spectra were recorded on a Horiba Jobin Yvon Fluorolog 3 spectrofluorimeter, equipped with a Hamamatsu R-928 photomultiplier tube and excitation and emission automated Glan-Thompson polarizers.

The luminescence quantum yields of the samples **Zn_1** and **Zn_3** in solution were determined by the optical dilution method [6] using 9,10-diphenylanthracene in cyclohexane solution as a reference standard (Φ = 0.78 [7]). The samples for solid-state measurements were prepared by placing a given amount of powder between two quartz slides and standardizing the layer. The emission quantum yields of the solid samples and **Zn_2** in solution were obtained by means of a 102 mm diameter integrating sphere coated with Spectralon® and mounted in the optical path of the spectrofluorimeter using, as the excitation source, a 450 W xenon lamp coupled with a double-grating monochromator for selecting wavelengths. The procedure for the measure of quantum yields with integrating sphere was based on De Mello method [8]. Time-resolved measurements were obtained by using the time-correlated single-photon counting (TCSPC) on the Fluorolog-3 apparatus. NanoLEDs pulse centred at 379 nm and 265 nm (FWHM 750 ps with 1 MHz repetition rate) were used as the excitation source and fixed directly on the sample chamber at 90° to a single-grating emission monochromator (2.1 nm mm^{-1} dispersion; 1200 grooves per mm). Data analysis was performed using the commercially available DAS6 software (Horiba Jobin Yvon IBH). The quality of the fit was assessed by minimizing the reduced χ^2 function and visual inspection of the weighted residuals.

Polarized emission

Thin film preparation: The thin film samples for GIWAXS and photophysical studies were deposited by dynamical spin-coating (WS-650Mz-23NPPB from Laurell Technologies Corporation) at a speed of 4000 RPM, on top of piranha solution etched silicon wafers and fused silica slides, respectively. Concentrations of **Zn_2** solutions were of 10 mg/ml for GIWAXS and 50 mg/ml for photophysical studies.

Measurements: The setup has been carefully prepared so that the plane of the support on which the film is homeotropically deposited and the plane of the emission polarizer are parallel. The dichroic ratio $I_{//}/I_{\perp}$ of **Zn_2** film was determined spectroscopically measuring the emission intensity at 550 nm (unpolarized excitation light at λ_{ex} = 440 nm) and varying the emission polarizer angle between 0° and 180° with an increment of 10 degrees. The angle α to which corresponds the maximum emission intensity value corresponds to angle at which electronic transition moment is parallel to the emission polarizer. Therefore, the parallel emission spectrum ($I_{//}$) was registered setting the polarizer at α angle, the perpendicular emission spectrum ($I_{\perp}$) was registered setting the excitation polarizer angle at α + 90°.

2. Synthesis and Characterization.

General synthesis for the Zn(II) precursors, Zn_P1-3: The complexes were obtained as previously reported for analogues derivatives [9]. In particular, a solution of $ZnCl_2$ (0.136 g, 1.00 mmol) in 50 mL of MeOH was added dropwise to a solution of ligand (0.833 mmol) in 50 mL $CHCl_3$. The reaction mixture was stirred for 1.5 h at r. t. The precipitate formed was filtered out, washed with MeOH and dried under vacuum.

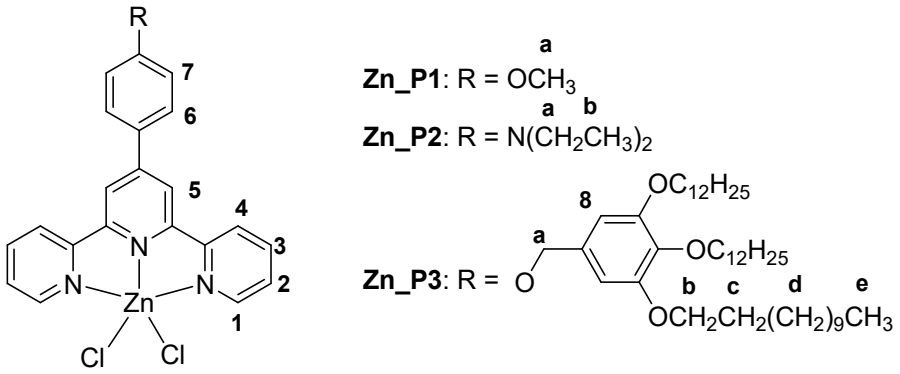

Figure SI-1. Chemical structure and related NMR numbering scheme of Zn(II) precursors **Zn_P1-3**.

Zn_P1: White solid (0.370 g, 90 %). Anal. Calcd. for $C_{22}H_{17}Cl_2N_3OZn \cdot 1.0\ H_2O$ (493.70 g·mol^{-1}): C, 53.52; H, 3.88; N, 8.51%. Found: C, 53.54; H, 3.72; N, 8.30%. IR (KBr, cm^{-1}): 3067, 3002 ($\nu_{\text{aromatic C-H}}$), 2937, 2845 ($\nu_{\text{methyl C-H}}$), 1250 ($\nu_{\text{as (C-O-C)}}$), 1023 ($\nu_{\text{s (C-O-C)}}$); ^{1}H-NMR (500 MHz, DMSO-d_6, δ/ppm): 8.86 (overlapped peaks, 6H, H^{1,4,5}), 8.25 (overlapped peaks, 4H, H^{3,6}), 7.83 (m, 2H, H^2), 7.12 (d, 2H, ^3J = 8.5 Hz, H^7), 3.87 (s, 3H, H^a). TGA: $T_{5\%}$ = 358^{o}C.

Zn_P2: Yellow solid (0.408 g, 88%). Anal. Calcd. for $C_{25}H_{24}Cl_2N_4Zn \cdot 0.5\ H_2O$ (525.78 g·mol^{-1}): C, 57.11; H, 4.79; N, 10.66. Found: C, 57.25; H, 4.50; N, 10.81%. IR (KBr, cm^{-1}): 3060 ($\nu_{\text{aromatic C-H}}$), 2970 ($\nu_{\text{methyl C-H}}$), 1250 ($\nu_{\text{as (C-O-C)}}$), 1068 ($\nu_{\text{s (C-O-C)}}$); ^{1}H-NMR (DMSO-$d_6$, δ/ppm): 8.89 (overlapped peaks, 6H, H^{1,4,5}), 8.32 (m, 4H, H^{3,6}), 8.20 (m, 2H, H^2), 6.87 (m, 2H, H^7), 1.20 (m, 6H, H^b). TGA: $T_{5\%}$ = 364^{o}C.

Zn_P3: Yellow solid (0.878 g, 90%). Anal. Calcd. for $C_{64}H_{93}Cl_2N_3O_4Zn$ (1104.74 g·mol^{-1}): C, 69.58; H, 8.49; N, 3.80. Found: C, 69.60; H, 8.44; N, 3.96%. IR (KBr, cm^{-1}): 2924 ($\nu_{\text{as,(-CH2-)}}$), 2854 ($\nu_{\text{s,(-CH2-)}}$), 1238 ($\nu_{\text{as (C-O-C)}}$), 1115 ($\nu_{\text{s (C-O-C)}}$); ^{1}H-NMR (DMSO-d_6, δ/ppm): 9.01 (dd, 2H, ^3J = 5.0 Hz, ^4J = 1.6 Hz, H^1), 8.06 (s, 2H, H^5), 8.01 (d, 2H, ^3J = 8.0 Hz, H^4), 7.71 (overlapped peaks, 4H, H^{3,6}), 7.45 (m, 2H, H^2), 6.91 (d, 2H, ^3J = 8.7 Hz, H^7), 6.68 (s, 2H, H^8), 4.98 (s, 2H, H^a), 4.03 (m, 6H, H^b), 1.83 (m, 6H, H^c), 1.29 (m, 54H, H^d), 0.89 (t, 9 H, ^3J = 6.5 Hz, H^e). TGA: $T_{5\%}$ = 288^{o}C.

General synthesis for the Zn(II) complexes, Zn_1-3: The complexes were obtained as previously reported for analogues derivatives[10]. In particular, to a suspension of the Zn(II) precursors **Zn_P1-3** (0.100 mmol) in 50 mL $CHCl_3$, a solution of the silver(I) salt of 3,4,5-tridodecyloxybenzoate (0.200 mmol) was added and the reaction mixture was stirred at room temperature for 2h. The AgCl precipitate formed is removed by filtration, the solvents were

evaporated and acetone was added. The unwanted precipitate formed was filtrated out, and the pure product was obtained from the mother solution by recrystallization from $CHCl_3$/MeOH.

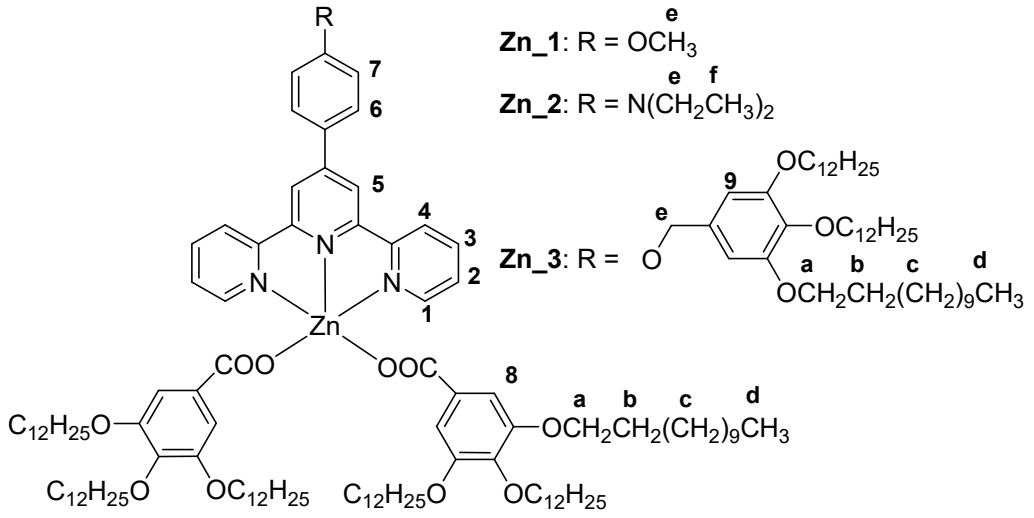

Figure SI-2. Chemical structure and related NMR numbering scheme of Zn(II) complexes **Zn_1-3**.

Zn_1: White solid (0.135 g, 75 %). Anal. Calcd. for $C_{108}H_{171}N_3O_{11}Zn$ (1752.92 g·mol^{-1}): C, 74.00; H, 9.83; N, 2.40%. Found: C, 73.92; H, 9.74; N, 2.59%. MS (*m*/*z*) = 1753.23. IR (KBr, cm^{-1}): 2923 ($\nu_{as,(-CH2-)}$), 2853 ($\nu_{s,(-CH2-)}$), 1616 ($\nu_{as\ COO}$-), 1359 ($\nu_{s\ COO}$-): Δ = 257 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$); δ/ppm: 8.98 (dd, 2H, ^3J = 5.0 Hz, ^4J = 1.7 Hz, H^1), 8.29 (s, 2H, H^5), 8.17 (d, 2H, ^3J = 8.0 Hz, H^4), 7.84 (td, 2H, ^3J = 7.8 Hz, 4H = 1.7 Hz, H^3), 7.73 (d, 2H, ^3J = 8.8 Hz, H^6), 7.47 (m, 2H, H^2), 7.32 (s, 4H, H^8), 6.95 (d, 2H, ^3J = 8.9 Hz, H^7), 3.93 (overlapped peaks, 12H, H^a), 3.87 (s, 3H, H^e), 1.75 (m, 12H, H^b), 1.42 – 1.26 (overlapped peaks, 108H, H^c), 0.89 (t, 18H, ^3J = 6.9 Hz, H^d). ^{13}C NMR (500 MHz, $CDCl_3$): 172.4, 161.5, 152.3, 149.2, 149.0, 148.3, 140.3, 138.9, 131.3, 128.7, 128.2, 126.0, 121.4, 118.5, 114.7, 108.5, 73.3, 69.1, 55.4, 31.9, 30.4, 29.8, 29.7, 29.7, 29.6, 29.5, 29.5, 29.4, 29.4, 26.2, 26.1, 22.7, 14.1.

