International Journal of
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MDPI

Supporting Information

1. *Bis*thiosemicarbazone ligands H_2L^{Me}, H_2L^{Ph} and H_2L^{PhNO2}

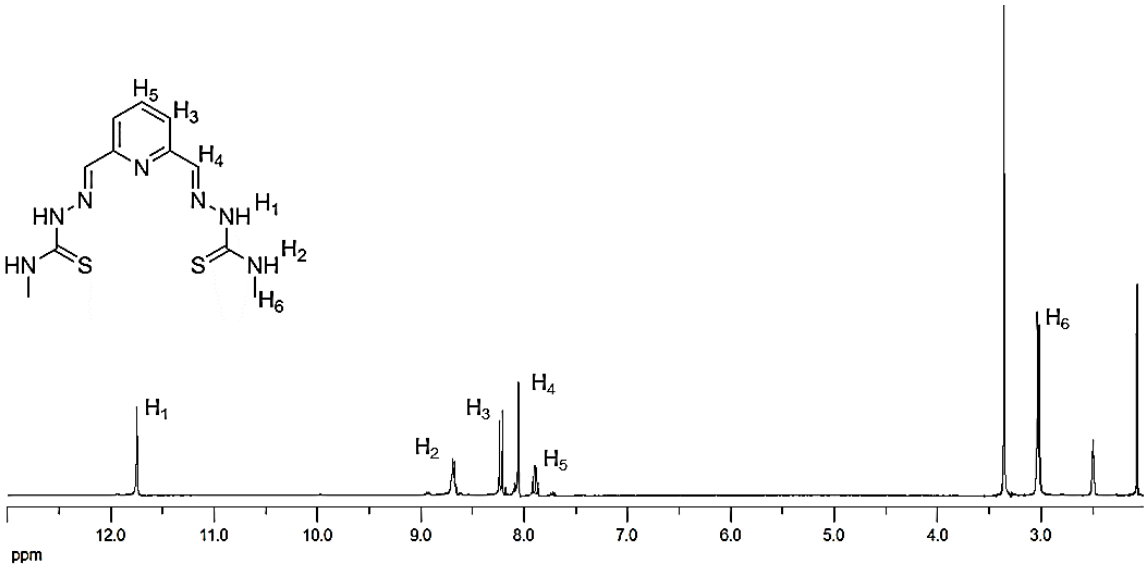

Figure S1. ^{1}H NMR spectra of $H_2L^{Me}\cdot 2H_2O$ (DMSO-d_6, r.t.). **^{1}H NMR [DMSO-d_6, δ (m, nH, Hx, J)]:** 11.76 (s, 2H, H_1), 8.71 (c_e, 2H, H_2, J= 4.4 Hz), 8.25 (d, 2H, H_3, J= 7.8 Hz), 8.06 (s, 2H, H_4), 7.90 (t, 1H, H_5, J= 7.8 Hz), 3.04 (d, 6H, H_6, J= 4.1 Hz).

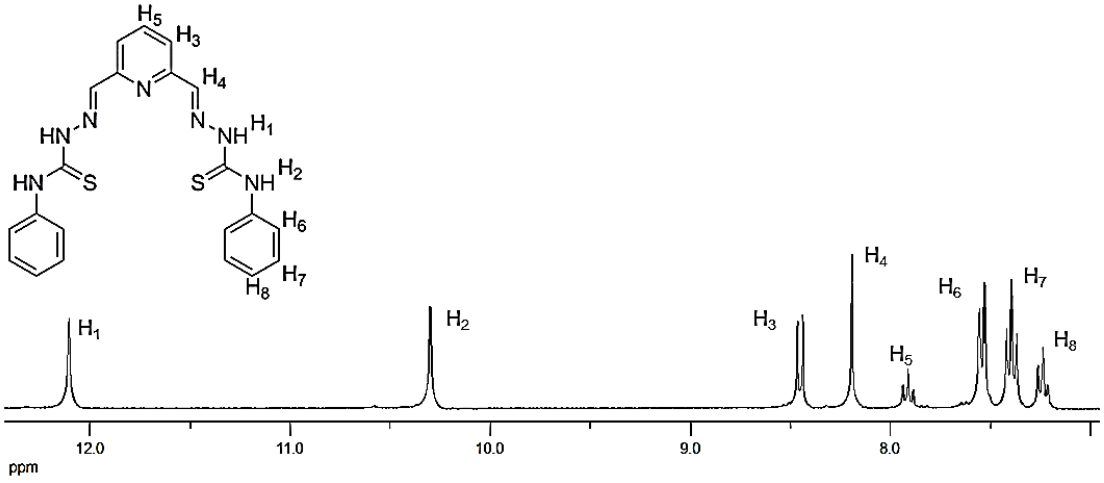

Figure S2. ^{1}H NMR spectra of $H_2L^{Ph}\cdot 2H_2O$ (DMSO-d_6, r.t.). **^{1}H NMR [DMSO-d_6, δ (m, nH, Hx, J)]:** 12.11 (s, 2H, H_1), 10.30 (s, 2H, H_2), 8.46 (d, 2H, H_3, J= 7.8 Hz), 8.19 (s, 2H, H_4), 7.91 (t, 1H, H_5, J= 7.8 Hz), 7.56 (d, 4H, H_6, J= 7.6 Hz), 7.40 (t_a, 4H, H_7, J_1= 7.6 Hz, J_2= 8.0 Hz), 7.24 (t, 2H, H_8, J_1= 7.4 Hz, J_2= 7.3 Hz).

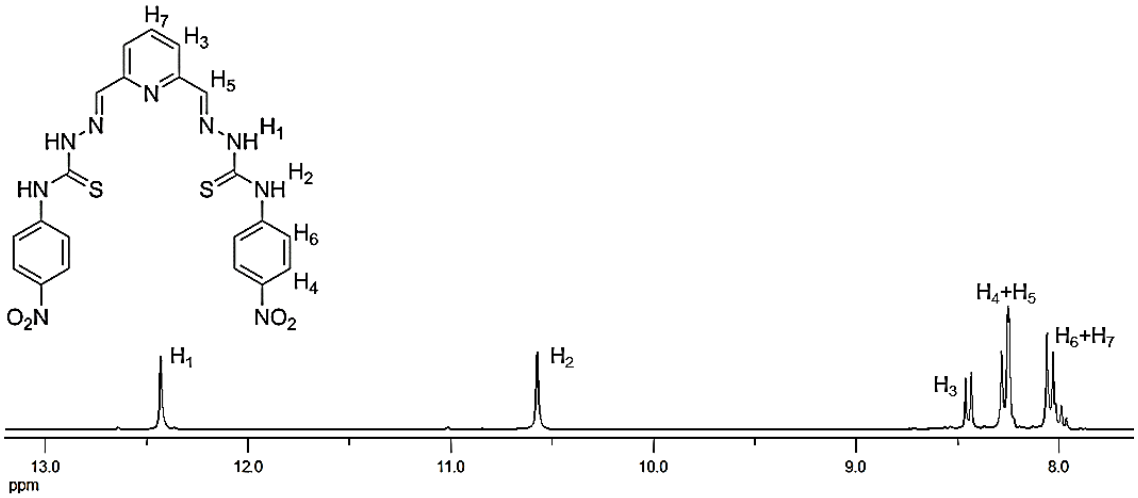

Figure S3. ^{1}H NMR spectra of H_2L^{PhNO2} (DMSO-d_6, r.t.). **^{1}H NMR [DMSO-d_6, δ (m, nH, Hx, J)]:** 12.43 (s, 2H, H_1), 10.57 (s, 2H, H_2), 8.46 (d, 2H, H_3, J= 7.8 Hz), 8.30-8.20 (m, 6H, H_4+H_5), 8.10-7.90 (m, 1H, H_6+H_7).

