Supporting Information

π-Extended Dipyrrins capable of highly fluorogenic complexation with metal ions

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Contents

I. Materials and Methods

All solvents and reagents were obtained from commercial sources and used as received. Column chromatography was performed on Merck silica gel. ^{1}H and ^{13}C NMR spectra were recorded on a Brucker Avance DMX 400 spectrometer, using tetramethylsilane as a standard. MALDI spectra were obtained on a MALDI-TOF Voyager-DE™ RP BioSpectrometry workstation, using α-cyano-4-hydroxycinnamic acid as the matrix. HRMS spectra were recorded on Thermo-Fisher LTQ Orbitrap XL mass-spectrometer. Solutions of analytes in THF were introduced directly into the ionization chamber. Typical parameter for analyses: ES, positive mode, ionization voltage 3.52 kV, capillary voltage 45 V, capillary temperature 200°C).

Quartz fluorometric cells (Starna, Inc, 1 cm optical path length) were used in optical experiments. The absorption spectra were recorded on a Perkin-Elmer Lambda 35 UV-Vis spectrophotometer. Steady state fluorescence measurements were performed on a FS900 specrtrofluorometer (Edinburgh Instruments, UK), equipped with R2658P PMT (Hamamatsu). Emission spectra were obtained using solutions with absorption at the excitation maxima of approximately 0.02 OD. Fluorescence quantum yields were measured relative to the fluorescence of Rhodamine 6G in ethanol at 22°C (ϕ_{fl}=0.94).[1] In all cases, the origin of the emitting species was confirmed by the excitation spectra.

Time-resolved fluorescence measurements were performed using the time-correlated single photon counting method (TCSPC). The TCSPC system consisted a picosecond diode laser source, MCP-PMT (Hamamatsu R2809U) and a TCSPC board (Becker & Hickl, SPC-730).

X-Ray diffraction experiments were carried out on a Bruker SMART APEX II CCD area detector, using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 100 K. The reflection intensities were integrated using SAINT software and absorption correction was applied semi-empirically using SADABS program. A sufficiently high value of R_{int} for toluene solvate is the consequence of extremely small crystal dimensions and weak reflection power. The structure of Zn-**2e** was solved by direct methods and refined by the full-matrix least-squares against F^2 using anisotropic approximation for non-hydrogen atoms.

Geometry optimizations were performed using the DFT method (B3LYP/6-31G(d)) as implemented in Gaussian 03 (Rev. D.01, Intel EM64T/AMD, Gaussian, Inc).[2] The stationary point was confirmed by running frequency calculations.

II. Synthesis

2,2'-di(ethoxycarbonyl)dibenzo[b,g]dipyrromethene (2a): Bis(3-ethoxycarbonyl-4,7-dihydro-2*H*-isoindolyl)methane[3] (0.20 g, 0.5 mmol) and DDQ (0.34 g, 1.5 mmol) were dissolved in dry THF (10 ml). The solution was stirred for 30 min at room temperature, diluted with CH_2Cl_2 (50 ml), washed with 10% aq. Na_2SO_3 (2×20 ml), brine (1×20 ml), dried over Na_2SO_4, and the solvent was evaporated in vacuum. The residue was chromatographed on silica gel using DCM as a solvent. The product was re-crystallized from CH_2Cl_2-MeOH mixture to yield dark blue crystals: 0.18 g, 93%. m. p. 168-170°C. ^{1}H NMR (400 MHz, $CDCl_3$) δH, ppm 9.3 (br. s, 1H), 8.16 (m, 2H), 7.81 (m, 2H), 7.57 (s, 1H), 7.38 (overlapp m, 4H), 4.53 (q, 4H, *J*=7.07 Hz), 1.55 (t, 6H, *J*=7.07 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δC, ppm 161.6, 138.1, 135.5, 135.3, 131.3, 127.2, 126.7, 122.9, 119.1, 116.5, 61.2, 14.5. UV/Vis (DMF): λ (log ε)=567 nm (4.85). Anal. calcd. for $C_{23}H_{20}N_2O_4$: C, 71.12; H, 5.19; N, 7.21. Found C, 71.25; H, 5.34; N, 7.10.

Characterization data for compounds **2b-2f** (for general synthetic scheme see the main text):

2b: purple crystals, yield 0.56 g, 88%, m. p. 208-210°C. ^{1}H NMR (400 MHz, $CDCl_3$) δH, ppm 14.7 (br. s, 1H), 8.15 (m, 2H), 7.72 (t, 1H, *J*=1.77 Hz), 7.36 (d, 2H, *J*=1.77 Hz), 7.21 (m, 2H), 6.94 (m, 2H), 6.16 (m, 2H), 1.77 (s, 18H), 1.37 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δC, ppm 161.2, 152.1, 140.5, 138.9, 135.9, 135.5, 134.7, 131.4, 130.8, 126.4, 125.6, 123.7, 122.7, 122.4, 122.2, 82.2, 35.2, 31.5, 28.4. *m/z* ES HRMS 633.3686 ($C_{41}H_{49}N_2O_4$, M+H, calc. 633.3687). Anal. Calcd. for $C_{41}H_{48}N_2O_4$ C, 77.82; H, 7.65; N, 4.43; Found C, 77.79; H, 7.71; N, 4.38.

2c: dark-brown crystals, yield 0.55 g, 92%, m. p. 248-250°C. ^{1}H NMR (400 MHz, $CDCl_3$) δH, ppm 14.76 (br. s, 1H), 8.15 (d, 2H, *J*=8.21 Hz), 7.81 (d, 2H, *J*=8.21 Hz), 7.42 (d, 2H, *J*=8.21 Hz), 7.23 (m, 2H), 7.02 (m, 2H), 6.19 (d, 2H, *J* = 8.21 Hz), 1.79 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δC, ppm 161.0, 139.5, 137.3, 135.5, 134.2, 132.8, 131.4, 131.1, 127.0, 125.9, 123.7, 123.1, 121.8, 82.6, 28.4. Anal. calcd. for $C_{33}H_{31}BrN_2O_4$ C, 66.11; H, 5.21; N, 4.67. Found C, 66.08; H, 5.39; N, 4.77.

2d: purple crystals, yield 0.50 g, 87%, m. p. 248-250°C. ^{1}H NMR (400 MHz, $CDCl_3$) δH, ppm 14.79 (br. s, 1H), 8.36 (d, 2H, *J*=8.08 Hz), 8.16 (d, 2H, *J*=8.08 Hz), 7.66 (d, 2H, *J*=8.08 Hz), 7.23 (m, 2H), 6.97 (m, 2H), 6.09 (d, 2H, *J* = 8.34 Hz), 4.08 (s, 3H), 1.78 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δC, ppm 166.7, 161.0, 141.3, 139.5, 137.5, 135.4, 133.9, 131.3, 131.1, 130.6, 129.6, 126.9, 125.9, 123.0, 121.7, 82.5, 52.5, 28.4. Anal. calcd. for $C_{35}H_{34}N_2O_6$ C, 72.65; H, 5.92; N, 4.84. Found C, 72.51; H, 5.79; N, 4.72.

2e: purple crystals, yield 0.49 g, 84%, m.p. 242-243°C. ^{1}H NMR (400 MHz, $CDCl_3$) δH, ppm 14.8 (br. s., 1H), 8.15 (dt, J_o=8.08 Hz, J_m=0.76 Hz, 2H), 7.24 (td, J_o=8.08 Hz, J_m=1.01 Hz, 2H), 7.04 (td, J_o=7.07 Hz, J_m=1.01 Hz, 2H), 6.78 (t, *J*=2.27 Hz, 1H), 6.68 (d, *J*=2.27 Hz, 2H), 6.39 (td, J_o=6.39 Hz, J_m not resolved, 2H), 3.83 (s, 6H), 1.76 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δC, ppm 161.7, 161.1, 135.5, 134.3, 131.3, 131.0, 126.9, 125.8, 122.8, 122.3, 106.9, 101.8, 82.4, 55.7, 28.4. Anal. calcd. for $C_{35}H_{36}N_2O_6$ C, 72.39; H, 6.25; N, 4.82. Found C, 72.01; H, 6.55; N, 4.61.

2f: dark-green crystals, yield 0.43 g, 82%. M.p. 252-253°C ^{1}H NMR (400 MHz, $CDCl_3$) δH, ppm 14.60 (br. s, 1H), 8.16 (m, 2H), 7.73 (m, 2H), 7.37 (m, 1H), 7.29 (m, 1H), 7.26 (m, 2H), 7.08 (m, 2H), 6.35 (m, 2H), 1.77 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δC, ppm 161.0, 139.6, 135.5, 131.4, 128.9, 128.1, 128.0, 127.0, 126.1, 123.0, 122.0, 82.4, 28.4. *m/z* ES HRMS 527.2001 ($C_{31}H_{31}N_2O_4S$, M+H, calc. 527.1999). Anal. calcd. for $C_{31}H_{30}N_2O_4S$ C, 70.70; H, 5.74; N, 5.32. Found C, 70.67; H, 5.80; N, 5.27.

5-(4-methoxycarbonylphenyl)-1,9-di(ethoxycarbonyl)dinaphtho[2,3-b,g]dipyrromethene (3). 2-ethoxycarbonyl-4,9-dihydrobenzo[*f*]isoindole (0.48 g, 2 mmol),[4] 4-methoxycarbonylbenzaldehyde (0.16 g, 1 mmol), *p*-toluenesulfonic acid (0.002 g, 0.1 mmol), and tetra-*n*-butylammonium chloride (0.003 g, 0.1 mmol) were dissolved in DCM (20 ml) and stirred ar room temperature under argon for 12 h. The reaction mixture was washed with water (1×20 ml), brine (1×20 ml), dried over Na_2SO_4, and the solvent was evaporated to dryness. The residue was dissolved in dry THF (20 ml), and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ, 0.68 g, 3 mmol) was added to the solution. The mixture was stirred for 1 h at room temperature, and the solvent was removed in vacuum. CH_2Cl_2(50 ml) was added to the residue, and the solution was washed with 10% aq. Na_2SO_3 (2×20 ml), brine (1×20 ml), dried over Na_2SO_4, and the solvent was evaporated in vacuum. The remaining solid was dissolved in dry THF (20 ml) and treated additionally with DDQ in the same manner. The product was purified on silica gel column using CH_2Cl_2 as a solvent and re-crystallized from MeOH-CH_2Cl_2. Dark-blue solid, yield 0.49 g, 78%. M.p. 262-264 C. ^{1}H NMR (400 MHz, $CDCl_3$) δH, ppm 15.18 (br. s, 1H), 8.74 (s, 2H), 8.50 (d, 2H, *J*=7.83 Hz), 7.92 (d, 2H, *J*=7.83 Hz), 7.83 (d, 2H, *J*=7.53 Hz), 7.30-7.45 (overlapp. m, 5H), 6.64 (s, 2H), 4.66 (q, 4H, *J*=7.07 Hz), 4.17 (s, 3H), 1.64 (t, 6H, *J*=7.07 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δC, ppm 161.7, 141.8, 137.1, 134.1, 132.5, 132.2, 132.0, 131.0, 130.9, 130.2, 129.7, 129.3, 129.2, 129.0, 127.3, 126.5, 126.2, 125.9, 123.7, 122.2, 121.1, 61.4, 52.6, 28.5, 27.7. *m/z* ES HRMS 623.2180 ($C_{39}H_{31}N_2O_6$, M+H, calc. 623.2177). Anal. calcd. for $C_{39}H_{30}N_2O_6$ C, 75.23; H, 4.86; N, 4.50; Found C, 75.18; H, 4.91; N, 4.48.

Zn-2d (ML_2): $Zn(OAc)_2{\cdot}2H_2O$ (100 mg) was added in one portion to a solution of **2d** (0.022 g, 0.038 mmol) in acetone (10 ml). The resulting mixture was vigorously shaken several times and placed in a freezer at -25°C overnight. The residue, containing dark blue crystals of Zn-**2d** was washed with ethanol and with water to remove the unreacted Zn acetate and dried in vacuum: 0.059 g, 93%. See the spectra below. UV/Vis (TolH): 599 (log ε 5.20). ^{1}H NMR (500 MHz, pyridine-d_5) δH, ppm 8.59 (d, 4H, *J*=10.00 Hz), 8.20 (m, 8H), 7.26 (t, 4H, *J*=10.00 Hz), 7.05 (t, 4H, *J*=10.00 Hz), 6.28 (d, 4H, *J*=10.50 Hz), 4.96 (s, 2H), 3.88 (s, 6H), 1.06 (s, 36H). *m/z* ES HRMS 1219.4047 ($C_{70}H_{66}N_4O_{12}Zn$, M+H, calc. 1219.4041). Anal. calcd. for $C_{70}H_{66}N_4O_{12}Zn$ C, 68.88; H, 5.45; N, 4.59; Found C, 68.80; H, 4.98; N, 4.51.

Zn-2a (ML_2): A solution of $Zn(OAc)_2{\cdot}2H_2O$ (0.0223 g, 0.1 mmol) in acetone (5 ml) was added dropwise to a vigorously stirred solution of **2a** (0.0776 g, 0.2 mmol) in acetone (10 ml). The resulting mixture was stirred at room temperature for 10 min, the solvent was evaporated and the remaining dark-blue crystals were dried in vacuum: 0.084 g, 100%, m.p. 272-273 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δH, ppm 8.40 (br. s, 2H), 8.16 (d, 8H, *J*=8.85 Hz), 7.50 (m, 4H), 7.35 (m, 4H), 3.92 (q, 8H,

J=7.03 Hz), 0.89 (t, 12H, *J*=7.16 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δC, ppm 162.9, 141.2, 139.0, 136.2, 131.6, 127.4, 125.8, 123.8, 123.4, 118.8, 61.4, 14.3. UV/Vis (THF): 626 nm (5.20). *m/z* ES HRMS 839.2058 ($C_{46}H_{39}N_4O_8Zn$, M+H, calc. 839.2054). Anal. calcd. for $C_{46}H_{38}N_4O_8Zn$ C, 65.76; H, 4.56; N, 6.67; Found C, 65.71; H, 4.61; N, 6.64.

Zn-2a(acac) (MLX): Zn acetylacetonate (0.0264 g, 0.1 mmol) was added in portions to a stirred solution of **2a** (0.0776 g, 0.2 mmol) in acetone (20 ml). The stirring was stopped after 10 min, and the reaction mixture was left for 1 h. The precipitate was filtered and dried in vacuum to yield the desired complex as a dark-blue powder: 0.052 g, 95%, m.p. 245-246^{o}C. ^{1}H NMR (400 MHz, d^6-DMSO) δH, ppm 8.88 (br. s, 1H), 8.55 (d, 2H, *J*=8.29 Hz), 8.04 (d, 2H, *J*=8.1 Hz), 7.55 (m, 2H), 7.38 (m, 2H), 5.24 (s, 1H), 3.83 (q, 4H, *J* = 6.78 Hz), 1.83 (s, 6H), 0.74 (t, 6H, *J*=6.97 Hz). ^{13}C NMR (100 MHz, d^6-DMSO) δC, ppm 191.5, 161.8, 139.5, 138.4, 135.8, 130.2, 127.0, 125.5, 122.5, 119.7, 98.9, 97.9, 60.7, 27.8, 13.5. UV/Vis (THF): 587 (4.41), 629 (4.90) nm. Anal. calcd. for $C_{28}H_{28}N_2O_6Zn$ C, 60.71; H, 5.10; N, 5.06; Found C, 60.66; H, 5.17; N, 4.98.

III. NMR spectra

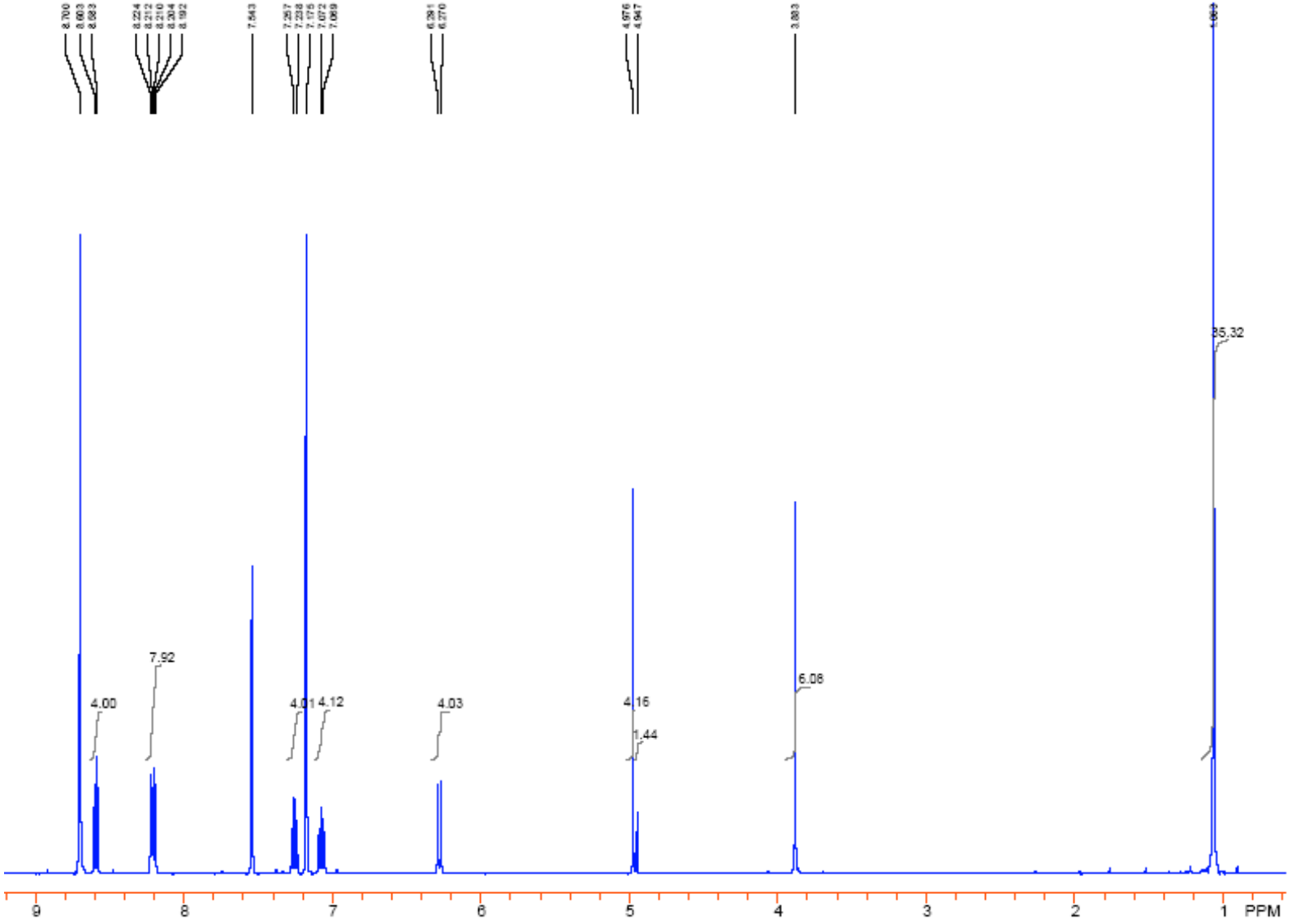


Figure S1. ^{1}H NMR spectrum of Zn-**2d** (ML_2) in pyridine-d_5.