Zn_2: Yellow solid (0.129 g, 72 %). Anal. Calcd. for $C_{111}H_{178}N_4O_{10}Zn$ (1794.01 g·mol^{-1}): C, 74.31; H, 10.00; N, 3.12%. Found: C, 74.14; H, 10.07; N, 3.02%. MS (*m*/*z*) = 1794.29. IR (KBr, cm^{-1}): 2922 ($\nu_{as,(-CH2-)}$), 2853 ($\nu_{s,(-CH2-)}$), 1615 ($\nu_{as\ COO}$-), 1216 ($\nu_{s\ COO}$-): Δ = 316 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$); δ/ppm: 8.97 (d, 2H, ^3J = 4.9 Hz, H^1), 8.26 (s, 2H, H^5), 8.14 (d, 2H, ^3J = 8.1 Hz, H^4), 7.76 (t, ^3J = 7.0 Hz, 2H, H^3), 7.67 (d, 2H, ^3J = 8.6 Hz, H^6), 7.40 (t, ^3J = 6.1 Hz, 2H, H^2), 7.32 (s, 4H, H^8), 6.63 (dd, 2H, ^3J = 9.0 Hz, ^4J = 5.4 Hz, H^7), 3.93 (q, 12H, ^3J = 6.3 Hz, H^a), 3.41

(q, 6H, ^{3}J = 7.1 Hz, H^{f}), 1.72 (m, 12H, H^{b}), 1.42 – 1.26 (overlapped peaks, 108H, H^{c}), 0.87 (t, ^{3}J = 6.9 Hz, 18H, H^{d}). ^{13}C NMR (500 MHz, $CDCl_3$): 172.3, 152.3, 149.4, 149.3, 148.8, 148.7, 140.2, 138.8, 131.4, 128.5, 125.9, 122.1, 121.1, 117.5, 111.7, 108.4, 73.3, 69.0, 44.5, 32.0, 30.4, 29.8, 29.7, 29.7, 29.5, 29.4, 29.4, 26.2, 22.7, 14.2, 12.7.

Zn_3: White solid (0.179 g, 75 %). Anal. Calcd. for $C_{150}H_{247}N_3O_{14}Zn$ (2382.01 g·mol^{-1}): C, 75.64; H, 10.45; N, 1.76%. Found: C, 75.84; H, 10.44; N, 2.06%. MS (*m*/*z*) = 2381.81. IR (KBr, cm^{-1}): 2922 ($\nu_{as,(-CH2-)}$), 2853 ($\nu_{s,(-CH2-)}$), 1616 ($\nu_{as\ COO-}$), 1371 ($\nu_{s\ COO-}$): Δ = 245 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$); δ/ppm: 9.01 (dd, 2H, ^{3}J = 5.0 Hz, ^{4}J = 1.7 Hz, H^{1}), 8.33 (s, 2H, H^{5}), 8.24 (d, 2H, ^{3}J = 8.1 Hz, H^{4}), 7.92 (td, 2H, ^{3}J = 7.8 Hz, ^{4}J = 1.8 Hz, H^{3}), 7.71 (m, 2H, H^{6}), 7.50 (m, 2H, H^{2}), 7.31 (s, 4H, H^{10}), 7.11 (d, 2H, ^{3}J = 8.8 Hz, H^{7}), 6.68 (s, 2H, H^{8}), 5.03 (s, 2H, H^{9}), 3.97 (overlapped peaks, 18H, H^{a}), 1.79 (m, 18H, H^{b}), 1.40 – 1.20 (overlapped peaks, 162H, H^{c}), 0.89 (m, 27H, H^{d}). ^{13}C NMR (500 MHz, $CDCl_3$): 160.8, 153.5, 152.3, 149.5, 149.2, 148.3, 140.4, 139.1, 138.4, 131.1, 128.8, 126.3, 121.2, 119.0, 115.8, 108.5, 106.3, 73.5, 73.3, 70.7, 69.3, 69.1, 32.0, 30.4, 30.4, 29.8, 29.7, 29.7, 29.5, 29.4, 29.4, 26.2, 26.2, 22.7, 14.1.

3. FT-IR spectra of complexes Zn P1-3 and Zn_1-3.

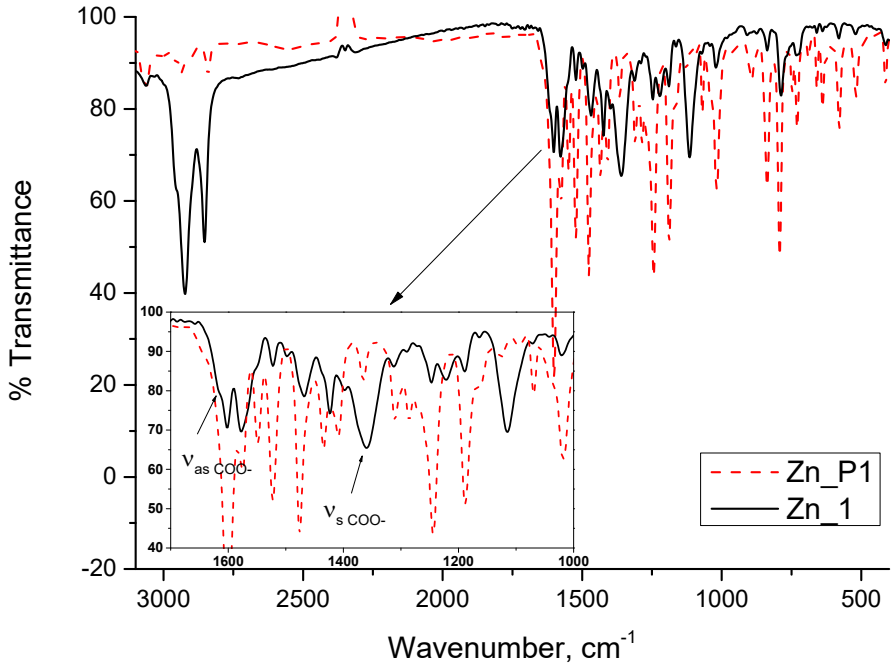

Figure SI-3. FT-IR spectra of complexes **Zn_P1** and **Zn_1**.

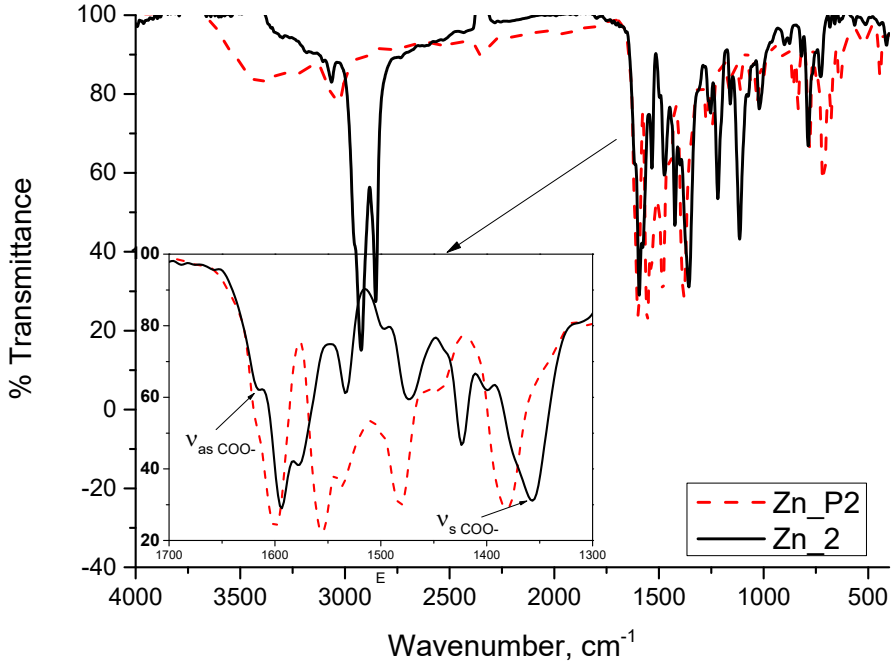

Figure SI-4. FT-IR spectra of complexes **Zn_P2** and **Zn_2**.

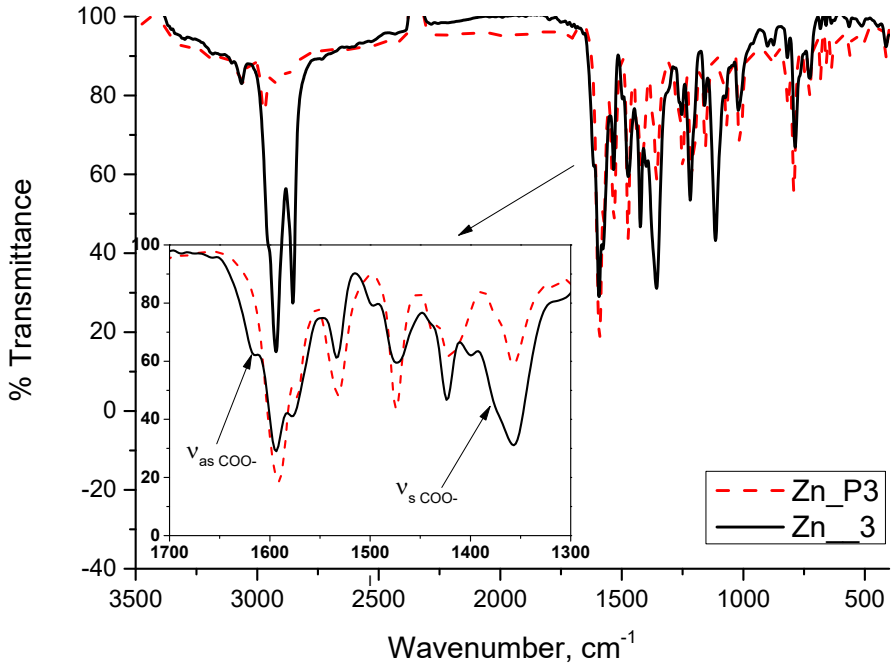

Figure SI-5. FT-IR spectra of complexes **Zn_P3** and **Zn_3**.

4. ^{1}H and ^{13}C NMR spectra of complexes Zn_1-3

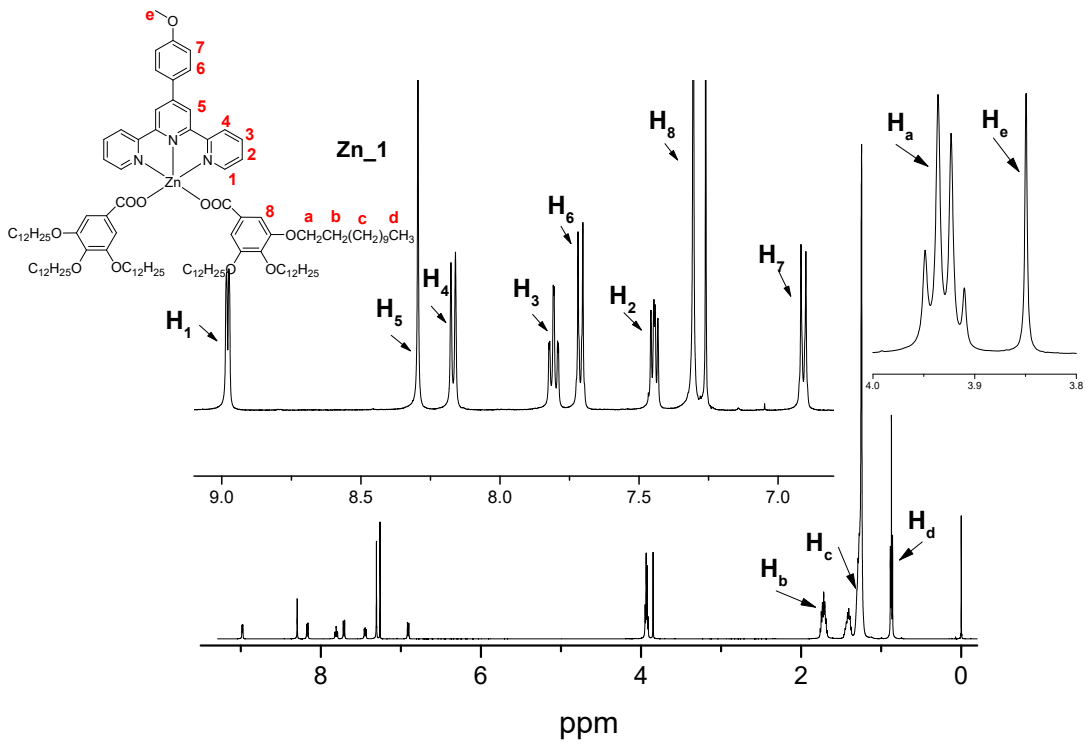

Figure SI-6. ^{1}H NMR spectra for complex **Zn_1**.

