Supplementary Information for

OFF-ON-OFF Fluorescent Response of *N,N,N′,N′*-Tetrakis(1-isoquinolylmethyl)-2-hydroxy-1,3-propanediamine (1-isoHTQHPN) toward Zn^{2+}

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Table S1 Crystallographic Data for 1-isoHTQHPN

1-isoHTQHPN	
Formula	$C_{43}H_{38}N_6O$
FW	654.81
Crystal system	triclinic
Space group	*P*-1
a, Å	8.1153(16)
b, Å	13.915(3)
c, Å	15.561(3)
α, deg	83.682(4)
β, deg	81.785(4)
γ, deg	89.608(5)
V, Å^3	1728.5(6)
Z	2
D_{calc}, g cm^{-3}	1.258
μ, mm^{-1}	0.0773
$2\theta_{max}$, deg	55
temp, K	153
no. reflns collected	13602
no. reflns used	7535
no. of params	603
R_{int}	0.0201
Final *R*1 ($I > 2\sigma(I)$)[a]	0.0553
*wR*2 (all data)[b]	0.1518
GOF	1.132

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table S2 Crystallographic Data for $[Zn(1\text{-isoHTQHPN})](ClO_4)_2 \cdot THF \cdot 3CH_3OH \cdot H_2O$ and $[Zn(1\text{-isoTQHPN})(OAc)](ClO_4)_2 \cdot 2CH_3CN$

	$[Zn(1\text{-isoHTQHPN})](ClO_4)_2 \cdot THF \cdot 3CH_3OH \cdot H_2O$	$[Zn(1\text{-isoTQHPN})(OAc)](ClO_4)_2 \cdot 2CH_3CN$
Formula	$C_{46.5}H_{49}Cl_2N_6O_{11.5}Zn$	$C_{49}H_{46}Cl_2N_8O_{11}Zn_2$
FW	1012.22	1124.62
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a, Å	11.2705(7)	18.4865(6)
b, Å	11.8818(6)	12.3565(3)
c, Å	35.6284(18)	21.1884(13)
β, deg	96.448(3)	92.618(2)
V, Å^3	4741.0(4)	4835.0(3)
Z	4	4
D_{calc}, g cm^{-3}	1.418	1.545
μ, mm^{-1}	0.6979	1.1734
$2\theta_{max}$, deg	55	55
temp, K	153	153
no. reflns collected	29943	36968
no. reflns used	10389	11000
no. of params	629	649
R_{int}	0.0316	0.0315
Final $R1$ ($I > 2\sigma(I)$)[a]	0.0740	0.0570
$wR2$ (all data)[b]	0.2349	0.1693
GOF	1.060	1.069

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table S3 Crystallographic Data for $[Zn_2(1\text{-isoTQHPN})(CH_3OH)(H_2O)](ClO_4)_3 \cdot 2CH_3OH$

	$[Zn_2(1\text{-isoTQHPN})(CH_3OH)(H_2O)](ClO_4)_3 \cdot 2CH_3OH$
Formula	$C_{46}H_{51}Cl_3N_6O_{17}Zn_2$
FW	1197.06
Crystal system	monoclinic
Space group	$P2_1$
a, Å	11.275(3)
b, Å	18.349(5)
c, Å	12.715(3)
β, deg	110.275(3)
V, Å^3	2467.6(11)
Z	2
D_{calc}, g cm^{-3}	1.611
μ, mm^{-1}	1.2145
$2\theta_{max}$, deg	54.9
temp, K	123
no. reflns collected	19314
no. reflns used	11172
no. of params	603
R_{int}	0.0386
Final *R*1 ($I > 2\sigma(I)$)[a]	0.0613
*wR*2 (all data)[b]	0.1588
GOF	1.101

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

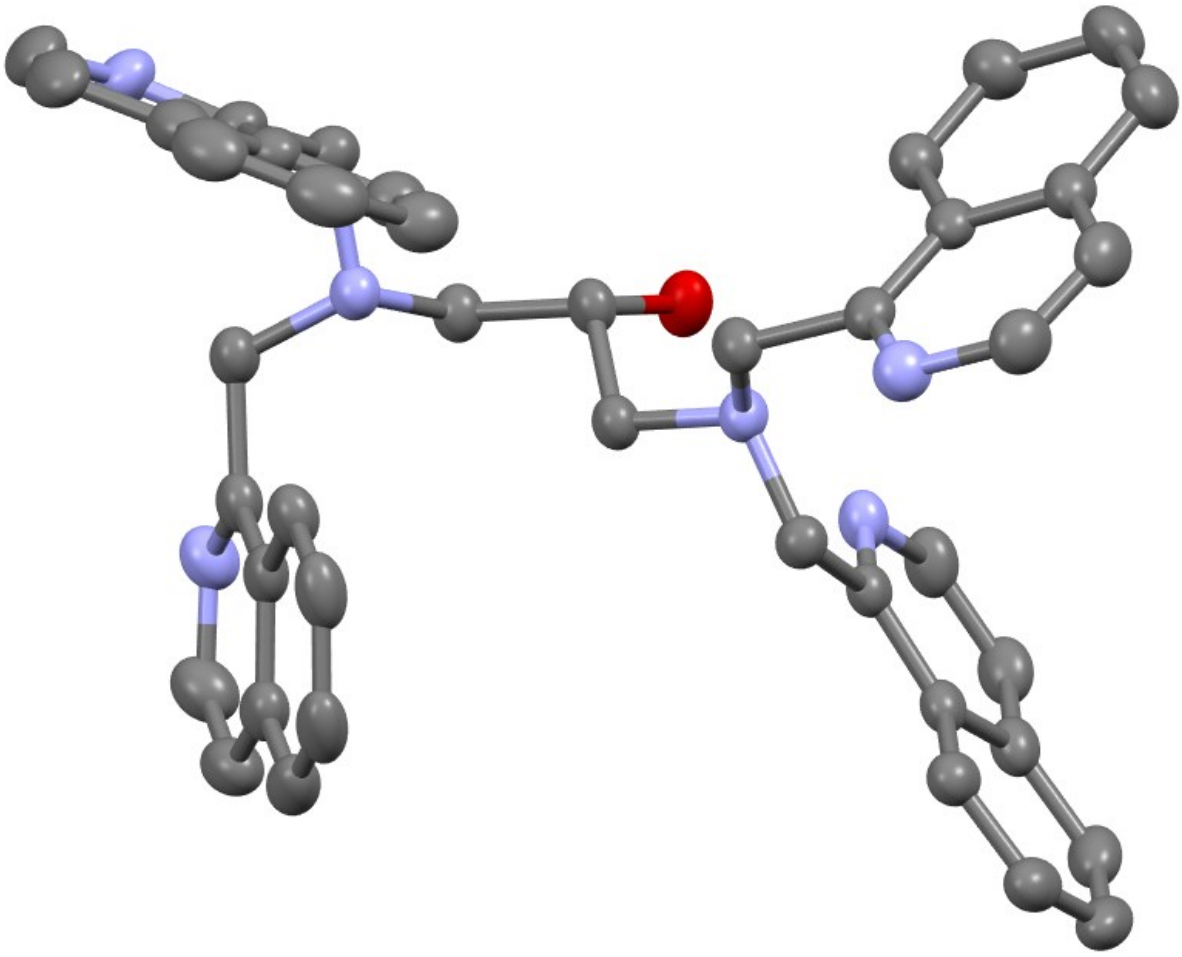


Fig. S1 ORTEP plot for 1-isoHTQHPN in 50% probability. Hydrogen atoms were omitted for clarity.