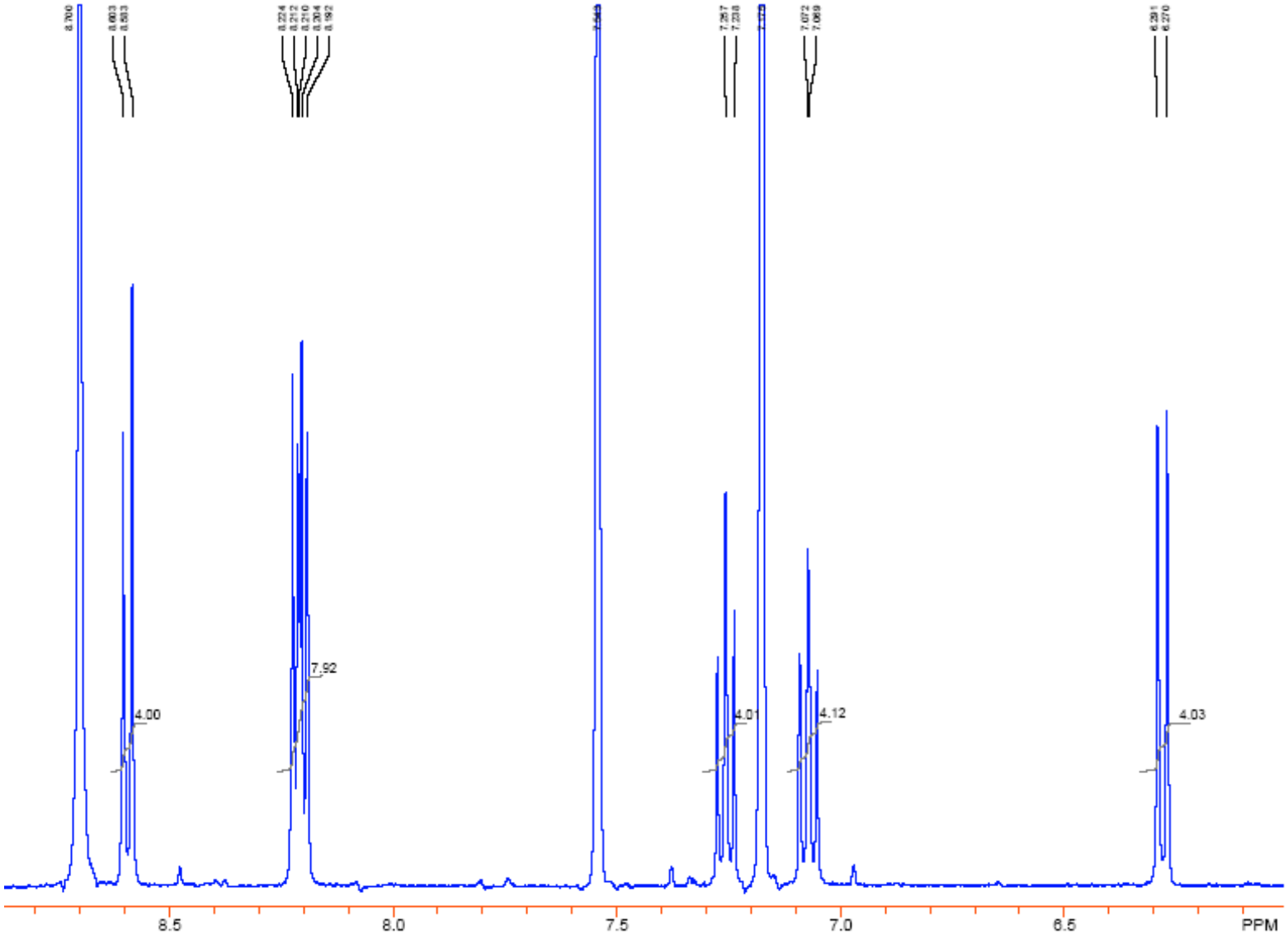


Figure S1a. ^{1}H NMR spectrum of Zn-**2d** (ML_2) - aromatic region.

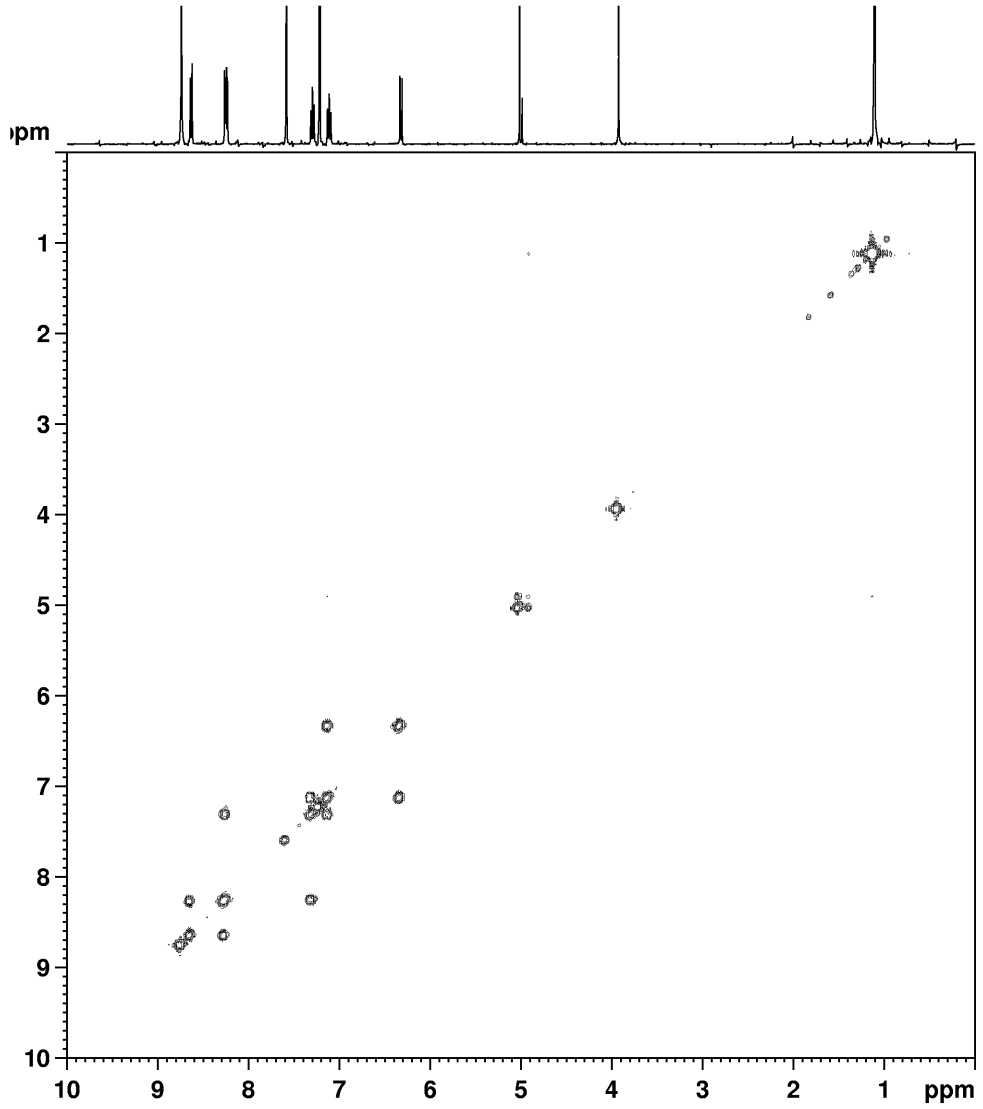


Figure S2. ^{1}H-^{1}H COSY NMR spectrum of Zn-**2d** (ML_2) in pyridine-d_5.

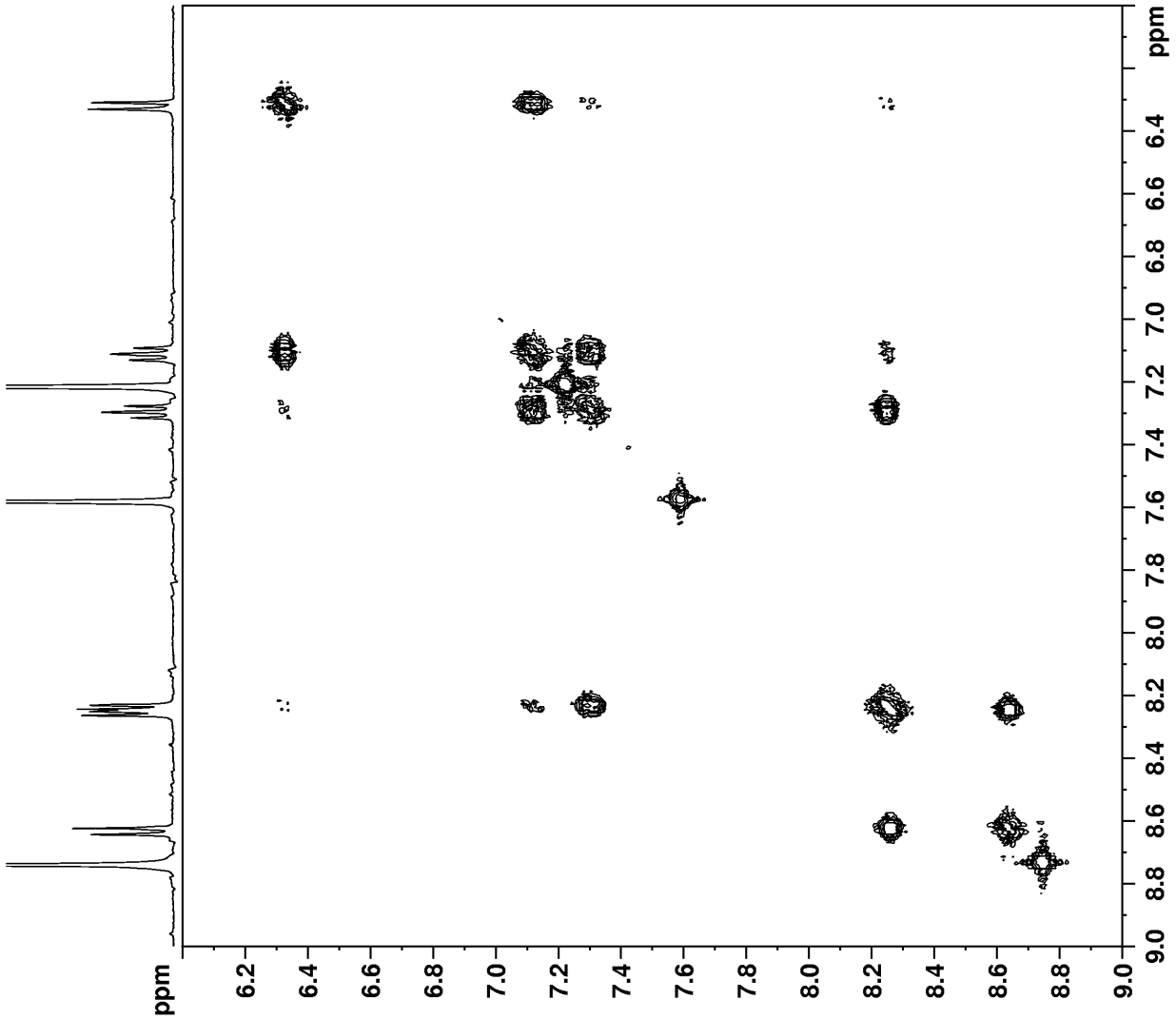


Figure S2a. ^{1}H-^{1}H COSY NMR spectrum of Zn-**2d** (ML_2) - aromatic region.

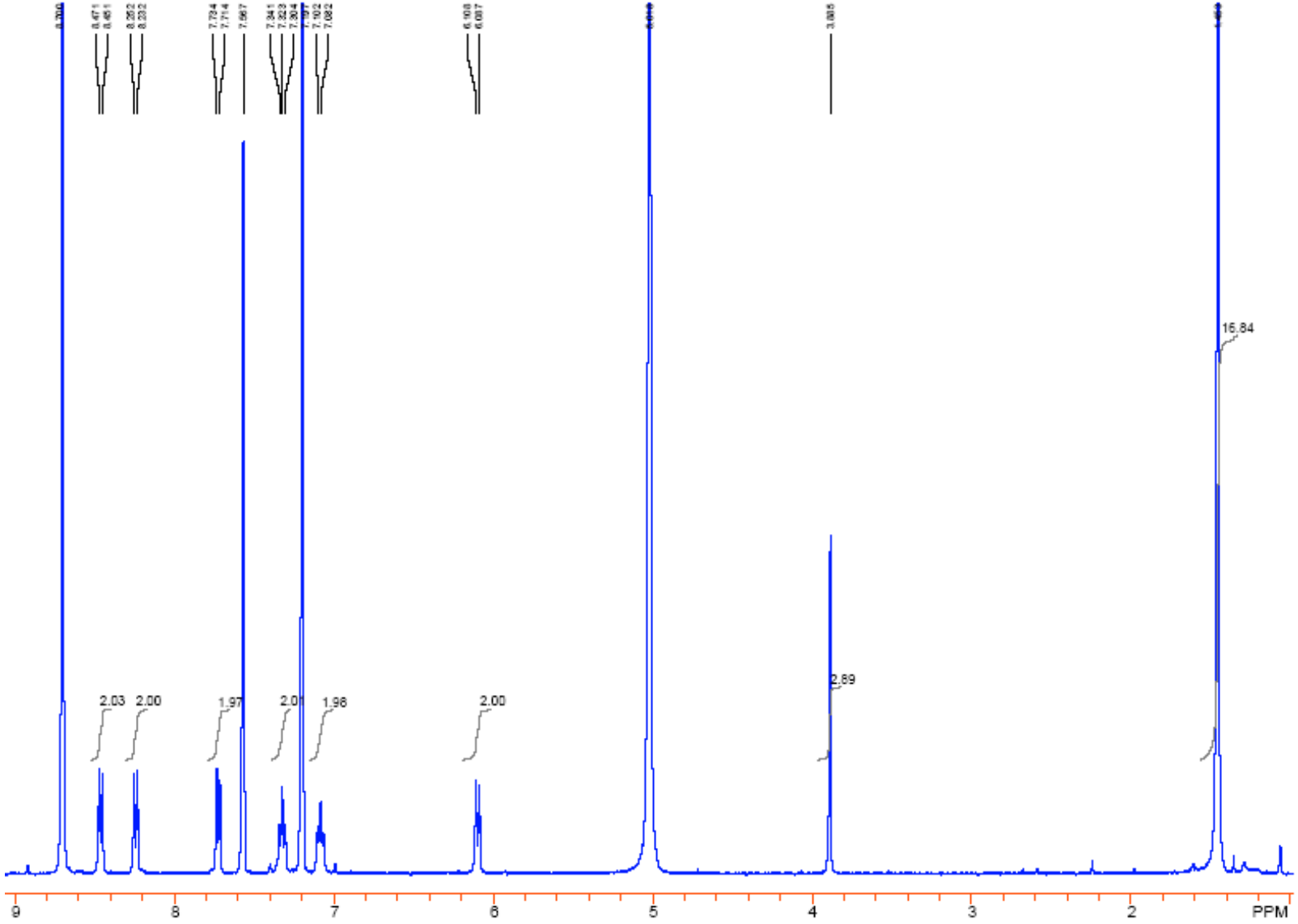


Figure S3. ^{1}H NMR spectrum of Zn-**2d** (MLX) in pyridine-d_5. (An excess of $ZnCl_2$ is added to a sample of ML_2.)

