Supplementary Information for

Quinoline-Based Fluorescent Zinc Sensors with Enhanced Fluorescence Intensity, Zn/Cd Selectivity and Metal Binding Affinity by Conformational Restriction

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Table S1. Crystallographic Data for TQDACH, $[Zn(TQDACH)](ClO_4)_2 \cdot CH_3OH$ and $[Zn(1\text{-isoTQDACH})](ClO_4)_2 \cdot 2CH_3OH$

	TQDACH	$[Zn(TQDACH)](ClO_4)_2 \cdot CH_3OH$	$[Zn(1\text{-isoTQDACH})](ClO_4)_2 \cdot 2CH_3OH$
Formula	$C_{46}H_{42}N_6$	$C_{47}H_{46}Cl_2N_6O_9Zn$	$C_{48}H_{50}Cl_2N_6O_{10}Zn$
FW	678.88	975.20	1007.24
Crystal system	triclinic	triclinic	monoclinic
Space group	*P*-1	*P*-1	$P2_1/n$
a, Å	9.953(2)	11.522(3)	10.8914(3)
b, Å	13.236(3)	11.821(3)	36.6116(12)
c, Å	13.693(3)	17.615(4)	23.0800(8)
α, deg	90.195(3)	102.860(3)	90
β, deg	91.519(3)	94.743(2)	93.212(2)
γ, deg	93.871(3)	112.892(2)	90
V, Å^3	1799.0(6)	2116.2(9)	9188.7(5)
Z	2	2	8
D_{calc}, g cm^{-3}	1.253	1.530	1.456
μ, mm^{-1}	0.0748	0.7744	0.7175
$2\theta_{max}$, deg	55.0	55.0	55.0
temp, K	123	123	123
no. reflns collected	14136	16476	89677
no. reflns used	7831	9221	20934
no. of params	637	586	1261
R_{int}	0.0204	0.0174	0.0456
Final *R*1 ($I > 2\sigma(I)$)[a]	0.0467	0.0370	0.0670
*wR*2 (all data)[b]	0.1193	0.0971	0.1710
GOF	1.134	1.051	1.084

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

Table S2. Crystallographic Data for $[Cu(TQDACH)](ClO_4)_2 \cdot 3CH_3OH$, $[Cd(TQDACH)](ClO_4)_2$ and $[Cd(1\text{-isoTQDACH})(CH_3OH)](ClO_4)_2 \cdot 0.5CH_3OH \cdot 2H_2O$

	$[Cu(TQDACH)](ClO_4)_2 \cdot 3CH_3OH$	$[Cd(TQDACH)](ClO_4)_2$	$[Cd(1\text{-isoTQDACH})(CH_3OH)](ClO_4)_2 \cdot 0.5CH_3OH \cdot 2H_2O$
Formula	$C_{49}H_{54}Cl_2CuN_6O_{11}$	$C_{46}H_{42}CdCl_2N_6O_8$	$C_{47.5}H_{52}CdCl_2N_6O_{11.5}$
FW	1037.45	990.19	1074.28
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$Pna2_1$	$C2/c$	$P2_1/c$
a, Å	18.493(5)	15.6590(6)	27.2692(7)
b, Å	12.269(3)	20.5854(5)	16.0487(3)
c, Å	20.647(5)	13.7274(5)	22.2666(5)
β, deg	90	112.878(2)	105.8950(10)
V, Å^3	4685(2)	4076.9(3)	9372.1(4)
Z	4	4	8
D_{calc}, g cm^{-3}	1.471	1.613	1.523
μ, mm^{-1}	0.6494	0.7334	0.6497
$2\theta_{max}$, deg	55.0	55.0	55.0
temp, K	123	123	123
no. reflns collected	29566	15626	71588
no. reflns used	8944	4560	21185
no. of params	631	285	1225
R_{int}	0.0356	0.0196	0.0248
Final $R1$ ($I > 2\sigma(I)$)[a]	0.0657	0.0546	0.0601
$wR2$ (all data)[b]	0.1832	0.1411	0.1683
GOF	1.079	1.049	1.034

[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 $[Cd(TQEN)](ClO_4)_2 \cdot 2CHCl_3$, $[Cd(1\text{-}isoTQEN)(CH_3CN)](ClO_4)_2 \cdot CH_3CN$ and $[Cd(TPEN)(H_2O)](ClO_4)_2$

	$[Cd(TQEN)](ClO_4)_2 \cdot 2CHCl_3$	$[Cd(1\text{-}isoTQEN)(CH_3CN)](ClO_4)_2 \cdot CH_3CN$	$[Cd(TPEN)(H_2O)](ClO_4)_2$
Formula	$C_{44}H_{38}CdCl_8N_6O_8$	$C_{46}H_{42}CdCl_2N_8O_8$	$C_{26}H_{30}CdCl_2N_6O_9$
FW	1174.85	1018.20	753.87
Crystal system	triclinic	monoclinic	monoclinic
Space group	*P*-1	$P2_1/n$	$C2/c$
a, Å	11.8217(10)	14.3782(5)	15.143(2)
b, Å	12.9831(9)	16.4845(5)	9.9383(13)
c, Å	16.441(2)	19.2641(7)	19.312(3)
α, deg	103.246(3)	90	90
β, deg	101.278(4)	101.197(2)	94.459(2)
γ, deg	96.489(3)	90	90
V, Å^3	2375.7(4)	4474.8(3)	2897.7(7)
Z	2	4	4
D_{calc}, g cm^{-3}	1.642	1.511	1.728
μ, mm^{-1}	0.9691	0.6717	1.0035
$2\theta_{max}$, deg	55.0	55.0	54.9
temp, K	223	223	123
no. reflns collected	23538	44004	10553
no. reflns used	10831	10239	3306
no. of params	604	586	260
R_{int}	0.0175	0.0229	0.0140
Final *R*1 ($I > 2\sigma(I)$)[a]	0.0447	0.0402	0.0198
*wR*2 (all data)[b]	0.1250	0.1087	0.0513
GOF	1.050	1.065	1.097

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

Table S4. Interatomic distances (Å) and angles (°) for TQDACH, $[Zn(TQDACH)](ClO_4)_2 \cdot CH_3OH$ and $[Zn(1\text{-}isoTQDACH)](ClO_4)_2 \cdot 2CH_3OH$

	$[Zn(TQDACH)](ClO_4)_2 \cdot CH_3OH$	$[Zn(1\text{-}isoTQDACH)](ClO_4)_2 \cdot 2CH_3OH$
Zn-N1	2.2043(19)	2.178(3), 2.210(3)
Zn-N2	2.1804(16)	2.174(3), 2.168(3)
Zn-N3	2.1421(14)	2.115(3), 2.171(3)
Zn-N4	2.2887(18)	2.175(3), 2.117(3)
Zn-N5	2.1269(17)	2.139(3), 2.148(3)
Zn-N6	2.4848(19)	2.171(3), 2.141(3)
N1-Zn-N2	80.02(6)	81.48(11), 80.82(11)
N1-Zn-N3	76.43(7)	79.88(11), 76.40(11)
N1-Zn-N4	79.89(7)	79.85(11), 80.60(11)
N1-Zn-N5	157.13(6)	151.75(10), 155.58(12)
N1-Zn-N6	89.78(7)	95.78(11), 105.44(11)
N2-Zn-N3	152.98(7)	157.90(11), 150.08(11)
N2-Zn-N4	91.71(7)	103.86(11), 109.13(12)
N2-Zn-N5	77.43(7)	77.04(11), 79.64(11)
N2-Zn-N6	78.29(6)	79.44(10), 80.47(11)
N3-Zn-N4	96.97(6)	84.42(11), 86.12(11)
N3-Zn-N5	126.39(8)	124.27(11), 126.66(12)
N3-Zn-N6	88.51(6)	90.73(11), 87.12(11)
N4-Zn-N5	96.95(7)	87.66(11), 92.12(11)
N4-Zn-N6	166.78(7)	173.96(11), 169.60(12)
N5-Zn-N6	89.36(6)	98.07(11), 85.60(12)

Zn-N3-C(4)	168.46(10)	173.60(15), 174.72(16)
Zn-N4-C(4)	152.57(10)	173.61(16), 163.64(16)
Zn-N5-C(4)	166.67(10)	166.90(15), 168.63(16)
Zn-N6-C(4)	139.56(10)	167.98(15), 175.69(16)

Table S5. Interatomic distances (Å) and angles (°) for [Cu(TQDACH)]$(ClO_4)_2 \cdot 3CH_3OH \cdot H_2O$, [Cd(TQDACH)]$(ClO_4)_2$ and [Cd(1-isoTQDACH)(CH_3OH)]$(ClO_4)_2 \cdot 0.5CH_3OH \cdot 2H_2O$