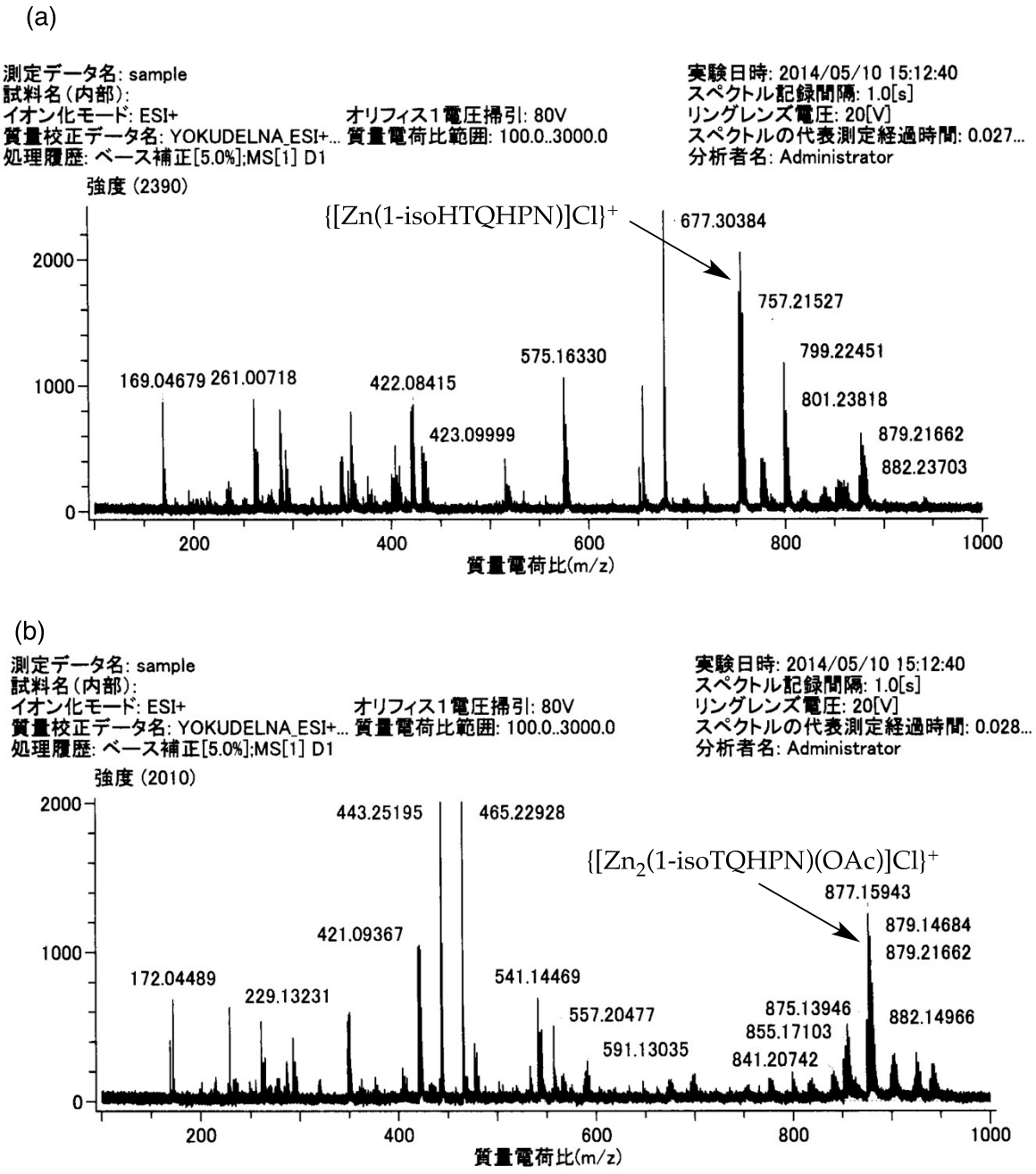


Fig. S2 ESI-MS spectra for 1-isoHTQHPN in the presence of (a) 1 equiv. or (b) 2 equiv. of $Zn(OAc)_2$ in CH_3OH. See Fig. S3 and S4 for simulation.

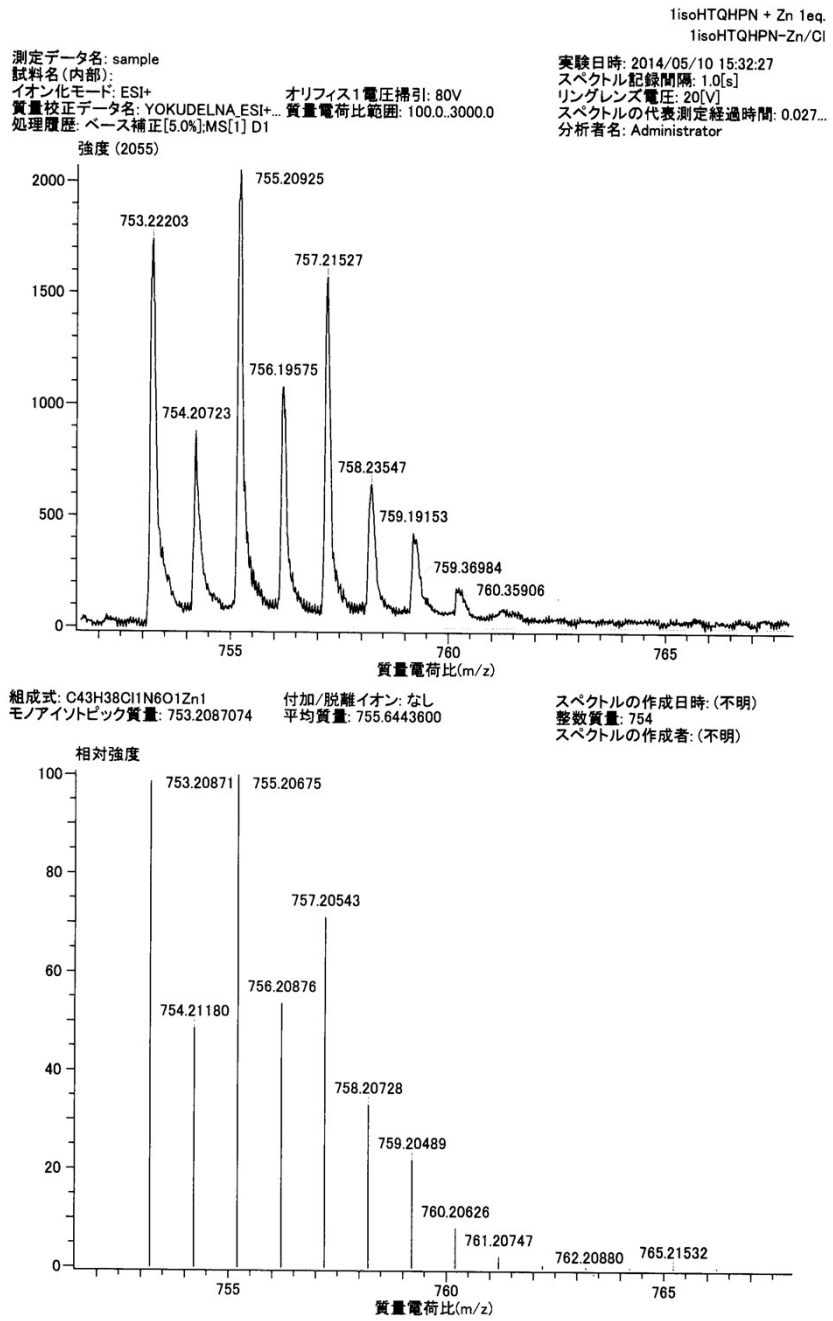


Fig. S3 (a) Experimental and (b) simulated ESI-MS spectra for {[Zn(1-isoHTQHPN)]Cl}$^{+}$ observed for 1-isoHTQHPN in the presence of 1 equiv. of $Zn(OAc)_2$ in CH_3OH. See Fig. S2a for whole spectrum.

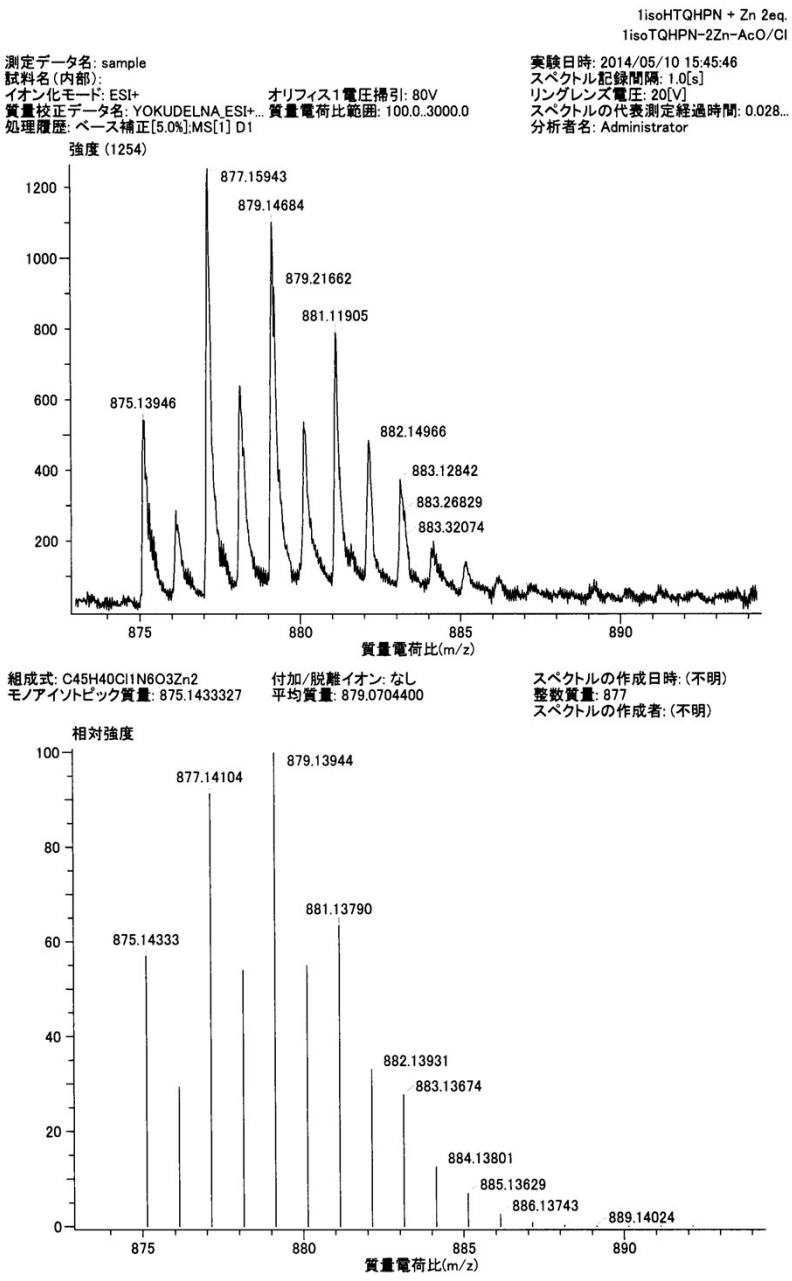


Fig. S4 (a) Experimental and (b) simulated ESI-MS spectra for $\{[Zn_2(1\text{-isoTQHPN})(OAc)]Cl\}^+$ observed for 1-isoHTQHPN in the presence of 2 equiv. of $Zn(OAc)_2$ in CH_3OH. See Fig. S2b for whole spectrum.