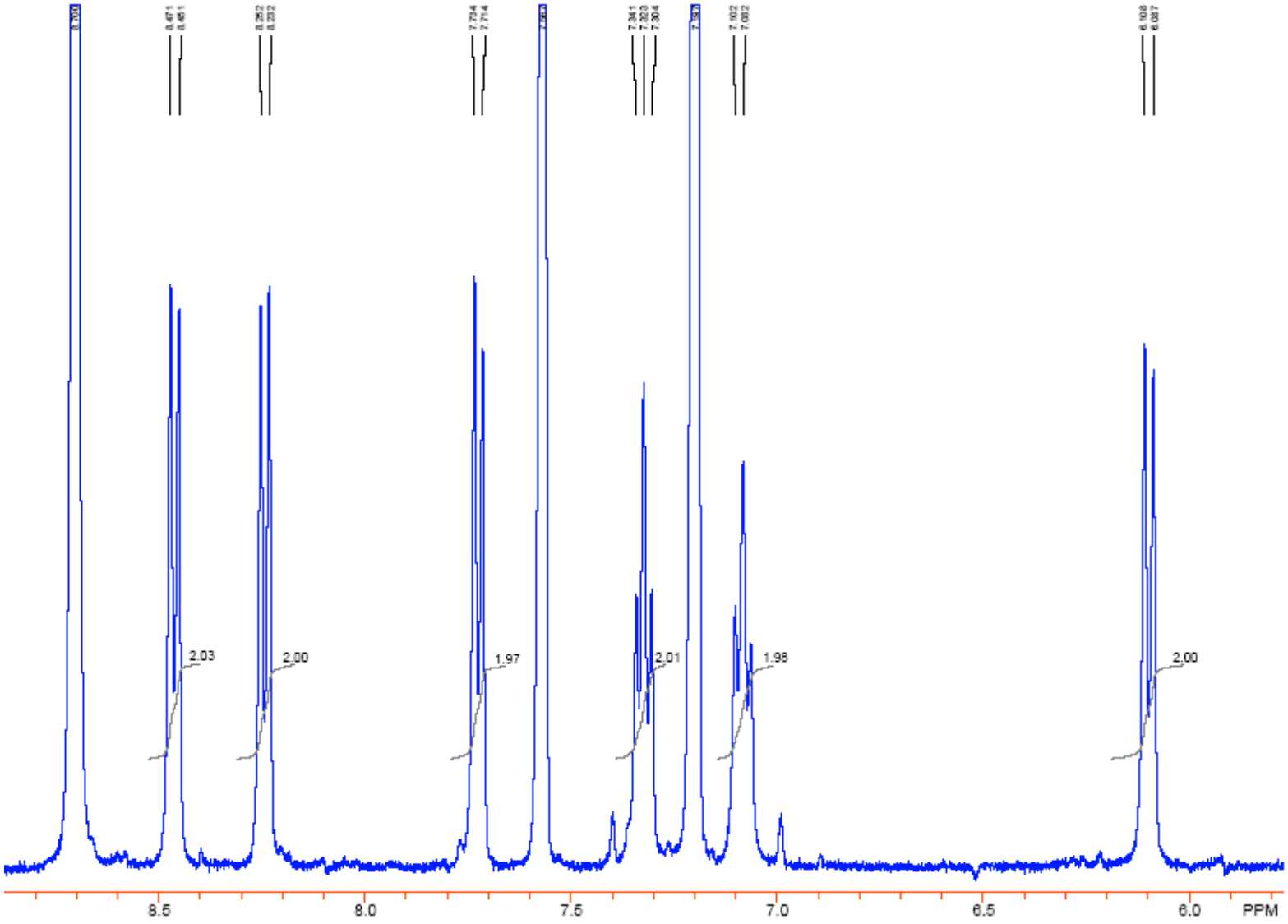


Figure S3a. ^{1}H NMR spectrum of Zn-**2d** (MLX) - aromatic region.

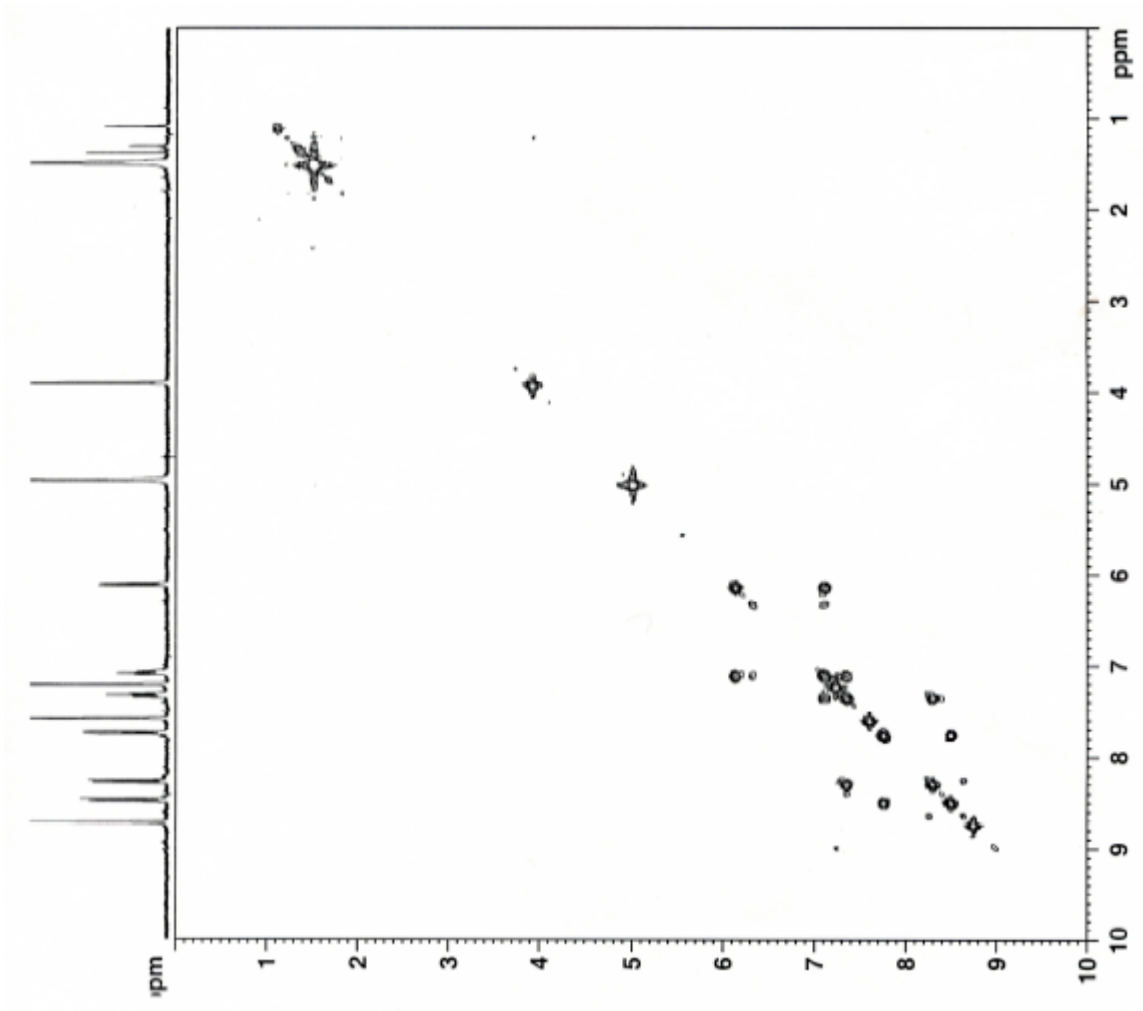


Figure S4. ^{1}H-^{1}H COSY NMR spectrum of Zn-**2d** (MLX) in pyridine-d_5.

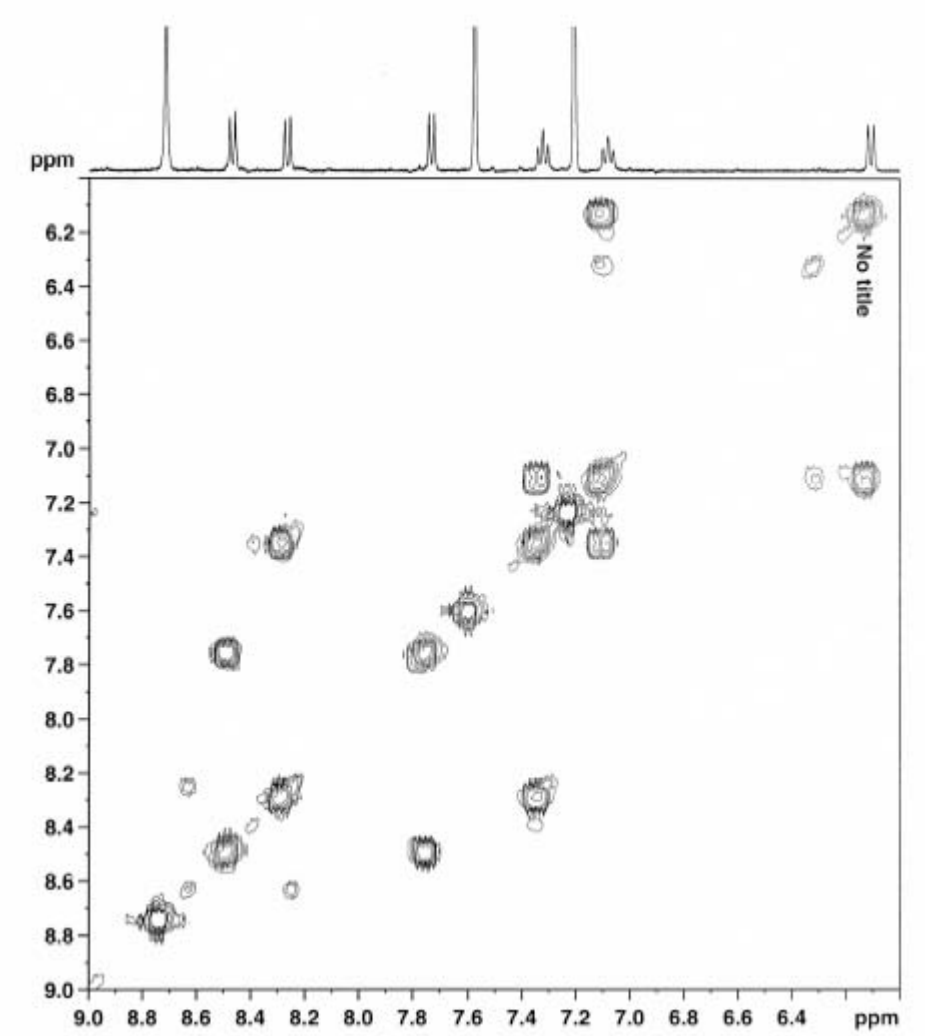


Figure S4a. ^{1}H-^{1}H COSY NMR spectrum of Zn-**2d** (MLX) in pyridine-d_5. - aromatic region.

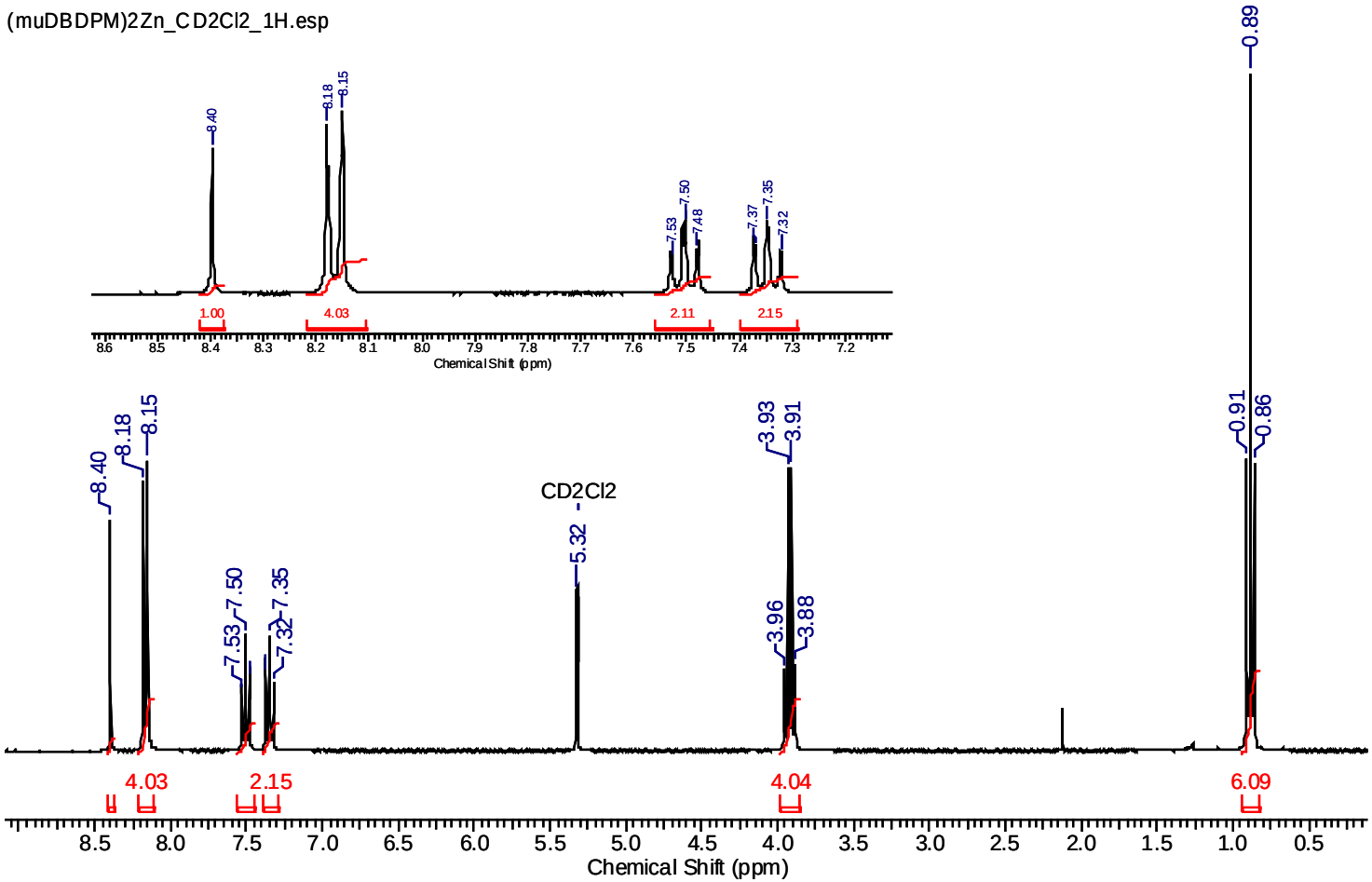


Figure S6. ^{1}H NMR spectrum of Zn-**2a** (ML_2) in CD_2Cl_2.

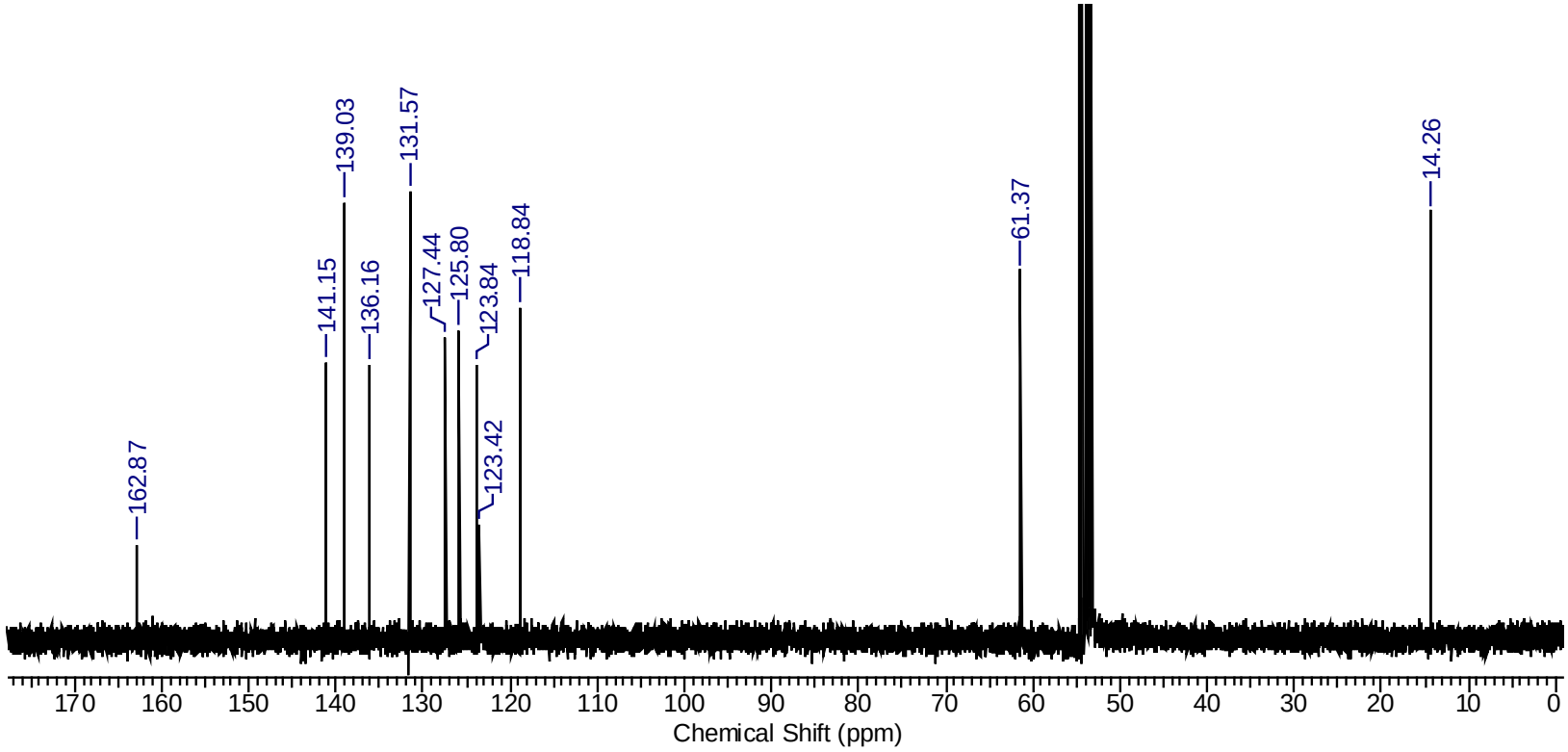


Figure S7. ^{13}C NMR spectrum of Zn-**2a** (ML_2) in CD_2Cl_2.