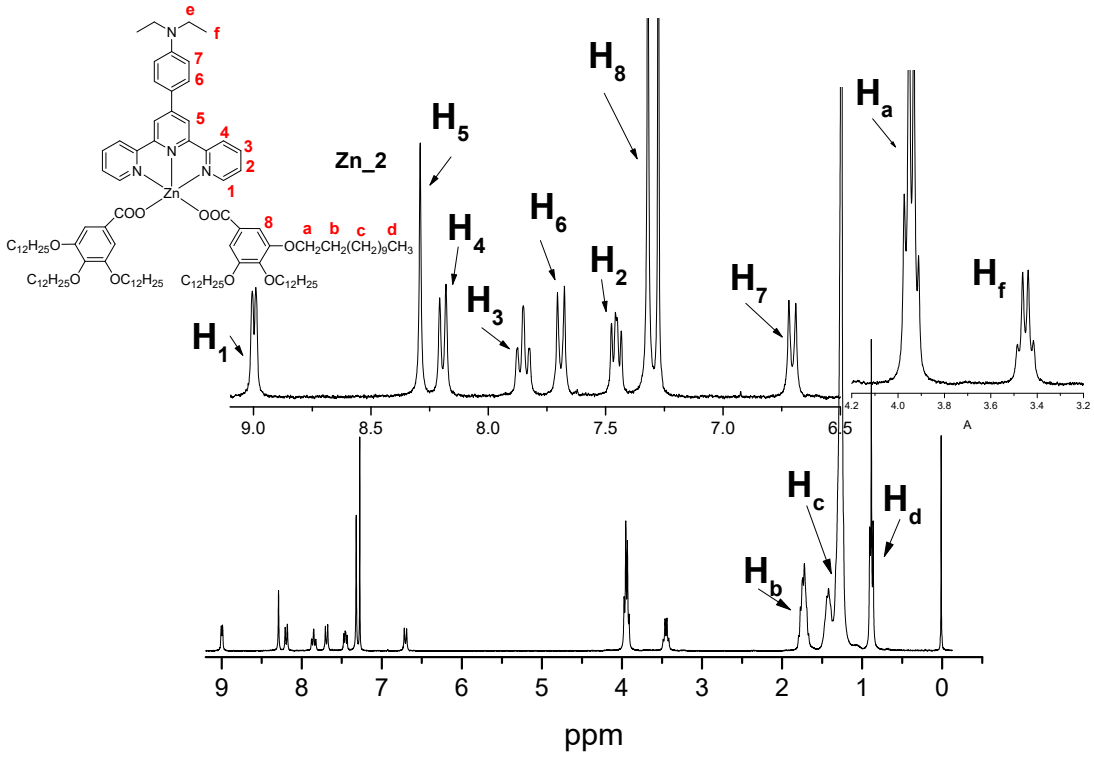

Figure SI-7. ^{1}H NMR spectra for complex **Zn_2**.

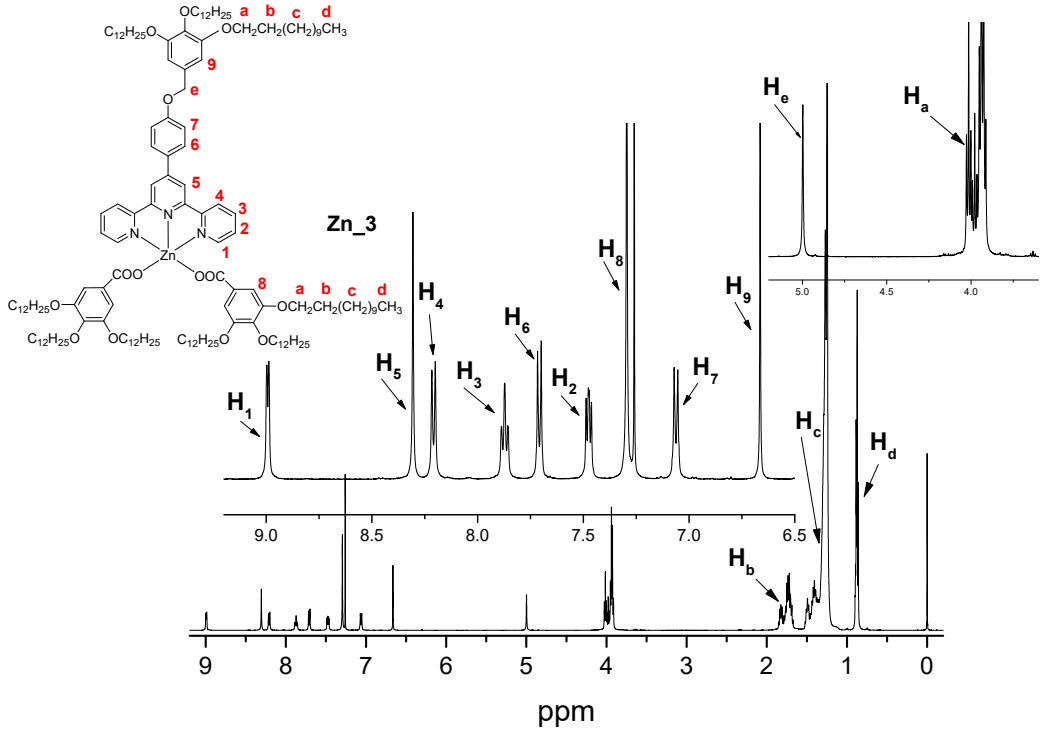

Figure SI-8. ^{1}H NMR spectra for complex **Zn_3**.

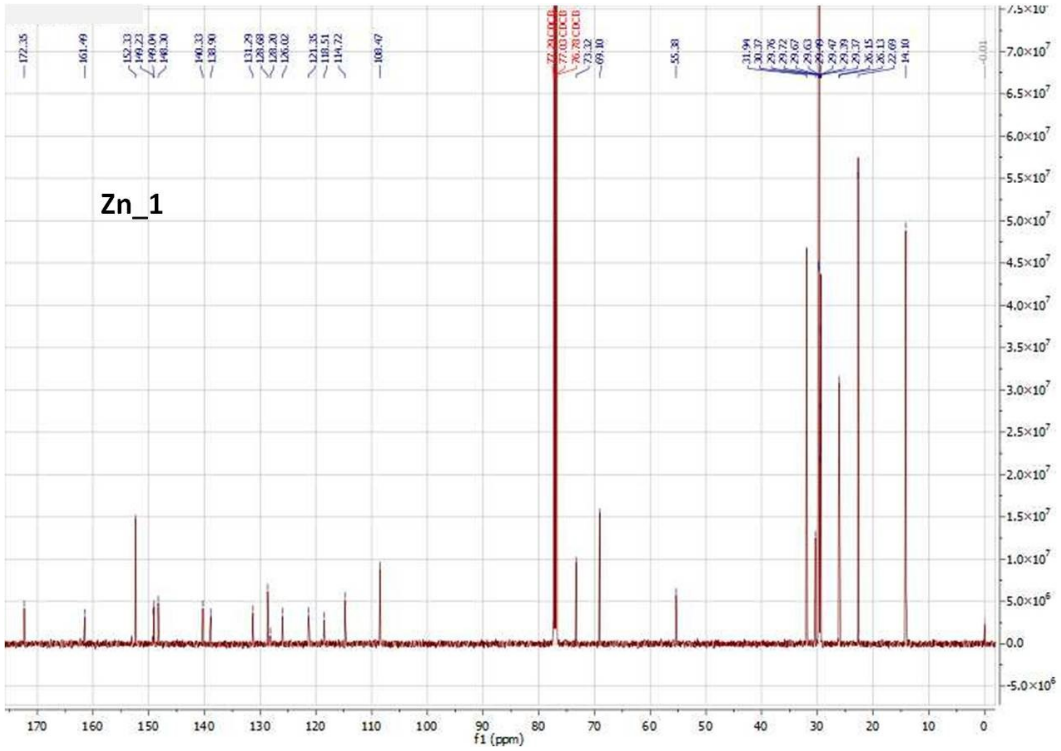

Figure SI-9. ^{13}C NMR spectra for complex **Zn_1**.

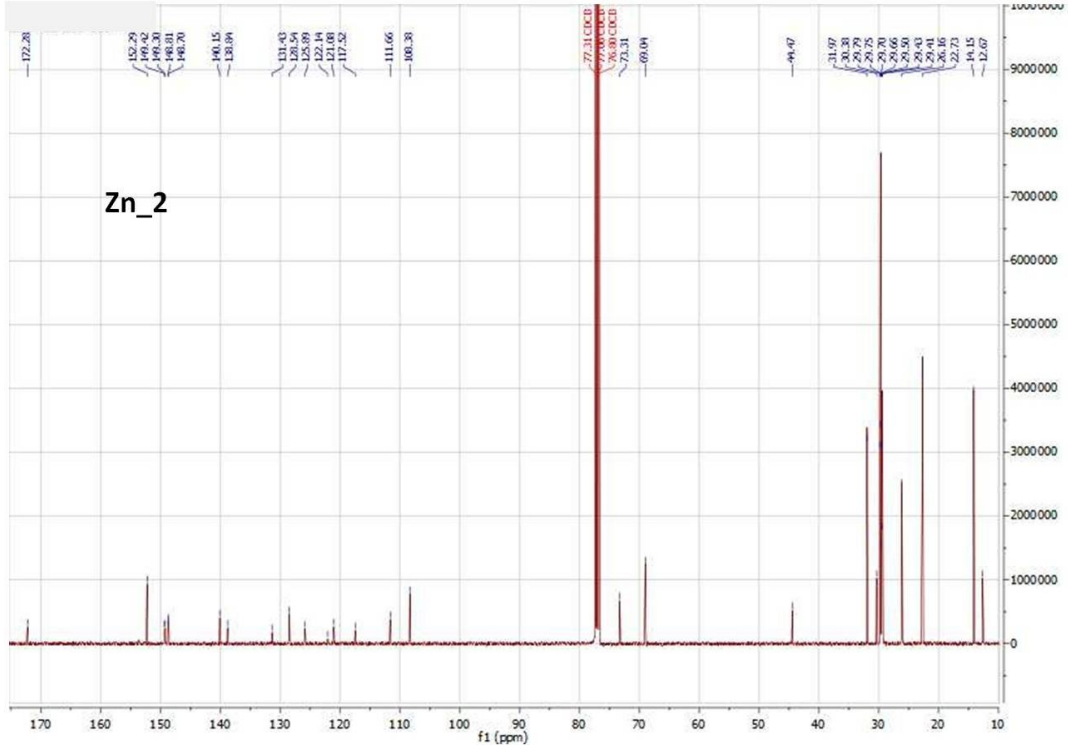

Figure SI-10. ^{13}C NMR spectra for complex **Zn_2**.

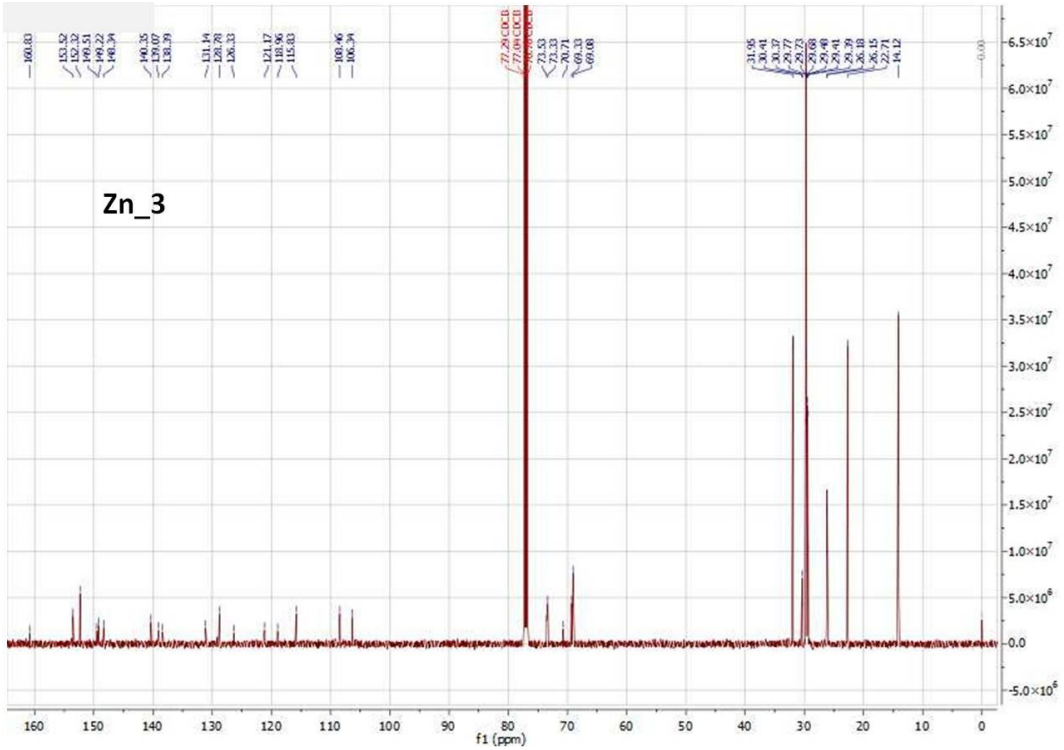

Figure SI-11. ^{13}C NMR spectra for complex **Zn_3**.