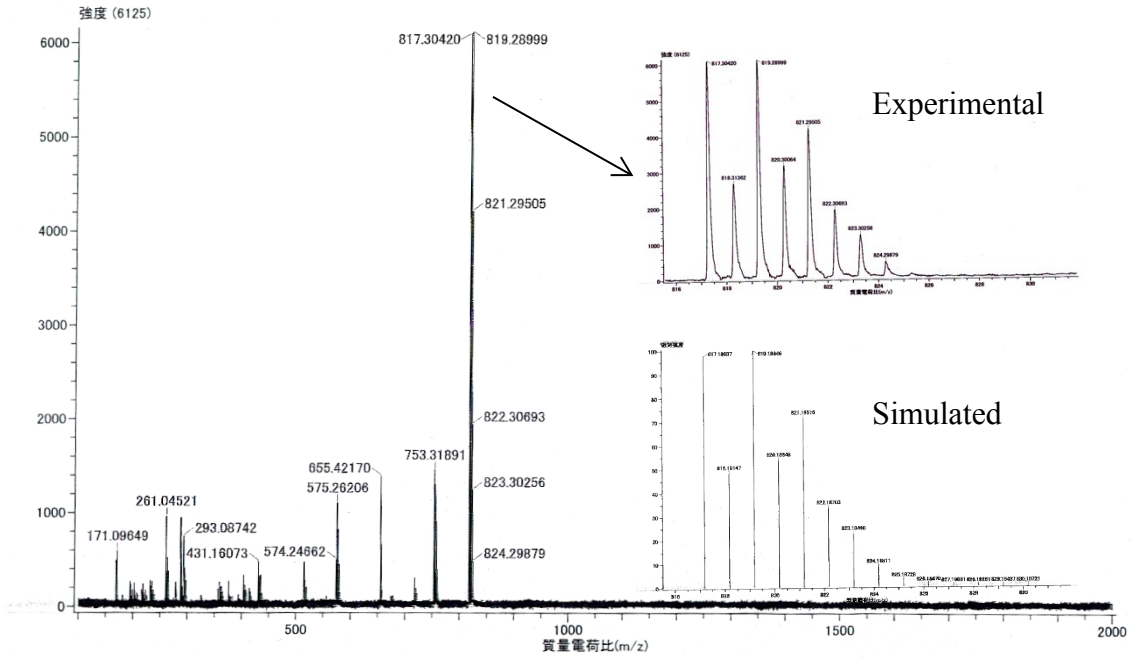


Fig. S5 ESI-MS spectrum for $[Zn(1\text{-isoHTQHPN})](ClO_4)_2$ in CH_3OH. Calcd for $\{[Zn(1\text{-isoHTQHPN})](ClO_4)\}^+$: m/z = 817.18837. Found: 817.30420.

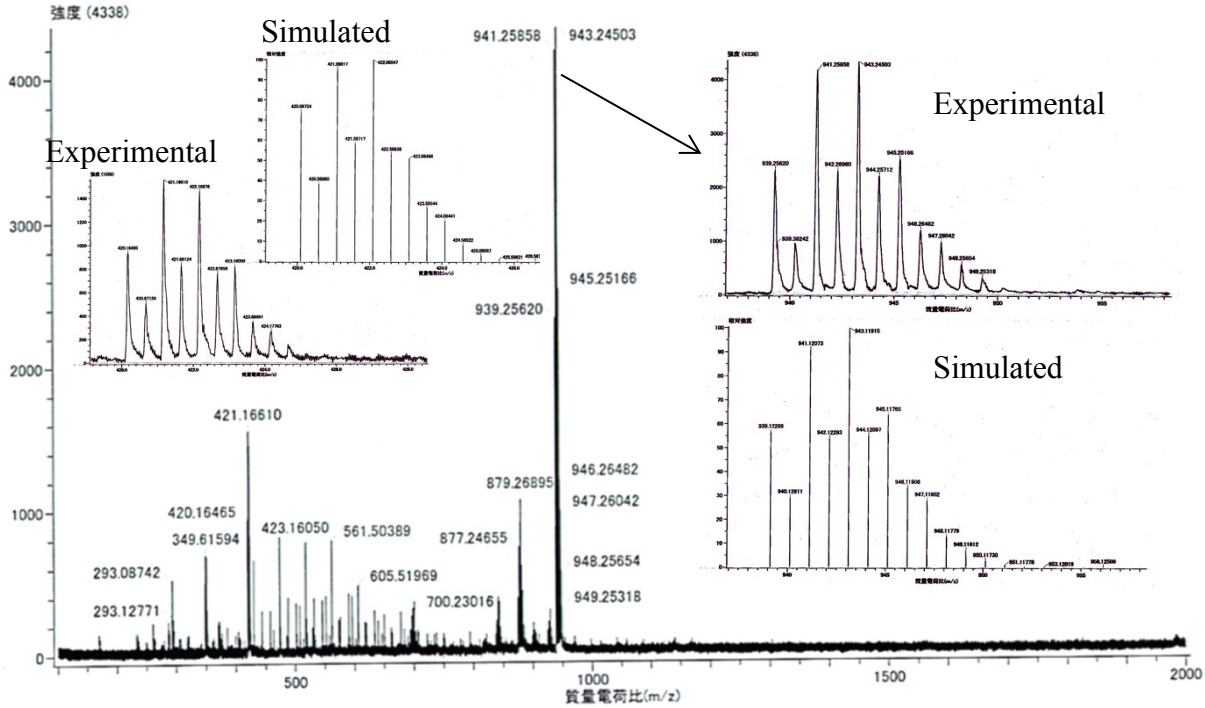


Fig. S6 ESI-MS spectrum for $[Zn_2(1\text{-isoTQHPN})(OAc)](ClO_4)_2$ in CH_3OH. Calcd for $\{[Zn_2(1\text{-isoTQHPN})(OAc)]\}^{2+}$: m/z = 420.08724. Found: 420.16465. Calcd for $\{[Zn(1\text{-isoTQHPN})(OAc)](ClO_4)\}^{+}$: m/z = 939.12299. Found: 939.25620.