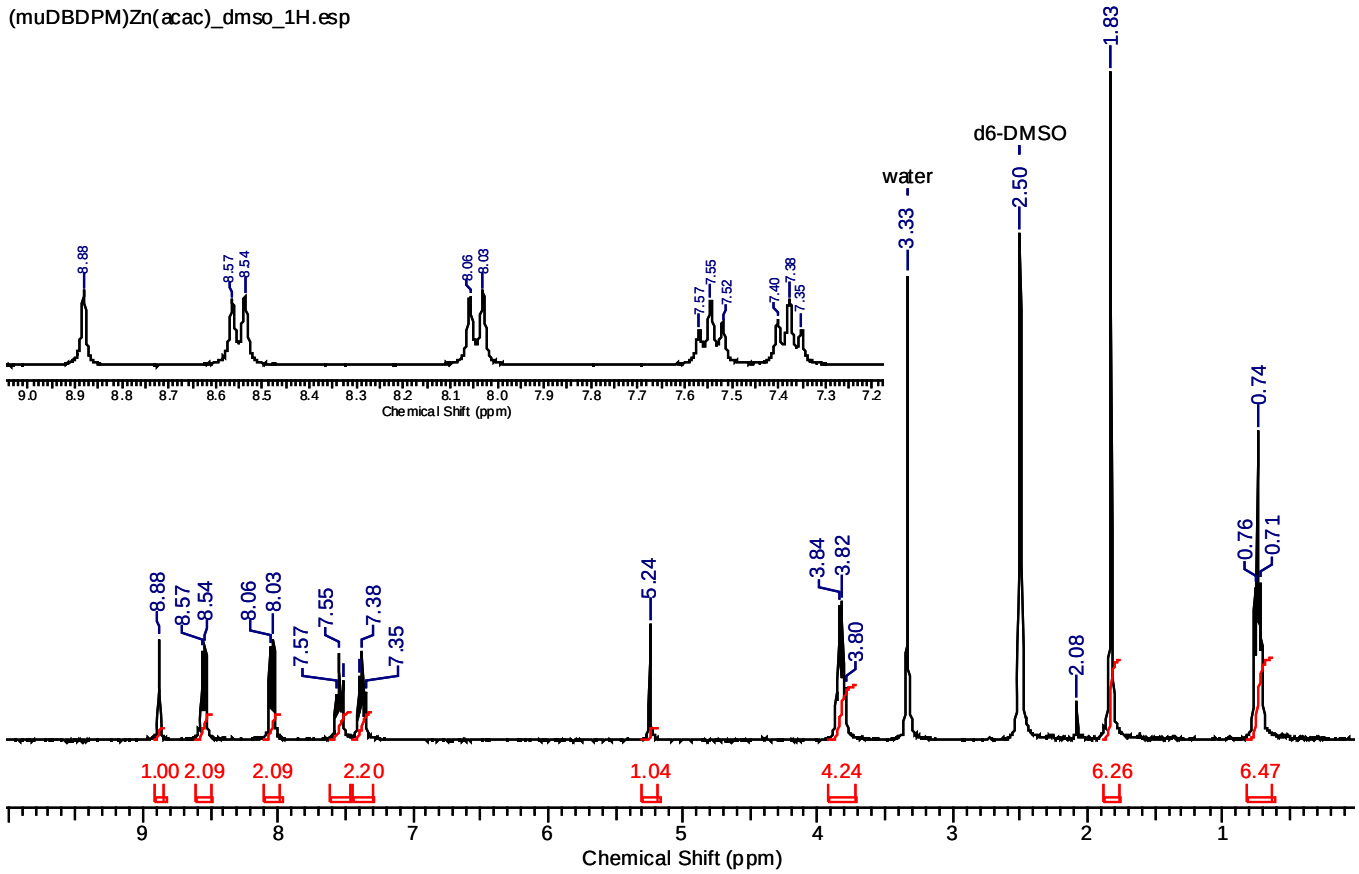


Figure S8. ^{1}H NMR spectrum of Zn-**2a**(acac) (MLX) in dmso-d_6.

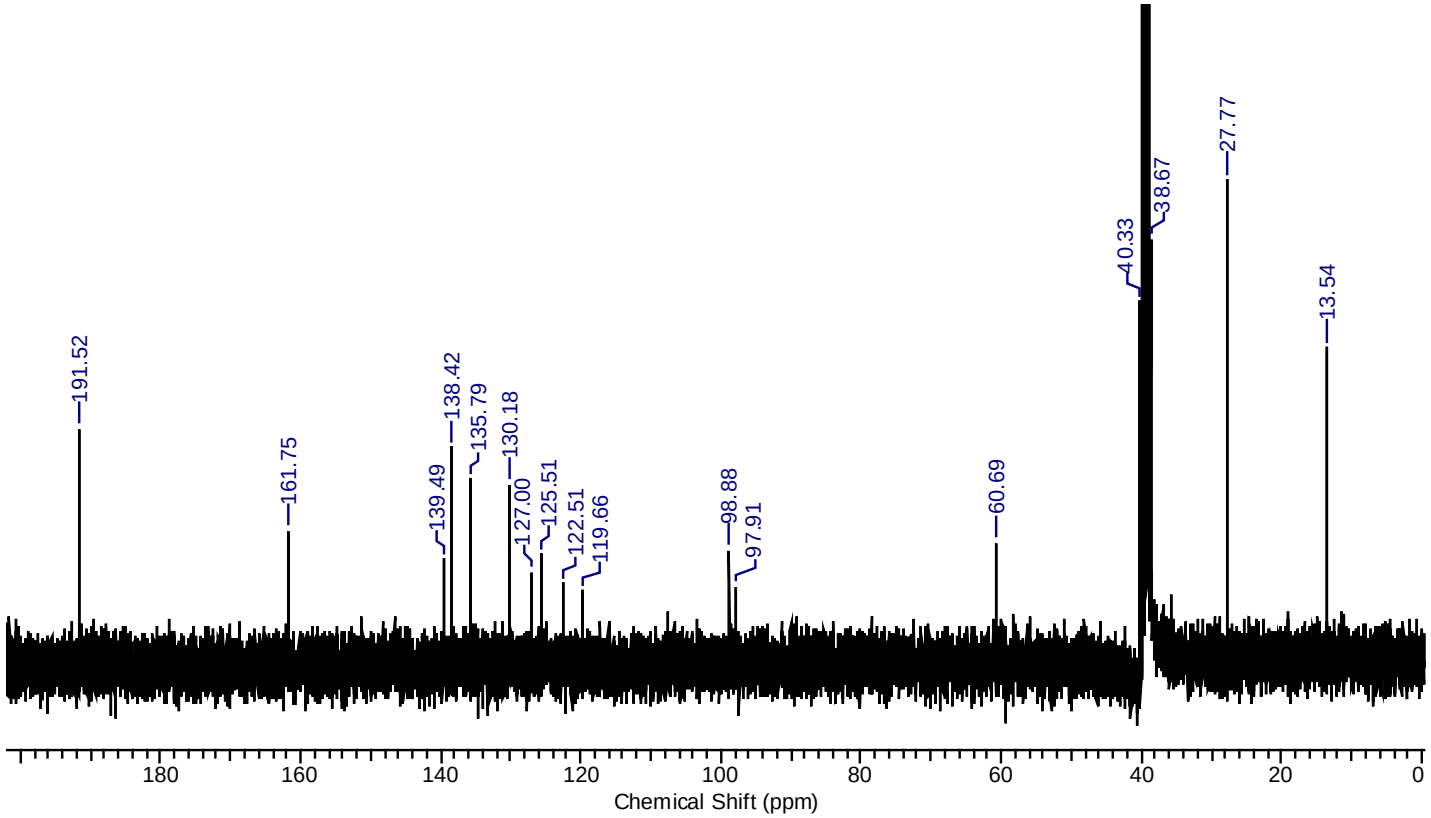


Figure S9. ^{13}C NMR spectrum of Zn-**2a**(acac) (MLX) in dmso-d_6.

IV. Interconversion between ML_2 and MLX

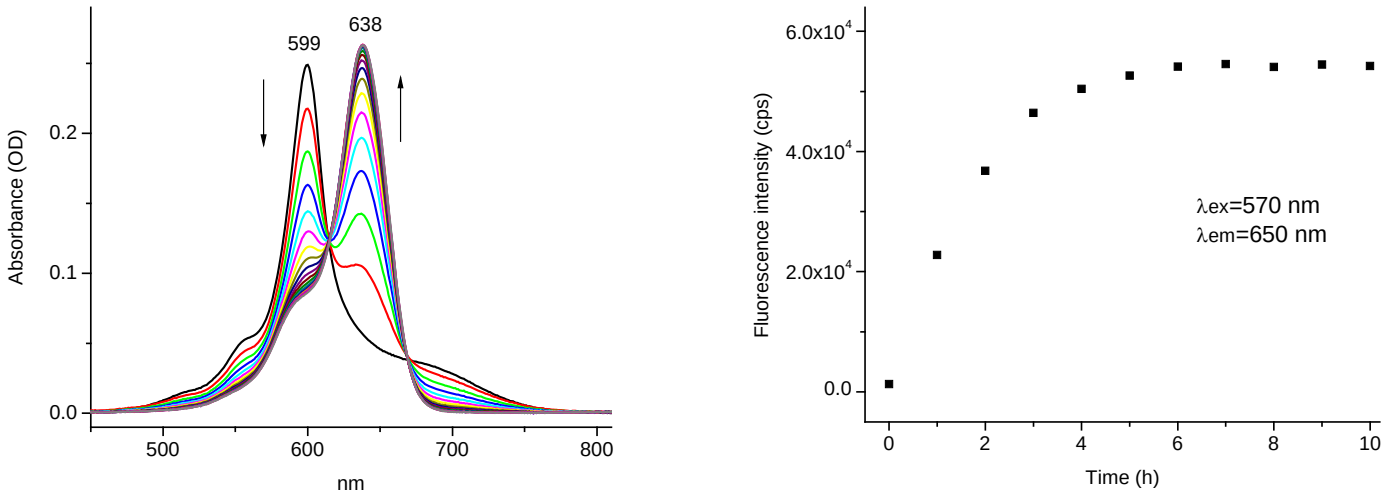


Figure S10. Changes in the absorption spectra (left) and in the fluorescence signal at 650 nm (λ_{ex}=570 nm) (right) upon addition of $ZnCl_2$ to Zn-**2d** (ML_2) in pyridine. The absorption and fluorescence data were recorded using different samples.

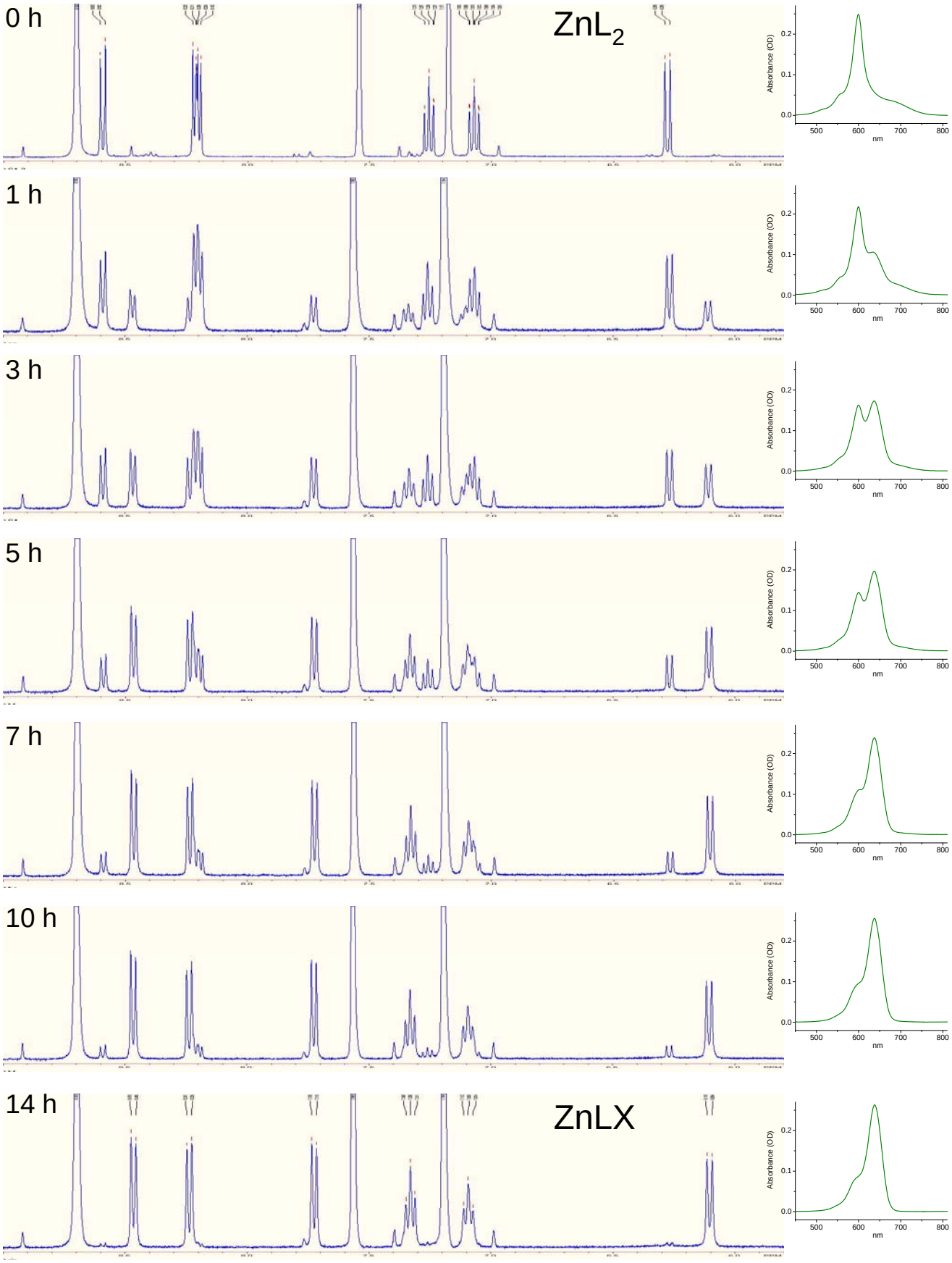
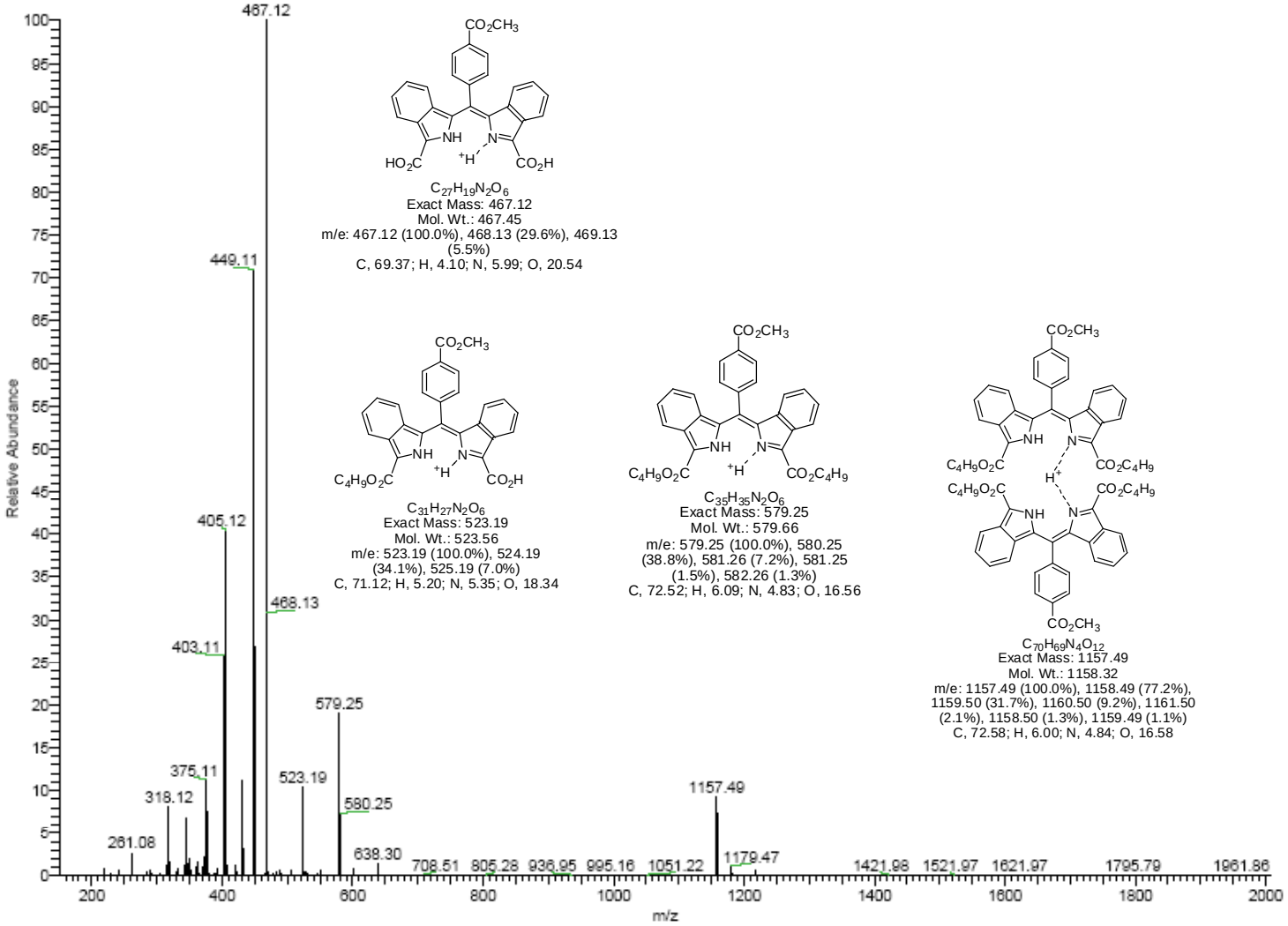


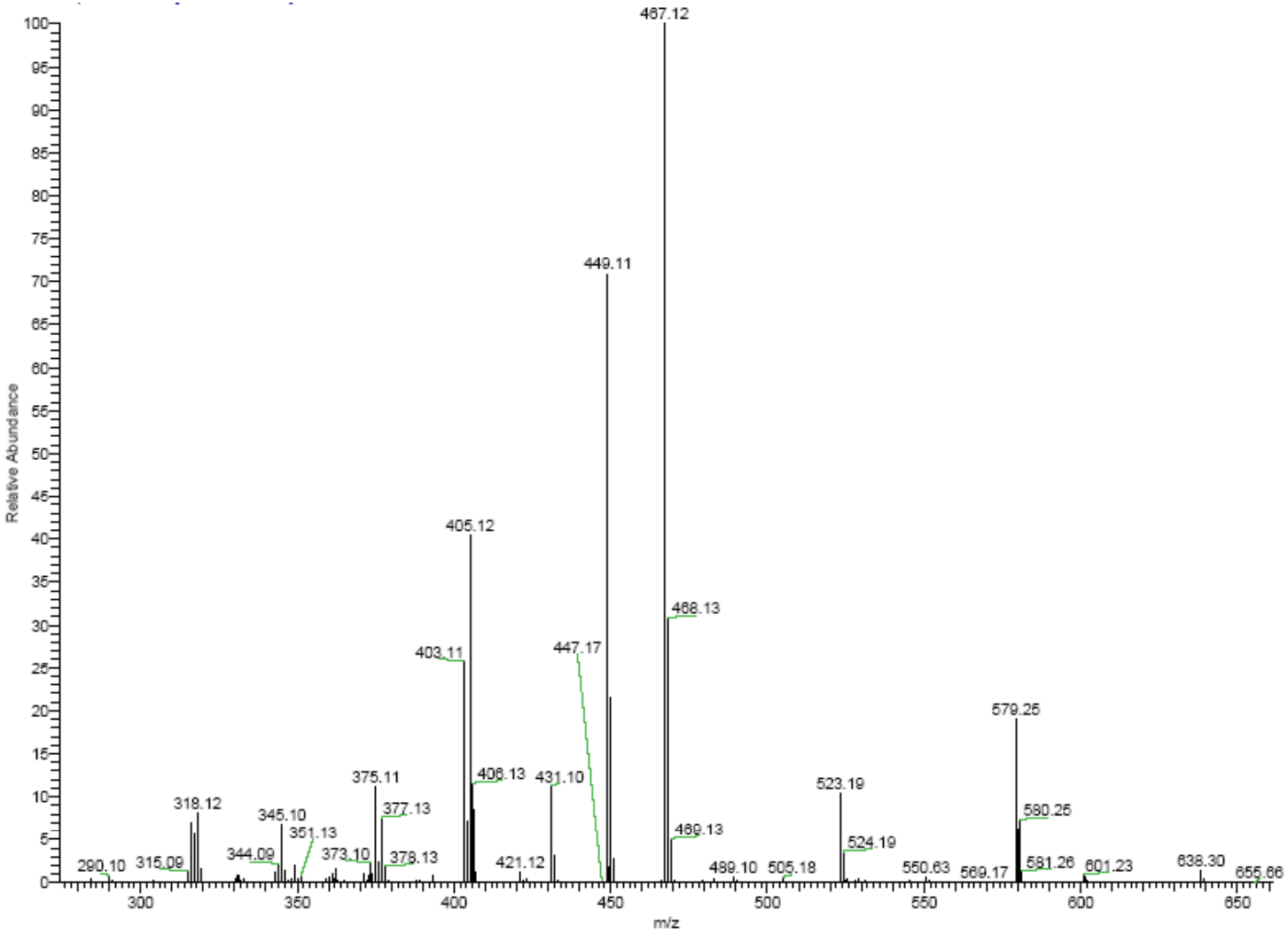
Figure S11. Changes in ^{1}H NMR spectra (aromatic region) and the absorption spectra (right) upon addition of $ZnCl_2$ to Zn-**2d** (ML_2) in pyridine. The NMR and absorption data were recorded using different samples.