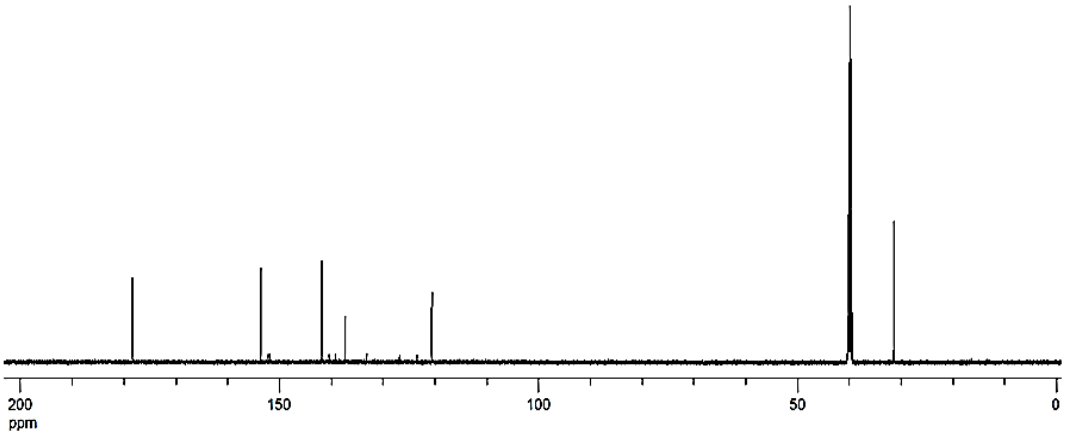

Figure S4. ^{13}C NMR spectra of H_2L^{Me}·2H_2O (DMSO-d_6, r.t.). **^{13}C NMR (DMSO-d_6, ppm):** 178.3 (C=S), 153.3 (C=N), 141.3 (C_{ar}), 137.5 (CH_{ar}), 120.6 (CH_{ar}), 31.26 (CH_3).

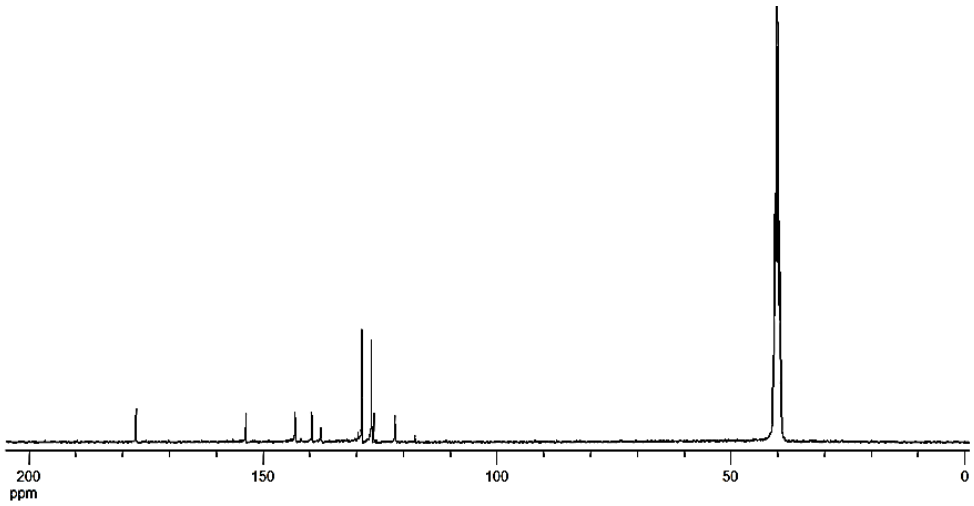

Figure S5. ^{13}C NMR spectra of H_2L^{Ph}·2H_2O (DMSO-d_6, r.t.). **^{13}C NMR (DMSO-d_6, ppm):** 177.1 (C=S), 153.7 (C=N), 143.1 (C_{ar}), 139.6 (C_{ar}), 137.7 (CH_{ar}), 128.8 (CH_{ar}), 126.8 (CH_{ar}), 126.3 (CH_{ar}), 121.8 (CH_{ar}).

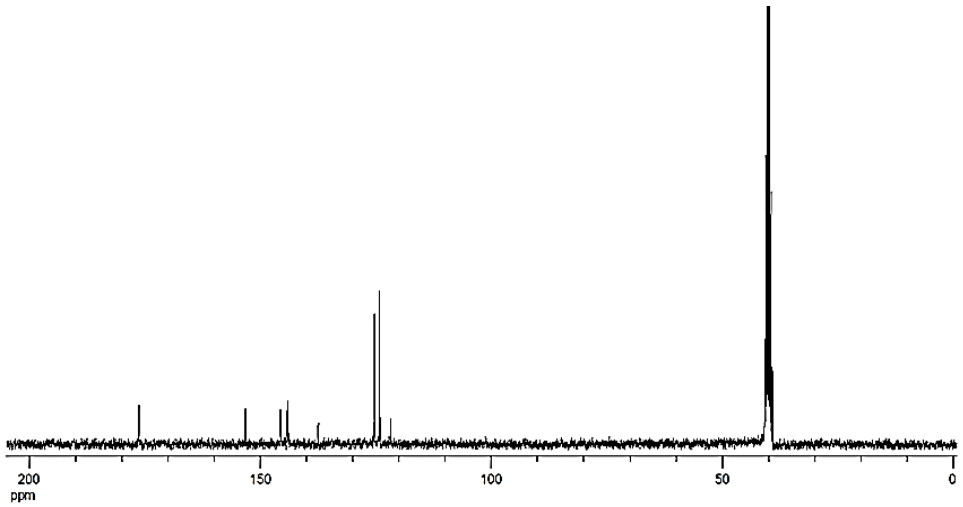

Figure S6. ^{13}C NMR spectra of H_2L^{PhNO2} (DMSO-d_6, r.t.). **^{13}C NMR (DMSO-d_6, ppm):** 176.4 (C=S), 153.3(C=N), 145.7(C_{ar}), 144.2 (C_{ar}), 144.0 (C_{ar}), 137.5 (CH_{ar}), 125.3 (CH_{ar}), 124.2 (CH_{ar}), 121.8 (CH_{ar}).