5. Mass Spectra of complexes Zn_1-3

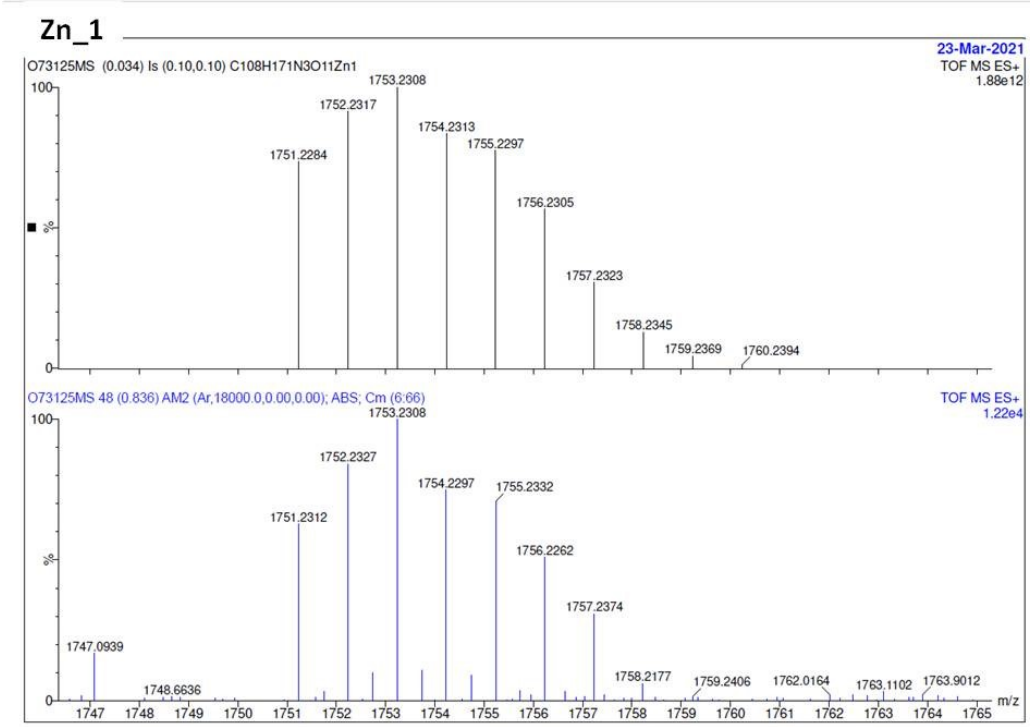

Figure SI_12. Simulation vs. measured MS for **Zn_1**.

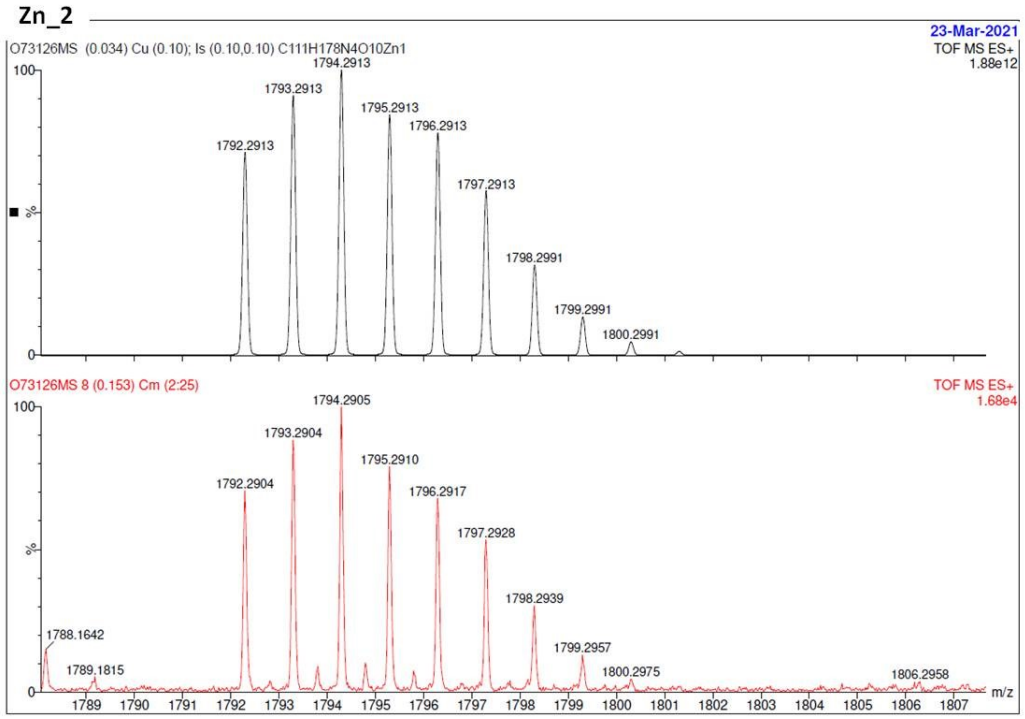

Figure SI_13. Simulation vs. measured MS for **Zn_2**.

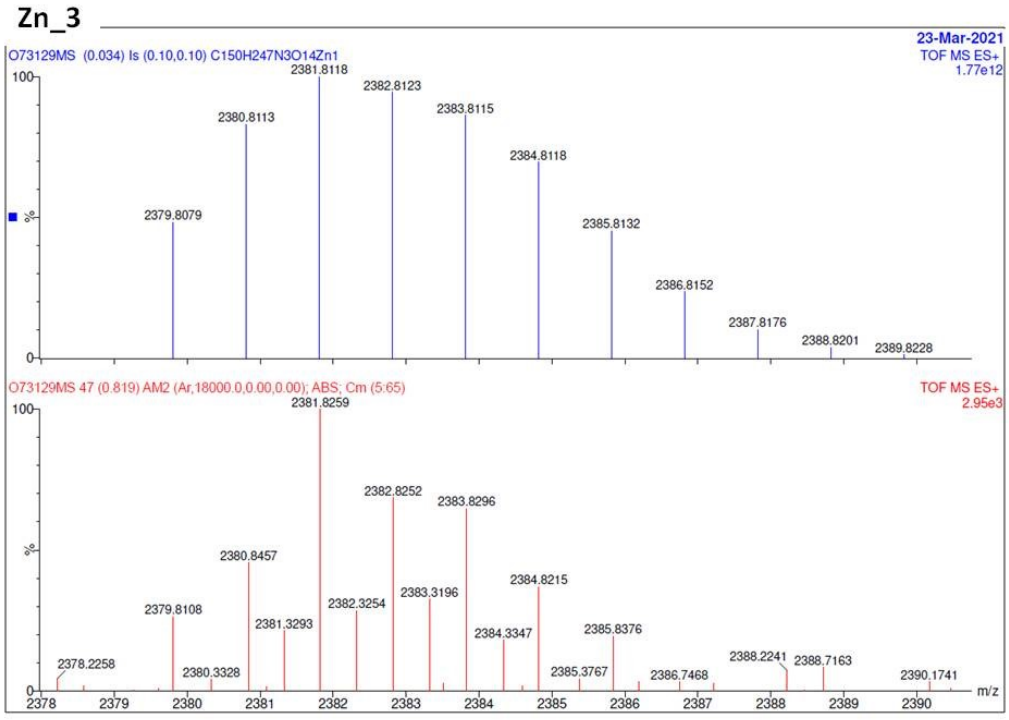

Figure SI_14. Simulation vs. measured MS for **Zn_3**.

6. TGA traces of precursor complexes Zn_P1-3 and complexes Zn_1-3

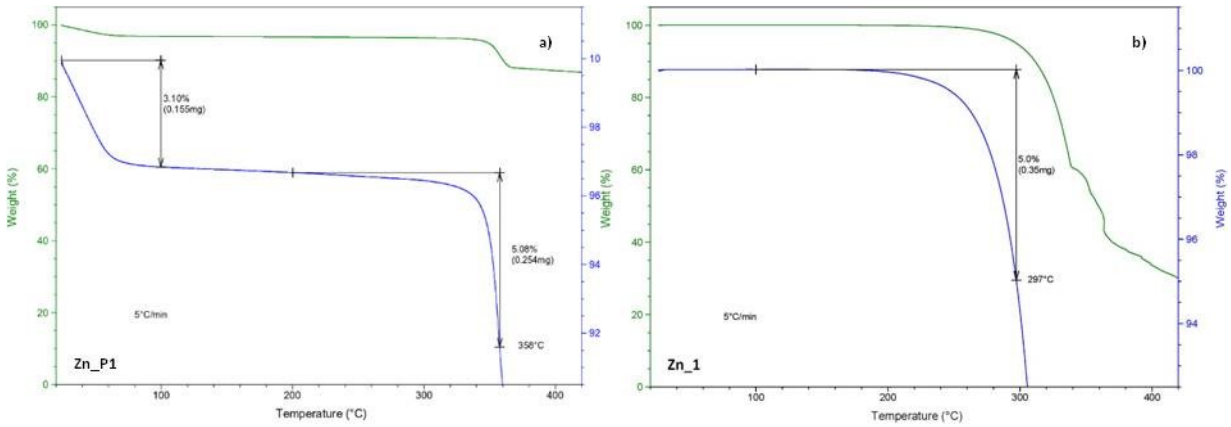

Figure SI_15. TGA trace for a) **Zn_P1**: initial weight loss from adsorbed water below 100°C; weight loss from degradation above ca. 320°C, 5% weight loss temperature at 5°C/min: $T_{5\%}$ = 358°C and b) **Zn_1**: weight loss from degradation becomes significant above ca. 230°C. The 5% weight loss temperatures at 5°C/min are $T_{5\%}$ = 295°C.

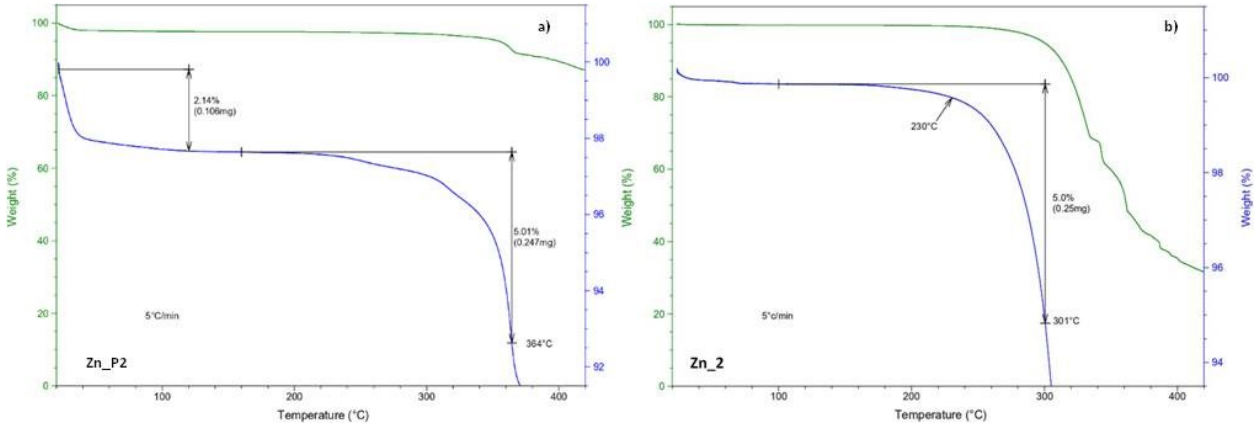

Figure SI_16. TGA trace for a) **Zn_P2**: initial weight loss from adsorbed water below 100°C; weight loss from degradation above 250°C, 5% weight loss temperature at 5°C/min: $T_{5\%}$ = 364°C; b) complex **Zn_2**: weight loss from degradation becomes significant above ca. 230°C. The 5% weight loss temperatures at 5°C/min are $T_{5\%}$ = 300°C.