V. High-resolution mass-spectroscopy data

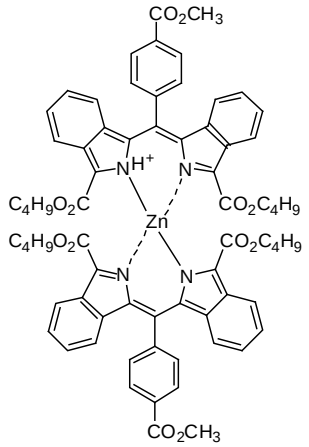
Note: The structures of the fragmentation ions are not proven, but merely are based on brutto formulaes suggested by the mass-spec software. These structures should not be considered as a proof of molecular identity.

Dipyrrin **2d**

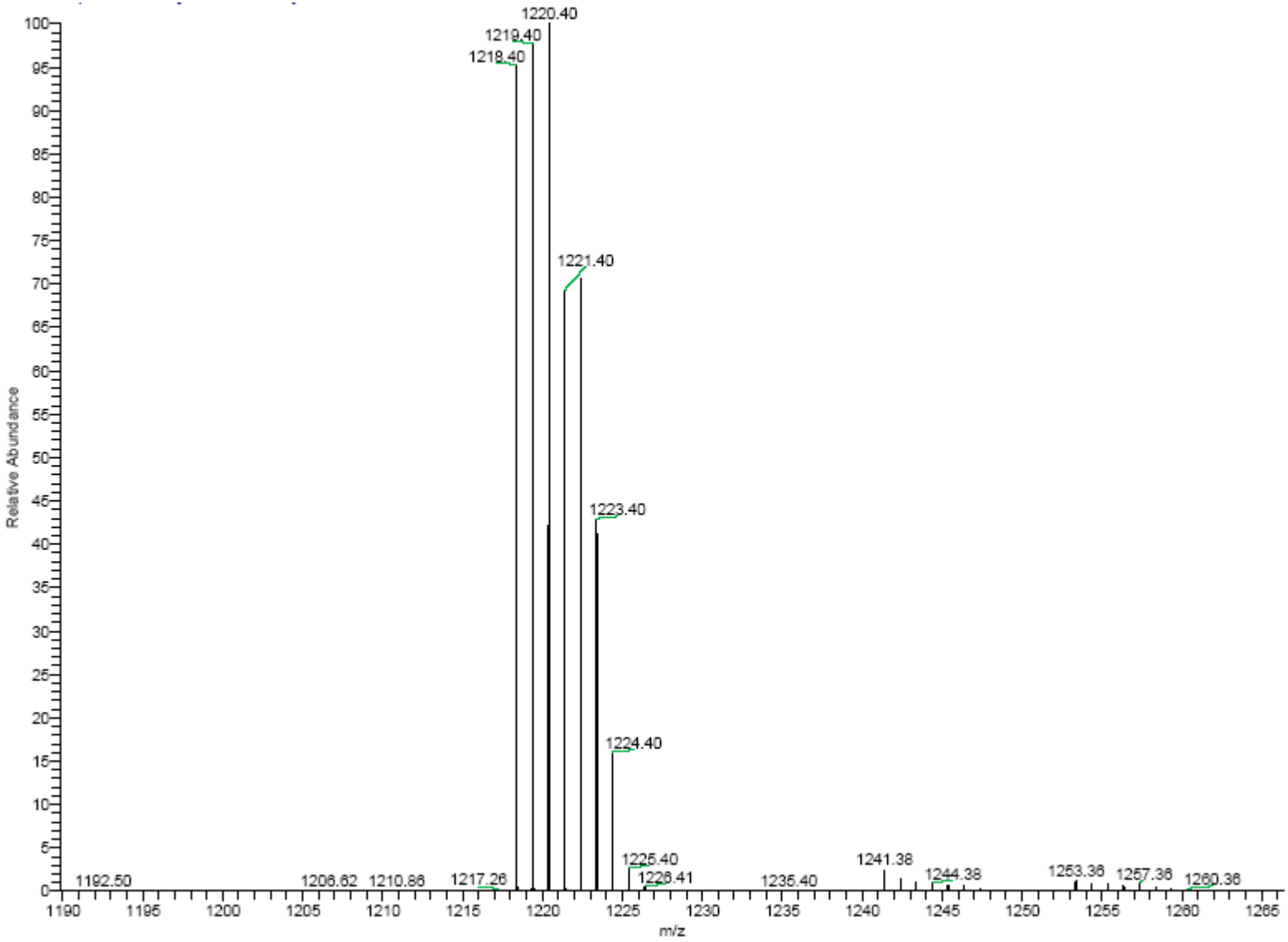


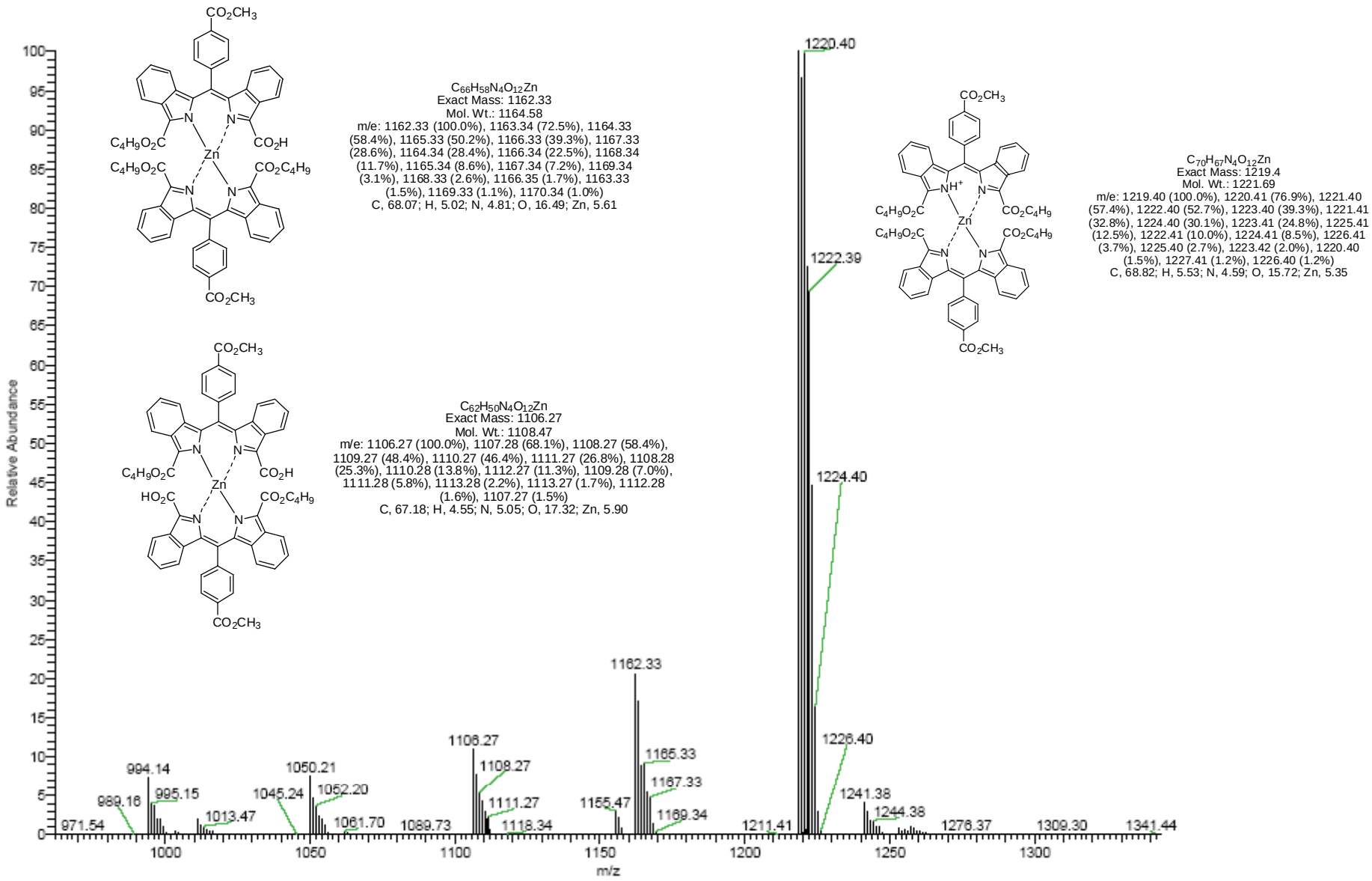

Relative Abundance
m/z
467.12
449.11
405.12
468.13
403.11
447.17
579.25
406.13
431.10
375.11
523.19
377.13
580.25
318.12
345.10
469.13
351.13
524.19
290.10
315.09
344.09
373.10
378.13
421.12
489.10
505.18
550.63
569.17
581.26
601.23
638.30
655.66

Zn-**2d** (ML_2)

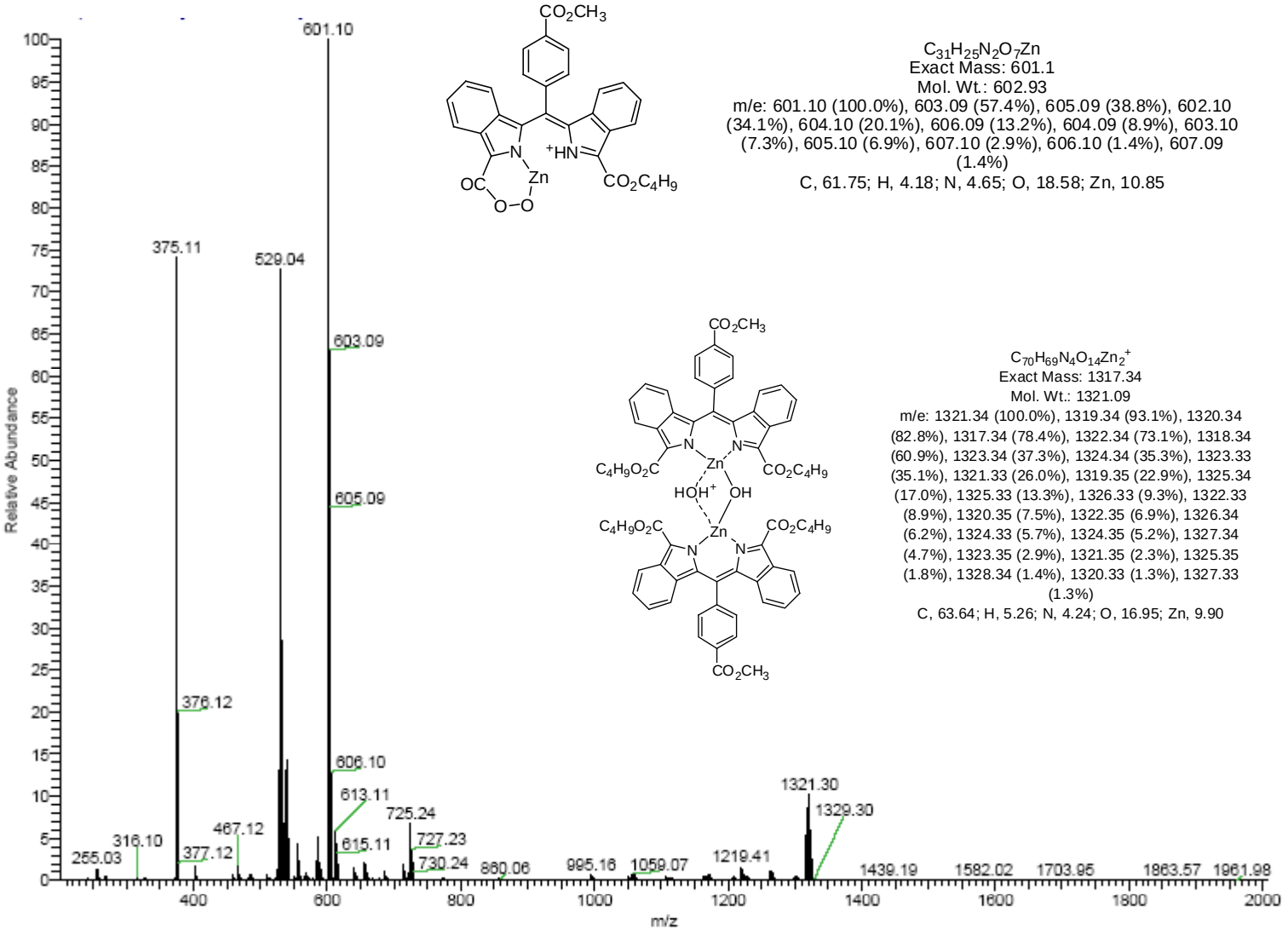


$C_{70}H_{67}N_4O_{12}Zn$
Exact Mass: 1219.4
Mol. Wt.: 1221.69
m/e: 1219.40 (100.0%), 1220.41 (76.9%), 1221.40 (57.4%), 1222.40 (52.7%), 1223.40 (39.3%), 1221.41 (32.8%), 1224.40 (30.1%), 1223.41 (24.8%), 1225.41 (12.5%), 1222.41 (10.0%), 1224.41 (8.5%), 1226.41 (3.7%), 1225.40 (2.7%), 1223.42 (2.0%), 1220.40 (1.5%), 1227.41 (1.2%), 1226.40 (1.2%)
C, 68.82; H, 5.53; N, 4.59; O, 15.72; Zn, 5.35


1220.40
1219.40
1218.40
1221.40
1223.40
1224.40
1225.40
1226.41
1241.38
1244.38
1253.36
1257.36
1260.36
1192.50
1206.62
1210.86
1217.26
1235.40
Relative Abundance
m/z