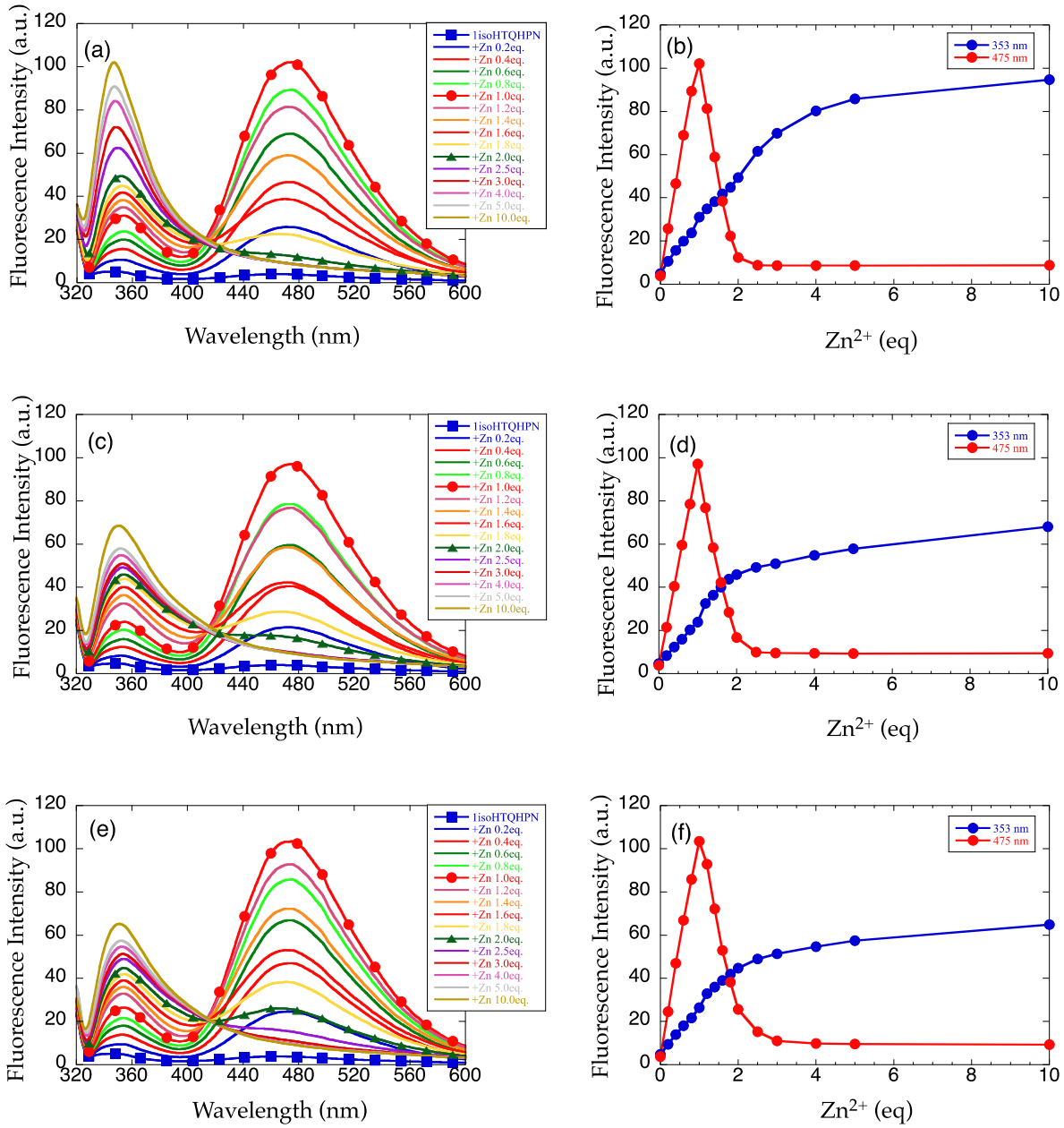


Fig. S7 (a, c, e) Fluorescence spectra and (b, d, e) fluorescence intensity plot for 1-isoHTQHPN in the presence of various concentration of (a, b) $Zn(OAc)_2{\cdot}2H_2O$, (c, d) $Zn(ClO_4)_2{\cdot}6H_2O$ and (e, f) $Zn(NO_3)_2{\cdot}6H_2O$ in DMF-H_2O (1:1) at 25 °C.

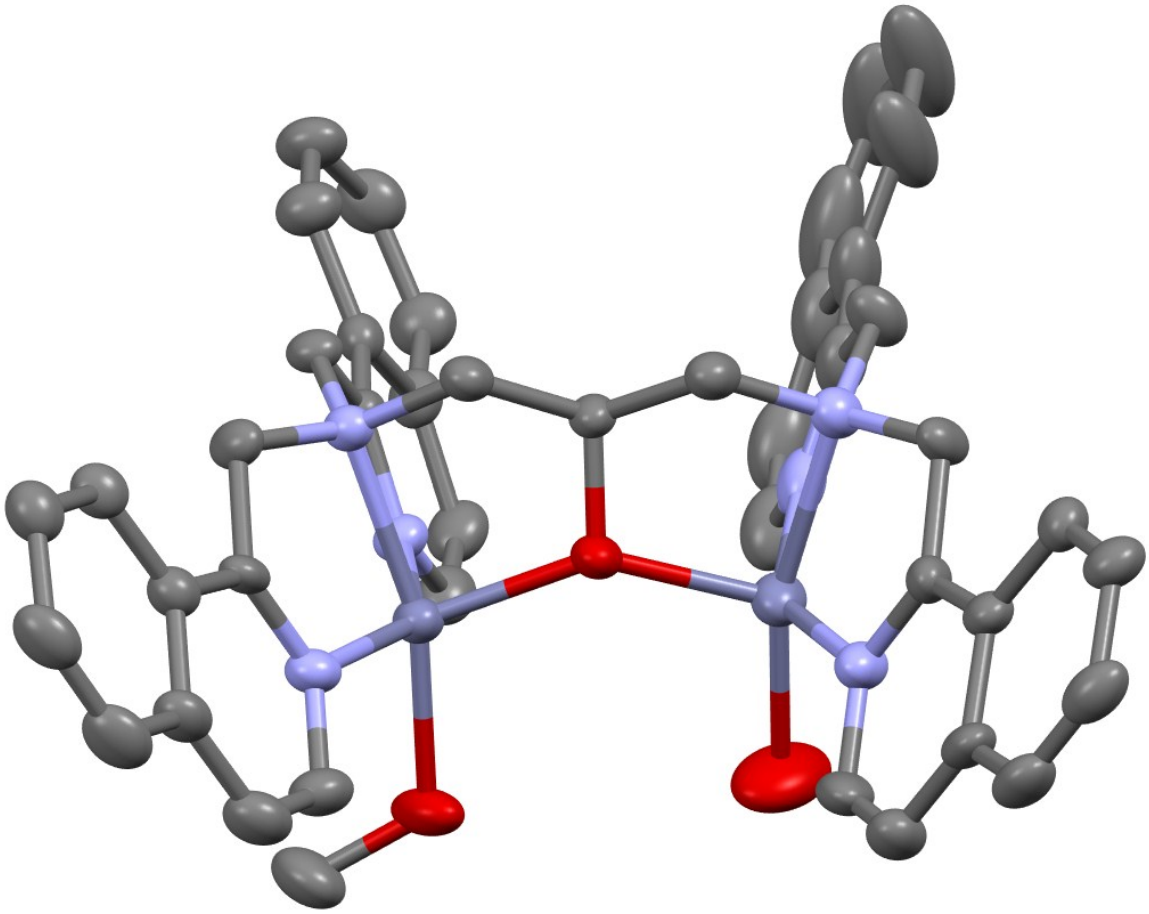


Fig. S8 ORTEP plot for $[Zn_2(1\text{-isoTQHPN})(CH_3OH)(H_2O)](ClO_4)_3 \cdot 2CH_3OH$ in 50% probability. Solvent molecules and hydrogen atoms were omitted for clarity.

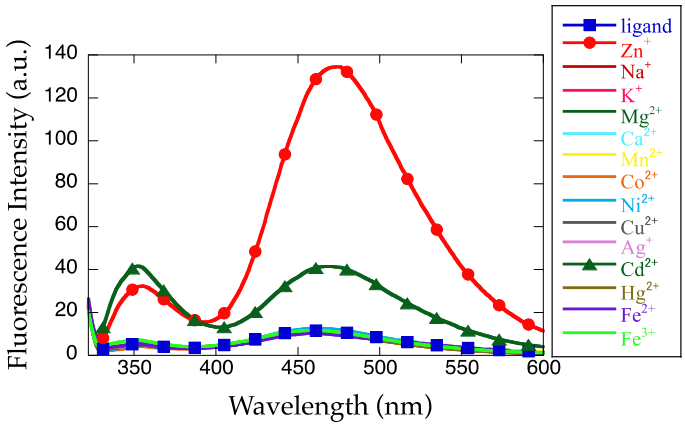


Fig. S9 Fluorescence spectra for 34 μM 1-isoHTQHPN in DMF-H_2O (1:1) at 25 °C in the presence of 1 equiv. of various metal ions.