2. *Bis*thiosemicarbazone derived zinc(II) dihelicates

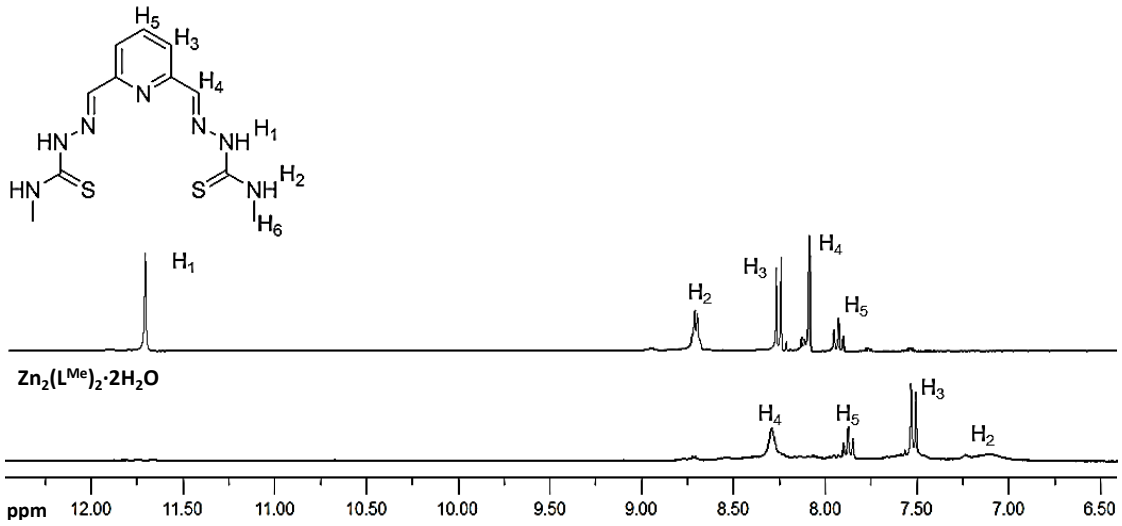

Figure S7. ^{1}H NMR spectra of $Zn_2(L^{Me})_2{\cdot}2H_2O$ (DMSO-d_6, r.t.). **^{1}H NMR [DMSO-d_6, δ (m, nH, Hx, J)]:** 8.26 (s, 2H, H_4), 7.83 (t, 1H, H_5, J= 7.7 Hz), 7.48 (d, 2H, H_3, J= 7.7 Hz), 7.22 (s_a, 1H, H_2), 2.75 (d, 6H, H_6, J= 4.2 Hz).

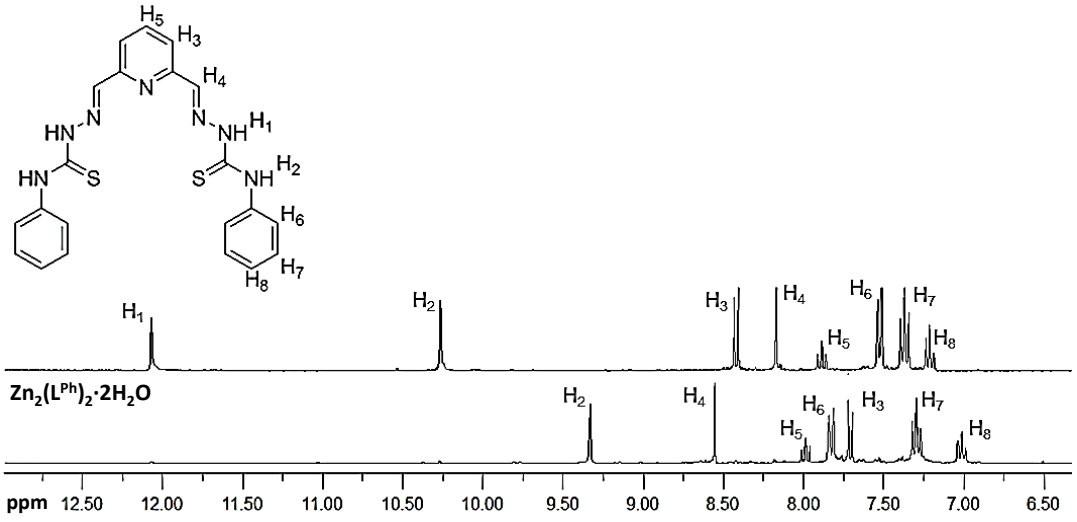

Figure S8. ^{1}H NMR spectra of $Zn_2(L^{Ph})_2 \cdot 2H_2O$ (DMSO-d_6, r.t.). **^{1}H NMR [DMSO-d_6, δ (m, nH, Hx, J)]:** 9.34 (s, 2H, H_2), 8.56 (s, 2H, H_4), 7.99 (d, 1H, H_5, J= 7.8 Hz), 7.84 (d, 4H, H_6, J= 7.8 Hz), 7.70 (d, 2H, H_3, J= 7.8 Hz), 7.30 (t_a, 4H, H_7, J_1= 7.8 Hz, J_2= 8.0 Hz), 7.01 (t_a, 2H, H_8, J_1= 7.4 Hz, J_2= 6.9 Hz).

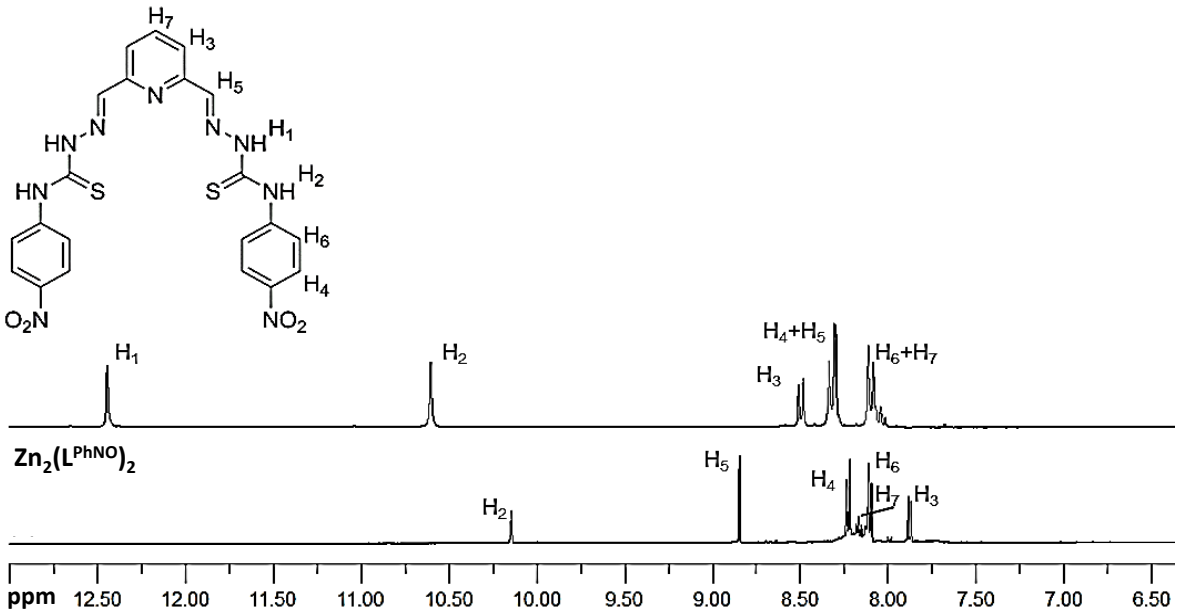

Figure S9. ^{1}H NMR spectra of $Zn_2(L^{PhNO2})_2$ (DMSO-d_6, r.t.). **^{1}H NMR [DMSO-d_6, δ (m, nH, Hx, J)]:** 10.11 (s, 2H, H_2), 8.80 (s, 2H, H_5), 8.17 (d, 1H, H_4, J= 7.7 Hz), 8.12 (t, 1H, H_7, J= 7.7 Hz), 8.05 (d, 4H, H_6, J= 9.3 Hz), 7.82 (d, 2H, H_3, J= 7.7 Hz).