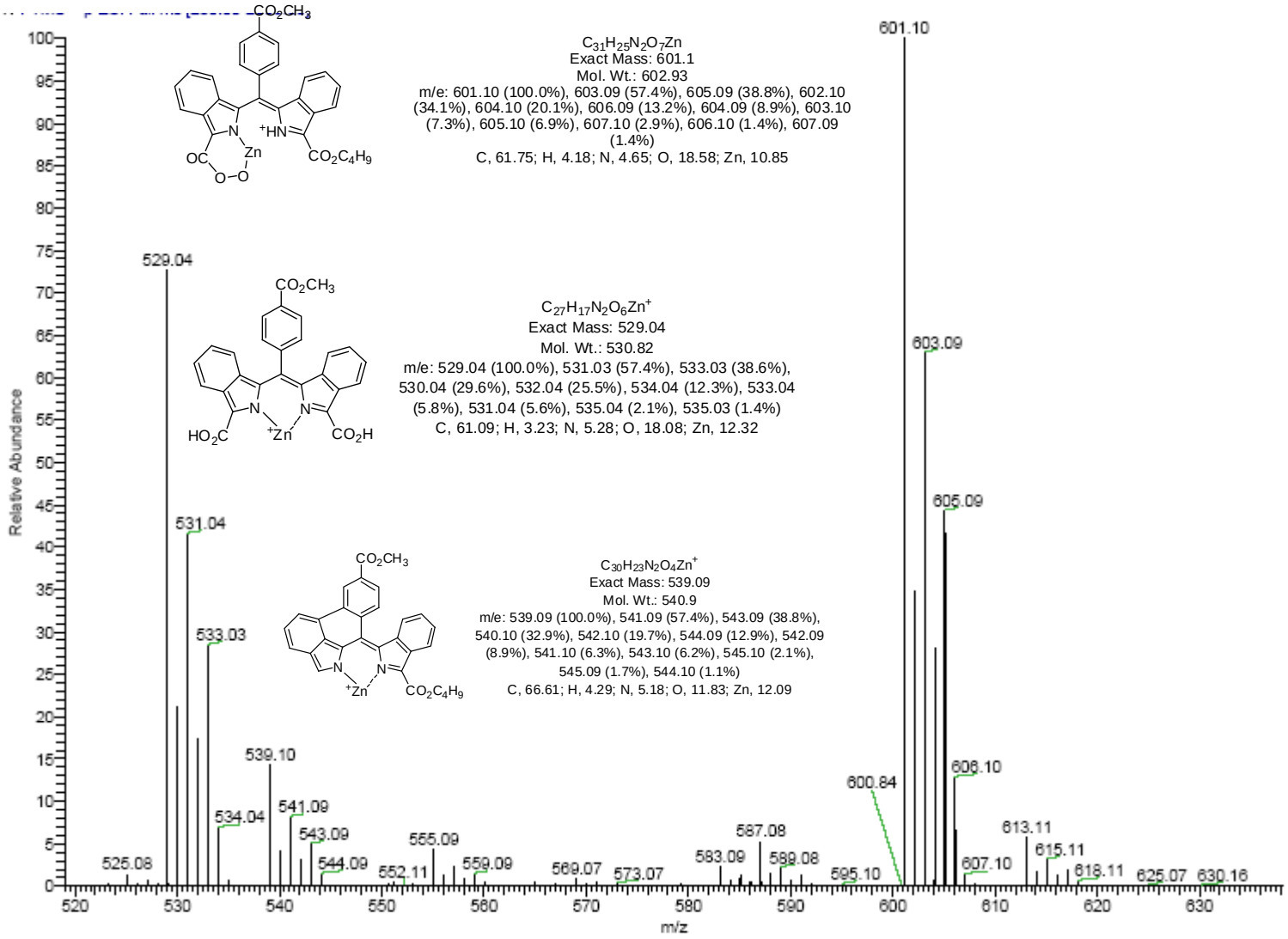


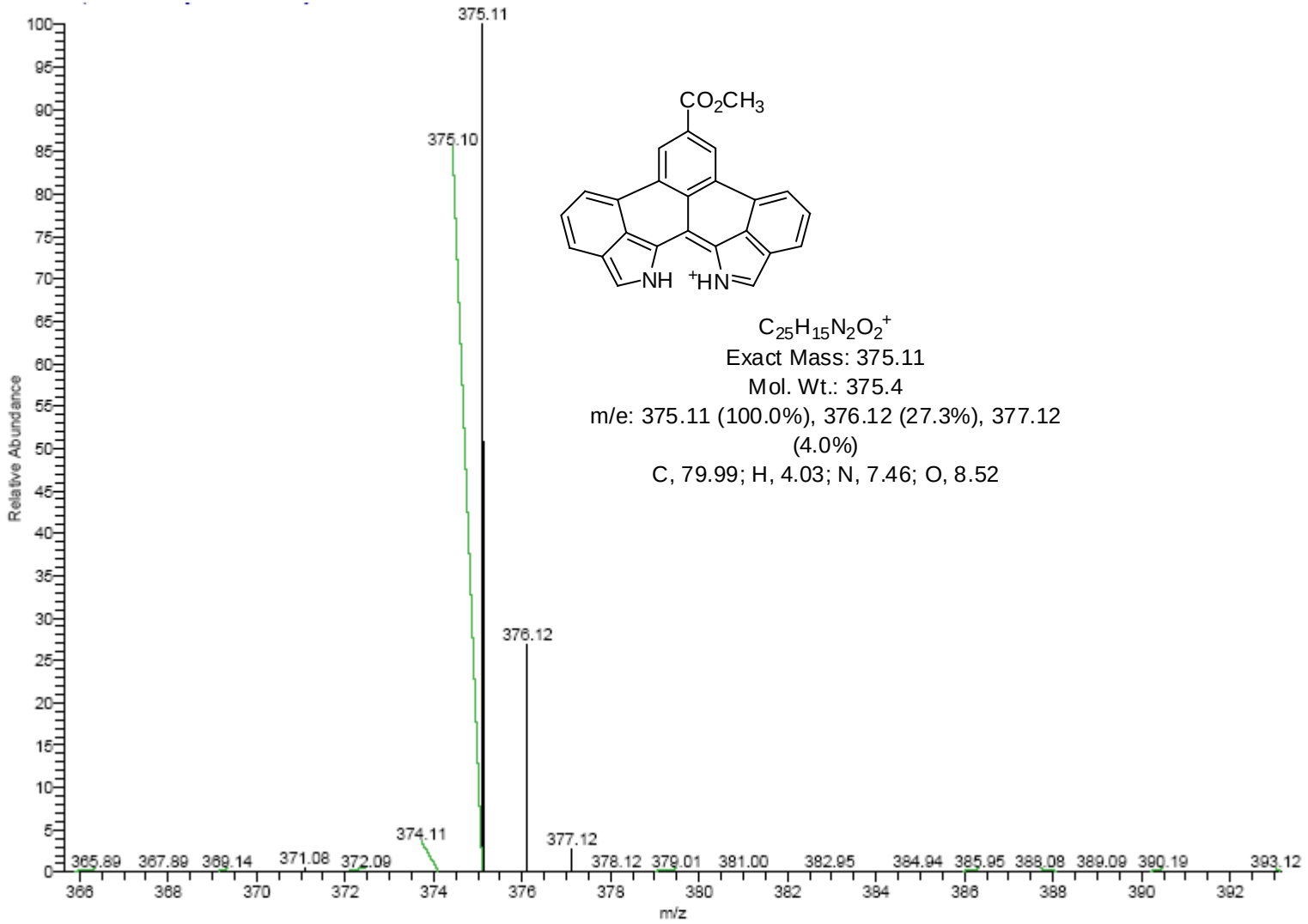
Zn-**2d** (MLX) ($ZnCl_2$ was added to **2d** in THF)



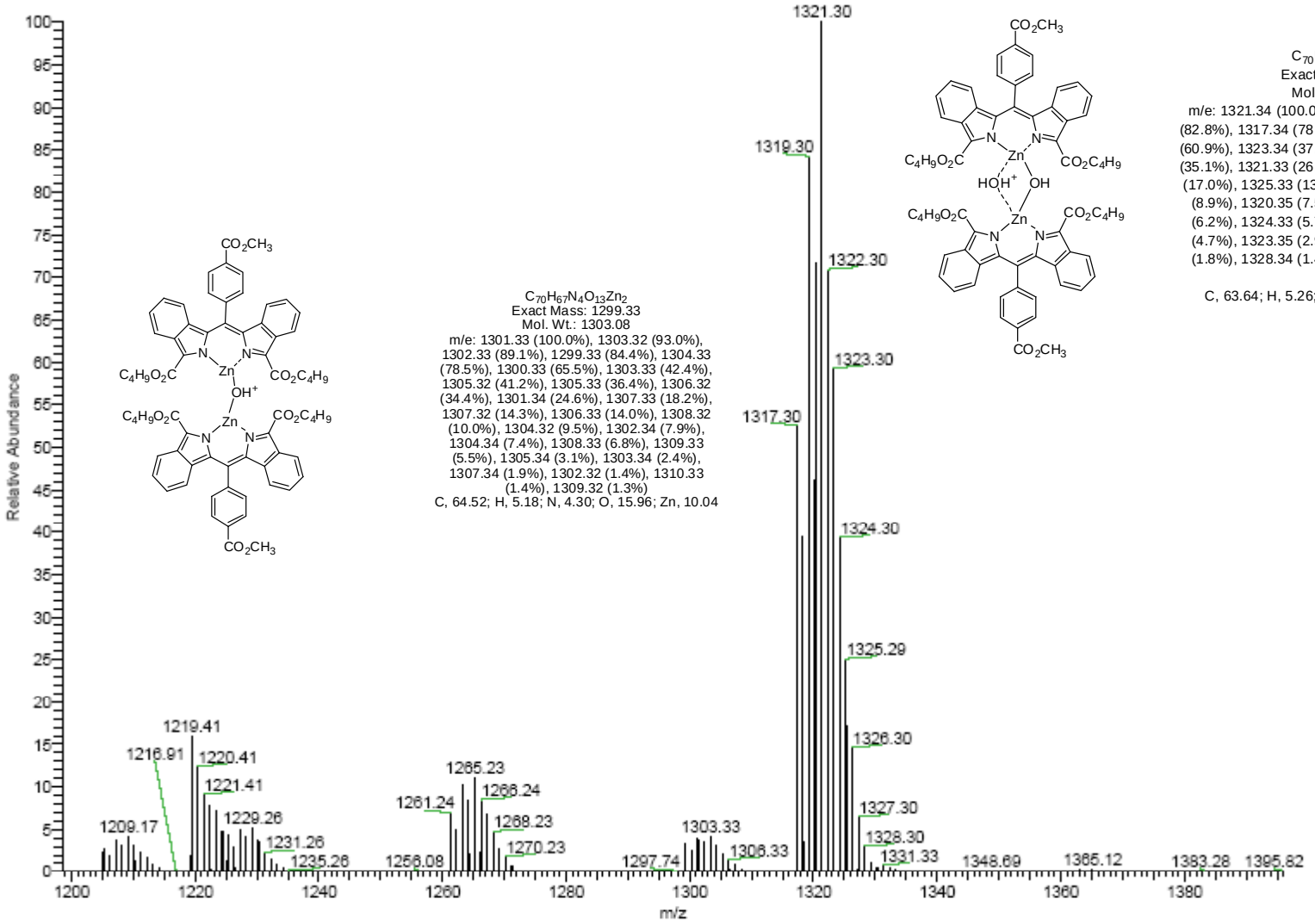
$C_{31}H_{25}N_2O_7Zn$
Exact Mass: 601.1
Mol. Wt.: 602.93
m/e: 601.10 (100.0%), 603.09 (57.4%), 605.09 (38.8%), 602.10 (34.1%), 604.10 (20.1%), 606.09 (13.2%), 604.09 (8.9%), 603.10 (7.3%), 605.10 (6.9%), 607.10 (2.9%), 606.10 (1.4%), 607.09 (1.4%)
C, 61.75; H, 4.18; N, 4.65; O, 18.58; Zn, 10.85

$C_{70}H_{69}N_4O_{14}Zn_2^+$
Exact Mass: 1317.34
Mol. Wt.: 1321.09
m/e: 1321.34 (100.0%), 1319.34 (93.1%), 1320.34 (82.8%), 1317.34 (78.4%), 1322.34 (73.1%), 1318.34 (60.9%), 1323.34 (37.3%), 1324.34 (35.3%), 1323.33 (35.1%), 1321.33 (26.0%), 1319.35 (22.9%), 1325.34 (17.0%), 1325.33 (13.3%), 1326.33 (9.3%), 1322.33 (8.9%), 1320.35 (7.5%), 1322.35 (6.9%), 1326.34 (6.2%), 1324.33 (5.7%), 1324.35 (5.2%), 1327.34 (4.7%), 1323.35 (2.9%), 1321.35 (2.3%), 1325.35 (1.8%), 1328.34 (1.4%), 1320.33 (1.3%), 1327.33 (1.3%)
C, 63.64; H, 5.26; N, 4.24; O, 16.95; Zn, 9.90

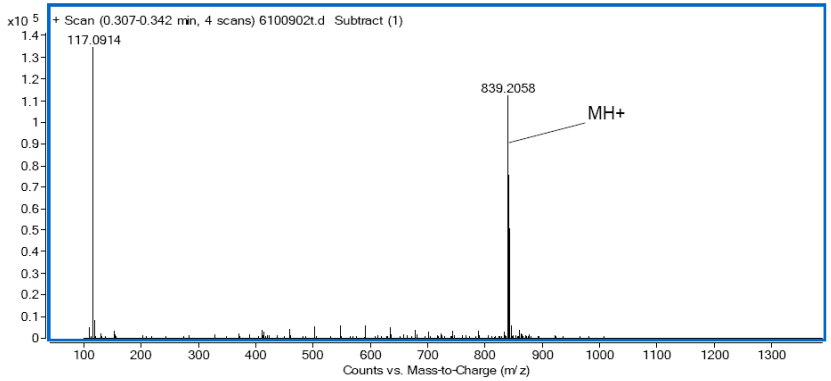

$C_{31}H_{25}N_2O_7Zn$
Exact Mass: 601.1
Mol. Wt.: 602.93
m/e: 601.10 (100.0%), 603.09 (57.4%), 605.09 (38.8%), 602.10 (34.1%), 604.10 (20.1%), 606.09 (13.2%), 604.09 (8.9%), 603.10 (7.3%), 605.10 (6.9%), 607.10 (2.9%), 606.10 (1.4%), 607.09 (1.4%)
C, 61.75; H, 4.18; N, 4.65; O, 18.58; Zn, 10.85
$C_{27}H_{17}N_2O_6Zn^+$
Exact Mass: 529.04
Mol. Wt.: 530.82
m/e: 529.04 (100.0%), 531.03 (57.4%), 533.03 (38.6%), 530.04 (29.6%), 532.04 (25.5%), 534.04 (12.3%), 533.04 (5.8%), 531.04 (5.6%), 535.04 (2.1%), 535.03 (1.4%)
C, 61.09; H, 3.23; N, 5.28; O, 18.08; Zn, 12.32
$C_{30}H_{23}N_2O_4Zn^+$
Exact Mass: 539.09
Mol. Wt.: 540.9
m/e: 539.09 (100.0%), 541.09 (57.4%), 543.09 (38.8%), 540.10 (32.9%), 542.10 (19.7%), 544.09 (12.9%), 542.09 (8.9%), 541.10 (6.3%), 543.10 (6.2%), 545.10 (2.1%), 545.09 (1.7%), 544.10 (1.1%)
C, 66.61; H, 4.29; N, 5.18; O, 11.83; Zn, 12.09
Relative Abundance
m/z
601.10
603.09
605.09
529.04
531.04
533.03
539.10
541.09
534.04
543.09
544.09
555.09
525.08
552.11
559.09
569.07
573.07
583.09
587.08
589.08
595.10
600.84
606.10
607.10
613.11
615.11
618.11
625.07
630.16

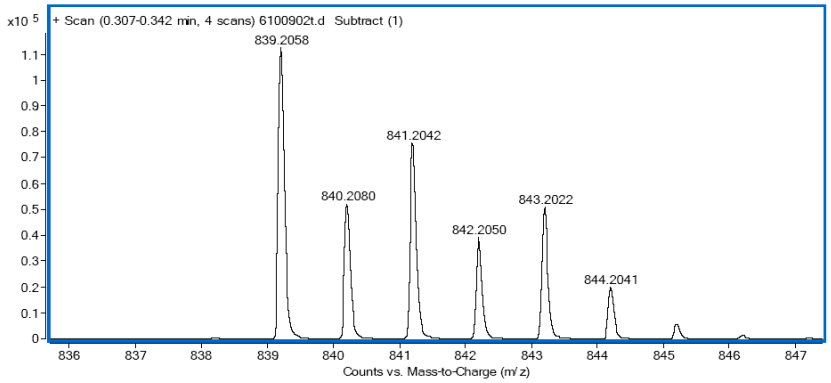


$C_{25}H_{15}N_2O_2^+$
Exact Mass: 375.11
Mol. Wt.: 375.4
m/e: 375.11 (100.0%), 376.12 (27.3%), 377.12 (4.0%)
C, 79.99; H, 4.03; N, 7.46; O, 8.52


Relative Abundance
m/z
1321.30
1319.30
1322.30
1323.30
1317.30
1324.30
1325.29
1326.30
1327.30
1328.30
1331.33
1219.41
1216.91
1220.41
1221.41
1229.26
1209.17
1231.26
1235.26
1265.23
1266.24
1261.24
1268.23
1270.23
1256.08
1303.33
1306.33
1297.74
1348.69
1365.12
1383.28
1395.82
C70H67N4O13Zn2
Exact Mass: 1299.33
Mol. Wt.: 1303.08
m/e: 1301.33 (100.0%), 1303.32 (93.0%), 1302.33 (89.1%), 1299.33 (84.4%), 1304.33 (78.5%), 1300.33 (65.5%), 1303.33 (42.4%), 1305.32 (41.2%), 1305.33 (36.4%), 1306.32 (34.4%), 1301.34 (24.6%), 1307.33 (18.2%), 1307.32 (14.3%), 1306.33 (14.0%), 1308.32 (10.0%), 1304.32 (9.5%), 1302.34 (7.9%), 1304.34 (7.4%), 1308.33 (6.8%), 1309.33 (5.5%), 1305.34 (3.1%), 1303.34 (2.4%), 1307.34 (1.9%), 1302.32 (1.4%), 1310.33 (1.4%), 1309.32 (1.3%)
C, 64.52; H, 5.18; N, 4.30; O, 15.96; Zn, 10.04
C70H69N4O14Zn2+
Exact Mass: 1317.34
Mol. Wt.: 1321.09
m/e: 1321.34 (100.0%), 1319.34 (93.1%), 1320.34 (82.8%), 1317.34 (78.4%), 1322.34 (73.1%), 1318.34 (60.9%), 1323.34 (37.3%), 1324.34 (35.3%), 1323.33 (35.1%), 1321.33 (26.0%), 1319.35 (22.9%), 1325.34 (17.0%), 1325.33 (13.3%), 1326.33 (9.3%), 1322.33 (8.9%), 1320.35 (7.5%), 1322.35 (6.9%), 1326.34 (6.2%), 1324.33 (5.7%), 1324.35 (5.2%), 1327.34 (4.7%), 1323.35 (2.9%), 1321.35 (2.3%), 1325.35 (1.8%), 1328.34 (1.4%), 1320.33 (1.3%), 1327.33 (1.3%)
C, 63.64; H, 5.26; N, 4.24; O, 16.95; Zn, 9.90

Zn-**2a** (ML_2)

