Supporting Information

Synthesis, structure and evaluation of spectral, luminescent and optoelectronic properties of Zn(II) hexafluoroacetylacetonate complexes of triphenodioxazines

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1. X-ray structural data

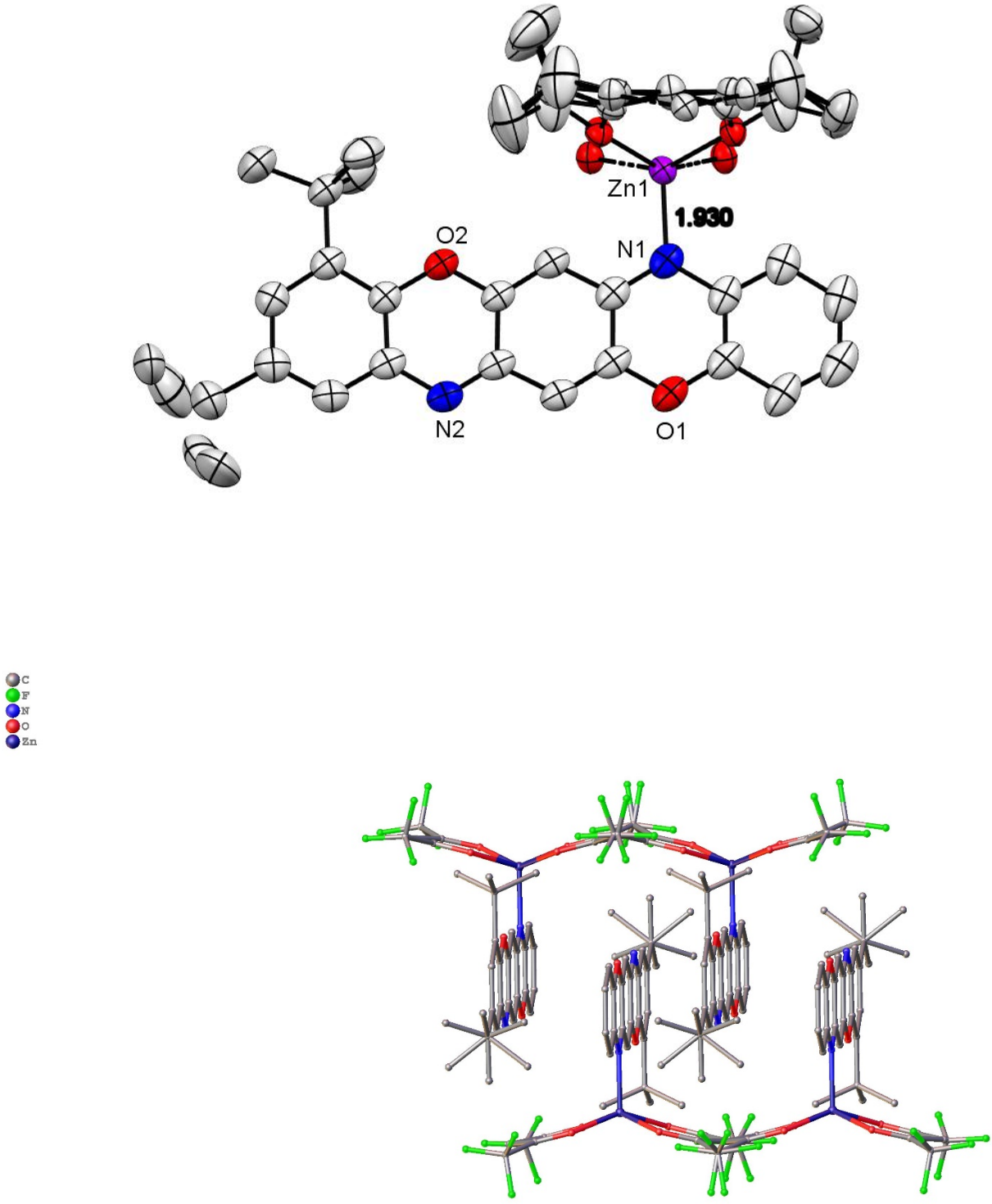


Fig S1. Molecular and crystalline structures of **4a**·**TPDO**. View of the molecule in the asymmetric unit (top); and crystal packing (down).