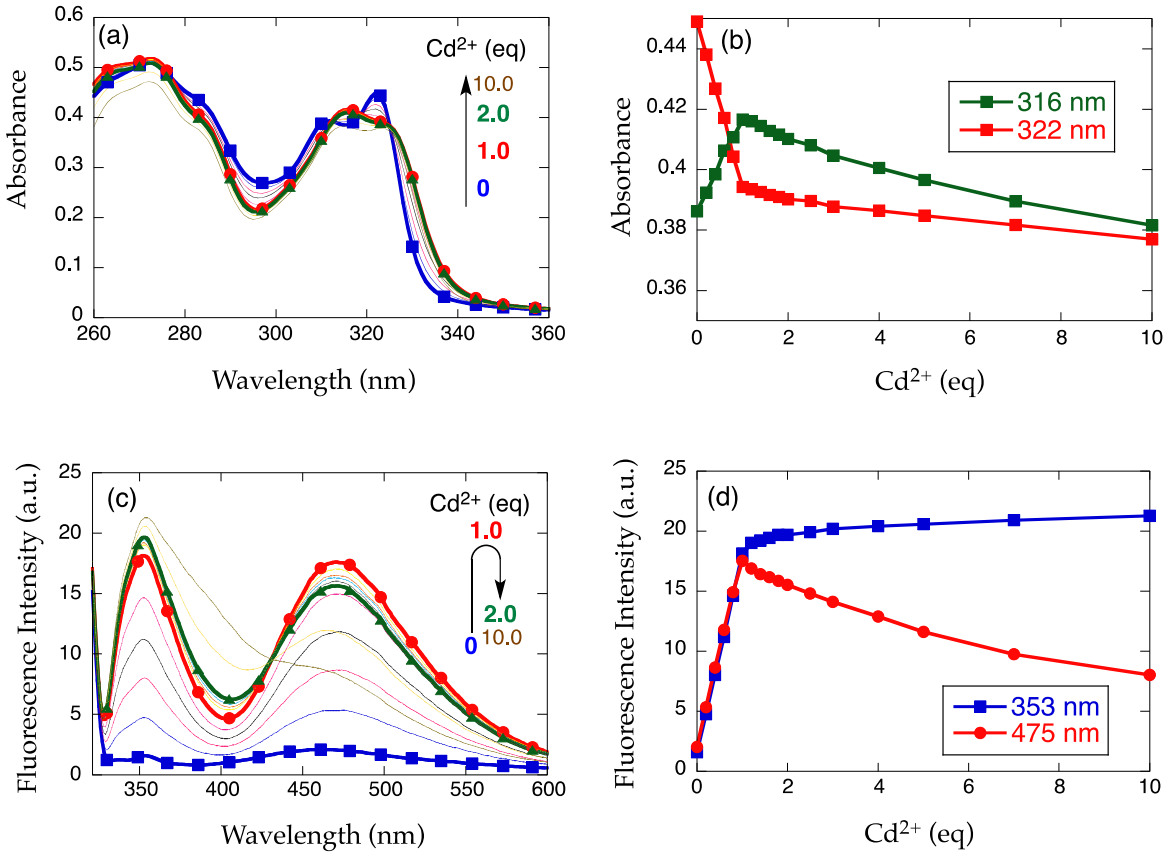


Fig. S10 (a, b) UV-vis absorption and (c, d) fluorescence (λ_{ex} = 320 nm) spectral changes of 34 μM 1-isoHTQHPN in DMF-H_2O (1:1) at 25 °C in the presence of various concentrations of Cd^{2+}.

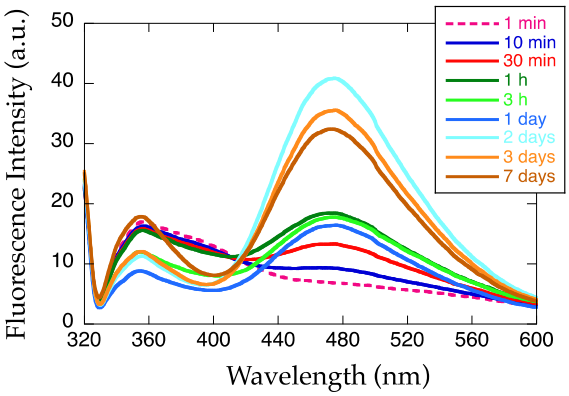
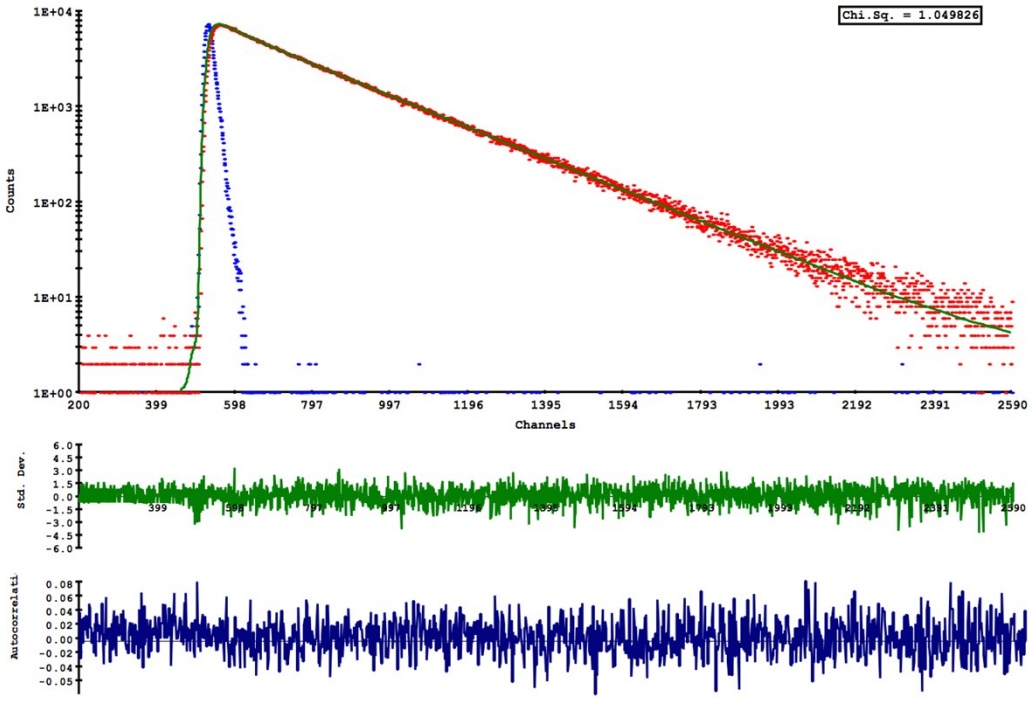


Fig. S11 Fluorescence spectral change for 34 μM $[Zn_2(1\text{-isoTQHPN})(OAc)](ClO_4)_2$ in DMF-H_2O (1:1) at 25 °C in the presence of 1 equiv. of TPEN.

DAS6 v6.8. - HORIBA Scientific IsoZn1_ex295_em475_slit32.das; fit2 [XSQ=1.049826] 19/02/2015

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Calculated using 2 exponentials

Prompt data : Prompt
Decay data : Decay

The initial parameters are:

 Shift Value = 0        ch;         0              sec
 Shift Limit = 10       ch;         2.743484E-10   sec

 T1 Estimate = 126.6362 ch;         3.474243E-09   sec
 T2 Estimate = 506.5447 ch;         1.389697E-08   sec

 A Free
 B1 Free
 B2 Free

 Prompt and decay LO = 200    ch;    5.486969E-09   sec
 Prompt and decay HI = 2600   ch;    7.133059E-08   sec

 Background on prompt = 0.3013245
 Time calibration = 2.743484E-11 sec/ch

The fitted parameters are:

 Hi reduced to: 2590 ch

 SHIFT = 0.7894002     ch;   2.165707E-11  sec     S.Dev = 1.055423E-12  sec
 T1    = 67.11081      ch;   1.841174E-09  sec     S.Dev = 9.431356E-11  sec
 T2    = 261.6785      ch;   7.179108E-09  sec     S.Dev = 7.688608E-12  sec
 A     = 0.7204295                                S.Dev = 0.0573779
 B1    = 5.767782E-03  [ 3.62 Rel.Ampl][ 0.13 Alpha] S.Dev = 1.038482E-04
 B2    = 3.941541E-02  [ 96.38 Rel.Ampl][ 0.87 Alpha] S.Dev = 3.830344E-05
 Average Life Time = 6.497703E-09  sec
 CHISQ = 1.049826           [ 2385 degrees of freedom ]


Chi-squared Probability =   4.436765 percent
Durbin-Watson Parameter =   1.926229
Negative residuals      =   43.91468 percent
Residuals < 1 s.dev     =   68.00502 percent
Residuals < 2 s.dev     =   94.77206 percent
Residuals < 3 s.dev     =   99.33083 percent
Residuals < 4 s.dev     =   99.87453 percent
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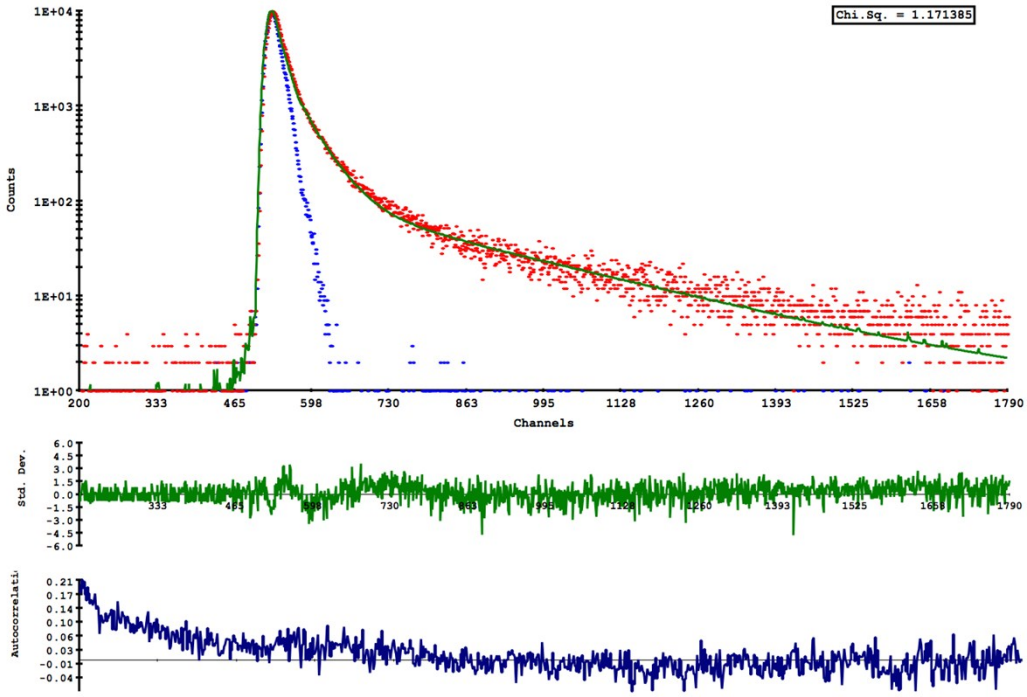
Fig. S12 Fluorescence lifetime measurement for $[Zn(1\text{-isoHTQHPN})]^{2+}$ at 475 nm in DMF-H_2O (1:1) at 25 °C.