Table S1. Main crystallographic data for helicates $[Zn_2(L^{Me})_2]\cdot 3H_2O$ **1***, $[Zn_2(L^{Ph})_2]\cdot 4CH_3CN$ **2*** and $[Zn_2(L^{PhNO2})_2]$ **3***.

	$[Zn_2(L^3\text{-}Me)_2]\cdot 3H_2O$	**$[Zn_2(L^3\text{-}Ph)_2]\cdot 4CH_3CN$**	**$[Zn_2(L^3\text{-}PhNO_2)_2]$**
Molecular formula	$Zn_2C_{22}H_{32}N_{14}S_4$	$Zn_2C_{50}H_{46}N_{18}S_4$	$Zn_2C_{42}H_{30}N_{18}O_8S_4$
Molecular weight	799.68	1158.03	1173.82
Spatial group	*I2/a*	P -1	*C2/c*
Crystalline system	Monoclinic	Triclinic	Monoclinic
Crystal size/mm	0.30 × 0.07 × 0.05	0.18 × 0.14 × 0.04	0.8 × 0.2 × 0.09
a/Å	14.424(4)	10.6496(5)	21.5284(13)
b/Å	12.7407(17)	15.3841(9)	14.0991(9)
c/Å	16.748(2)	18.3830(10)	15.6869(8)
α/º	90	97.235(2)	90
β/º	99.930(7)	105.836(2)	94.982(4)
γ/º	90	108.760(3)	90
Temperature/K	100	373(2)	100
Volume/Å^3	3031.6(10)	2667.0(2)	4743.5(5)
Z	4	2	4
Density/g cm^{-3}	1.752	1.442	1.644
Intervale θ/º	2.5 - 19.1	2.4 - 21.6	2.9 - 26.2
Measured reflexions	23453	40098	24181
Unique reflexions [R_{int}]	2896 [0.150]	10094 [0.086]	3478 [0.054]
μ/mm^{-1}	1.91	1.110	1.262
F(000)	1640	1192	2384
Residues/e Å^{-3}	0.56 and -0.94	0.794 and -0.537	1.18 and -0.63
R Final Index [I>2sigma(I)]	0.0612 [0.1383]	0.0545 [0.1138]	0.0342 [0.0779]
R Index [all data]	0.1108 [0.1682]	0.1038 [0.1298]	0.0522 [0.0845]

Table S2. Main bond distances and angles for $[Zn_2(L^{Me})_2]\cdot 3H_2O$ **1*** zinc helicate.

Bond distances (Å)					
N(3)-Zn(1)	2.114(5)	S(3)-Zn(1)	2.3865(19)	C(9)-N(5)	1.263(8)
N(5)-Zn(1)	2.124(5)	C(3)-N(3)	1.290(8)	C(10)-S(2)	1.747(7)
N(4)-Zn(1)	2.485(5)	C(2)-S(3)	1.739(6)	S(2)-Zn(1)	2.3423(19
Bond angles (º)					
N(3)-Zn(1)-S(3)	80.53(15)	N(3)-Zn(1)-N(4)	70.94(18)	C(9)-N(5)-N(6)	116.0(5)
N(5)-Zn(1)-S(2)	82.37(15)	N(5)-Zn(1)-N(4)	102.64(18)	C(10)-N(5)-N(6)	112.8(5)
S(3)-Zn(1)-S(2)	112.48(7)	C(3)-N(3)-N(2)	116.3(5)	N(1)-C(2)-S(3)	115.7(5)
C(2)-N(2)-N(3)	113.2(5)				

Table S3. Main bond distances and angles for $[Zn_2(L^{Ph})_2]\cdot 4CH_3CN$ **2*** zinc helicate.

Bond distances (Å)					
N(3)-Zn(1)	2.081(4)	S(1)-Zn(1)	2.3593(12)	C(14)-N(5)	1.280(6)
N(4)-Zn(1)	2.463(3)	S(2)-Zn(2)	2.3381(13)	C(15)-S(2)	1.741(5)
N(5)-Zn(2)	2.081(4)	S(3)-Zn(1)	2.3384(13)	C(28)-S(3)	1.741(5)
N(10)-Zn(1)	2.084(4)	S(4)-Zn(2)	2.3777(12)	C(29)-N(10)	1.284(5)
N(11)-Zn(2)	2.446(3)	C(7)-S(1)	1.738(5)	C(35)-N(12)	1.287(5)
N(12)-Zn(2)	2.080(4)	C(8)-N(3)	1.278(5)		
Bond angles (⁰)					
N(10)-Zn(1)-S(3)	83.30(11)	N(5)-Zn(2)-S(2)	83.58(11)	N(13)-N(12)-Zn(2)	123.2(3)
N(3)-Zn(1)-S(1)	81.96(10)	N(12)-Zn(2)-S(4)	81.23(10)	C(36)-N(13)-N(12)	112.7(4)
S(3)-Zn(1)-S(1)	111.71(5)	S(2)-Zn(2)-S(4)	110.53(5)	C(35)-N(12)-N(13)	116.1(4)
N(3)-Zn(1)-N(4)	72.07(13)	N(12)-Zn(2)-N(11)	72.20(13)	N(14)-C(36)-S(4)	114.4(3)
N(10)-Zn(1)-N(4)	94.92(13)	N(5)-Zn(2)-N(11)	97.47(13)	C(14)-N(5)-N(6)	115.4(4)
C(8)-N(3)-N(2)	116.7(4)	C(29)-N(10)-N(9)	116.0(4)	C(15)-N(6)-N(7)	117.3(4)
C(7)-N(2)-N(3)	112.7(4)	C(28)-N(9)-N(10)	113.3(4)	N(7)-C(15)-S(2)	114.3(4)
N(1)-C(7)-S(1)	94.97(16)	N(8)-C(28)-S(3)	113.6(3)		

Table S4. Main bond distances and angles for $[Zn_2(L^{PhNO2})_2]$ **3*** zinc helicate.