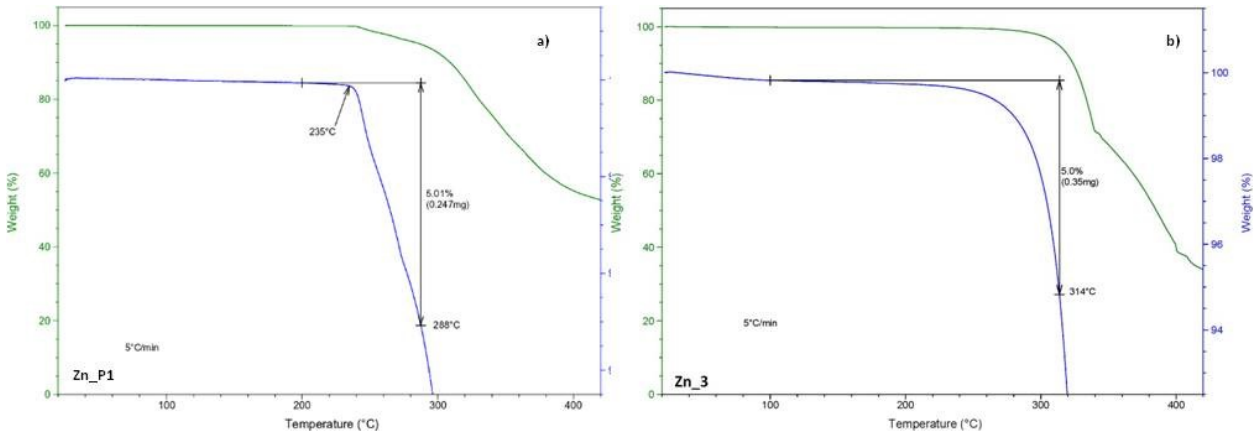

Figure SI_17. TGA trace for a) **Zn_P3**: weight loss from degradation above 235°C. 5% weight loss temperature at 5°C/min: $T_{5\%}$ = 288°C; b) **Zn_3**: weight loss from degradation becomes significant above ca. 260°C; the 5% weight loss temperatures at 5°C/min are $T_{5\%}$ = 315°C.

7. DSC traces of complexes Zn_1-3

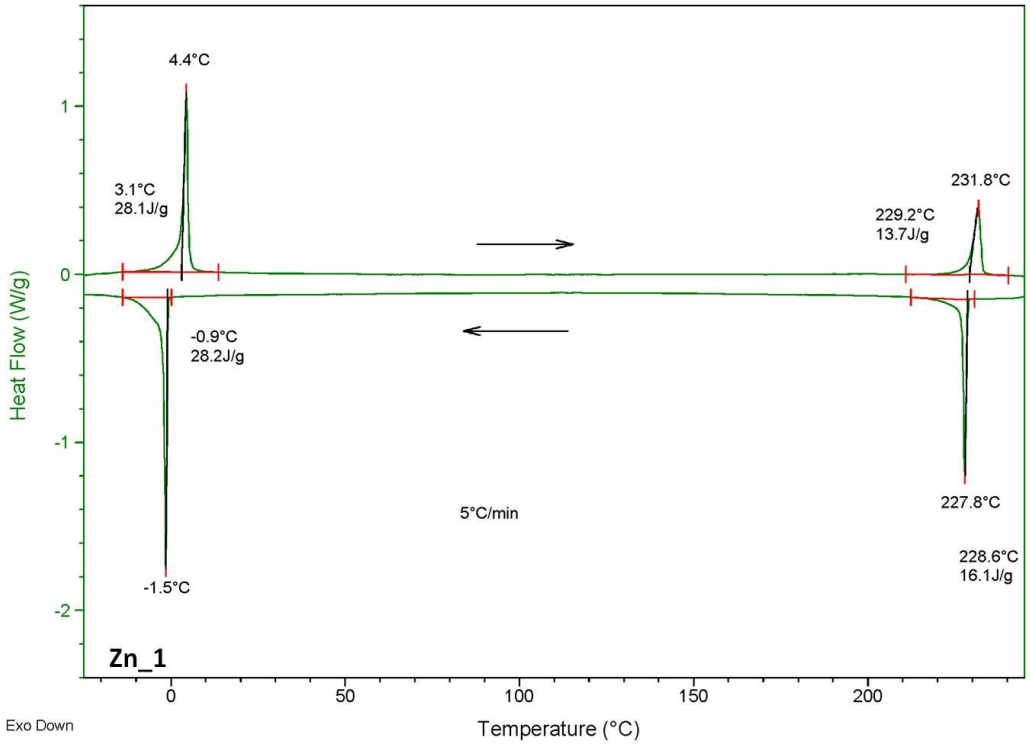

Figure SI_18. DSC trace for complex **Zn_1**, second cycle.

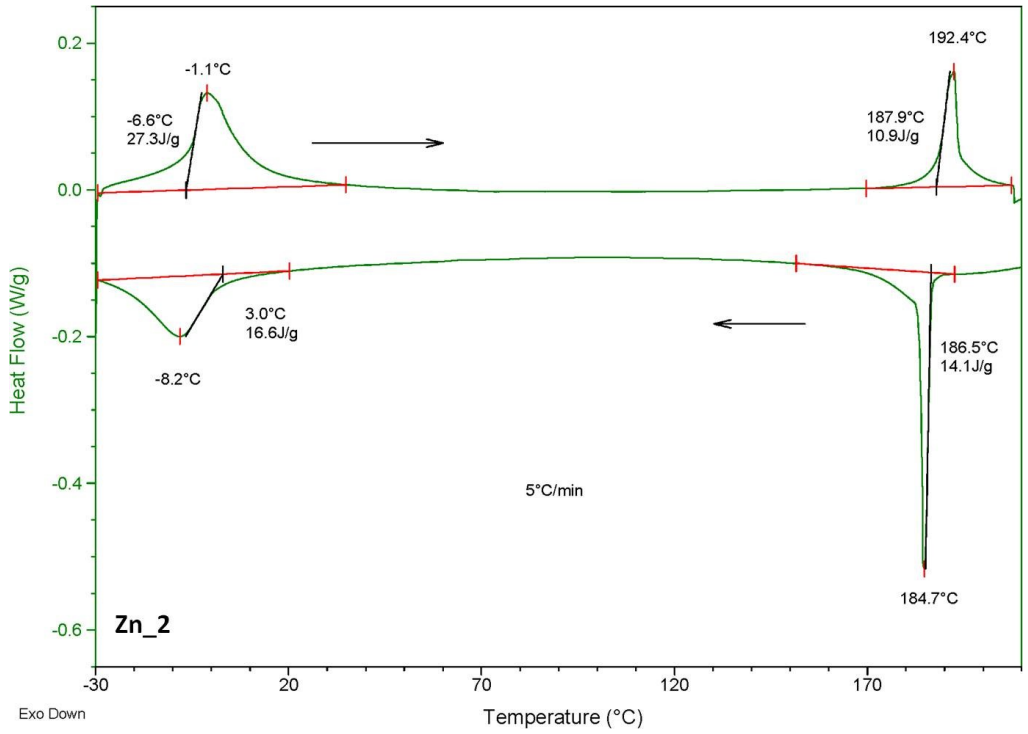

Figure SI_19. DSC trace for complex **Zn_2**, second cycle.

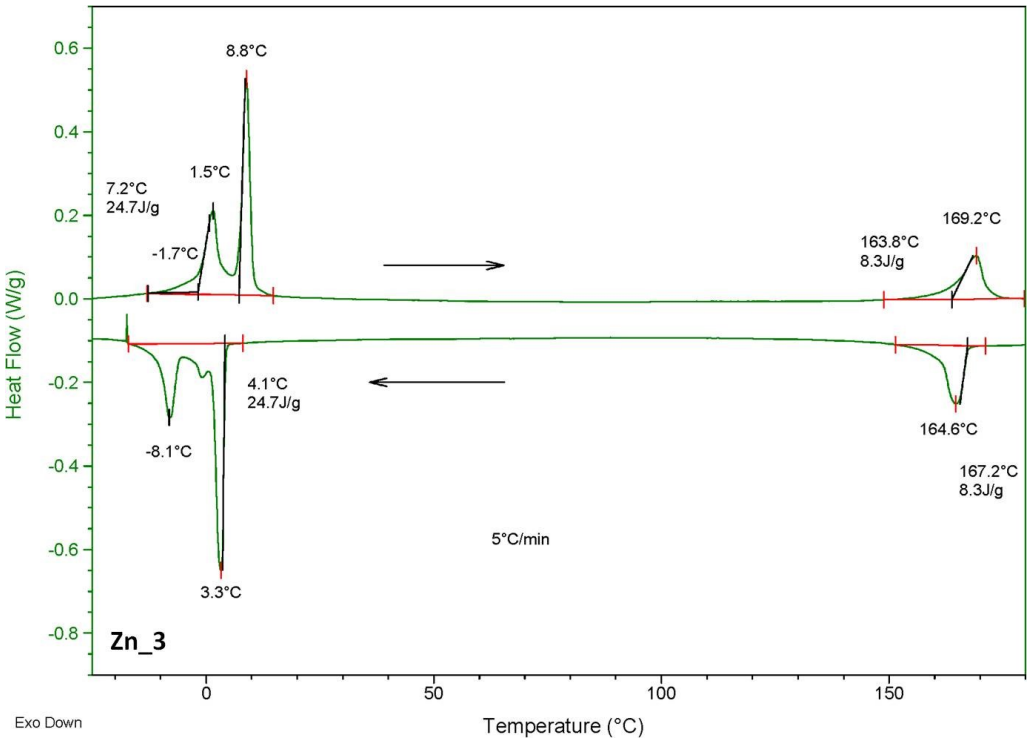

Figure SI_20. DSC trace for complex **Zn_3**, second cycle.

8. S/WAXS patterns of complexes Zn_1-3

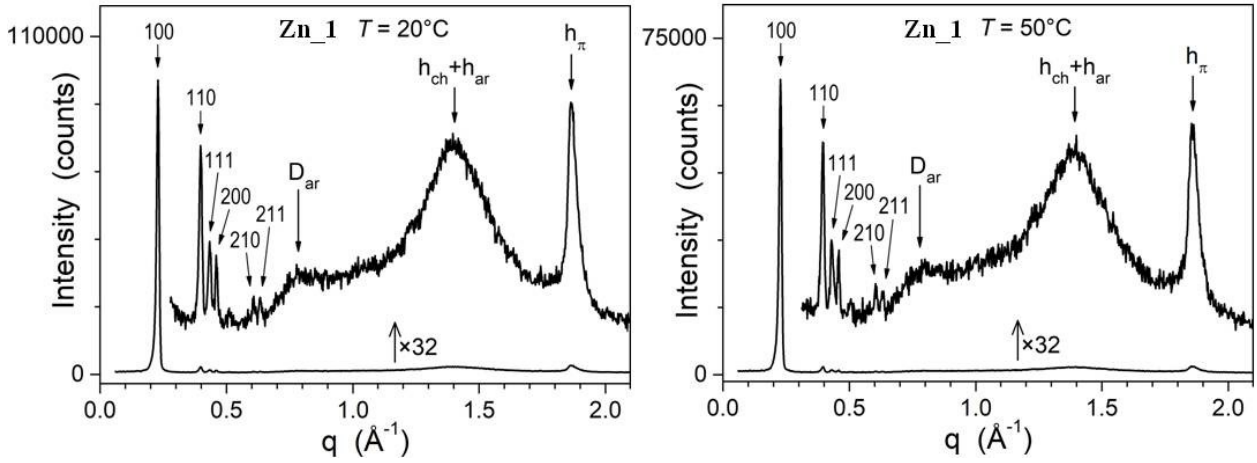

Figure SI_21. S/WAXS patterns of the **Zn_1** complex at: room temperature in the pasty state of the M_{hex} mesophase (left) showing the same structure as in the higher temperature fluid state (right).