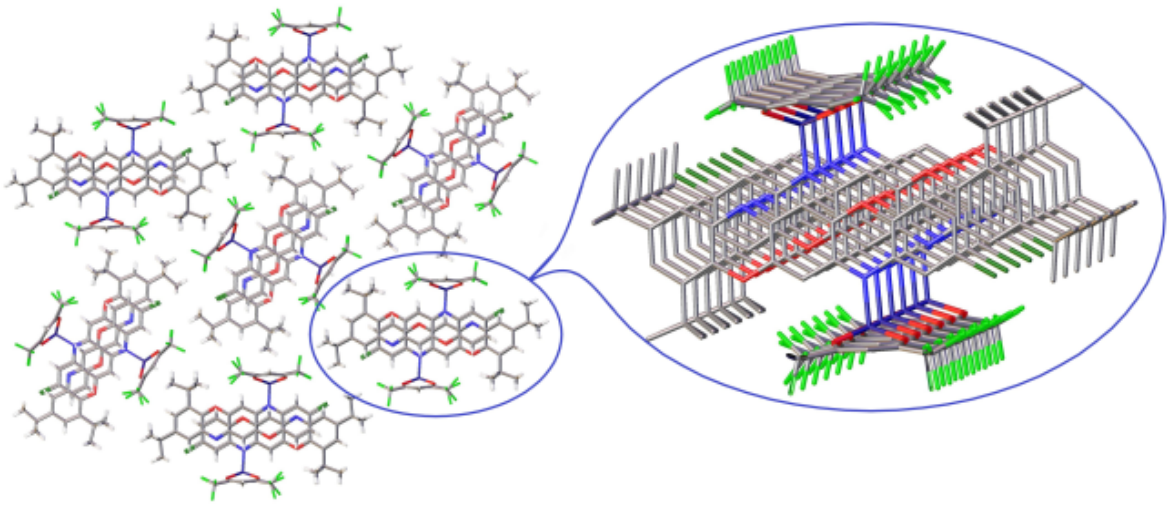


Fig S2. Crystal packing of complex **5d**.

Table S1. Crystallographic parameters of **4a·TPDO**, **4b·TPDO** and **5d**.

Parameter	**4a·TPDO**	**4b·TPDO**	**5d**
Empirical formula	$C_{62}H_{54}F_{12}N_4O_8Zn$	$C_{62}H_{52}Cl_2F_{12}N_4O_8Zn$	$C_{54}H_{46}F_{24}N_2O_{10}Zn_2$
Color	dark brown	-	red
Formula weight, g/mol	1276.46	1345.34	1469.67
Temperature, K	293(2)	100(2)	100(10)
Crystal system	orthorhombic	monoclinic	triclinic
Space group	P n m a	P 1 21/c 1	P-1
a, Å	17.5047(3)	13.3529(3)	9.2874(2)
b, Å	6.79920(10)	25.4867(5)	13.0910(2)
c, Å	25.4483(4)	17.6734(3)	13.6559(3)
α, °	90.000	90.000	100.796(2)
β, °	90.000	90.040(2)	103.403(2)
γ, °	90.000	90.000	107.607(2)
Volume, $Å^3$	3028.80(8)	6014.6(2)	1478.90(6)
Z	2	4	1
Calculated density, g/cm^3	1.400	1.486	1.650
μ(MoK α), mm^{-1}	1.387	2.226	2.218
Theta range for data collection	≤ 67.684	≤ 67.684	≤ 67.684
Reflections collected	24874	35219	25663
Independent reflections	3450/2792	11223/9093	6156/5817
Index ranges	-22 < h < 18 -8 < k < 8 -31 < l < 32	-16 < h < 12 -31 < k < 31 -21 < l < 21	-11 < h < 10 -14 < k < 16 -17 < l < 16
Parameters	325	1038	421
Goodness-of-fit	1.056	1.040	1.050
R indixes (all data)	0.0744	0.0708	0.0317

Table S2. Bond lengths [Å] and valence angles [rad] for **4a·TPDO**.