Bond distances (Å)					
N(4)-Zn(1)	2.062(2)	S(3)-Zn(2)	2.3857(7)	C(14)-N(6)	1.287(3)
S(4)-Zn(1)	2.3203(7)	C(7)-S(4)	1.737(3)	C(15)-S(3)	1.737(3)
N(6)-Zn(2)	2.116(2)	C(8)-N(4)	1.279(3)		
Bond angles (⁰)					
N(4)-Zn(1)-S(4)	84.14(6)	N(6)-Zn(2)-S(3)	110.45(6)	C(8)-N(4)-N(3)	115.1(2)
S(4)-Zn(1)-S(4)	122.23(4)	S(3)-Zn(2)-S(3)	118.20(4)	C(14)-N(6)-N(7)	114.5(2)
N(4)-Zn(1)-N(4)	145.32(12)	N(6)-Zn(2)-N(6)	158.14(12)	N(3)-C(7)-S(4)	127.9(2)
N(7)-C(15)-S(3)	127.7(2)	N(2)-C(7)-N(3)	117.3(2)	N(7)-C(15)-N(8)	116.6(2)

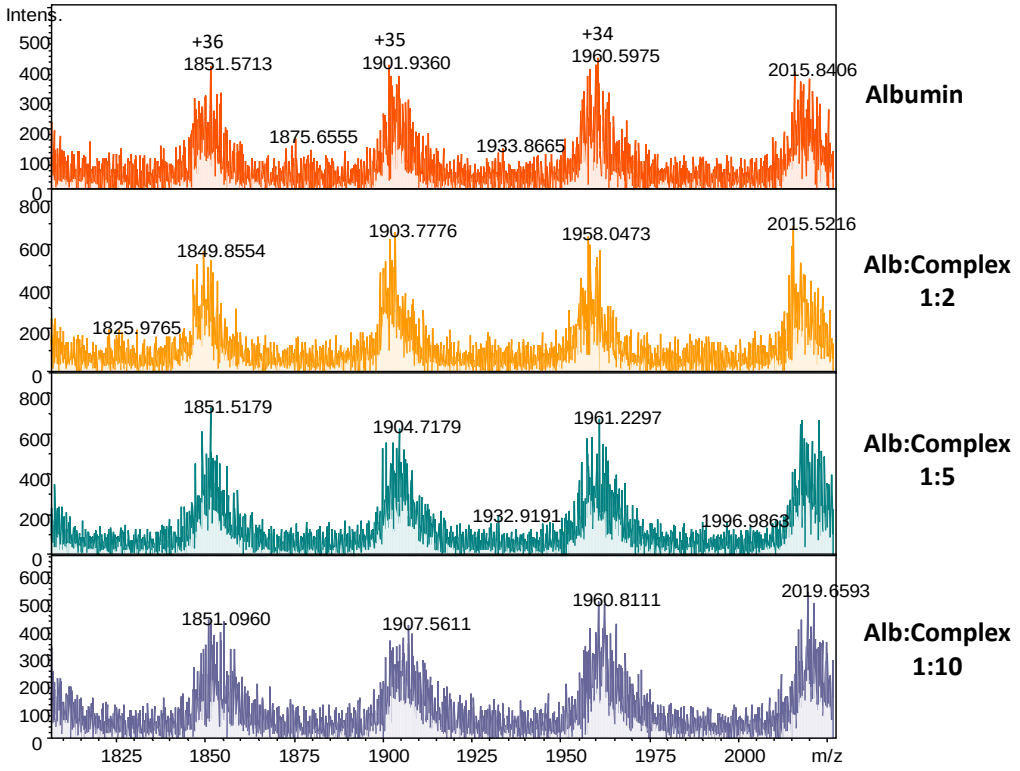

Figure S10. ESI MS-TOF titration of human serum albumin (MW= 66550 Da) with $Zn_2(L^{Ph})_2{\cdot}2H_2O$ **2** helicate.

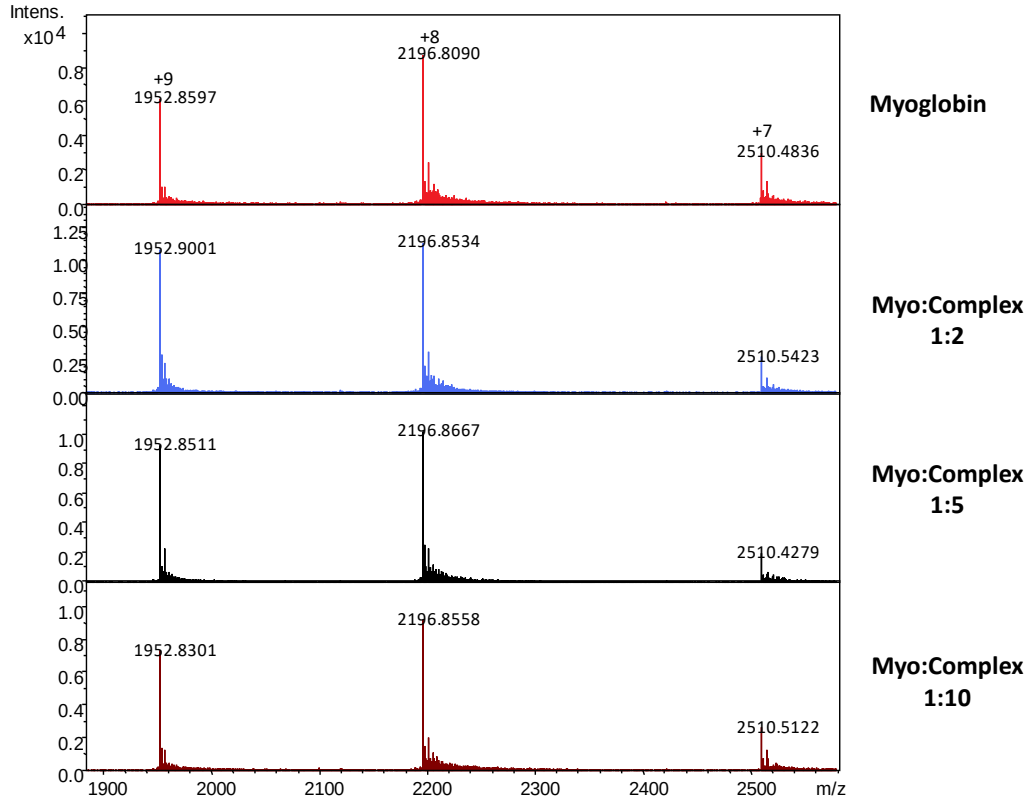

Figure S11. ESI MS-TOF titration of myoglobin (MW= 17567 Da) with $Zn_2(L^{Ph})_2{\cdot}2H_2O$ **2** helicate.