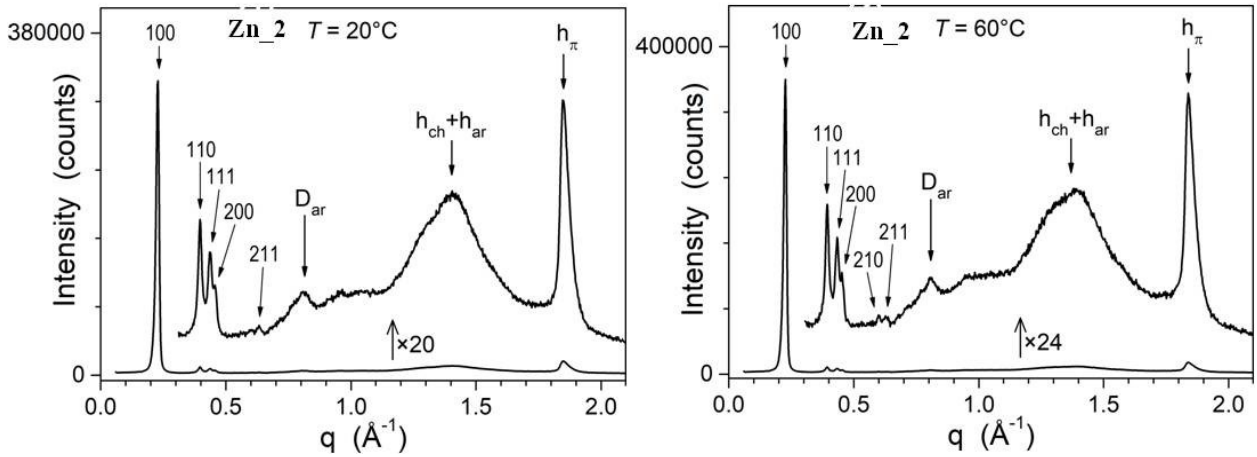

Figure SI_22. SWAXS patterns of the **Zn_2** complex at: room temperature in the pasty state of the M_{hex} mesophase (left) showing the same structure as in the higher temperature fluid state (right).

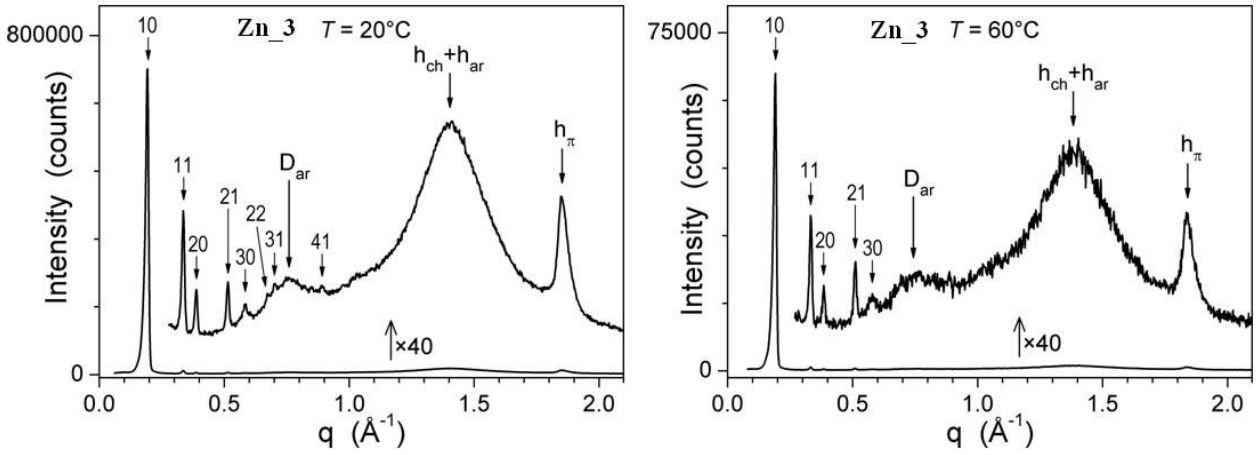

Figure SI_23. SWAXS patterns of the **Zn_3** complex at: room temperature in the pasty state of the M_{hex} mesophase (left) showing the same structure as in the higher temperature fluid state (right).

9. Photophysical data for complexes Zn_1-3

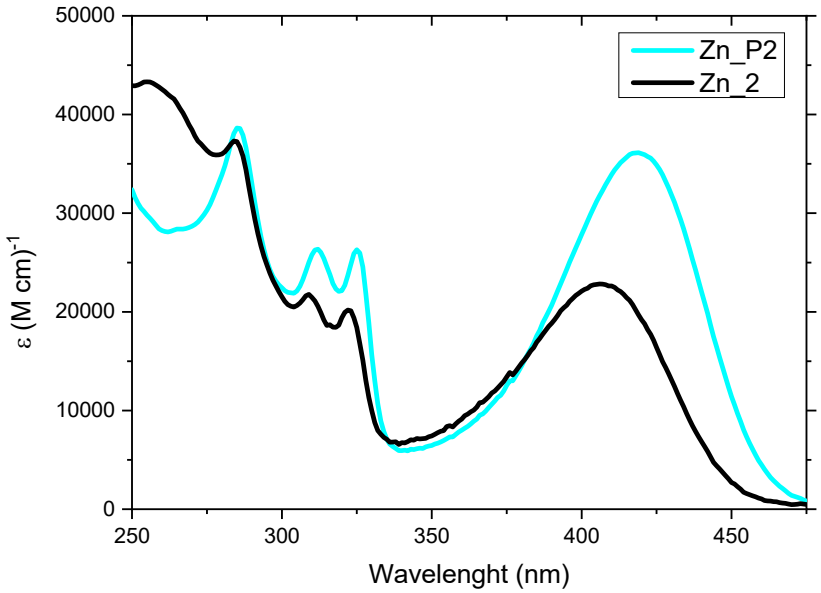

Figure SI_24. Absorption spectra of **Zn_2** (black line) and its chlorinated precursor **Zn_P2** (cyan line) in CH_2Cl_2 solution.

Table SI_1. Emission maximum and quantum yields for **Zn_1** by varying the temperature (λ_{ex}= 340 nm)

Heating		
T /°C	λem/nm	ϕ (%)
30	**435**	**4**
80	**435**	**2.9**
150	**435**	**1.7**
180	**435**	**1.35**

Table SI_2. Emission maximum and quantum yields for **Zn_2** by varying the temperature (λ_{ex}= *430 nm)*

Heating			Cooling		
T/°C	λem/nm	ϕ (%)	T /°C	λem/nm	ϕ (%)
100	**544**	**14.7**	100	**544**	**14.4**
150	**546**	**11.3**	30	**542**	**20.2**

Table SI_3. Emission maximum and quantum yields for **Zn_3** by varying the temperature (λ_{ex}= 350 nm)

Heating			Cooling		
T/°C	λem/nm	ϕ (%)	T /°C	λem/nm	ϕ (%)
30	**435**	**2.3**	150	**435**	**0.4**
80	**435**	**1.2**	80	**436**	**1.1**
150	**435**	**0.3**	30	**434**	**1.5**
180	**435**	**0.07**			

10. Computational studies

Table SI_4. Computed Cartesian coordinates of **Zn_1** model (angstrom) computed in vacuum and CH_2Cl_2 and **Zn_2** model computed in vacuum, *n*-hexane and CH_2Cl_2.

Zn_1 model in vacuum

N	-1.561993	-0.017783	0.038118
C	-2.237708	-0.039792	-1.110655
C	-3.627965	-0.095998	-1.125013
C	-4.334361	-0.126737	0.080721
C	-3.591084	-0.100974	1.264192
C	-2.201745	-0.047993	1.207136
C	-1.399038	-0.019902	-2.342855
H	-4.167059	-0.147102	-2.059137
C	-5.811695	-0.188999	0.103852
H	-4.103318	-0.096662	2.214708
C	-1.326049	-0.011066	2.412936
N	-0.010931	0.066525	2.166758
C	0.852364	0.105242	3.178632
C	0.446488	0.067397	4.507197
C	-0.913529	-0.014775	4.775866
C	-1.813128	-0.054348	3.719193
H	1.899362	0.167241	2.906931
H	1.179716	0.099860	5.302101
H	-1.272996	-0.048793	5.796918
H	-2.873496	-0.119893	3.916437
C	-1.928161	-0.005690	-3.633315
C	-1.060917	0.010224	-4.717262
C	0.309235	0.012186	-4.491000
C	0.757630	-0.000982	-3.175691
N	-0.074719	-0.016744	-2.137666
H	-2.996186	-0.004733	-3.797214
H	-1.453188	0.022116	-5.726706
H	1.018091	0.025120	-5.308271
H	1.814373	0.002134	-2.936605
C	-6.489797	-0.960192	1.061591
C	-7.869969	-1.026957	1.083861
C	-8.625230	-0.311420	0.147392
C	-7.971241	0.465851	-0.810334
C	-6.580747	0.515253	-0.825203
H	-5.925982	-1.542483	1.780020
H	-8.388120	-1.636055	1.813505
O	-9.977476	-0.437420	0.252744
H	-8.527487	1.039592	-1.537570
H	-6.092880	1.143706	-1.560298
Zn	0.570129	0.032745	0.004838
O	1.745271	1.612434	-0.040455
O	1.775680	-1.525881	0.017194
C	1.149305	-2.655278	0.139753
C	1.090276	2.726990	-0.151098
O	-0.079788	-2.768720	0.238794
O	-0.143062	2.810951	-0.221064
C	2.026911	-3.885078	0.159554
C	1.939111	3.976069	-0.194785
C	1.426770	-5.135361	0.292116
C	2.215175	-6.283338	0.314766
C	3.611144	-6.182215	0.209573
C	4.203298	-4.918188	0.067408
C	3.411265	-3.771382	0.045323
H	0.351405	-5.172707	0.374543
O	1.724247	-7.556389	0.434468
O	4.395005	-7.307076	0.306419
O	5.568660	-4.916958	-0.043769
H	3.837015	-2.785656	-0.057149
C	1.308875	5.211884	-0.322640
C	2.070857	6.377082	-0.365430
C	3.470333	6.307667	-0.284363
C	4.093152	5.057827	-0.147503
C	3.327635	3.893771	-0.105855
H	0.231572	5.224837	-0.385019
O	1.549516	7.638150	-0.483109
O	4.226606	7.449505	-0.399725
O	5.459971	5.087779	-0.061308
H	3.777195	2.918348	-0.006912
C	-10.796526	0.262925	-0.682219
H	-11.821925	0.016033	-0.420082
H	-10.651982	1.343619	-0.603934
H	-10.594985	-0.061746	-1.706327
C	0.317071	-7.705779	0.583096
H	0.141489	-8.775044	0.678586
H	-0.045986	-7.196190	1.479787
H	-0.221526	-7.324936	-0.289263
C	4.685115	-7.933274	-0.948538
H	5.304895	-8.799627	-0.723214
H	3.765443	-8.261580	-1.440136
H	5.235055	-7.252930	-1.604062
C	6.218233	-3.656005	-0.155469
C	0.137213	7.755361	-0.610249
H	-0.063722	8.819898	-0.708379
H	-0.228321	7.232854	-1.498471
H	-0.379041	7.367381	0.272429
C	4.528829	8.084762	0.847874
H	5.123849	8.964487	0.608107
H	3.612450	8.393132	1.358175
H	5.107697	7.418490	1.492753
C	6.140095	3.842237	0.041646
H	7.199449	4.085879	0.080887
H	5.857026	3.303844	0.950647
H	5.945120	3.207544	-0.827098
H	7.281901	-3.875303	-0.216210
H	5.905210	-3.121362	-1.056837
H	6.025927	-3.028627	0.719171