	[Cu(TQDACH)]-$(ClO_4)_2 \cdot 3CH_3OH$	[Cd(TQDACH)]-$(ClO_4)_2$	[Cd(1-isoTQDACH)-(CH_3OH)]$(ClO_4)_2 \cdot 0.5CH_3OH \cdot 2H_2O$
M-N1	2.045(4)	2.386(4)	2.417(3), 2.419(3)
M-N2	2.039(4)		2.428(4), 2.417(3)
M-N3	2.032(4)	2.289(4)	2.447(3), 2.432(3)
M-N4	2.345(4)	2.472(3)	2.319(4), 2.314(4)
M-N5	2.068(4)		2.411(4), 2.449(3)
M-N6	2.824(4)		2.330(4), 2.339(4)
M-O1	-	-	2.434(3), 2.407(3)
N1-M-N2	85.53(15)	73.78(12)	73.77(10), 74.65(10)
N1-M-N3	79.39(16)	72.18(14)	68.21(10), 68.48(11)
N1-M-N4	80.32(14)	74.40(12)	74.22(12), 73.43(11)
N1-M-N5	165.26(15)	137.72(15)	127.09(11), 128.11(10)
N1-M-N6	91.77(13)	102.02(12)	98.02(12), 97.56(11)
N2-M-N3	159.03(17)	137.72(15)	134.51(12), 133.71(12)
N2-M-N4	96.90(14)	102.02(12)	109.48(11), 108.24(11)
N2-M-N5	80.21(16)	72.18(14)	68.91(12), 68.54(11)
N2-M-N6	75.90(13)	74.40(12)	71.26(12), 71.36(11)
N3-M-N4	94.85(15)	92.25(11)	83.47(11), 87.29(11)
N3-M-N5	113.34(17)	148.53(14)	156.33(13), 157.74(13)
N3-M-N6	89.99(14)	88.93(11)	90.01(11), 86.54(11)
N4-M-N5	104.99(15)	88.93(11)	84.29(12), 84.66(10)
N4-M-N6	169.78(12)	175.65(9)	171.29(11), 170.50(11)
N5-M-N6	81.18(14)	92.25(11)	103.80(12), 103.65(10)
O1-M-N1	-	-	150.46(9), 149.69(9)
O1-M-N2	-	-	131.04(10), 131.72(9)
O1-M-N3	-	-	82.31(10), 81.23(10)
O1-M-N4	-	-	105.08(12), 104.90(11)
O1-M-N5	-	-	81.43(11), 80.86(10)
O1-M-N6	-	-	79.64(12), 81.27(11)

M-N3-C(4)	166.9(3)	164.75(18)	157.84(17), 157.14(17)
M-N4-C(4)	162.9(2)	140.48(14)	178.00(18), 175.44(14)
M-N5-C(4)	167.1(3)		157.97(17), 154.00(15)
M-N6-C(4)	116.57(18)		171.70(18), 156.50(18)

Table S6. Interatomic distances (Å) and angles (°) for $[Cd(TQEN)](ClO_4)_2 \cdot 2CHCl_3$, $[Cd(1\text{-}isoTQEN)(CH_3CN)](ClO_4)_2 \cdot CH_3CN$ and $[Cd(TPEN)(H_2O)](ClO_4)_2$

	$[Cd(TQEN)](ClO_4)_2 \cdot 2CHCl_3$	$[Cd(1\text{-}isoTQEN)(CH_3CN)](ClO_4)_2 \cdot CH_3CN$	$[Cd(TPEN)(H_2O)](ClO_4)_2$
Cd-N1	2.400(3)	2.406(2)	2.4637(13)
Cd-N2	2.377(3)	2.4088(18)	
Cd-N3	2.354(3)	2.504(3)	2.4890(13)
Cd-N4	2.370(2)	2.338(2)	2.3568(12)
Cd-N5	2.376(3)	2.426(3)	
Cd-N6	2.435(2)	2.378(3)	
Cd-X	-	2.366(3)[a]	2.3884(18)[b]
N1-Cd-N2	74.69(10)	75.83(7)	73.96(5)
N1-Cd-N3	70.83(10)	67.43(7)	68.86(4)
N1-Cd-N4	75.53(8)	72.82(7)	71.35(4)
N1-Cd-N5	147.01(10)	124.72(7)	125.98(4)
N1-Cd-N6	88.81(8)	97.17(8)	106.58(4)
N2-Cd-N3	142.12(9)	131.42(7)	125.98(4)
N2-Cd-N4	92.00(9)	115.54(7)	106.58(4)
N2-Cd-N5	72.72(10)	68.68(7)	68.86(4)
N2-Cd-N6	74.25(8)	70.08(7)	71.35(4)
N3-Cd-N4	94.17(8)	83.07(8)	97.13(4)
N3-Cd-N5	141.81(10)	159.84(8)	163.67(5)
N3-Cd-N6	89.68(8)	83.85(8)	83.22(4)
N4-Cd-N5	100.57(8)	85.77(8)	83.22(4)
N4-Cd-N6	161.57(10)	165.87(8)	177.53(5)
N5-Cd-N6	87.22(8)	108.28(8)	97.13(4)
X-Cd-N1	-	150.84(8)[a]	143.02(3)[b]
X-Cd-N2	-	129.12(8)[a]	143.02(3)[b]
X-Cd-N3	-	83.48(9)[a]	81.83(3)[b]
X-Cd-N4	-	102.59(9)[a]	91.23(3)[b]
X-Cd-N5	-	82.63(9)[a]	81.83(3)[b]
X-Cd-N6	-	81.16(9)[a]	91.23(3)[b]
Cd-N3-C(4)	162.57(11)	159.24(11)	170.23(7)
Cd-N4-C(4)	164.21(15)	177.69(11)	172.52(7)

Cd-N5-C(4)	165.98(13)	163.59(11)
Cd-N6-C(4)	147.24(13)	163.46(13)

[a] X = N.

[b] X = O.

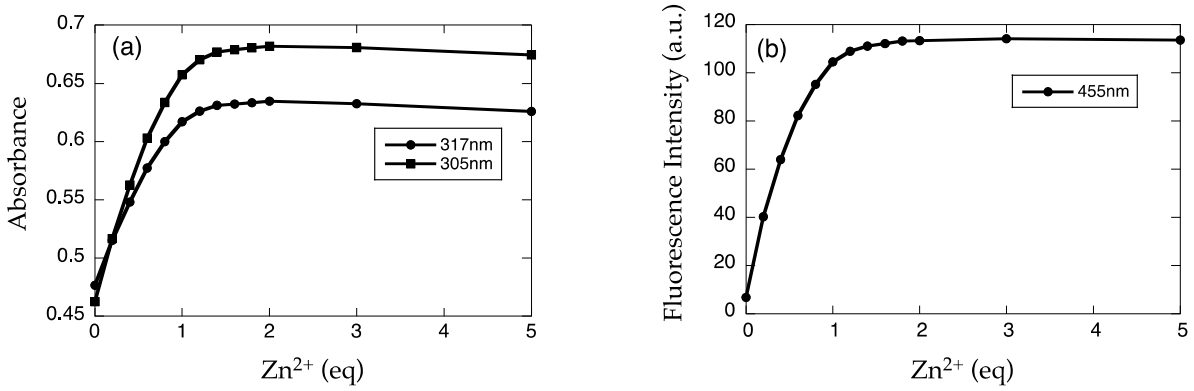

Figure S1. Zinc titration profile for 34 μM TQDACH in DMF/H_2O (1:1) at 25 °C. (a) UV-vis absorbance changes at 305 and 317 nm. (b) Fluorescence intensity changes (λ_{ex} = 317 nm) at 455 nm.

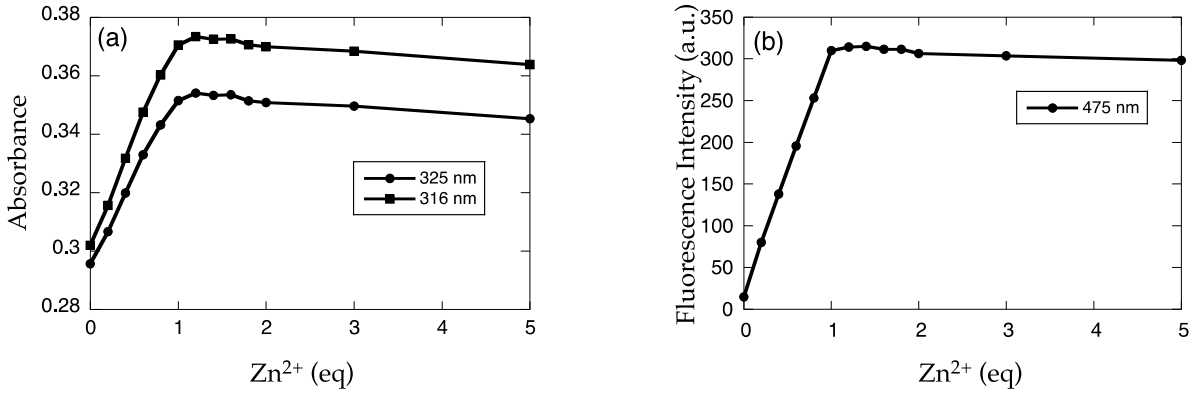

Figure S2. Zinc titration profile for 34 μM 1-isoTQDACH in DMF/H_2O (1:1) at 25 °C. (a) UV-vis absorbance changes at 316 and 325 nm. (b) Fluorescence intensity changes (λ_{ex} = 325 nm) at 475 nm.