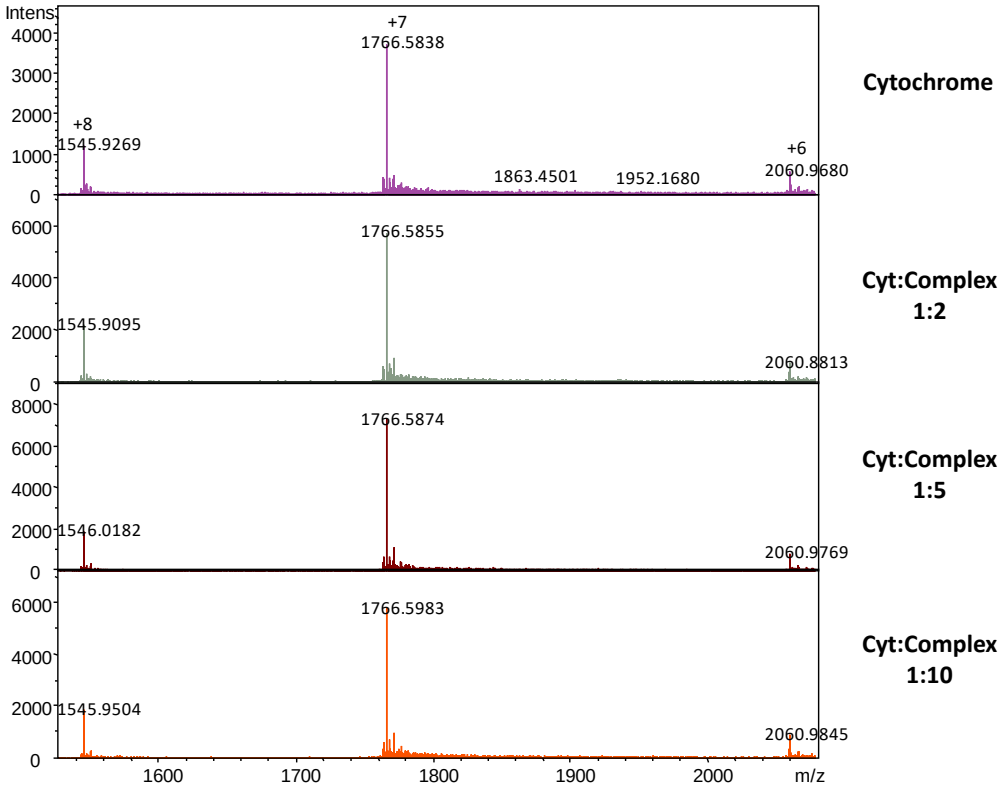

Figure S12. ESI MS-TOF titration of cytochrome C (MW= 12359 Da) with $Zn_2(L^{Ph})_2{\cdot}2H_2O$ **2** helicate.

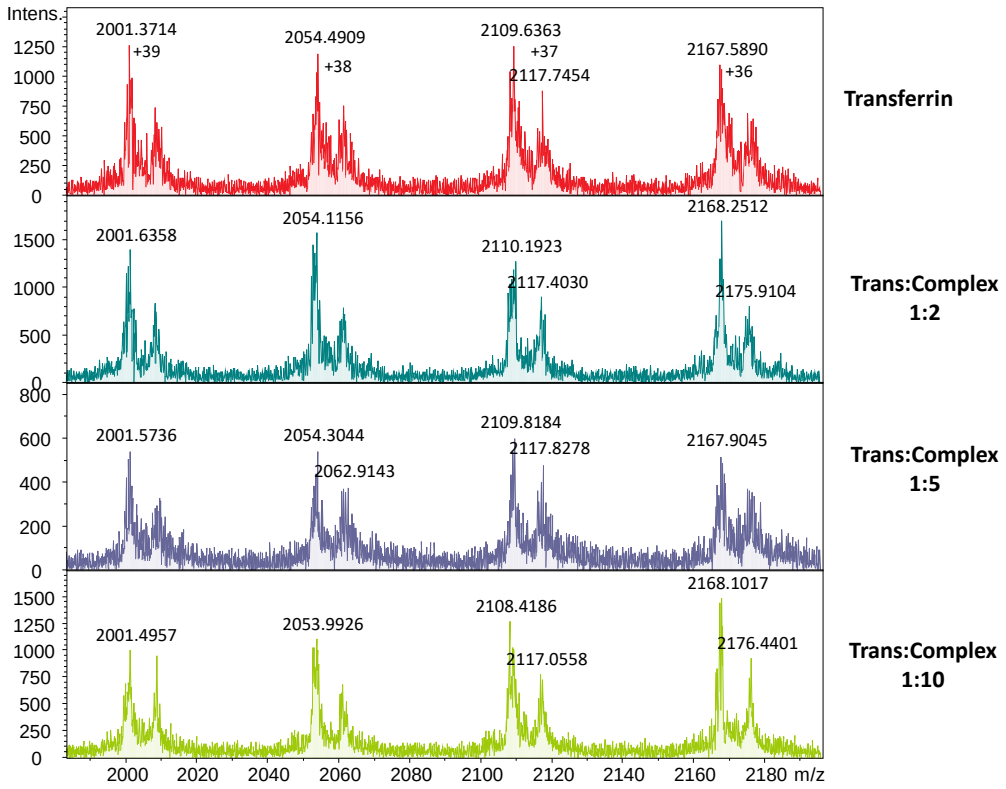

Figure S13. ESI MS-TOF titration of transferrin (MW= 78019 Da) with $Zn_2(L^{Ph})_2{\cdot}2H_2O$ **2** helicate.

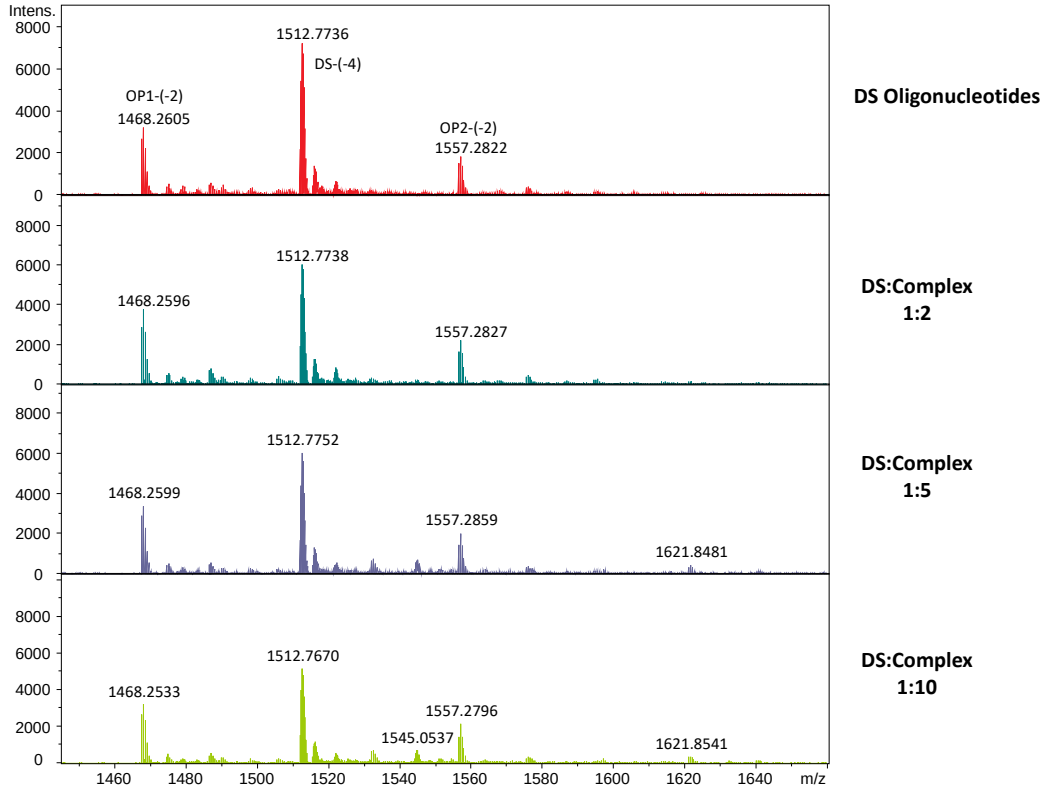

Figure S14. ESI MS-TOF titration of double-stranded oligonucleotides (DS) with $Zn_2(L^{Ph})_2{\cdot}2H_2O$ **2** helicate.