Zn_2 model in vacuum

N	0.000000	0.000000	-1.421820
C	-0.043914	1.157707	-2.082205
C	-0.042793	1.193570	-3.472258
C	0.000000	0.000000	-4.201826
C	0.042793	-1.193570	-3.472258
C	0.043914	-1.157707	-2.082205
C	-0.074115	2.377013	-1.224994
H	-0.043837	2.137319	-3.996684
C	0.000000	0.000000	-5.676198
H	0.043837	-2.137319	-3.996684
C	0.074115	-2.377013	-1.224994
N	0.012241	-2.154563	0.095181
C	0.029900	-3.180087	0.942920
C	0.112326	-4.499803	0.515679
C	0.180552	-4.743990	-0.849887
C	0.161154	-3.673257	-1.733100
H	-0.022145	-2.926723	1.995074
H	0.124947	-5.306427	1.236641

H	0.249571	-5.757311	-1.226031
H	0.216848	-3.850927	-2.797452
C	-0.161154	3.673257	-1.733100
C	-0.180552	4.743990	-0.849887
C	-0.112326	4.499803	0.515679
C	-0.029900	3.180087	0.942920
N	-0.012241	2.154563	0.095181
H	-0.216848	3.850927	-2.797452
H	-0.249571	5.757311	-1.226031
H	-0.124947	5.306427	1.236641
H	0.022145	2.926723	1.995074
C	0.726564	-0.947603	-6.409077
C	0.738541	-0.952004	-7.792459
C	0.000000	0.000000	-8.530878
C	-0.738541	0.952004	-7.792459
C	-0.726564	0.947603	-6.409077
H	1.328564	-1.682242	-5.887689
H	1.334606	-1.694975	-8.301634
N	0.000000	0.000000	-9.906303
H	-1.334606	1.694975	-8.301634
H	-1.328564	1.682242	-5.887689
Zn	0.000000	0.000000	0.705410
O	-1.567402	-0.004247	1.900516
O	1.567402	0.004247	1.900516
C	2.694007	-0.106863	1.267149
C	-2.694007	0.106863	1.267149
O	2.802109	-0.201945	0.037585
O	-2.802109	0.201945	0.037585
C	3.928972	-0.119378	2.138376
C	-3.928972	0.119378	2.138376
C	5.176942	-0.240039	1.531065
C	6.329304	-0.256927	2.313126
C	6.235040	-0.157812	3.709955
C	4.973231	-0.027506	4.309434
C	3.822008	-0.011153	3.523728
H	5.208668	-0.318124	0.455171
O	7.600724	-0.365082	1.814667
O	7.365119	-0.248746	4.487415
O	4.978538	0.078498	5.675385
H	2.837734	0.081962	3.954984
C	-5.176942	0.240039	1.531065
C	-6.329304	0.256927	2.313126
C	-6.235040	0.157812	3.709955
C	-4.973231	0.027506	4.309434
C	-3.822008	0.011153	3.523728
H	-5.208668	0.318124	0.455171
O	-7.600724	0.365082	1.814667
O	-7.365119	0.248746	4.487415
O	-4.978538	-0.078498	5.675385
H	-2.837734	-0.081962	3.954984
C	-0.768375	0.993022	-10.637521
C	0.768375	-0.993022	-10.637521
H	-0.636715	0.830799	-11.704023
H	-1.838459	0.923497	-10.415371
H	-0.438455	2.011684	-10.408126
H	0.636715	-0.830799	-11.704023
H	1.838459	-0.923497	-10.415371
H	0.438455	-2.011684	-10.408126
C	7.743048	-0.506565	0.406098
H	8.812005	-0.592917	0.223857
H	7.238312	-1.405622	0.042062
H	7.352178	0.364986	-0.126613
C	7.982619	1.010143	4.778540
H	8.854151	0.789840	5.392896
H	8.301929	1.507674	3.858858
H	7.299980	1.658289	5.334385
C	3.720188	0.178313	6.331819
C	-7.743048	0.506565	0.406098
H	-8.812005	0.592917	0.223857
H	-7.238312	1.405622	0.042062
H	-7.352178	-0.364986	-0.126613
C	-7.982619	-1.010143	4.778540
H	-8.854151	-0.789840	5.392896
H	-8.301929	-1.507674	3.858858
H	-7.299980	-1.658289	5.334385
C	-3.720188	-0.178313	6.331819
H	-3.944508	-0.236811	7.394585
H	-3.177106	-1.076717	6.024894
H	-3.098354	0.700282	6.139500
H	3.944508	0.236811	7.394585
H	3.177106	1.076717	6.024894
H	3.098354	-0.700282	6.139500

Zn_2 in *n*-hexane

N	0.000000	0.000000	-1.520858
C	-0.001319	1.159452	-2.182325
C	0.003158	1.194920	-3.571488
C	0.000000	0.000000	-4.303171
C	-0.003158	-1.194920	-3.571488
C	0.001319	-1.159452	-2.182325
C	0.005501	2.378315	-1.324056
H	0.036761	2.139745	-4.091916
C	0.000000	0.000000	-5.776136
H	-0.036761	-2.139745	-4.091916
C	-0.005501	-2.378315	-1.324056
N	-0.026051	-2.151969	-0.001809
C	-0.033801	-3.179028	0.846044
C	-0.021055	-4.500608	0.417720
C	0.001693	-4.747542	-0.948981
C	0.009687	-3.676702	-1.832670
H	-0.050313	-2.926939	1.899406
H	-0.027718	-5.306641	1.139109
H	0.013738	-5.762507	-1.325901
H	0.028778	-3.856886	-2.897624
C	-0.009687	3.676702	-1.832670
C	-0.001693	4.747542	-0.948981
C	0.021055	4.500608	0.417720
C	0.033801	3.179028	0.846044
N	0.026051	2.151969	-0.001809
H	-0.028778	3.856886	-2.897624
H	-0.013738	5.762507	-1.325901
H	0.027718	5.306641	1.139109
H	0.050313	2.926939	1.899406
C	0.607912	-1.028248	-6.511220
C	0.618161	-1.035188	-7.894093
C	0.000000	0.000000	-8.634385
C	-0.618161	1.035188	-7.894093
C	-0.607912	1.028248	-6.511220
H	1.118219	-1.831244	-5.993440
H	1.120135	-1.844883	-8.402998
N	0.000000	0.000000	-10.006343
H	-1.120135	1.844883	-8.402998
H	-1.118219	1.831244	-5.993440
Zn	0.000000	0.000000	0.592853
O	-1.544159	0.009676	1.832966
O	1.544159	-0.009676	1.832966
C	2.694291	-0.079409	1.245647
C	-2.694291	0.079409	1.245647
O	2.855049	-0.137416	0.017332
O	-2.855049	0.137416	0.017332
C	3.895283	-0.088941	2.165447
C	-3.895283	0.088941	2.165447

C	5.169527	-0.188646	1.610057
C	6.288663	-0.201973	2.440069
C	6.133078	-0.116513	3.832205
C	4.846217	-0.009239	4.380708
C	3.729097	0.001717	3.546556
H	5.253426	-0.254724	0.536385
O	7.579569	-0.295131	1.995571
O	7.231995	-0.195576	4.657042
O	4.792436	0.078609	5.745498
H	2.727264	0.077101	3.938795
C	-5.169527	0.188646	1.610057
C	-6.288663	0.201973	2.440069
C	-6.133078	0.116513	3.832205
C	-4.846217	0.009239	4.380708
C	-3.729097	-0.001717	3.546556
H	-5.253426	0.254724	0.536385
O	-7.579569	0.295131	1.995571
O	-7.231995	0.195576	4.657042
O	-4.792436	-0.078609	5.745498
H	-2.727264	-0.077101	3.938795
C	-0.626481	1.089158	-10.739847
C	0.626481	-1.089158	-10.739847
H	-0.505139	0.915276	-11.805302
H	-1.698266	1.157937	-10.527630
H	-0.168442	2.053755	-10.499838
H	0.505139	-0.915276	-11.805302
H	1.698266	-1.157937	-10.527630
H	0.168442	-2.053755	-10.499838
C	7.786340	-0.400216	0.587013
H	8.862849	-0.469477	0.451474
H	7.309549	-1.295852	0.181810
H	7.408393	0.480963	0.062810
C	7.820445	1.076014	4.975112
H	8.667265	0.868409	5.626509
H	8.169797	1.576106	4.068853
H	7.103277	1.712122	5.498956
C	3.504019	0.179055	6.351296
C	-7.786340	0.400216	0.587013
H	-8.862849	0.469477	0.451474
H	-7.309549	1.295852	0.181810
H	-7.408393	-0.480963	0.062810
C	-7.820445	-1.076014	4.975112
H	-8.667265	-0.868409	5.626509
H	-8.169797	-1.576106	4.068853
H	-7.103277	-1.712122	5.498956
C	-3.504019	-0.179055	6.351296
H	-3.684651	-0.233396	7.421997
H	-2.979832	-1.080448	6.023967
H	-2.891558	0.698223	6.129417
H	3.684651	0.233396	7.421997
H	2.979832	1.080448	6.023967
H	2.891558	-0.698223	6.129417

Zn_1 model in CH_2Cl_2

N	-1.831751	-0.113022	0.013934
C	-2.513728	-0.145555	-1.134317
C	-3.903449	-0.130605	-1.142645
C	-4.606148	-0.074237	0.066745
C	-3.856759	-0.044149	1.248573
C	-2.468336	-0.067250	1.187385
C	-1.676624	-0.201113	-2.365535
H	-4.443178	-0.180630	-2.075618
C	-6.083198	-0.041943	0.095665
H	-4.358581	0.026348	2.201195
C	-1.584283	-0.029078	2.385857
N	-0.265455	-0.006093	2.129369
C	0.602143	0.028001	3.141169
C	0.199330	0.040897	4.470611
C	-1.161837	0.015114	4.745936
C	-2.066904	-0.020835	3.693144
H	1.650993	0.044962	2.872099
H	0.936662	0.068744	5.261254
H	-1.518449	0.021493	5.767795
H	-3.127647	-0.044500	3.894684
C	-2.209046	-0.286027	-3.650574
C	-1.344705	-0.330801	-4.736770
C	0.026101	-0.289076	-4.516473
C	0.479576	-0.206169	-3.205980
N	-0.348782	-0.164758	-2.162031
H	-3.276764	-0.320211	-3.809196
H	-1.740089	-0.397950	-5.742086
H	0.732489	-0.320859	-5.334732
H	1.537958	-0.172688	-2.979087
C	-6.802365	-0.625721	1.152232
C	-8.184186	-0.595696	1.182734
C	-8.898498	0.031715	0.154616
C	-8.203712	0.621860	-0.903415
C	-6.813858	0.575660	-0.924290
H	-6.276694	-1.135972	1.949244
H	-8.730310	-1.060976	1.993746
O	-10.256426	0.015743	0.272860
H	-8.726830	1.122583	-1.704963
H	-6.297430	1.060066	-1.743239
Zn	0.271403	-0.064548	-0.028957
O	1.519182	1.486318	-0.104853
O	1.614945	-1.534822	-0.001727
C	1.145357	-2.730080	0.099018
C	0.962617	2.647612	-0.130709
O	-0.065779	-3.008819	0.160831
O	-0.267032	2.839231	-0.121504
C	2.174940	-3.838082	0.144572
C	1.908019	3.828013	-0.174913
C	1.746643	-5.156605	0.293441
C	2.682362	-6.188592	0.345117
C	4.051750	-5.898861	0.243834
C	4.473434	-4.569616	0.089357
C	3.533465	-3.540608	0.042061
H	0.688073	-5.349976	0.370152
O	2.367712	-7.509768	0.495334
O	4.981918	-6.909633	0.351331
O	5.824487	-4.385645	-0.002648
H	3.829988	-2.510131	-0.070962
C	1.381852	5.118663	-0.212697
C	2.239791	6.216517	-0.256362
C	3.629472	6.020885	-0.263049
C	4.150163	4.718680	-0.222696
C	3.287417	3.623892	-0.179375
H	0.309909	5.239831	-0.208995
O	1.826574	7.518351	-0.299085
O	4.479295	7.100746	-0.363175
O	5.513725	4.626826	-0.232896
H	3.660188	2.612566	-0.149852
C	-11.034542	0.633764	-0.763905
H	-12.072088	0.497804	-0.473302
H	-10.810683	1.699385	-0.836576
H	-10.856195	0.149717	-1.725582
C	0.980205	-7.857434	0.588401
H	0.954788	-8.938240	0.696202
H	0.515683	-7.392119	1.459768
H	0.441250	-7.566843	-0.315441
C	5.326025	-7.526835	-0.907096
H	6.057557	-8.299265	-0.680201