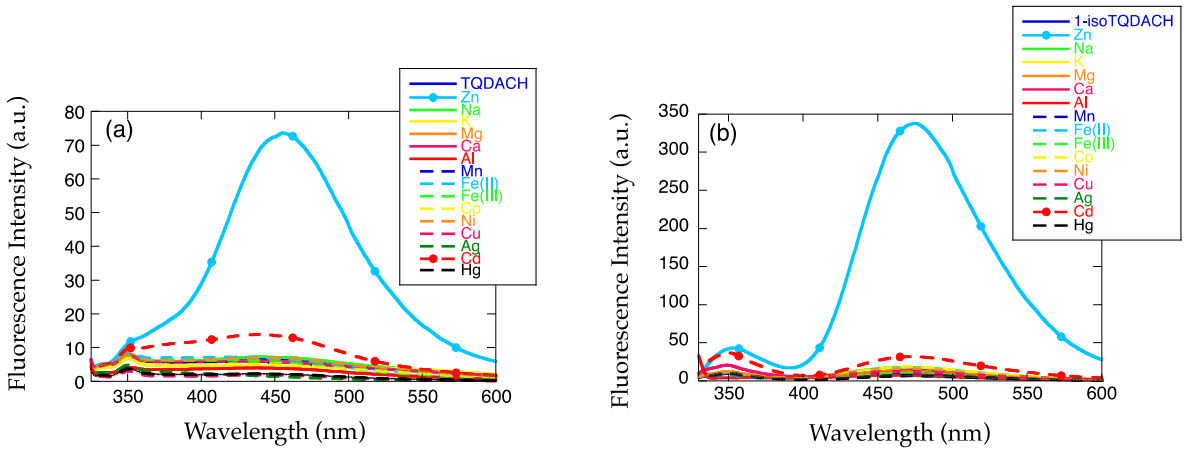

Figure S3. Fluorescence spectra of 34 μM (a) TQDACH (λ_{ex} = 317 nm) and (b) 1-isoTQDACH (λ_{ex} = 325 nm) in DMF/H_2O (1:1) at 25 °C in the presence of one equivalent of zinc (light blue, solid line with marks), cadmium (red, broken line with marks) and other metal ions (various colors, no marks).

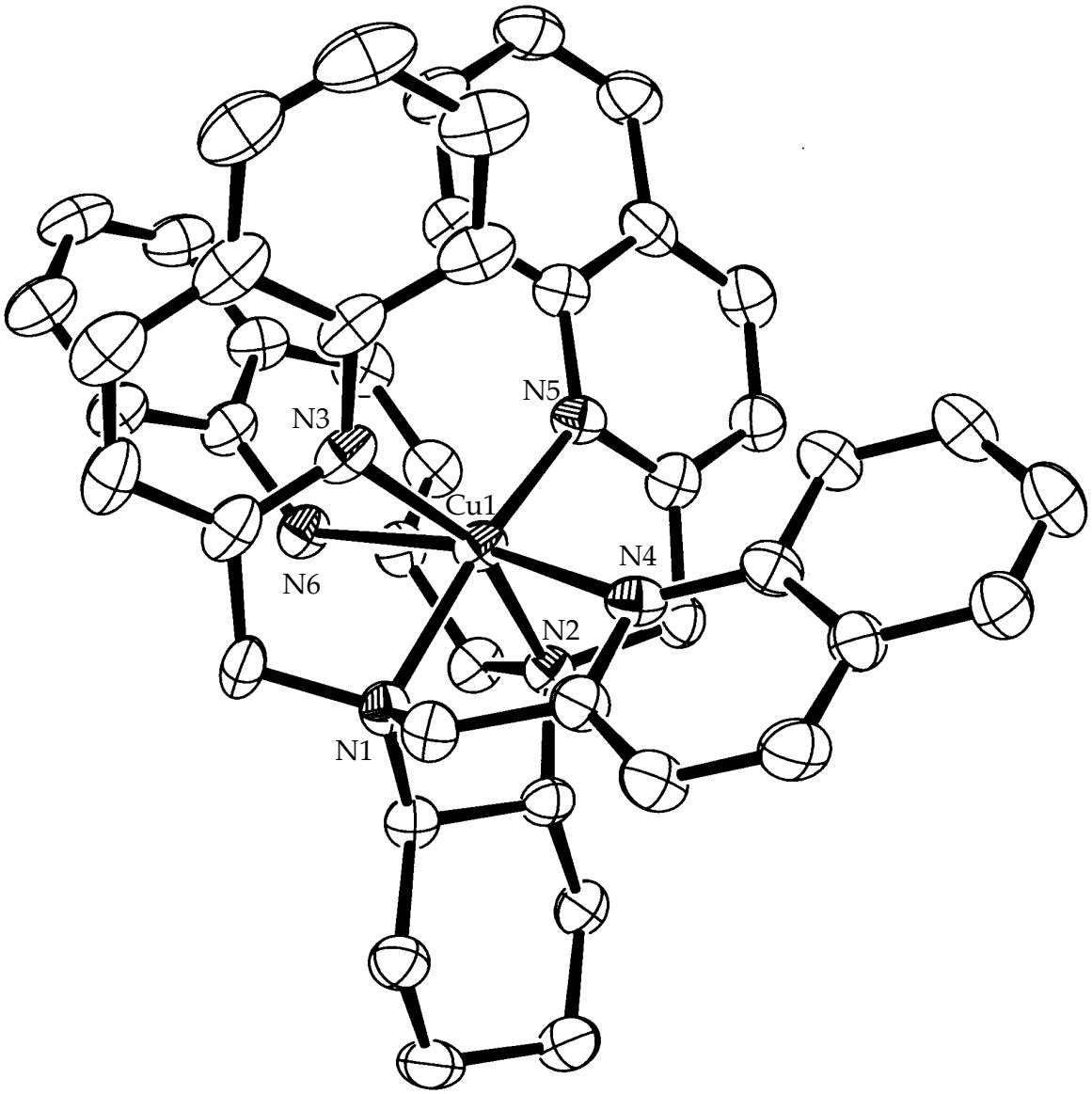

Figure S4. ORTEP plot for $[Cu(TQDACH)](ClO_4)_2 \cdot 3CH_3OH$ with 50% probability ellipsoids. Counter anions, hydrogen atoms and solvents were omitted for clarity.

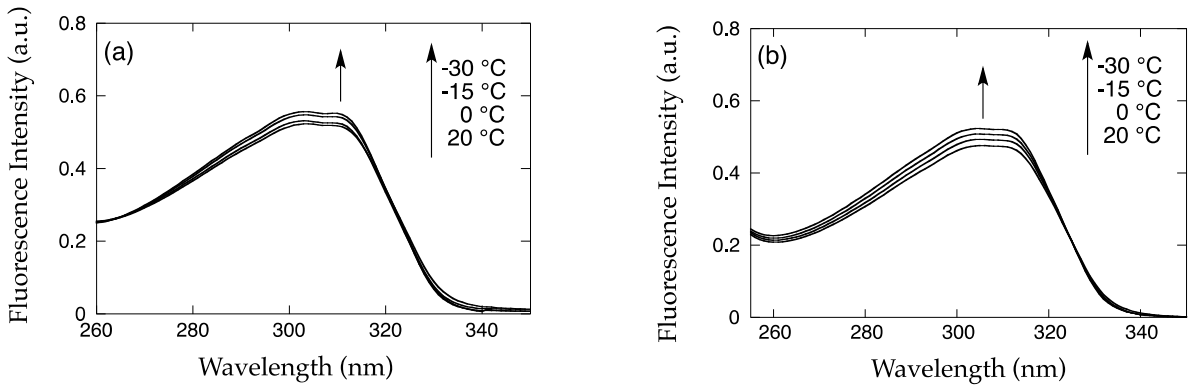

Figure S5. Temperature-dependent UV-vis spectra of 34 μM (a) TQEN-Zn complex and (b) TQDACH-Zn complex in acetonitrile.