DAS6 v6.8. - HORIBA Scientific IsoZn2_ex295_em353_slit32.das; fit3fix1 [XSQ=1.171385] 19/02/2015

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Calculated using 3 exponentials

Prompt data : Prompt
Decay data : Decay

The initial parameters are:

 Shift Value = 0         ch;          0              sec
 Shift Limit = 10        ch;          2.743484E-10   sec

 T1 Estimate = 1         ch;          2.743484E-11   sec (Fixed)
 T2 Estimate = 27.29742 ch;           7.489006E-10   sec
 T3 Estimate = 54.59485 ch;           1.497801E-09   sec

 A Free
 B1 Free
 B2 Free
 B3 Free

 Prompt and decay LO = 200    ch;    5.486969E-09   sec
 Prompt and decay HI = 1800   ch;    4.938272E-08   sec

 Background on prompt = 0.3189369
 Time calibration = 2.743484E-11 sec/ch

The fitted parameters are:

 Hi reduced to: 1790 ch

 SHIFT = 0.7129513     ch;   1.955971E-11  sec     S.Dev = 6.813048E-13  sec
 T1    = 1             ch;   2.743484E-11  sec     Fixed
 T2    = 38.86188      ch;   1.066169E-09  sec     S.Dev = 1.110948E-11  sec
 T3    = 284.8678      ch;   7.815303E-09  sec     S.Dev = 1.037415E-10  sec
 A     = 0.8284459                                S.Dev = 5.456821E-02
 B1    = 1.581689      [ 74.67 Rel.Ampl][ 0.99 Alpha] S.Dev = 3.990023E-03
 B2    = 1.066079E-02  [ 19.56 Rel.Ampl][ 0.01 Alpha] S.Dev = 5.393351E-05


 B3    = 4.296041E-04  [ 5.78 Rel.Ampl][ 0.00 Alpha] S.Dev = 3.599953E-06
 Average Life Time = 3.648784E-11  sec
 CHISQ = 1.171385            [ 1584 degrees of freedom ]

 Chi-squared Probability = 2.2811E-04 percent
 Durbin-Watson Parameter =   1.610259
 Negative residuals      =   38.71779 percent
 Residuals < 1 s.dev     =   66.56191 percent
 Residuals < 2 s.dev     =   94.02892 percent
 Residuals < 3 s.dev     =   99.12005 percent
 Residuals < 4 s.dev     =   99.87429 percent
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Fig. S13 Fluorescence lifetime measurement for $[Zn_2(1\text{-isoTQHPN})(OAc)]^{2+}$ at 353 nm in DMF-H_2O (1:1) at 25 °C.

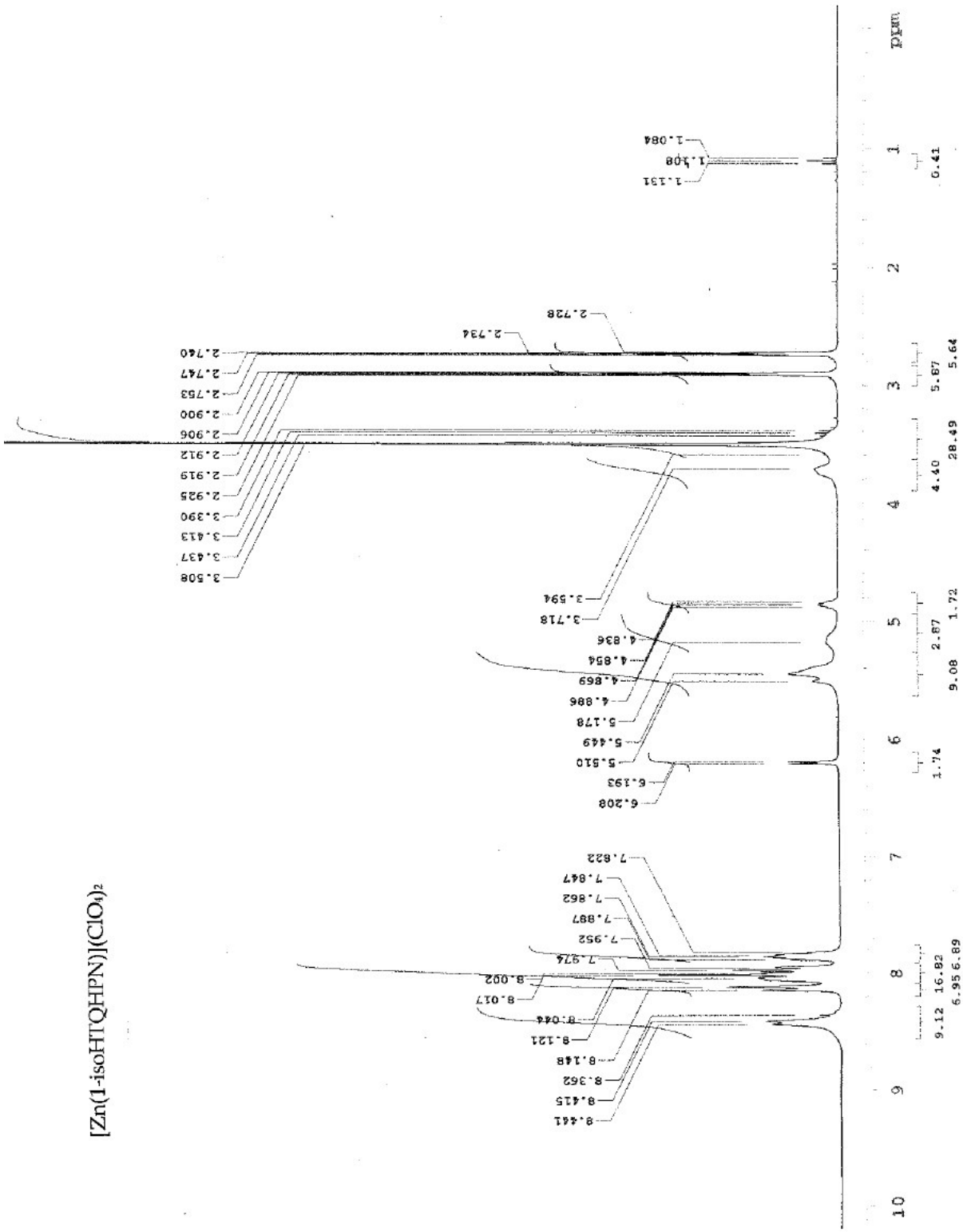

Fig. S14 ^{1}H NMR spectrum for [Zn(1-isoHTQHPN)]$(ClO_4)_2$ in DMF-d_7.