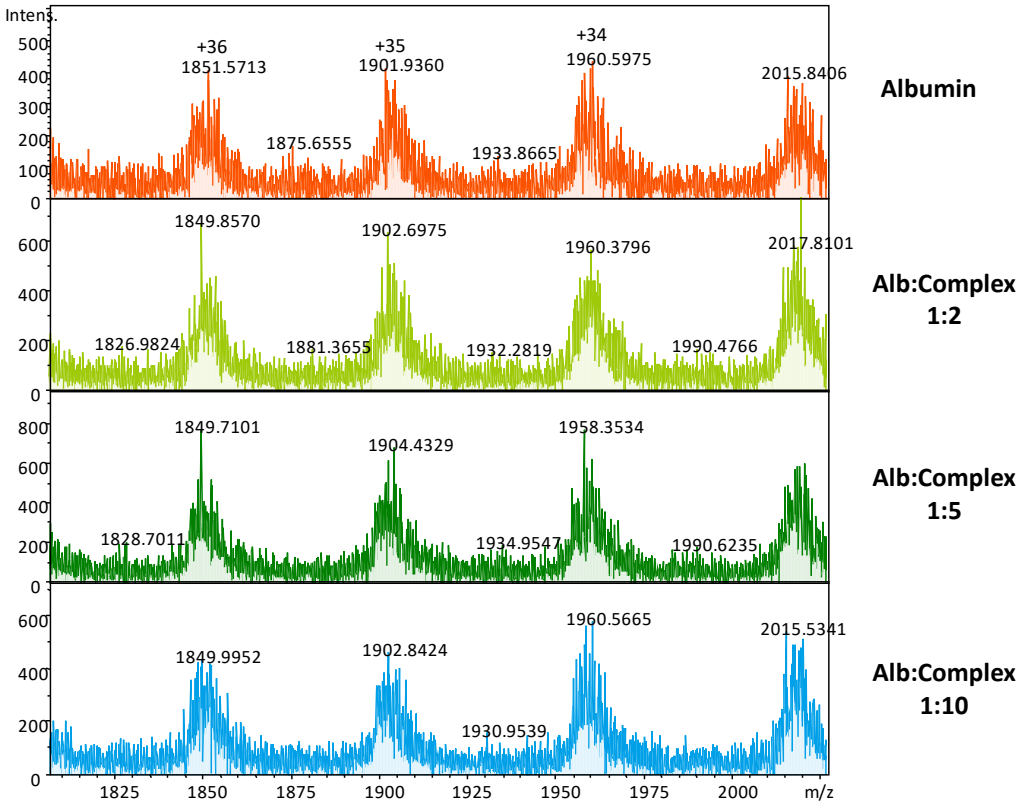

Figure S15. ESI MS-TOF titration of human serum albumin (MW= 66550 Da) with $Zn_2(L^{PhNO2})_2$ **3** helicate.

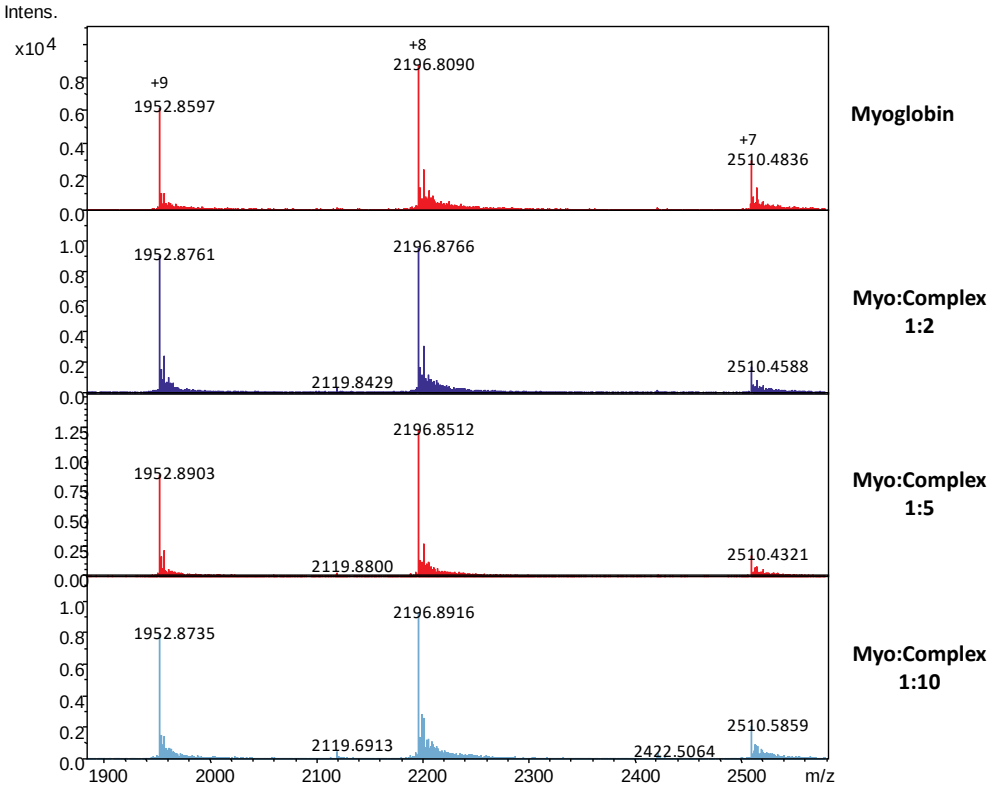

Figure S16. ESI MS-TOF titration of myoglobin (MW= 17567 Da) with $Zn_2(L^{PhNO2})_2$ **3** helicate.