H	4.443831	-7.977819	-1.364638
H	5.764144	-6.791900	-1.584755
C	6.303845	-3.046212	-0.175107
C	0.415549	7.770193	-0.277223
H	0.309849	8.850997	-0.310039
H	-0.076469	7.328235	-1.145704
H	-0.037738	7.385455	0.638363
C	4.867966	7.660597	0.909071
H	5.529203	8.495561	0.687931
H	3.991503	8.018284	1.452135
H	5.399846	6.917418	1.505867
C	6.093539	3.317158	-0.181482
H	7.168949	3.471127	-0.195304
H	5.810127	2.797969	0.736255
H	5.798649	2.722135	-1.048043
H	7.385835	-3.126654	-0.232099
H	5.920483	-2.607806	-1.098633
H	6.028431	-2.417483	0.673897

Zn_2 model in CH_2Cl_2

N	0.000000	0.000000	-1.711612
C	0.003808	1.161127	-2.374666
C	0.007539	1.196092	-3.762606
C	0.000000	0.000000	-4.495905
C	-0.007539	-1.196092	-3.762606
C	-0.003808	-1.161127	-2.374666
C	0.016281	2.378414	-1.515141
H	0.042293	2.142259	-4.279706
C	0.000000	0.000000	-5.966883
H	-0.042293	-2.142259	-4.279706
C	-0.016281	-2.378414	-1.515141
N	-0.029177	-2.149808	-0.191047
C	-0.041444	-3.179437	0.656186
C	-0.041324	-4.500339	0.226648
C	-0.026871	-4.747248	-1.140341
C	-0.013975	-3.676095	-2.023927
H	-0.051715	-2.931633	1.710399
H	-0.051704	-5.306242	0.947767
H	-0.025244	-5.761676	-1.517806
H	-0.001750	-3.855654	-3.088754
C	0.013975	3.676095	-2.023927
C	0.026871	4.747248	-1.140341
C	0.041324	4.500339	0.226648
C	0.041444	3.179437	0.656186
N	0.029177	2.149808	-0.191047
H	0.001750	3.855654	-3.088754
H	0.025244	5.761676	-1.517806
H	0.051704	5.306242	0.947767
H	0.051715	2.931633	1.710399
C	0.549595	-1.061812	-6.703643
C	0.560390	-1.069024	-8.085901
C	0.000000	0.000000	-8.828048
C	-0.560390	1.069024	-8.085901
C	-0.549595	1.061812	-6.703643
H	1.011910	-1.894692	-6.188461
H	1.015108	-1.906160	-8.594840
N	0.000000	0.000000	-10.195951
H	-1.015108	1.906160	-8.594840
H	-1.011910	1.894692	-6.188461
Zn	0.000000	0.000000	0.385854
O	-1.503776	0.007818	1.690474
O	1.503776	-0.007818	1.690474
C	2.693957	-0.078284	1.204239
C	-2.693957	0.078284	1.204239
O	2.959302	-0.138640	-0.009979
O	-2.959302	0.138640	-0.009979
C	3.815732	-0.086591	2.220469
C	-3.815732	0.086591	2.220469
C	5.132563	-0.206445	1.778362
C	6.176228	-0.222105	2.702438
C	5.899856	-0.114639	4.074091
C	4.572025	0.011063	4.509599
C	3.531561	0.022295	3.581393
H	5.315715	-0.288329	0.718345
O	7.497169	-0.341305	2.373547
O	6.923905	-0.187622	4.993145
O	4.401058	0.112336	5.861851
H	2.501904	0.112345	3.888453
C	-5.132563	0.206445	1.778362
C	-6.176228	0.222105	2.702438
C	-5.899856	0.114639	4.074091
C	-4.572025	-0.011063	4.509599
C	-3.531561	-0.022295	3.581393
H	-5.315715	0.288329	0.718345
O	-7.497169	0.341305	2.373547
O	-6.923905	0.187622	4.993145
O	-4.401058	-0.112336	5.861851
H	-2.501904	-0.112345	3.888453
C	-0.574232	1.118639	-10.932003
C	0.574232	-1.118639	-10.932003
H	-0.468536	0.932269	-11.996522
H	-1.638903	1.242427	-10.712150
H	-0.064905	2.058311	-10.698588
H	0.468536	-0.932269	-11.996522
H	1.638903	-1.242427	-10.712150
H	0.064905	-2.058311	-10.698588
C	7.830779	-0.438292	0.982881
H	8.913698	-0.517655	0.945556
H	7.383389	-1.326089	0.532027
H	7.509880	0.452313	0.439112
C	7.505524	1.090439	5.326486
H	8.291713	0.890238	6.051131
H	7.933576	1.558036	4.438107
H	6.754558	1.747102	5.769355
C	3.063654	0.260723	6.354482
C	-7.830779	0.438292	0.982881
H	-8.913698	0.517655	0.945556
H	-7.383389	1.326089	0.532027
H	-7.509880	-0.452313	0.439112
C	-7.505524	-1.090439	5.326486
H	-8.291713	-0.890238	6.051131
H	-7.933576	-1.558036	4.438107
H	-6.754558	-1.747102	5.769355
C	-3.063654	-0.260723	6.354482
H	-3.154753	-0.331794	7.434817
H	-2.600734	-1.169966	5.965791
H	-2.450869	0.605112	6.095815
H	3.154753	0.331794	7.434817
H	2.600734	1.169966	5.965791
H	2.450869	-0.605112	6.095815

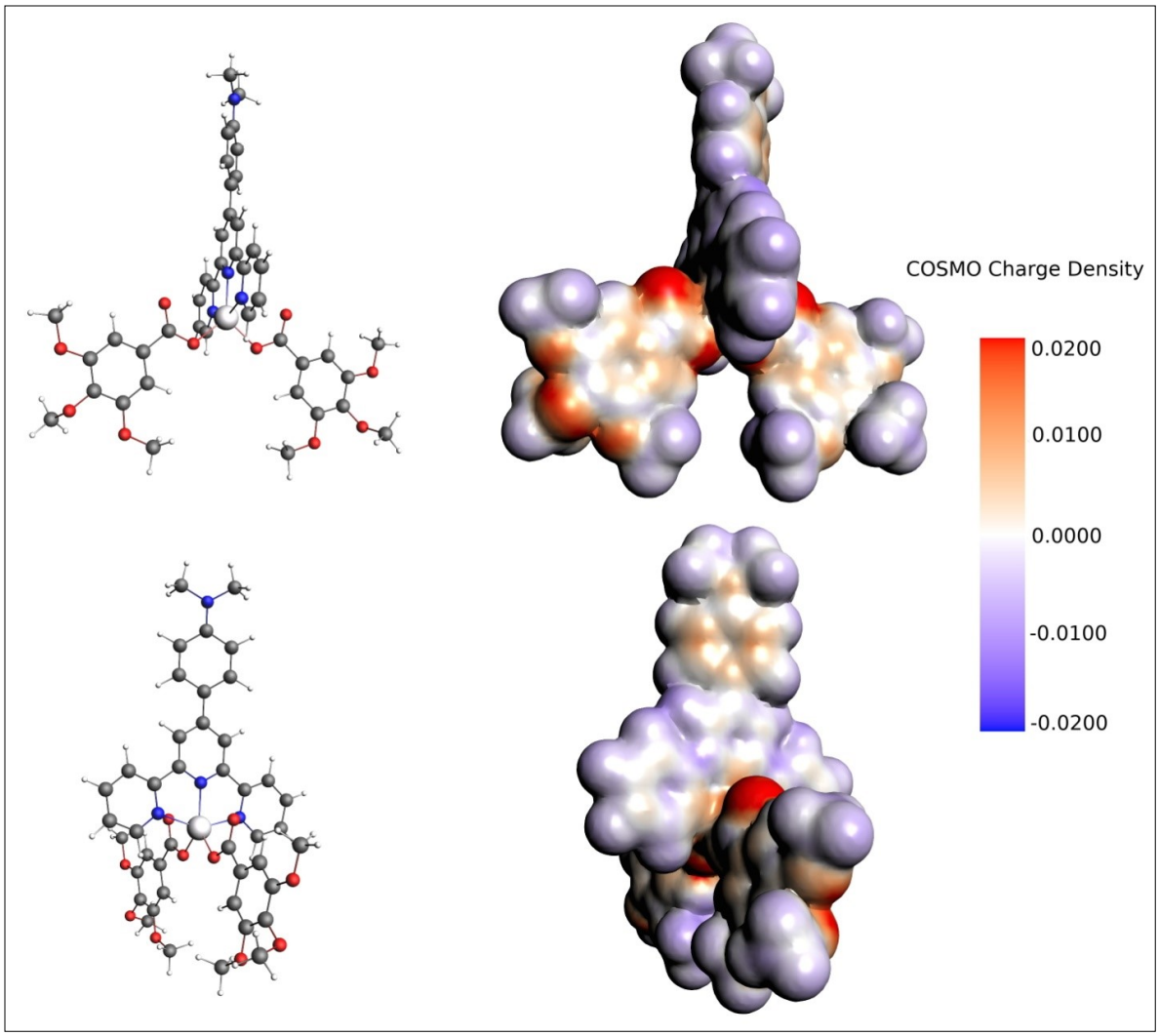

Figure SI_25. The computed COSMO charge density of **Zn_2** model in CH_2Cl_2 is sketched from two different viewpoints. Positive solvent polarization is in red, negative in blue. Positive polarization is more evident on the gallate ligands (apart from the methyl substituents). This is likely due to the gallate negative charge and, consequently, gallate-localized MOs are stabilized by solvation. The *tpy*-localized MOs, at contrary, are destabilized due to the predominant negative solvent polarization in proximity of the *tpy* ligand. Figure 5 shows the MOs energy shifts in different environments. The diethylaniline-localized HOMO is exposed to a destabilizing environment; hence, more polarizable solvents induce energy destabilization of diethylaniline-localized MOs (like the HOMO, 106b in Figure 9). At contrary, the more "internal" LUMO on the *tpy* ligand probably feels the positive (red) polarization in correspondence of the gallate oxygen atoms (it could be equivalently considered a solvent-induced screening of the partially-negative oxygen atoms). This stabilizing part of the COSMO surface can partially counterbalance the effect of the negatively polarized surface around the *tpy* ligand. As a consequence, the LUMO is less affected by the environment in comparison to the HOMO.

References

1. Chen, F.; Tian, Y.-K.; Chen, Y. Controlled formation of main chain supramolecular polymer based on metal–ligand interaction and thiol-ene click reaction, *Chem. Asian J.* **2018**, *13*, 3169-3172.
2. Liu, Y.; Li, C.; Miao, W.; Tang, W.; Xue, D.; Xiao, J.; Zhang, T.; Wang, C. Rhodium-terpyridine catalyzed redox-neutral depolymerization of lignin in water, *Green Chem.* **2020**, *22*, 33-38.
3. Liu D., Zhang M., Du W., Hu L., Li F., Tian X., Wang A., Zhang Q., Zhang Z., Wu J., Tian Y. A Series of Zn(II) Terpyridine-Based Nitrate Complexes as Two-Photon Fluorescent Probe for Identifying Apoptotic and Living Cells via Subcellular Immigration, *Inorg. Chem*. **2018**, *57, 13*, 7676–7683.
4. PubChem CID: 101474225
5. Szerb E. I., Pucci D., Crispini A., La Deda M. Soft Luminescent Materials Based on Ag(I) Coordination Complexes, *Mol. Cryst. Liq. Cryst*. **2013**, *573*, 34–45.
6. Demas J. N., Crosby G. A. Measurement of photoluminescence quantum yields. Review, *J. Phys. Chem*. **1971**, *75*, 991-1024.
7. Heinrich G., Schoof S., Gusten H., 9,10-diphenylanthracene as a fluorescence quantum yield standard, *J. Photochem*. **1974/75**, *3*, 315 – 320.
8. de Mello., J. C.; Wittmann, H. F.; Friend, R. H. An improved experimental determination of external photoluminescence quantum efficiency, *Adv. Mater*. **1997**, *9*, 230-232.
9. Andelescu, A.-A.; Heinrich, B.; Spirache, M. A.; Voirin, E.; La Deda, M.; Di Maio, G.; Szerb, E. I.; Donnio, B.; Costisor, O. Playing with Pt(II) and Zn(II) Coordination to Obtain Luminescent Metallomesogens, *Chem. Eur. J.* **2020**, *26*, 4850 – 4860.