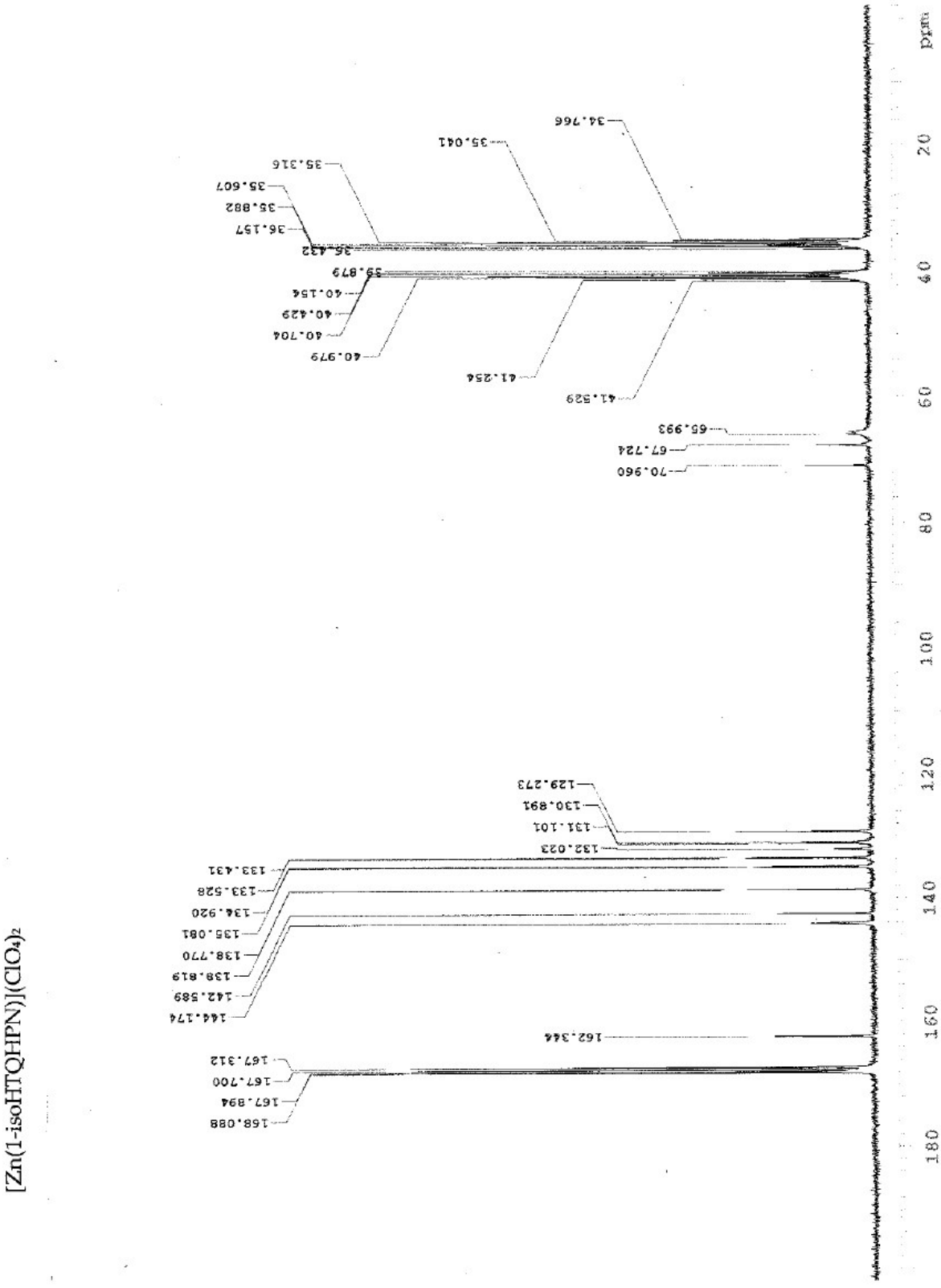

Fig. S15 ^{13}C NMR spectrum for [Zn(1-isoHTQHPN)]$(ClO_4)_2$ in DMF-d_7.

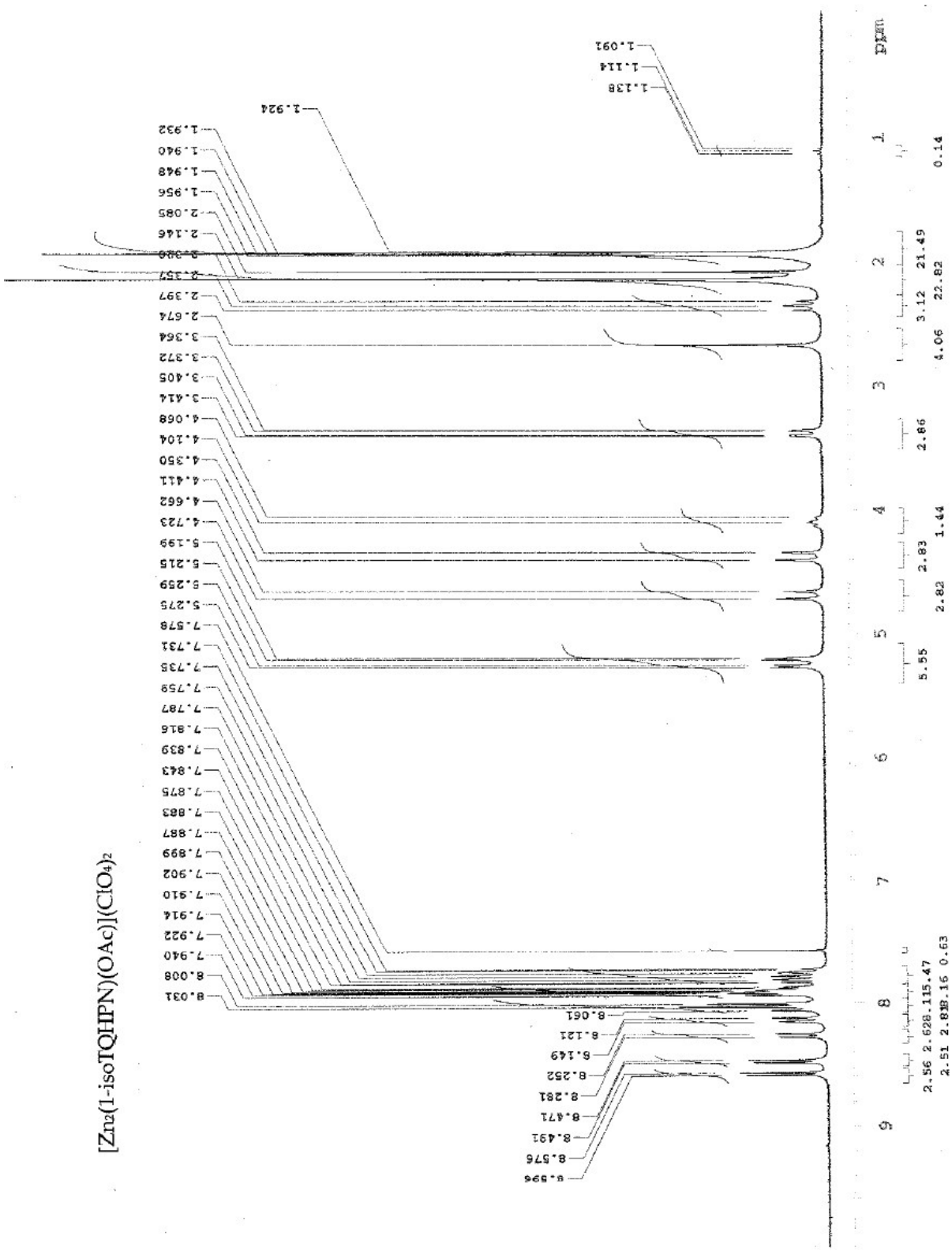

Fig. S16 ^{1}H NMR spectrum for $[Zn_2(1\text{-isoTQHPN})(OAc)](ClO_4)_2$ in CD_3CN.

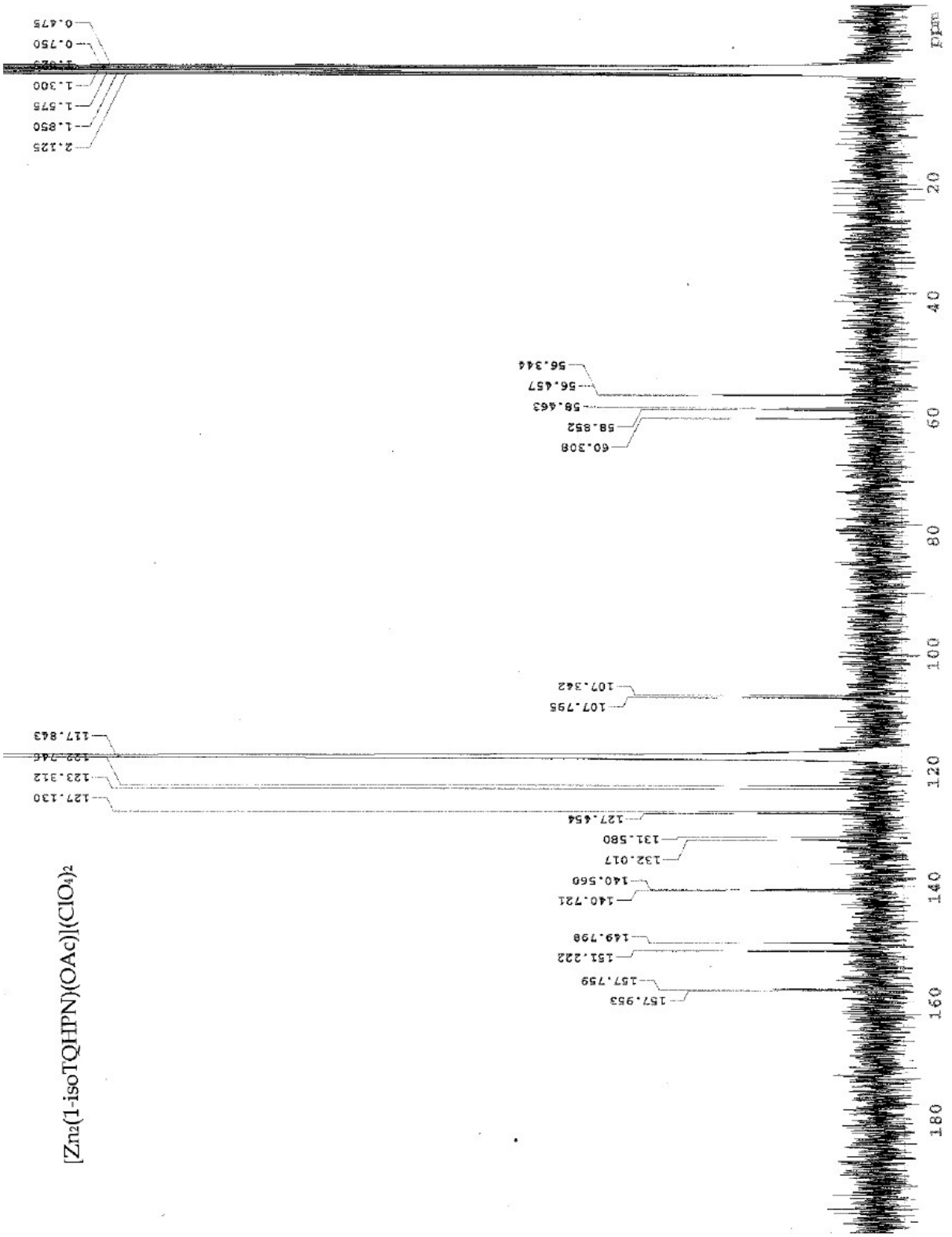

Fig. S17 ^{13}C NMR spectrum for $[Zn_2(1\text{-isoTQHPN})(OAc)](ClO_4)_2$ in CD_3CN.