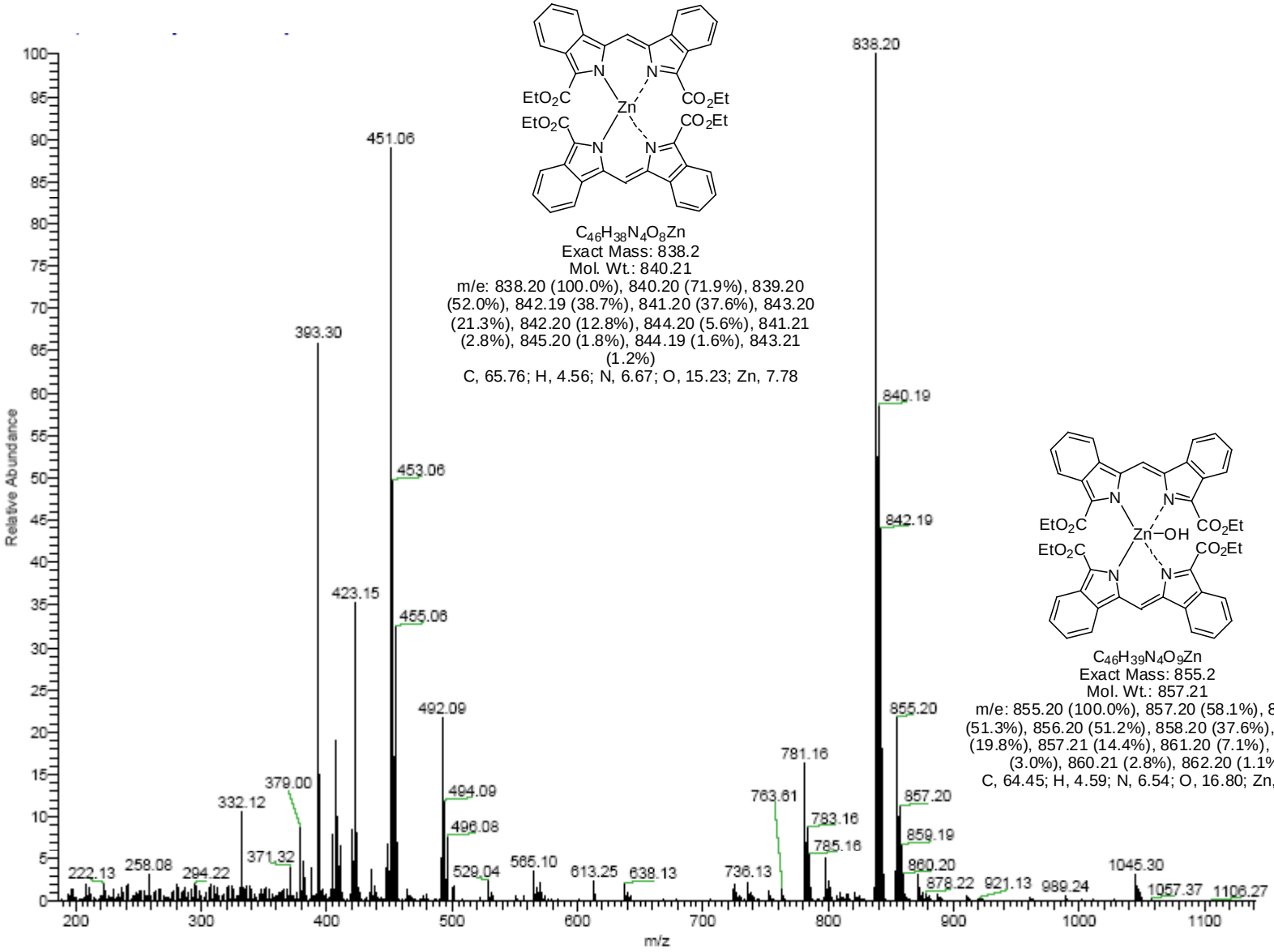




Measured Mass 839.2058

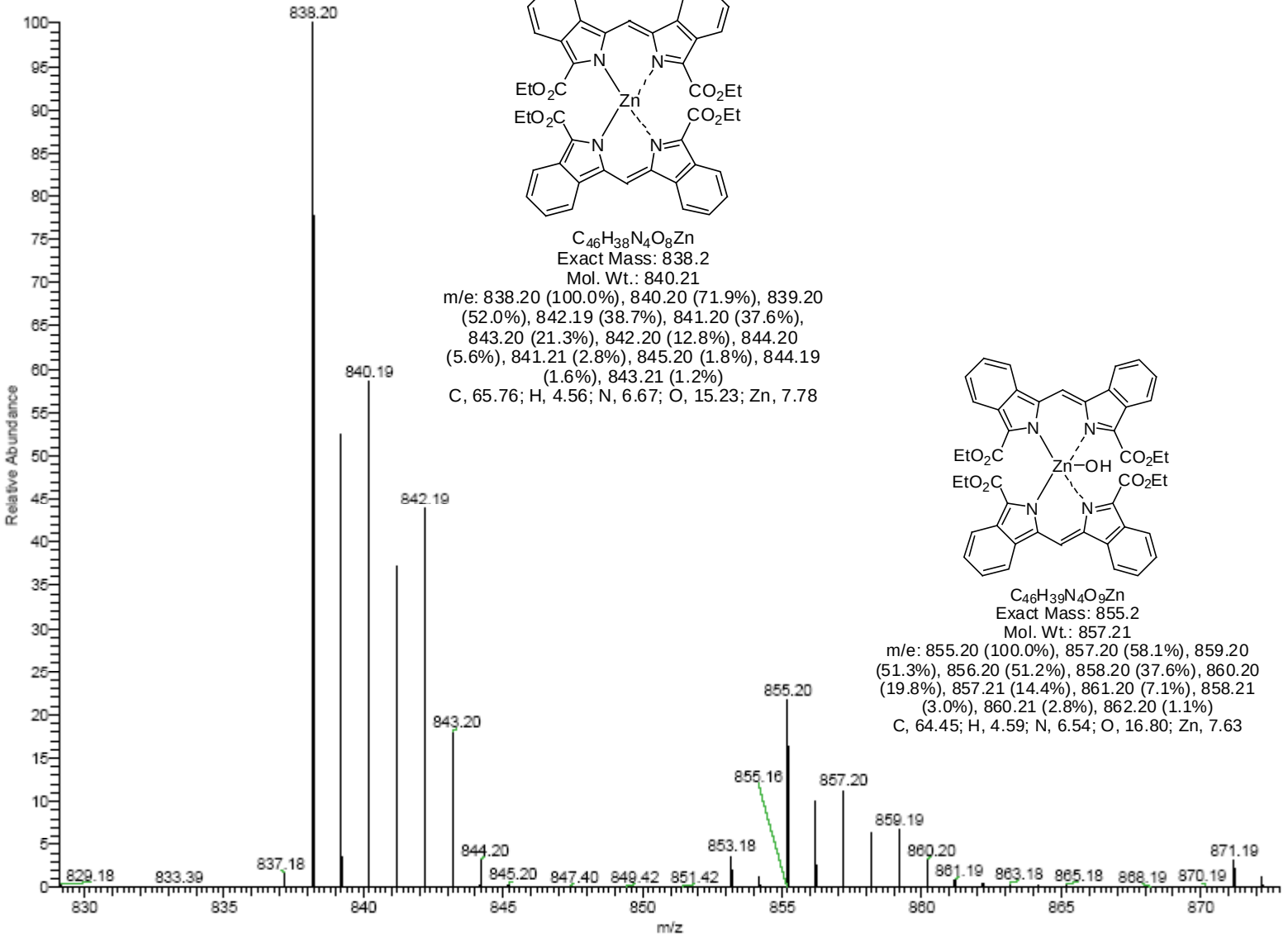
Element	Low Limit	High Limit
C	41	51
H	30	50
O	6	10
N	0	5
Zn	0	1

Formula	Calculated Mass	mDaError	ppmError	RDB
C46 H39 N4 O8 Zn	839.2054	0.4	0.5	29.5
C48 H41 N O9 Zn	839.2067	-0.9	-1.1	29
C51 H39 N2 O6 Zn	839.2094	-3.6	-4.3	33.5



$C_{46}H_{38}N_4O_8Zn$
Exact Mass: 838.2
Mol. Wt.: 840.21
m/e: 838.20 (100.0%), 840.20 (71.9%), 839.20 (52.0%), 842.19 (38.7%), 841.20 (37.6%), 843.20 (21.3%), 842.20 (12.8%), 844.20 (5.6%), 841.21 (2.8%), 845.20 (1.8%), 844.19 (1.6%), 843.21 (1.2%)
C, 65.76; H, 4.56; N, 6.67; O, 15.23; Zn, 7.78

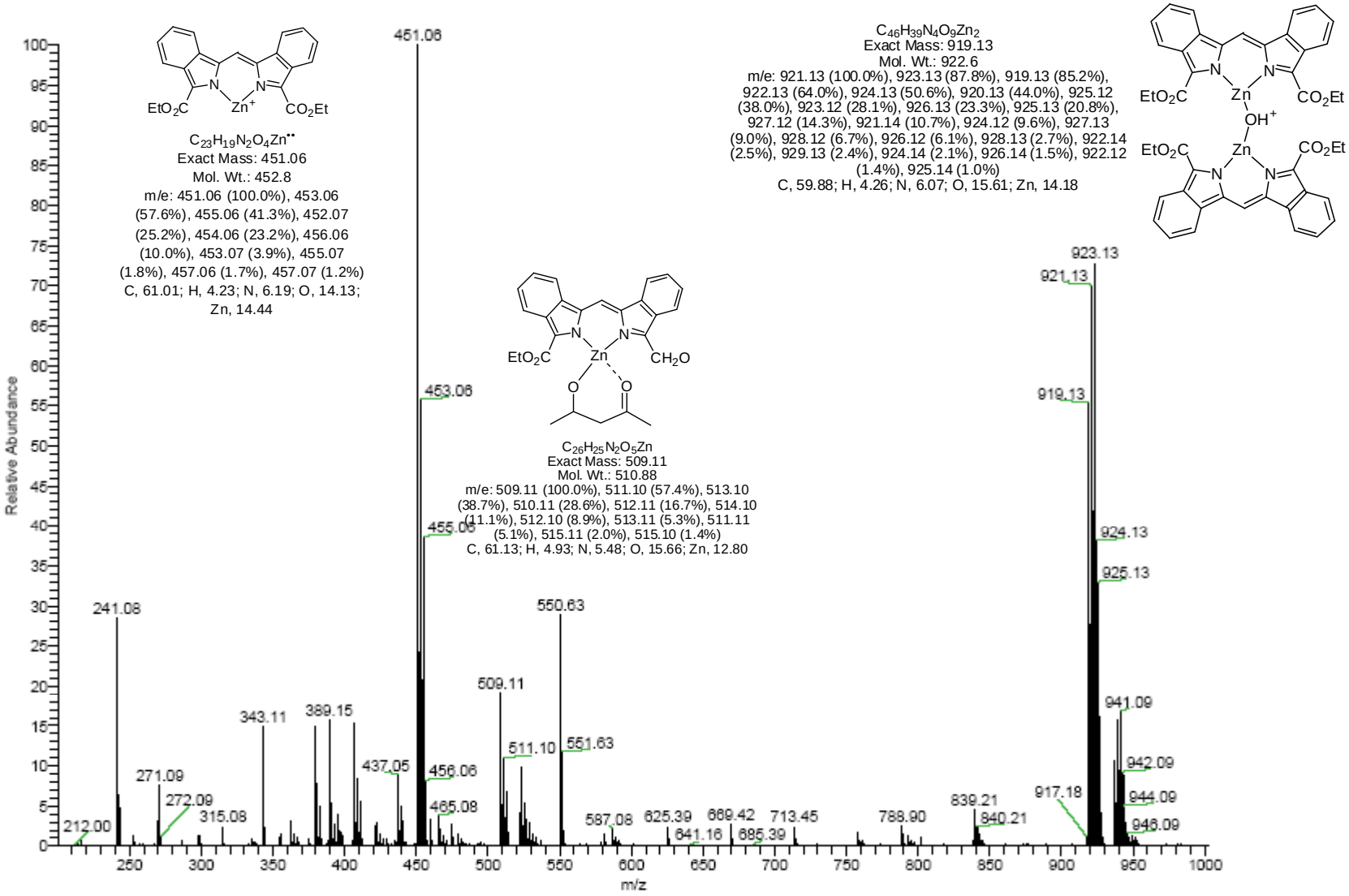
$C_{46}H_{39}N_4O_9Zn$
Exact Mass: 855.2
Mol. Wt.: 857.21
m/e: 855.20 (100.0%), 857.20 (58.1%), 859.20 (51.3%), 856.20 (51.2%), 858.20 (37.6%), 860.20 (19.8%), 857.21 (14.4%), 861.20 (7.1%), 858.21 (3.0%), 860.21 (2.8%), 862.20 (1.1%)
C, 64.45; H, 4.59; N, 6.54; O, 16.80; Zn, 7.63

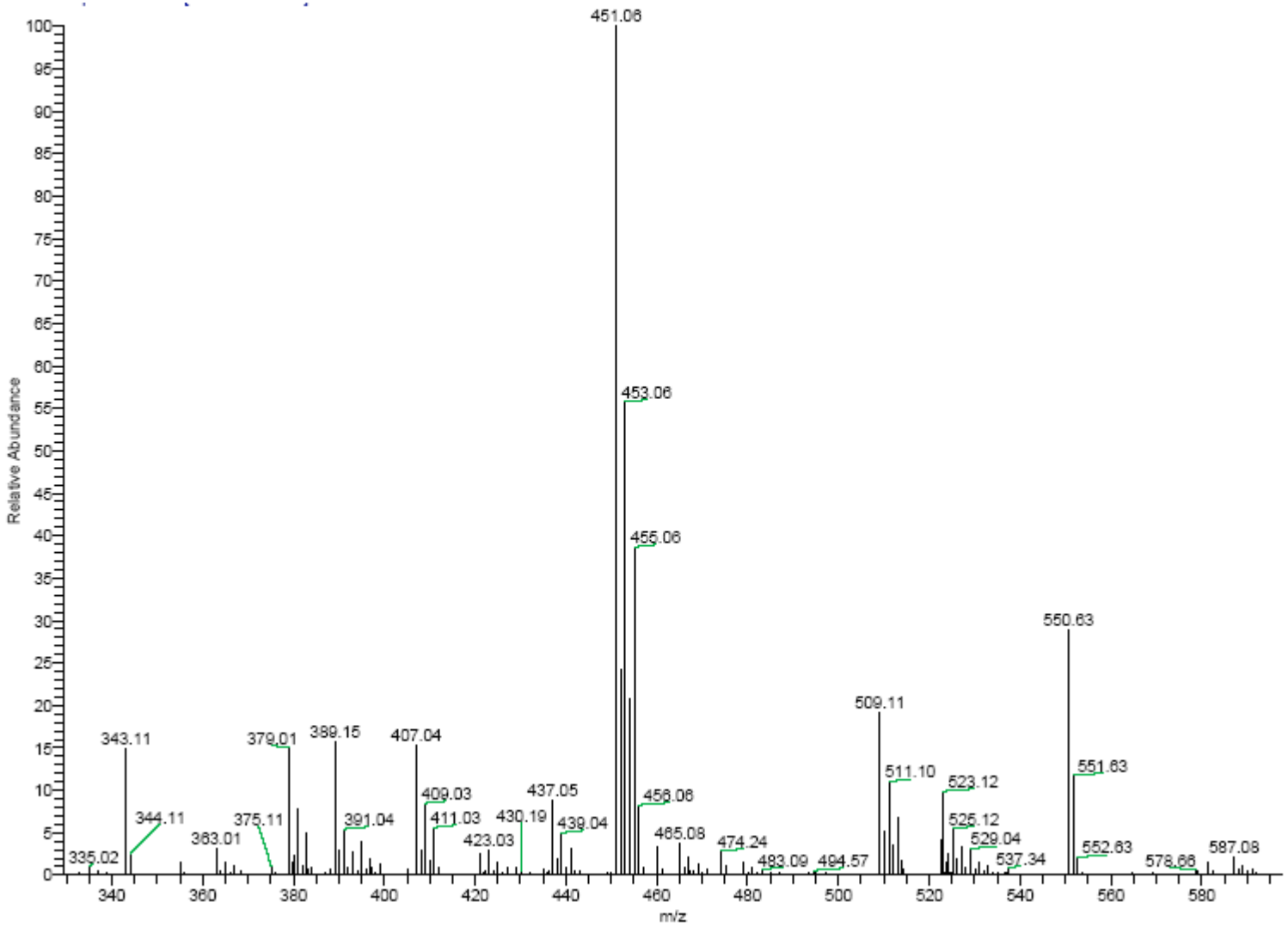


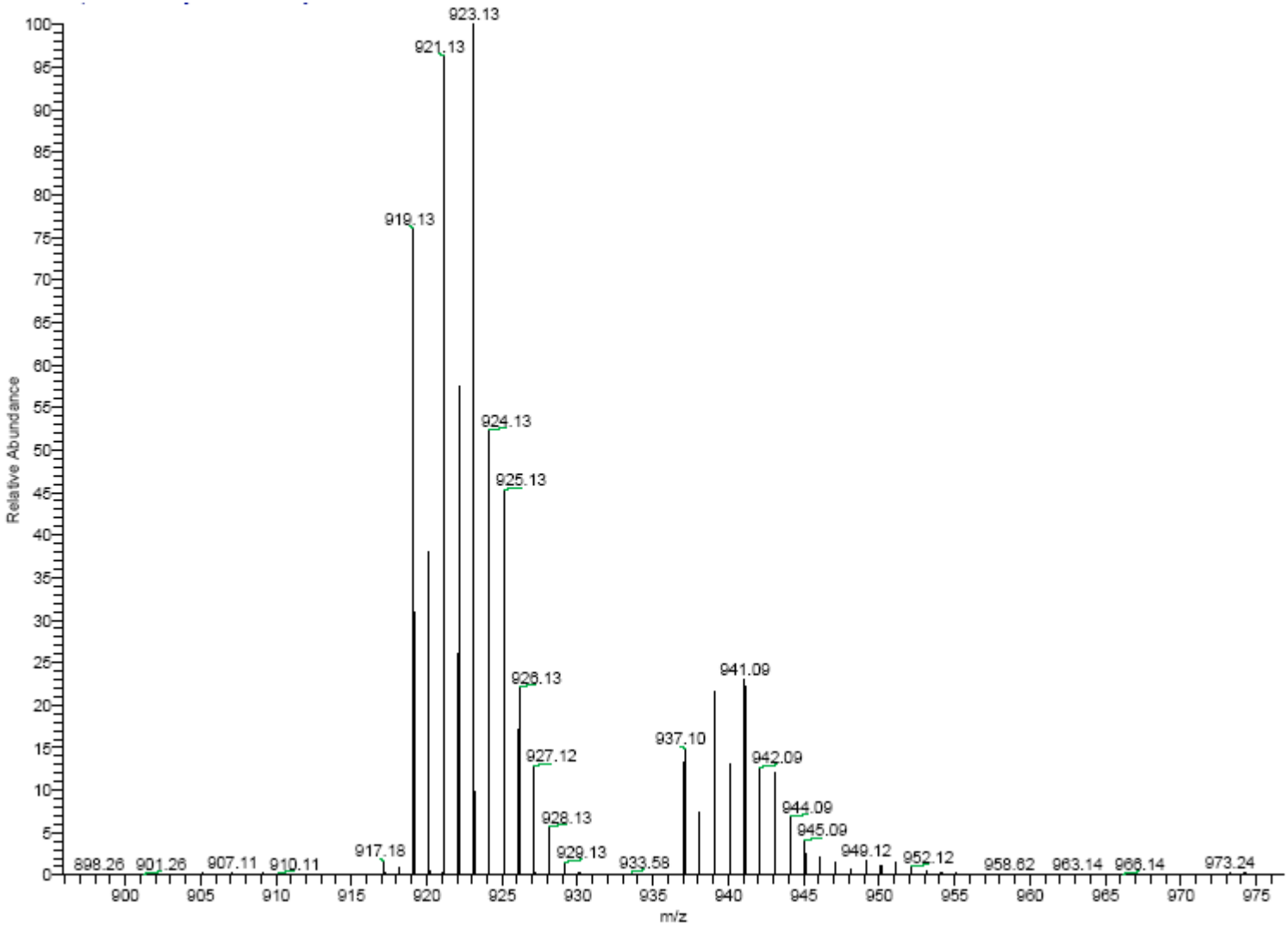
$C_{46}H_{38}N_4O_8Zn$
Exact Mass: 838.2
Mol. Wt.: 840.21
m/e: 838.20 (100.0%), 840.20 (71.9%), 839.20 (52.0%), 842.19 (38.7%), 841.20 (37.6%), 843.20 (21.3%), 842.20 (12.8%), 844.20 (5.6%), 841.21 (2.8%), 845.20 (1.8%), 844.19 (1.6%), 843.21 (1.2%)
C, 65.76; H, 4.56; N, 6.67; O, 15.23; Zn, 7.78