Atom	Atom	Distance, Å	Atom	Atom	Distance, Å
Zn1	N1	1.930(4)	C16	C20	1.549(6)
Zn1	O4	2.045(3)	C16	C15	1.397(6)
Zn1	O3	2.051(3)	C27	F5	1.267(7)

O2	C18	1.358(4)	C27	F4	1.248(6)
O2	C17	1.381(5)	C27	C26	1.524(8)
O1	C9	1.367(4)	C27	F6	1.272(12)
O1	C8	1.365(6)	C8	C7	1.393(6)
N2	C12	1.381(5)	C14	C13	1.371(6)
N2	C11	1.289(5)	C14	C15	1.400(6)
F2	C23	1.309(6)	C14	C19	1.537(7)
N1	C3	1.415(5)	C25	C26	1.542(13)
N1	C2	1.326(5)	C25	C24	1.542(12)
C23	F1	1.302(6)	C20	C22	1.538(5)
C23	C24	1.537(7)	C20	C22	1.538(5)
C23	F3	1.298(12)	C20	C21	1.527(7)
C18	C1	1.339(6)	C6	C5	1.383(8)
C18	C11	1.457(5)	C6	C7	1.357(8)
C12	C17	1.400(5)	C5	C4	1.400(6)
C12	C13	1.391(6)	O4	C24	1.247(6)
C17	C16	1.388(5)	O3	C26	1.244(5)
C9	C2	1.456(5)	C19	C29	1.531(10)
C9	C10	1.336(6)	C19	C29	1.531(10)
C1	C2	1.422(5)	C19	C28	1.447(16)
C11	C10	1.439(5)	C19	C31	1.451(19)
C3	C8	1.388(6)	C19	C30	1.592(17)
C3	C4	1.386(6)	C19	C30	1.592(17)

Atom	Atom	Atom	Angle, °	Atom	Atom	Atom	Angle, °
N1	Zn1	O4	104.66(12)	F4	C27	F6	107.7(8)
N1	Zn1	O3	106.39(12)	F6	C27	C26	116.1(6)
O4	Zn1	O3	86.12(13)	C9	C10	C11	121.6(4)
C18	O2	C17	119.5(3)	O1	C8	C3	121.8(4)
C8	O1	C9	118.9(4)	O1	C8	C7	117.3(5)
C11	N2	C12	117.6(3)	C3	C8	C7	120.9(5)
C3	N1	Zn1	122.5(3)	C13	C14	C15	118.1(4)
C2	N1	Zn1	119.8(3)	C13	C14	C19	122.1(4)
C2	N1	C3	117.7(4)	C15	C14	C19	119.8(4)
F2	C23	C24	108.5(7)	C26	C25	C24	102.3(11)
F1	C23	F2	104.2(6)	C14	C13	C12	121.3(4)
F1	C23	C24	111.9(7)	C22	C20	C16	110.5(2)
F3	C23	F2	108.5(10)	C22	C20	C16	110.5(2)
F3	C23	F1	109.4(6)	C22	C20	C22	109.6(4)
F3	C23	C24	113.9(5)	C21	C20	C16	112.1(5)
O2	C18	C11	118.2(4)	C21	C20	C22	107.1(3)
C1	C18	O2	118.1(3)	C21	C20	C22	107.1(3)
C1	C18	C11	123.8(3)	C16	C15	C14	123.8(4)
N2	C12	C17	122.4(4)	C7	C6	C5	120.6(5)
N2	C12	C13	119.3(4)	C6	C5	C4	119.8(5)

C13	C12	C17	118.3(4)	C6	C7	C8	119.9(6)
O2	C17	C12	119.0(3)	C24	O4	Zn1	127.1(3)
O2	C17	C16	117.7(3)	C26	O3	Zn1	127.6(3)
C16	C17	C12	123.2(4)	C14	C19	C30	108.5(7)
O1	C9	C2	119.0(4)	C14	C19	C30	108.5(7)
C10	C9	O1	118.4(4)	C29	C19	C14	105.6(5)
C10	C9	C2	122.6(4)	C29	C19	C14	105.6(5)
C18	C1	C2	120.6(4)	C29	C19	C29	110.1(12)
N2	C11	C18	123.4(3)	C29	C19	C30	62.0(11)
N2	C11	C10	121.7(3)	C29	C19	C30	145.9(8)
C10	C11	C18	115.0(4)	C28	C19	C14	112.1(8)
C8	C3	N1	120.4(4)	C28	C19	C29	111.6(7)
C4	C3	N1	120.8(4)	C28	C19	C29	111.6(7)
C4	C3	C8	118.8(4)	C28	C19	C30	52.9(10)
N1	C2	C9	122.2(3)	C31	C19	C14	118.9(10)
N1	C2	C1	121.3(4)	C31	C19	C30	107.7(10)
C1	C2	C9	116.5(4)	C30	C19	C30	105(2)
C17	C16	C20	122.6(4)	C27	C26	C25	108.5(7)
C17	C16	C15	115.3(4)	O3	C26	C27	114.2(5)
C15	C16	C20	122.1(4)	O3	C26	C25	137.3(7)
F5	C27	C26	106.6(7)	C23	C24	C25	107.9(7)
F5	C27	F6	109.6(8)	O4	C24	C23	114.2(5)
F4	C27	F5	104.9(7)	O4	C24	C25	137.9(7)
F4	C27	C26	111.4(6)	C3	C4	C5	120.0(5)