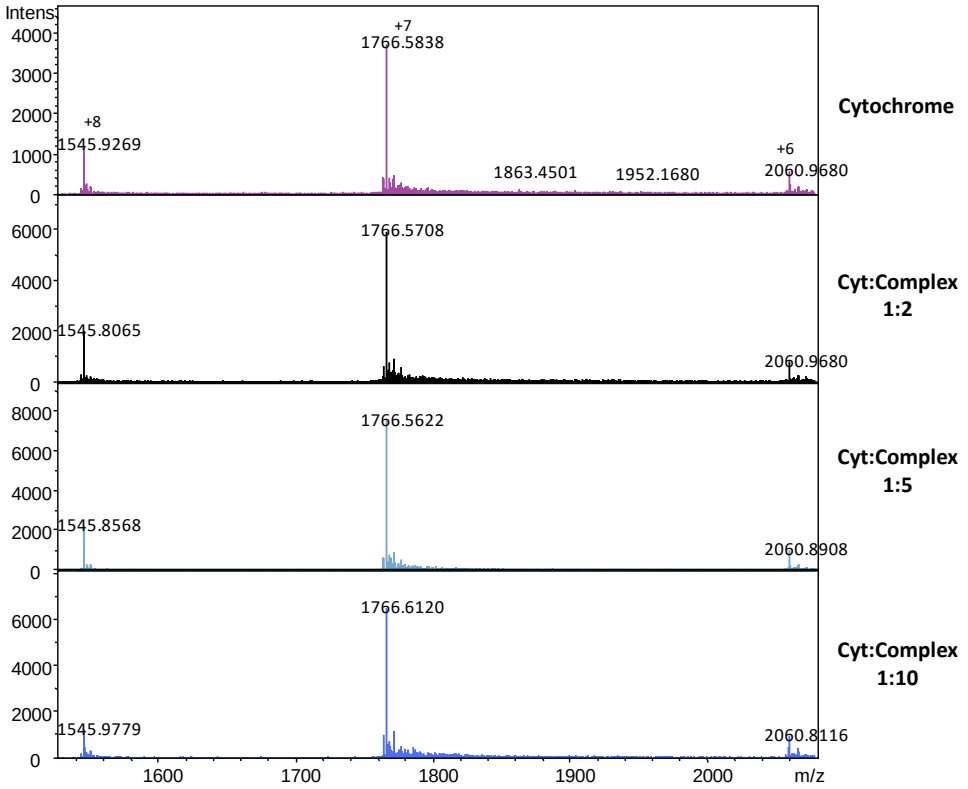

Figure S17. ESI MS-TOF titration of cytochrome C (MW= 12359 Da) with $Zn_2(L^{PhNO2})_2$ **3** helicate.

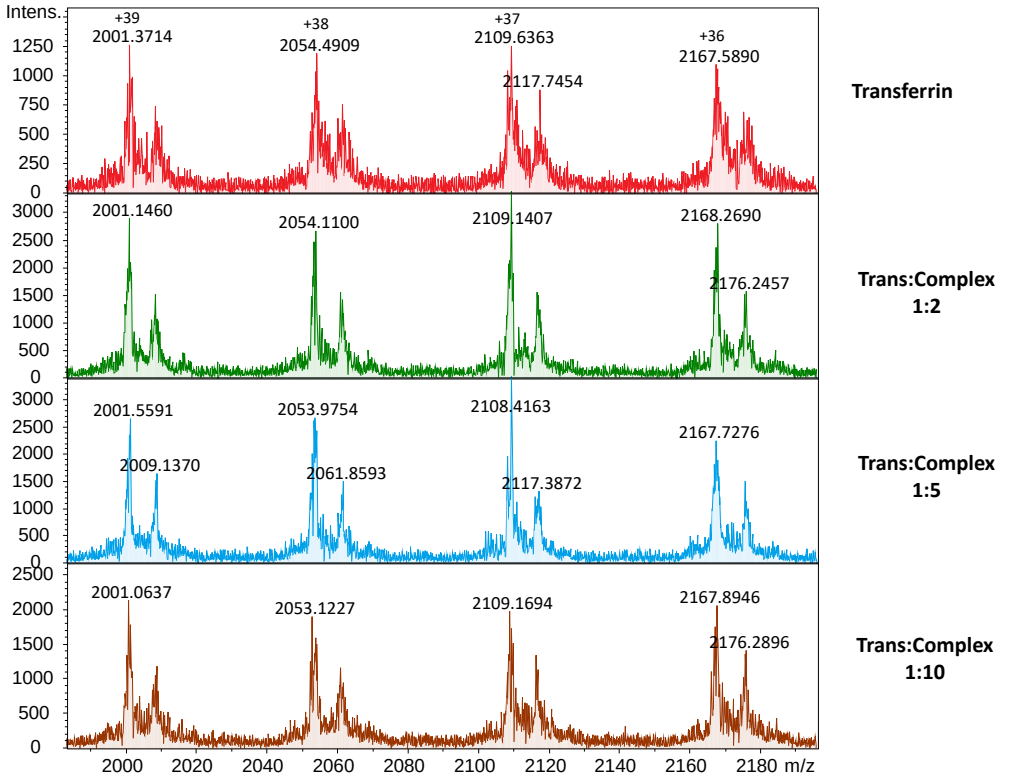

Figure S18. ESI MS-TOF titration of transferrin (MW= 78019 Da) with $Zn_2(L^{PhNO2})_2$ **3** helicate.

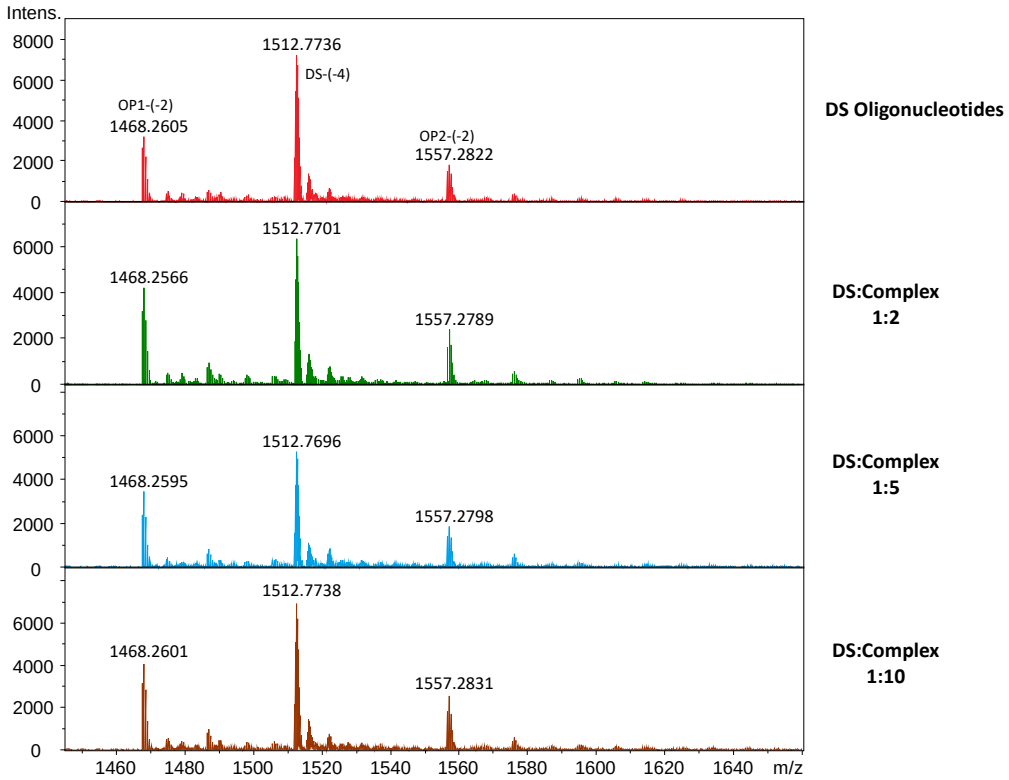

Figure S19. ESI MS-TOF titration of double-stranded oligonucleotides (DS) with $Zn_2(L^{PhNO2})_2$ **3** helicate.