$C_{46}H_{39}N_4O_9Zn$
Exact Mass: 855.2
Mol. Wt.: 857.21
m/e: 855.20 (100.0%), 857.20 (58.1%), 859.20 (51.3%), 856.20 (51.2%), 858.20 (37.6%), 860.20 (19.8%), 857.21 (14.4%), 861.20 (7.1%), 858.21 (3.0%), 860.21 (2.8%), 862.20 (1.1%)
C, 64.45; H, 4.59; N, 6.54; O, 16.80; Zn, 7.63

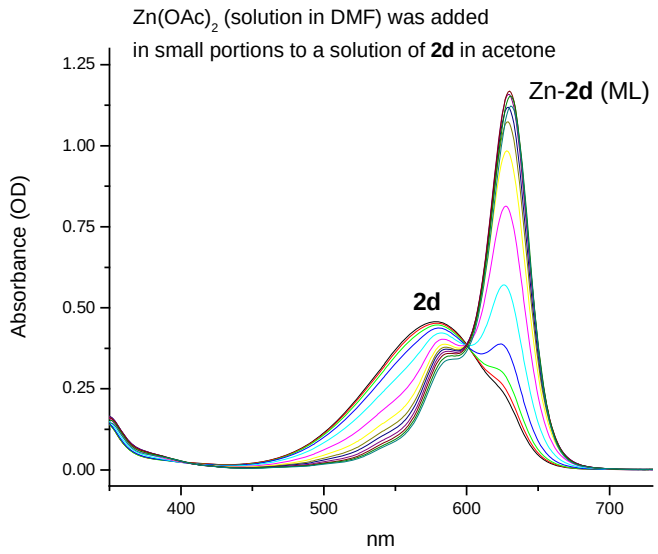
Zn(acac)-**2a**


C23H19N2O4Zn••
Exact Mass: 451.06
Mol. Wt.: 452.8
m/e: 451.06 (100.0%), 453.06 (57.6%), 455.06 (41.3%), 452.07 (25.2%), 454.06 (23.2%), 456.06 (10.0%), 453.07 (3.9%), 455.07 (1.8%), 457.06 (1.7%), 457.07 (1.2%)
C, 61.01; H, 4.23; N, 6.19; O, 14.13; Zn, 14.44
C26H25N2O5Zn
Exact Mass: 509.11
Mol. Wt.: 510.88
m/e: 509.11 (100.0%), 511.10 (57.4%), 513.10 (38.7%), 510.11 (28.6%), 512.11 (16.7%), 514.10 (11.1%), 512.10 (8.9%), 513.11 (5.3%), 511.11 (5.1%), 515.11 (2.0%), 515.10 (1.4%)
C, 61.13; H, 4.93; N, 5.48; O, 15.66; Zn, 12.80
C46H39N4O9Zn2
Exact Mass: 919.13
Mol. Wt.: 922.6
m/e: 921.13 (100.0%), 923.13 (87.8%), 919.13 (85.2%), 922.13 (64.0%), 924.13 (50.6%), 920.13 (44.0%), 925.12 (38.0%), 923.12 (28.1%), 926.13 (23.3%), 925.13 (20.8%), 927.12 (14.3%), 921.14 (10.7%), 924.12 (9.6%), 927.13 (9.0%), 928.12 (6.7%), 926.12 (6.1%), 928.13 (2.7%), 922.14 (2.5%), 929.13 (2.4%), 924.14 (2.1%), 926.14 (1.5%), 922.12 (1.4%), 925.14 (1.0%)
C, 59.88; H, 4.26; N, 6.07; O, 15.61; Zn, 14.18
Relative Abundance
m/z
451.06
453.06
455.06
241.08
271.09
272.09
315.08
343.11
389.15
437.05
456.06
465.08
509.11
511.10
550.63
551.63
587.08
625.39
641.16
669.42
685.39
713.45
788.90
839.21
840.21
917.18
919.13
921.13
923.13
924.13
925.13
941.09
942.09
944.09
946.09

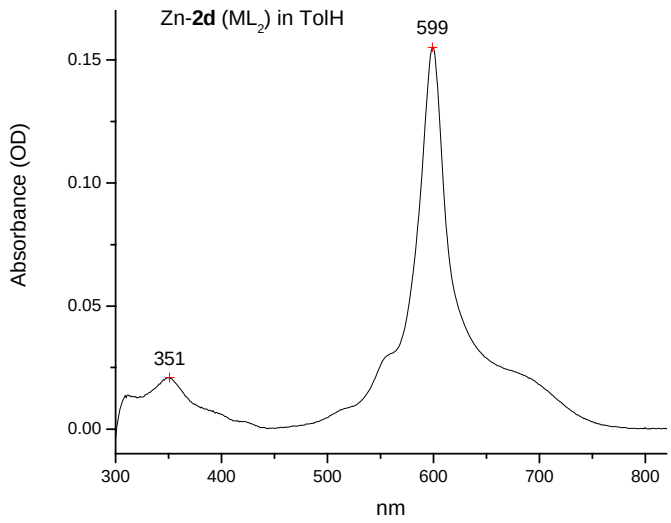

Relative Abundance
m/z
451.06
453.06
455.06
343.11
344.11
335.02
363.01
375.11
379.01
389.15
391.04
407.04
409.03
411.03
423.03
430.19
437.05
439.04
456.08
465.08
474.24
483.09
494.57
509.11
511.10
523.12
525.12
529.04
537.34
550.63
551.63
552.63
578.66
587.08


Relative Abundance
m/z
923.13
921.13
919.13
924.13
925.13
926.13
927.12
928.13
929.13
941.09
937.10
942.09
944.09
945.09
898.26
901.26
907.11
910.11
917.18
933.58
949.12
952.12
958.62
963.14
966.14
973.24

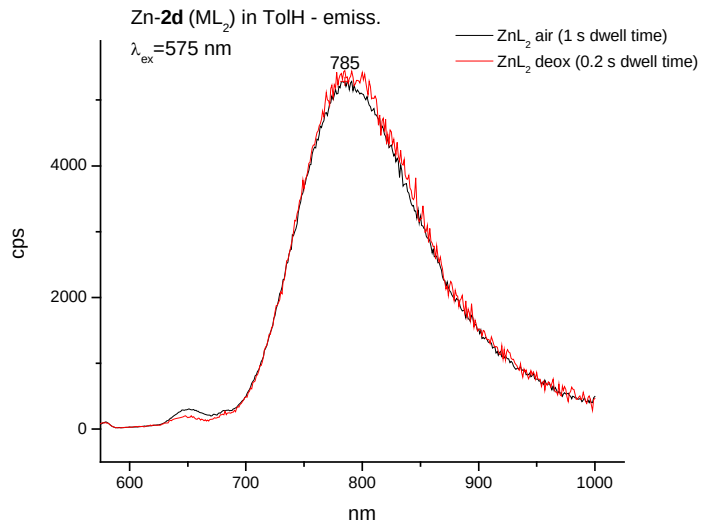
VI. Optical spectroscopic data



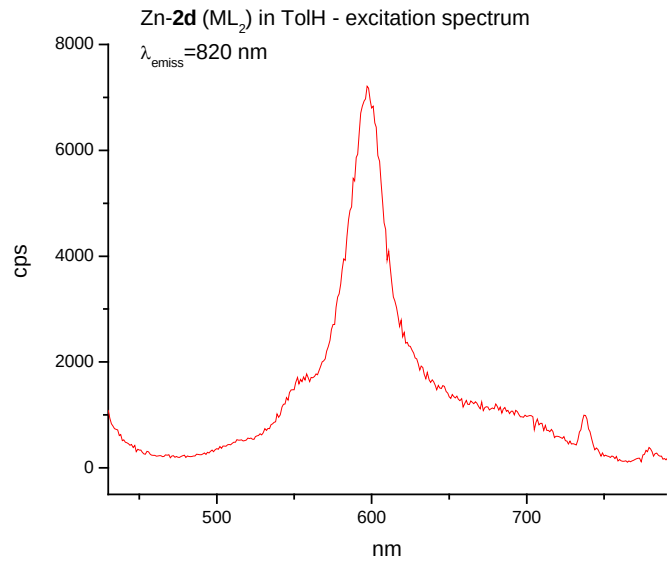
a) Zn acetate was added in small portions to a solution of **2d** in acetone, yielding the brightly fluorescent Zn-**2d** MLX complex.



b) Overnight dark blue crystals precipitated from the acetone solution. These crystals are poorly soluble in acetone, but well soluble in toluene, CH_2Cl_2, pyridine. The absorption spectrum in toluene is shown.



c) Emission spectrum of ML_2 complex corresponding to the absorption spectrum in b).



d) Excitation spectrum corresponding to the emission spectrum shown in c).

Figure S12. Spectral changes accompanying formation of Zn-**2d** *mono*- (MLX) and *bis*- (ML_2) complexes.

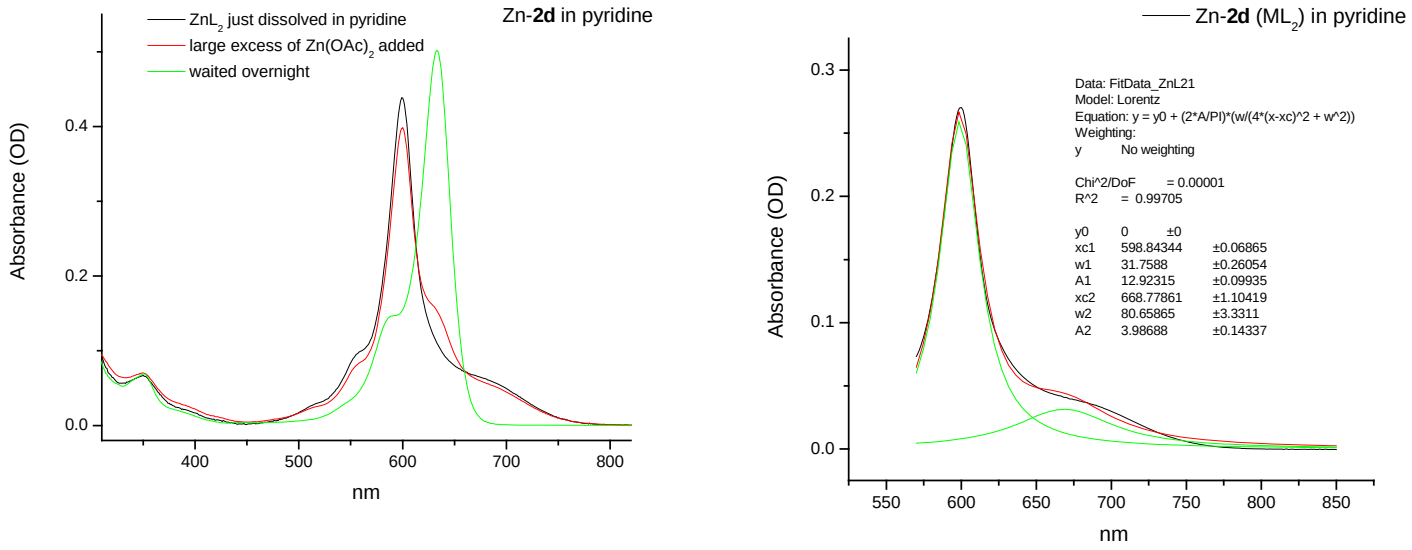


Figure S13. a) Spectral changes accompanying conversion Zn-**2d** ML_2 complex into MLX complex in pyridine upon addition of excess of $Zn(OAc)_2$. b) Fit of the absorption spectrum of Zn-**2d** ML_2 complex with two Lorentzians.

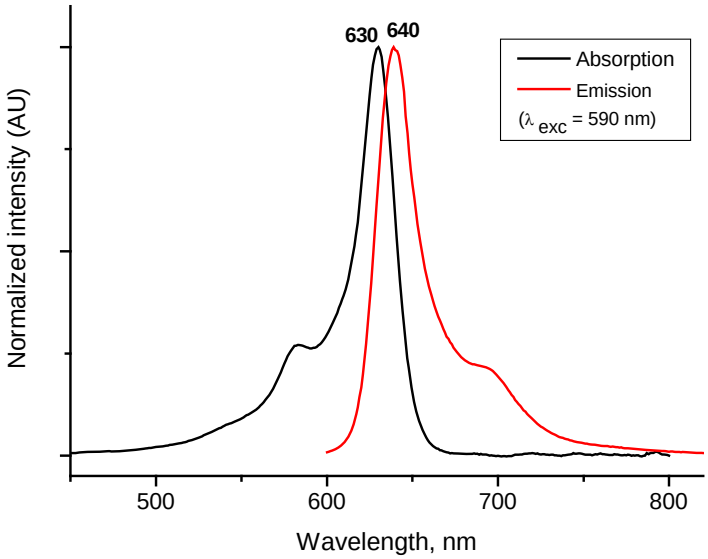
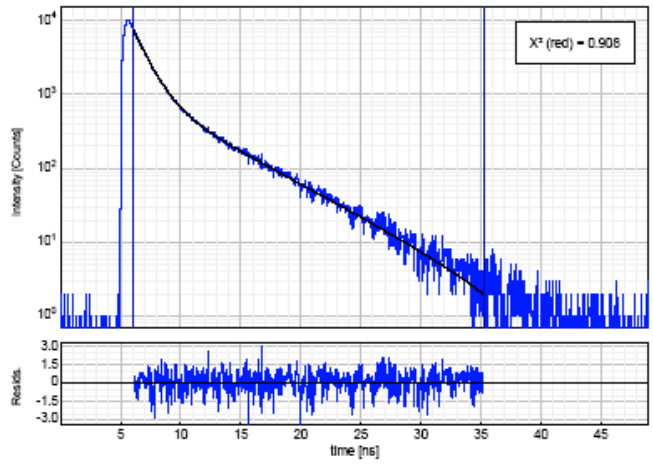


Figure S14. Absorption and emission spectra of Zn(acac)-**2a** in THF.

VII. Fluorescence decays

a)



$$I(t) = \sum_{i=1}^{n} A_i \, e^{-\frac{t}{\tau_i}}$$

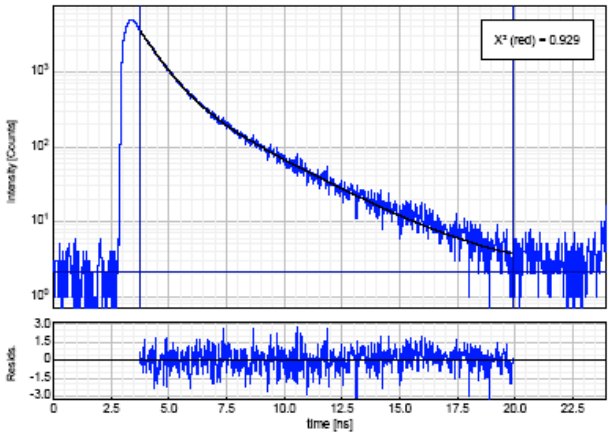
Parameter	Value	Conf. Lower	Conf. Upper	Conf. Estimation
A_1 [Cnts]	1014	-15	+15	Fitting
τ_1 [ns]	4.983	-0.043	+0.043	Fitting
A_2 [Cnts]	6258	-70	+70	Fitting
τ_2 [ns]	1.133	-0.012	+0.012	Fitting
Bkgr. Dec [Cnts]	-0.97	-0.66	+0.66	Fitting

Average Lifetime:

$\tau_{Av.1}$=2.735 ns (intensity weighted)

$\tau_{Av.2}$=1.670 ns (amplitude weighted)

b)



$$I(t) = \sum_{i=1}^{n} A_i \, e^{-\frac{t}{\tau_i}}$$

Parameter	Value	Conf. Lower	Conf. Upper	Conf. Estimation
A_1 [Cnts]	646	-13	+13	Fitting
τ_1 [ns]	2.699	-0.033	+0.033	Fitting
A_2 [Cnts]	2937	-44	+44	Fitting
τ_2 [ns]	0.818	-0.011	+0.011	Fitting
Bkgr. Dec [Cnts]	2.09	-0.66	+0.66	Fitting

Average Lifetime:

$\tau_{Av.1}$=1.609 ns (intensity weighted)

$\tau_{Av.2}$=1.157 ns (amplitude weighted)

Figure S15. Fluorescence decays of Zn-**2d** MLX in pyridine (a) and ML_2 in toluene (b).

VIII. References

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