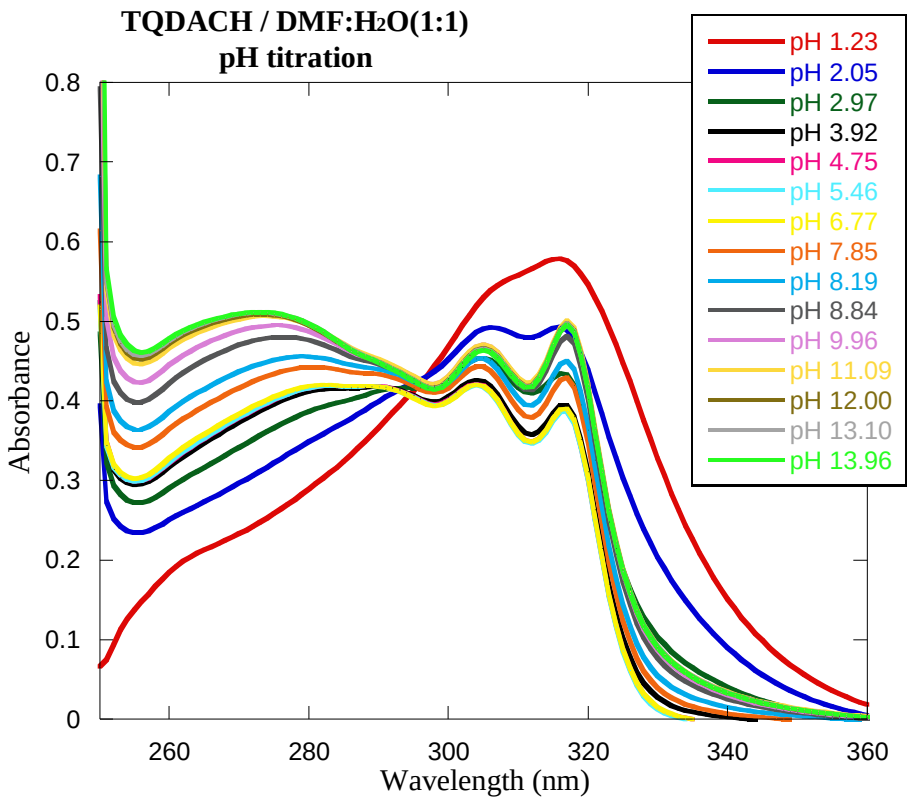

Figure S6. UV-vis spectra of 34 μM TQDACH in DMF/water (1:1) at various pHs at 25 °C.

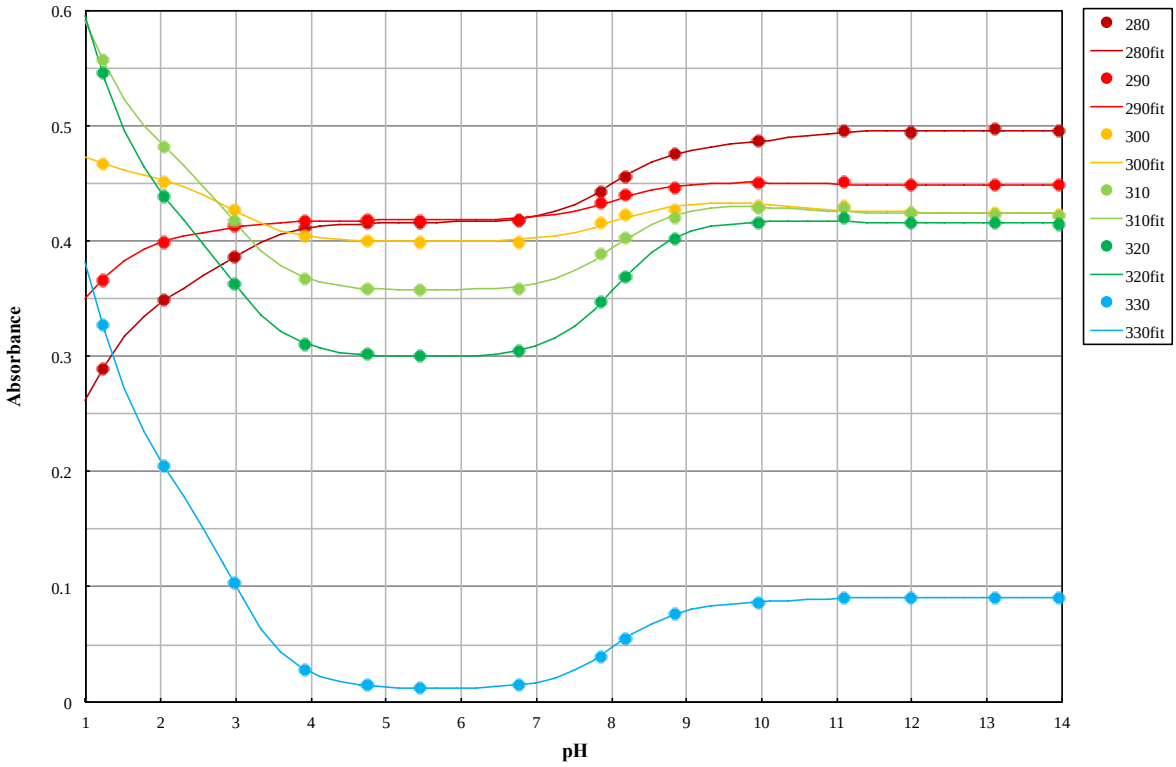

Figure S7. Curve fitting of the pH-dependent absorbance change of TQDACH in DMF/water (1:1) using SPECFIT[1] analysis.

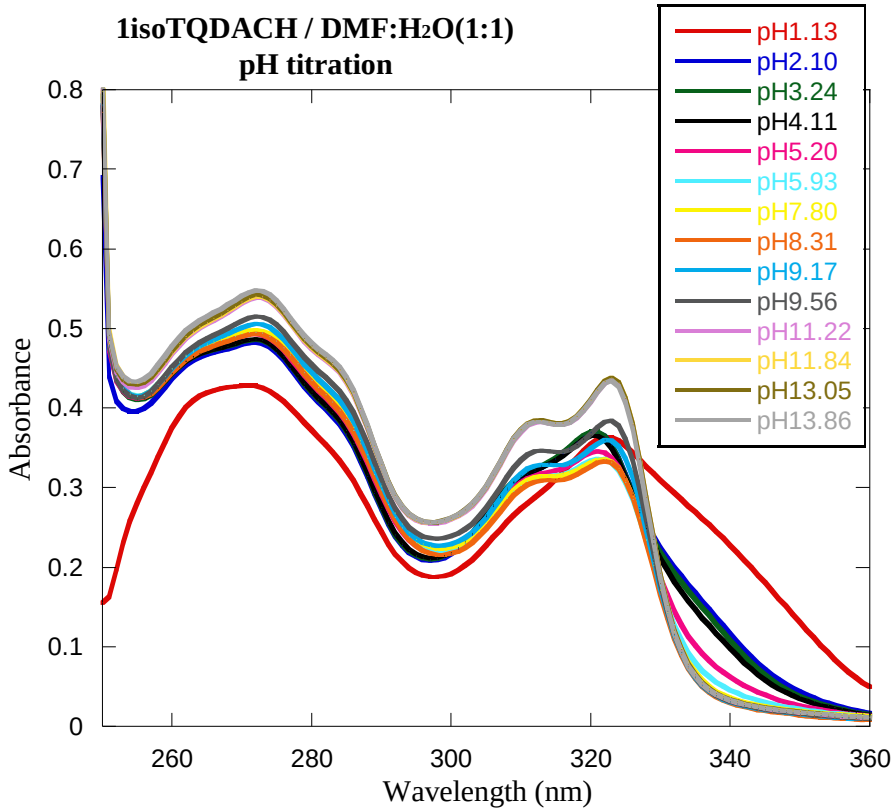

Figure S8. UV-vis spectra of 34 μM 1-isoTQDACH in DMF/water (1:1) at various pHs at 25 °C.