Table S3. Bond lengths [Å] and valence angles [rad] for **4b·TPDO**.

Atom	Atom	Distance, Å	Atom	Atom	Distance, Å	Atom	Atom	Distance, Å
Zn1A	O3A	2.057(5)	C4A	C9A	1.398(4)	C32B	F8B	1.36(3)
Zn1A	O4A	2.052(6)	C5A	C6A	1.391(5)	C32B	F9B	1.29(2)
Zn1A	O5A	2.046(5)	C5A	C19A	1.539(5)	C33B	C34B	1.38(3)
Zn1A	O6A	2.034(5)	C6A	C7A	1.405(5)	C34B	C35B	1.39(3)
Zn1A	N1A	1.979(3)	C7A	C8A	1.384(5)	C36B	F1B	1.35(2)
O3A	C28A	1.250(9)	C7A	C23A	1.538(4)	C36B	F2B	1.51(2)
O4A	C30A	1.243(9)	C8A	C9A	1.413(4)	C36B	F3B	1.50(3)
O5A	C33A	1.242(8)	C10A	C11A	1.436(4)	Cl1B	C16B	1.740(4)
O6A	C35A	1.247(9)	C11A	C12A	1.345(5)	O1B	C3B	1.351(4)
C28A	C29A	1.387(17)	C13A	C14A	1.387(5)	O1B	C4B	1.378(4)
C28A	C27A	1.490(9)	C13A	C18A	1.383(5)	O2B	C12B	1.379(4)
C29A	C30A	1.406(18)	C14A	C15A	1.396(5)	O2B	C13B	1.375(4)
C30A	C31A	1.594(11)	C15A	C16A	1.378(6)	N1B	C1B	1.328(4)
C31A	F4A	1.356(12)	C16A	C17A	1.383(5)	N1B	C18B	1.392(5)
C31A	F5A	1.315(15)	C17A	C18A	1.401(5)	N2B	C9B	1.388(5)

C31A	F6A	1.224(11)	C19A	C20A	1.550(8)	N2B	C10B	1.314(4)
C32A	C33A	1.551(12)	C19A	C21A	1.526(8)	C1B	C2B	1.417(5)
C32A	F7A	1.317(13)	C19A	C22A	1.536(5)	C1B	C12B	1.454(5)
C32A	F8A	1.327(14)	C23A	C24A	1.530(5)	C2B	C3B	1.368(5)
C32A	F9A	1.370(14)	C23A	C25A	1.487(9)	C3B	C10B	1.451(4)
C33A	C34A	1.397(17)	C23A	C26A	1.585(8)	C4B	C5B	1.399(5)
C34A	C35A	1.420(16)	C27A	C35B	1.541(14)	C4B	C9B	1.407(5)
C35A	C36A	1.564(11)	C27A	F10B	1.370(12)	C5B	C6B	1.394(5)
C36A	F10A	1.220(13)	C27A	F11B	1.410(11)	C5B	C19B	1.534(4)
C36A	F11A	1.401(13)	C27A	F12B	1.358(8)	C6B	C7B	1.419(5)
C36A	F12A	1.304(11)	Zn1B	O3B	2.047(11)	C7B	C8B	1.376(5)
F1A	C27A	1.281(7)	Zn1B	O4B	2.037(12)	C7B	C23B	1.533(5)
F2A	C27A	1.285(8)	Zn1B	O5B	2.029(12)	C8B	C9B	1.402(4)
F3A	C27A	1.359(8)	Zn1B	O6B	1.994(11)	C10B	C11B	1.415(5)
Cl1A	C16A	1.736(4)	Zn1B	N1B	1.896(3)	C11B	C12B	1.354(4)
O1A	C3A	1.355(4)	O3B	C28B	1.28(2)	C13B	C14B	1.379(5)
O1A	C4A	1.375(4)	O4B	C30B	1.288(19)	C13B	C18B	1.407(5)
O2A	C12A	1.367(4)	O5B	C33B	1.262(16)	C14B	C15B	1.393(5)
O2A	C13A	1.382(4)	O6B	C35B	1.278(17)	C15B	C16B	1.391(6)
N1A	C1A	1.315(4)	C28B	C29B	1.35(4)	C16B	C17B	1.385(6)
N1A	C18A	1.410(4)	C28B	C36B	1.26(3)	C17B	C18B	1.395(5)
N2A	C9A	1.387(4)	C29B	C30B	1.44(4)	C19B	C20B	1.521(9)
N2A	C10A	1.315(4)	C30B	C31B	1.40(3)	C19B	C21B	1.524(6)
C1A	C2A	1.419(5)	C31B	F4B	1.46(4)	C19B	C22B	1.542(8)
C1A	C12A	1.460(5)	C31B	F5B	1.39(3)	C23B	C24B	1.581(9)
C2A	C3A	1.350(4)	C31B	F6B	1.30(3)	C23B	C25B	1.488(8)
C3A	C10A	1.451(4)	C32B	C33B	1.42(2)	C23B	C26B	1.535(5)
C4A	C5A	1.401(5)	C32B	F7B	1.57(2)			