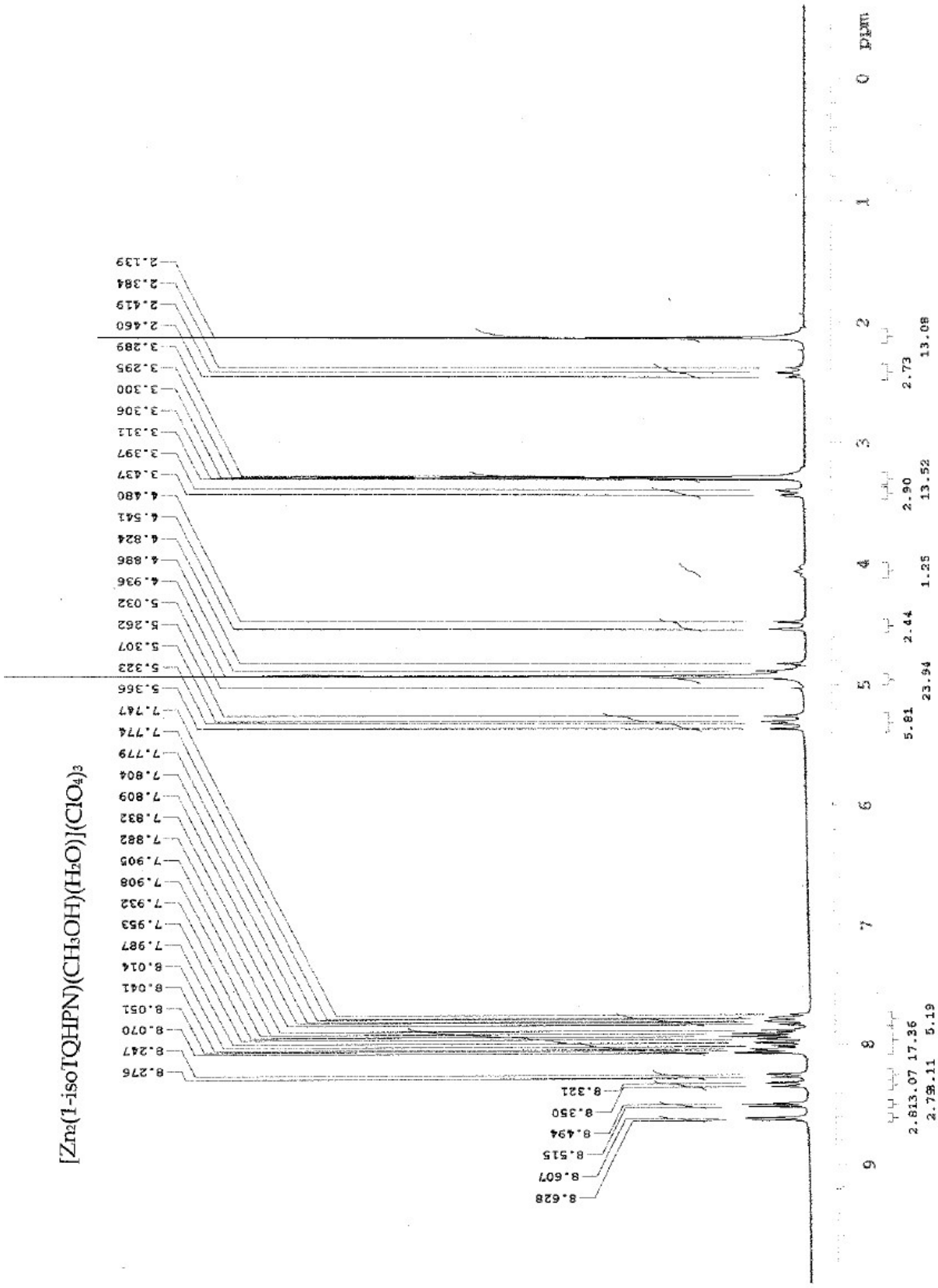

Fig. S18 ^{1}H NMR spectrum for $[Zn_2(1\text{-isoTQHPN})(CH_3OH)(H_2O)](ClO_4)_3$ in CD_3OD.

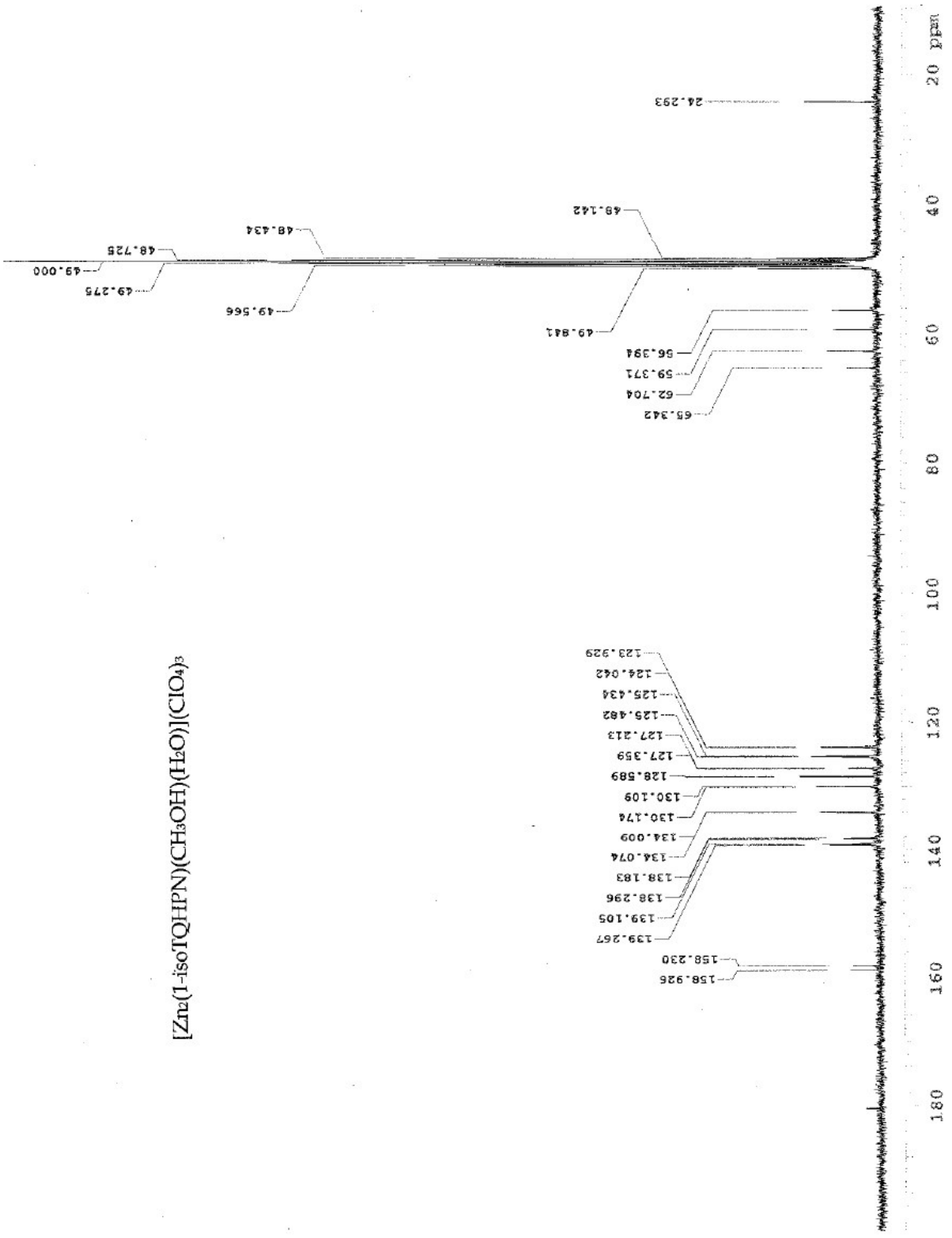

Fig. S19 ^{13}C NMR spectrum for $[Zn_2(1\text{-isoTQHPN})(CH_3OH)(H_2O)](ClO_4)_3$ in CD_3OD.