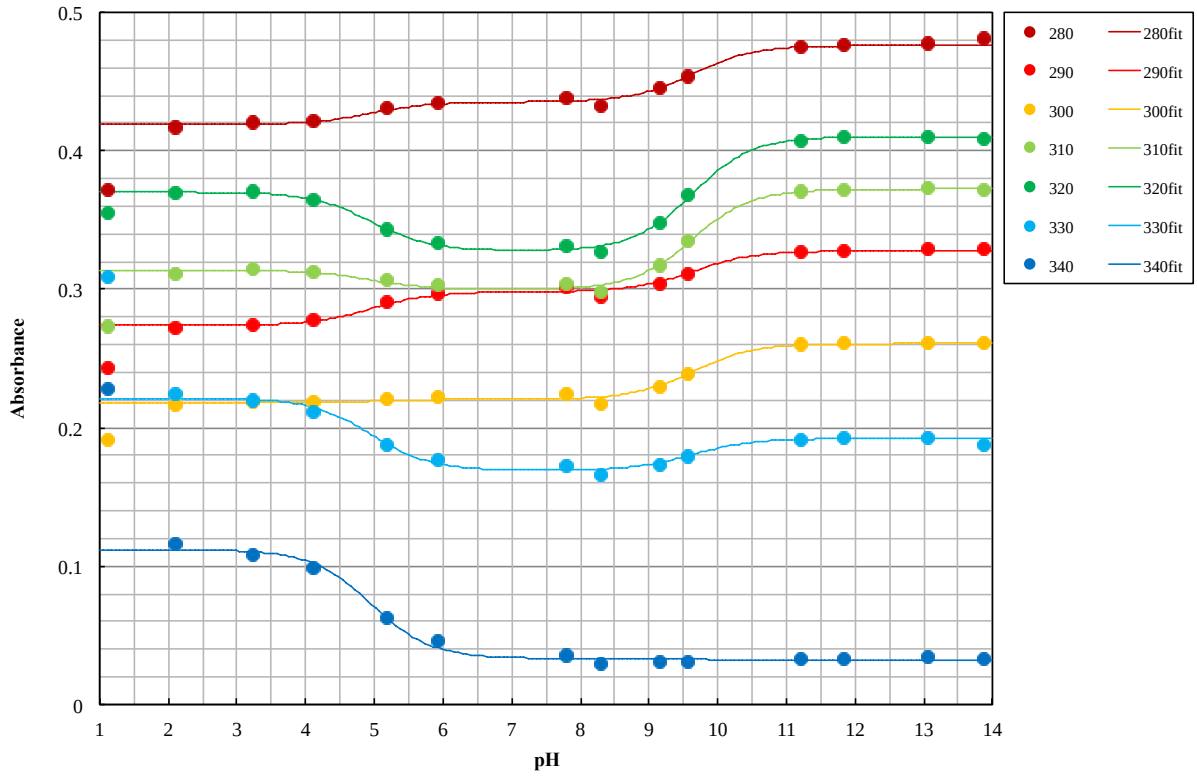

Figure S9. Curve fitting of the pH-dependent absorbance change of 1-isoTQDACH in DMF/water (1:1) using SPECFIT[1] analysis.

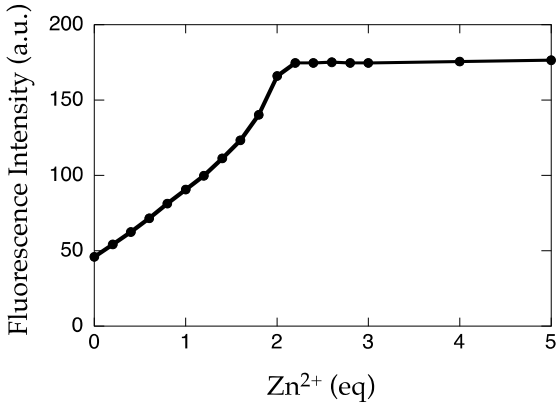

Figure S10. Competitive fluorescence intensity change of 34 μM 1-isoTQEN at 477 nm (λ_{ex} = 328 nm) in the presence of one equivalent of TPEN with increasing amount of zinc in DMF/H_2O (1:1) at 25 °C.

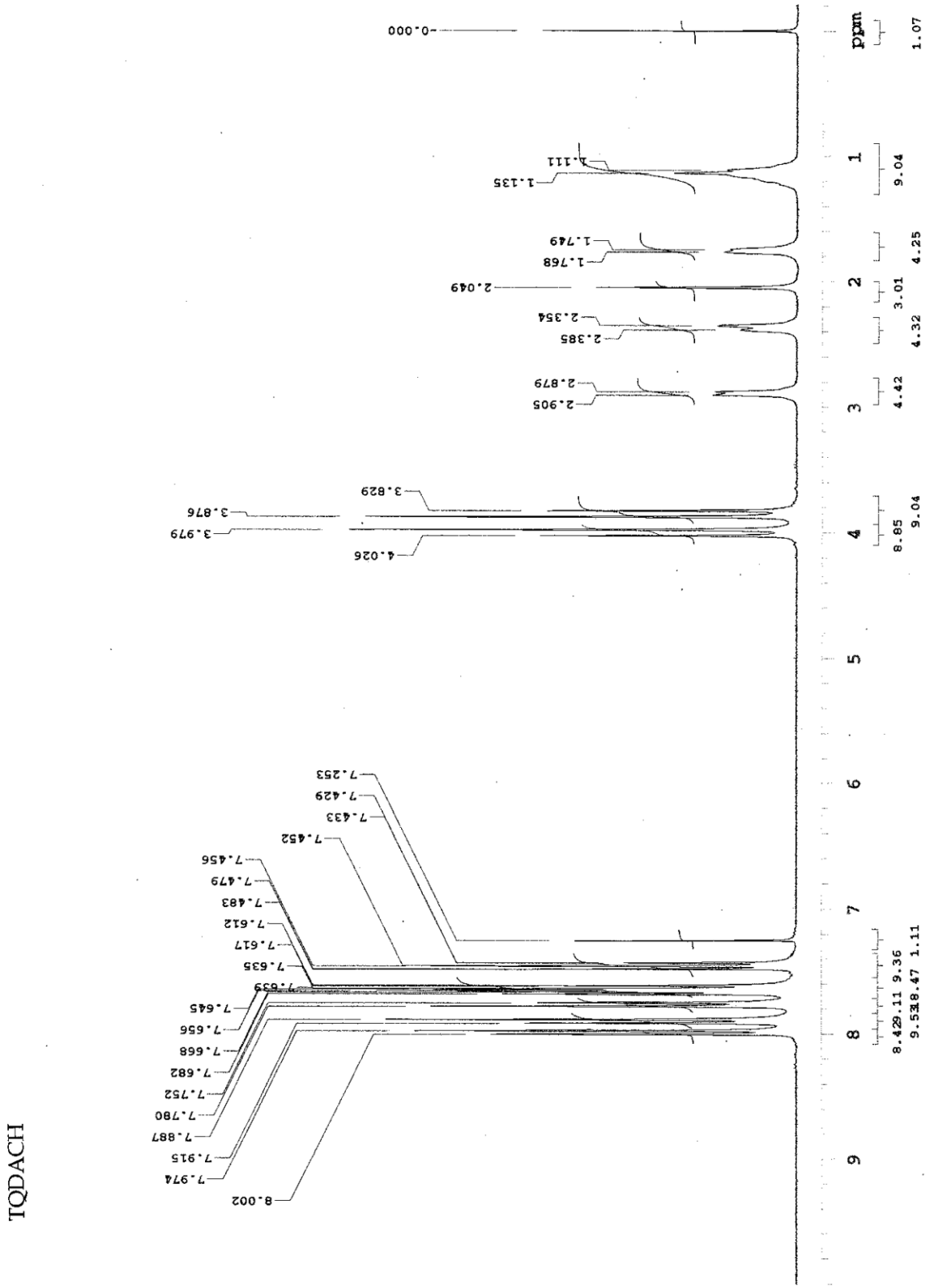

Figure S11. ^{1}H NMR spectrum of TQDACH in $CDCl_3$.

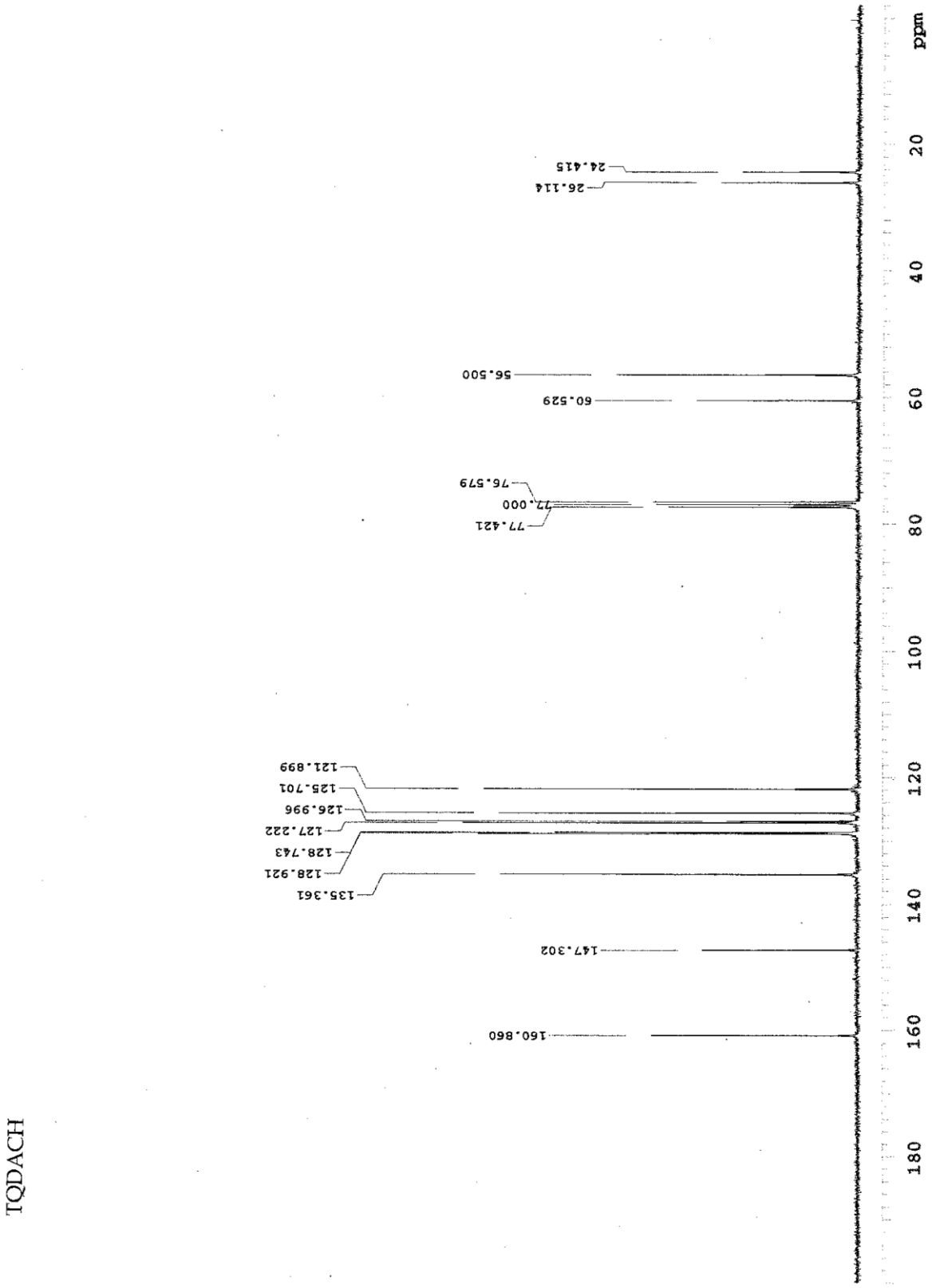

Figure S12. ^{13}C NMR spectrum of TQDACH in $CDCl_3$.

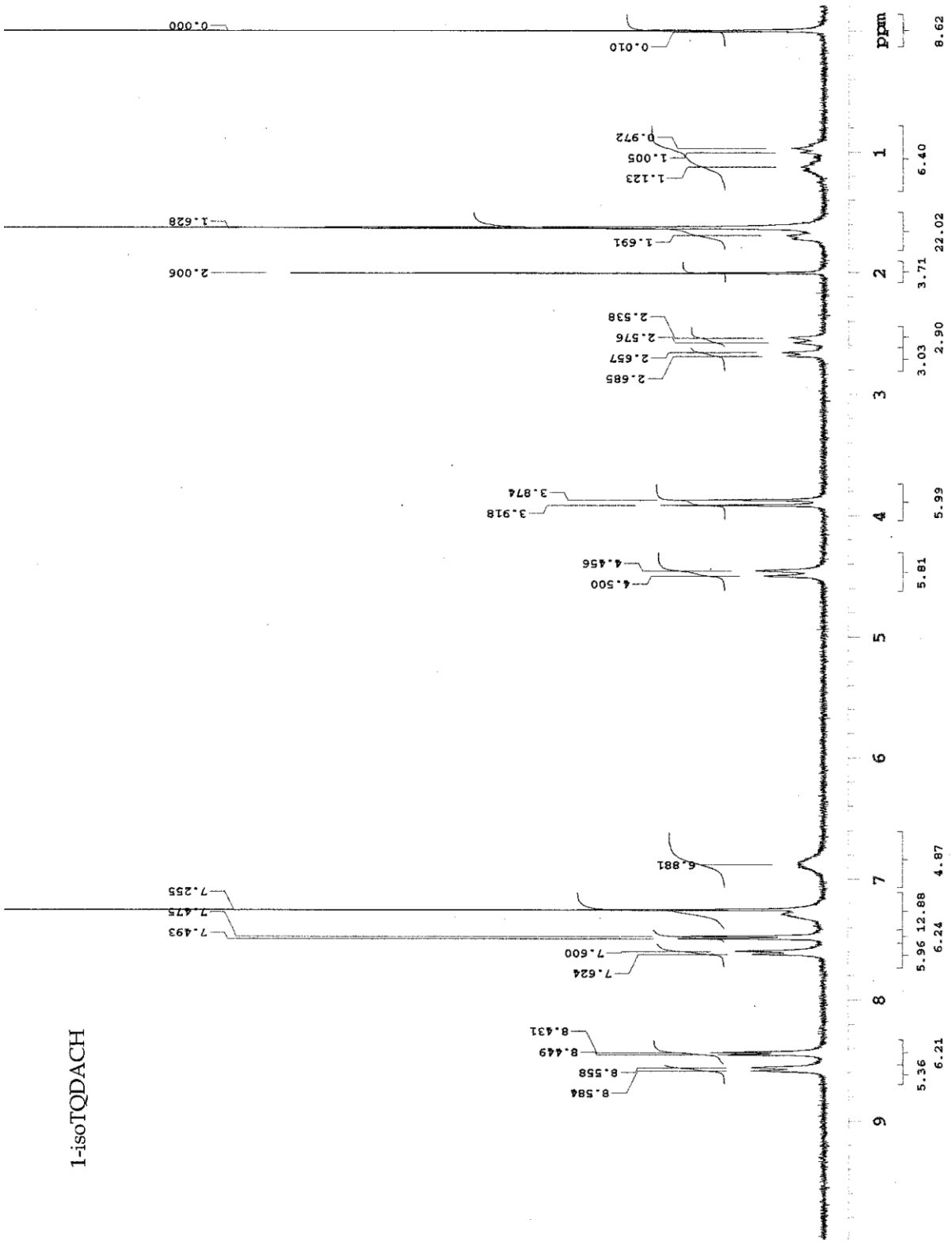

Figure S13. ^{1}H NMR spectrum of 1-isoTQDACH in $CDCl_3$.

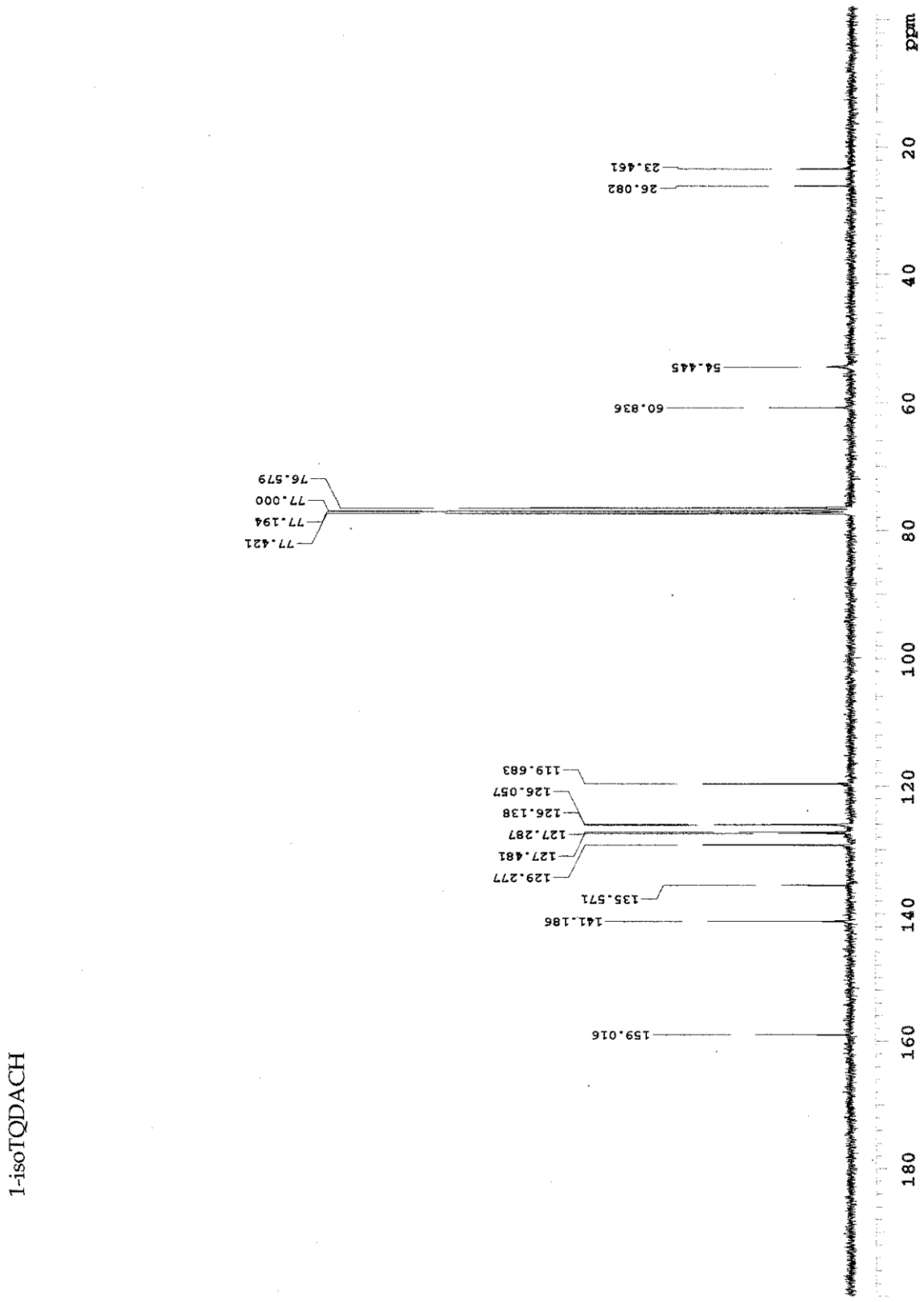

Figure S14. ^{13}C NMR spectrum of 1-isoTQDACH in $CDCl_3$.

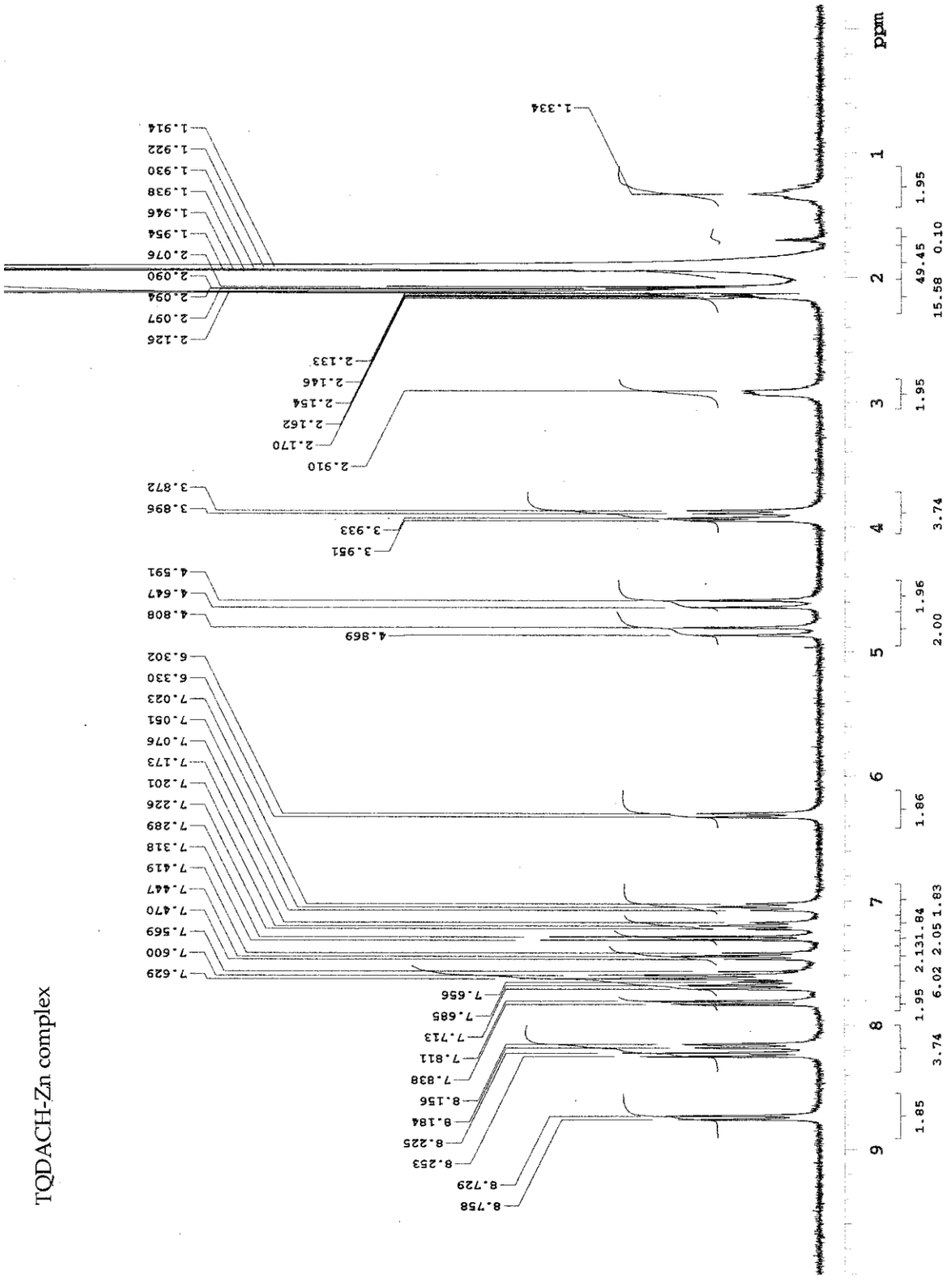

Figure S15. ^{1}H NMR spectrum of $[Zn(TQDACH)](ClO_4)_2$ in CD_3CN.

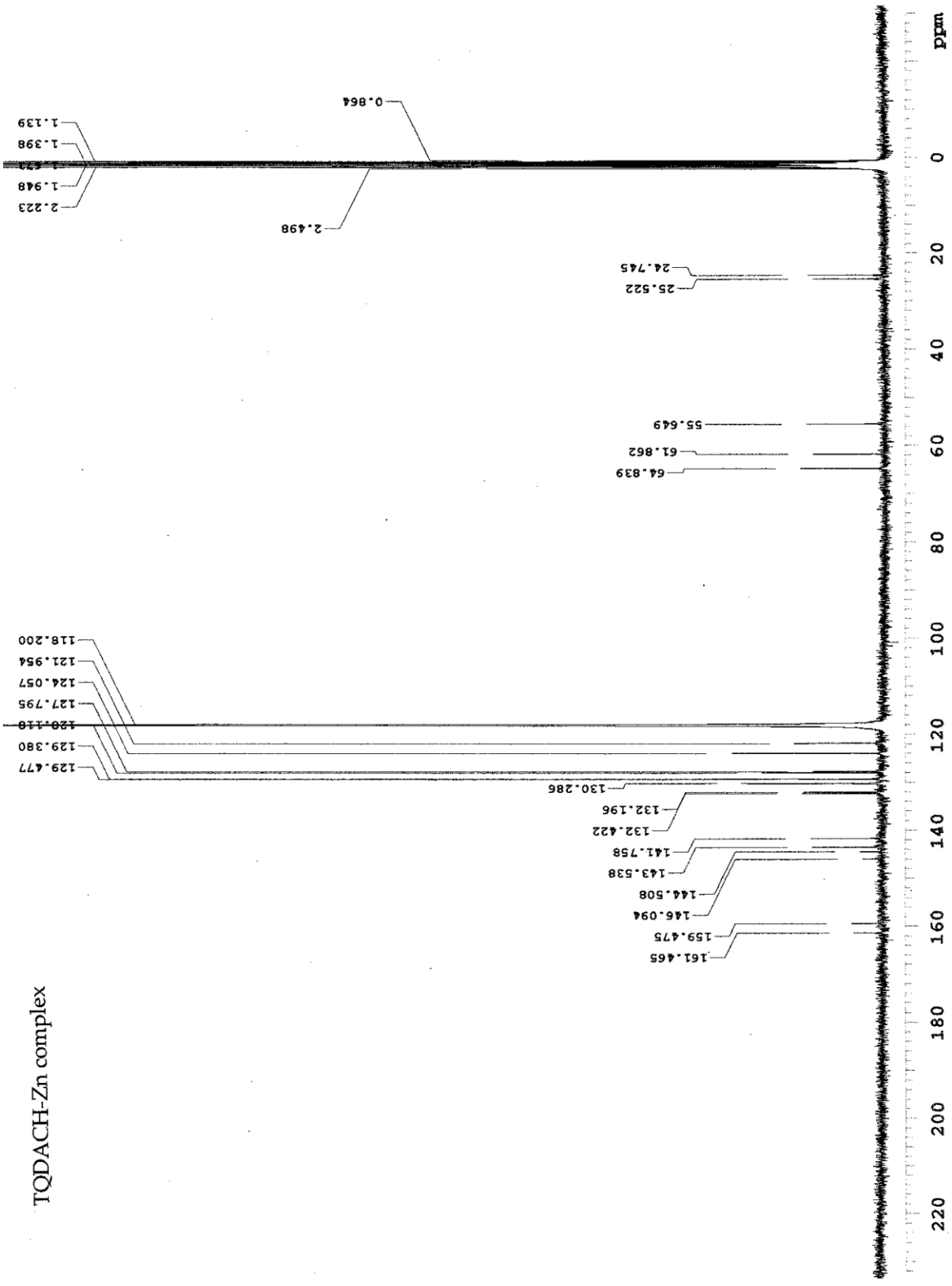

Figure S16. ^{13}C NMR spectrum of $[Zn(TQDACH)](ClO_4)_2$ in CD_3CN.

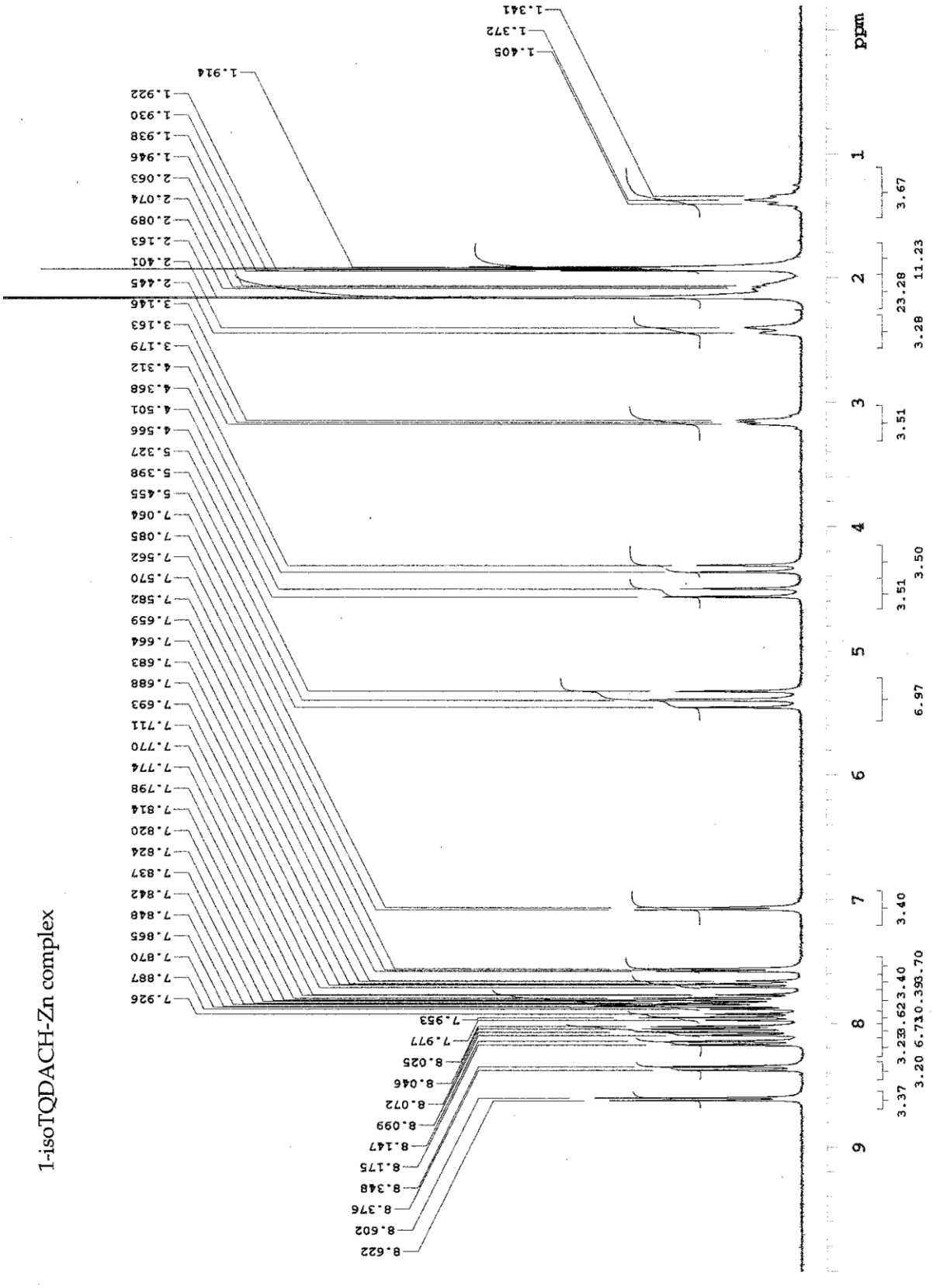

Figure S17. ^{1}H NMR spectrum of [Zn(1-isoTQDACH)]$(ClO_4)_2$ in CD_3CN.

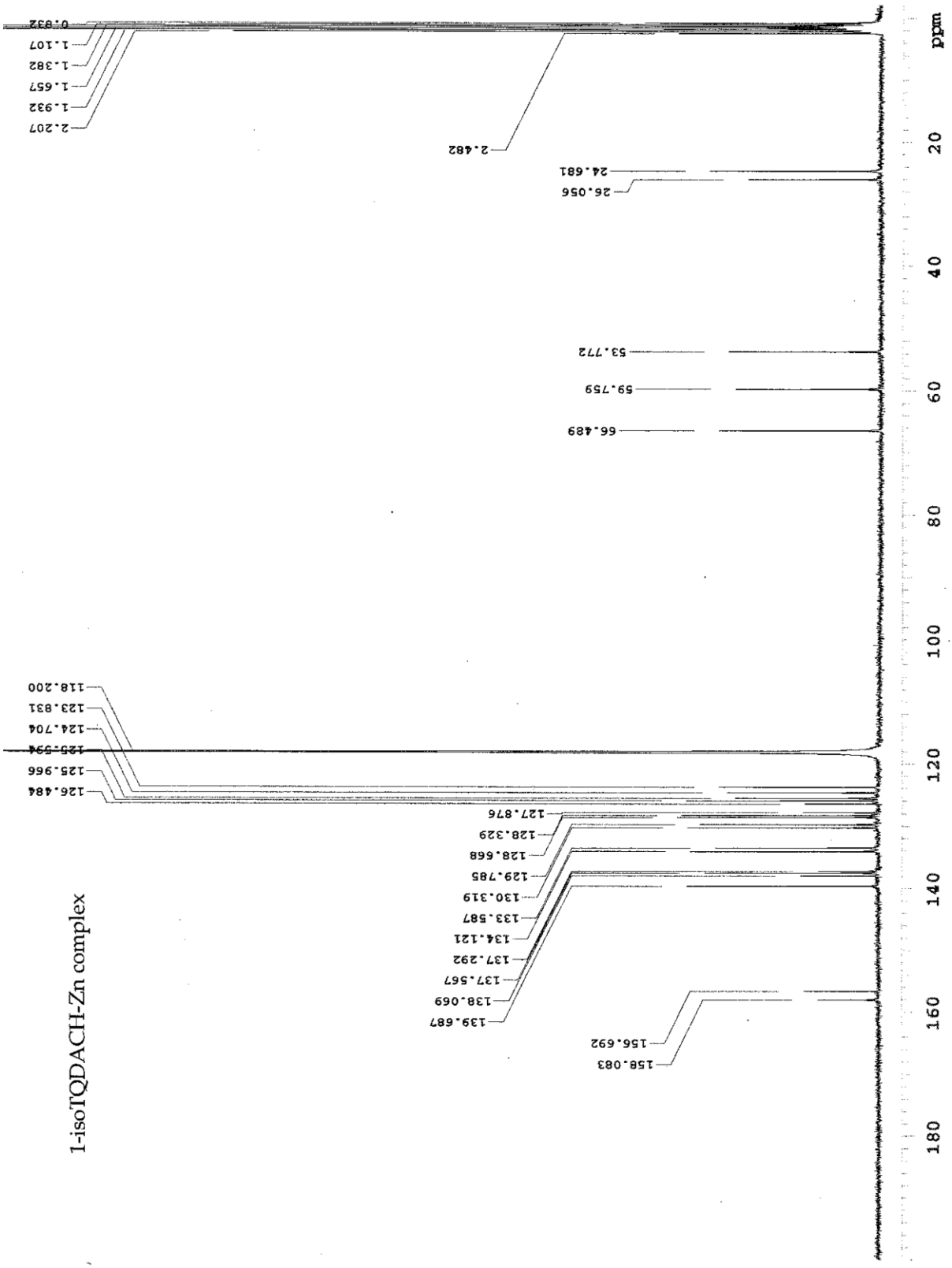

Figure S18. ^{13}C NMR spectrum of $[Zn(1\text{-isoTQDACH})](ClO_4)_2$ in CD_3CN.

References

(1) R. A. Binstead, B. Jung, A. D. Zuverbühler, *SPECFIT/32, Global Analysis System, ver 3.0; Spectrum Software Associates: Marlborough, USA* **2000**.