Atom	Atom	Atom	Angle, °	Atom	Atom	Atom	Angle, °
O4A	Zn1A	O3A	86.8(2)	F10B	C27A	C35B	102.7(7)
O5A	Zn1A	O3A	151.4(2)	F10B	C27A	F11B	102.9(7)
O5A	Zn1A	O4A	85.10(12)	F11B	C27A	C35B	110.0(7)
O6A	Zn1A	O3A	86.61(12)	F12B	C27A	C35B	113.3(7)
O6A	Zn1A	O4A	150.0(2)	F12B	C27A	F10B	130.4(7)
O6A	Zn1A	O5A	86.8(2)	F12B	C27A	F11B	95.8(8)
N1A	Zn1A	O3A	103.1(2)	O4B	Zn1B	O3B	86.9(5)
N1A	Zn1A	O4A	105.7(2)	O5B	Zn1B	O3B	151.3(4)
N1A	Zn1A	O5A	105.49(19)	O5B	Zn1B	O4B	84.6(3)
N1A	Zn1A	O6A	104.3(2)	O6B	Zn1B	O3B	86.5(3)
C28A	O3A	Zn1A	126.6(5)	O6B	Zn1B	O4B	149.9(5)
C30A	O4A	Zn1A	126.7(5)	O6B	Zn1B	O5B	87.3(5)
C33A	O5A	Zn1A	127.9(5)	N1B	Zn1B	O3B	102.4(3)
C35A	O6A	Zn1A	127.4(5)	N1B	Zn1B	O4B	107.9(4)
O3A	C28A	C29A	128.7(9)	N1B	Zn1B	O5B	106.3(3)

O3A	C28A	C27A	111.9(7)	N1B	Zn1B	O6B	102.2(4)
C29A	C28A	C27A	118.9(8)	C28B	O3B	Zn1B	127.6(11)
C28A	C29A	C30A	120.9(11)	C30B	O4B	Zn1B	125.2(11)
O4A	C30A	C29A	128.5(9)	C33B	O5B	Zn1B	128.1(10)
O4A	C30A	C31A	111.0(7)	C35B	O6B	Zn1B	127.7(10)
C29A	C30A	C31A	120.2(8)	O3B	C28B	C29B	129(2)
F4A	C31A	C30A	108.1(7)	C36B	C28B	O3B	110.7(18)
F5A	C31A	C30A	109.8(9)	C36B	C28B	C29B	120(3)
F5A	C31A	F4A	96.6(9)	C28B	C29B	C30B	119(3)
F6A	C31A	C30A	115.0(8)	O4B	C30B	C29B	130(2)
F6A	C31A	F4A	113.7(7)	O4B	C30B	C31B	107.0(19)
F6A	C31A	F5A	112.1(10)	C31B	C30B	C29B	123(2)
F7A	C32A	C33A	110.3(9)	C30B	C31B	F4B	115(2)
F7A	C32A	F8A	113.1(8)	F5B	C31B	C30B	117(3)
F7A	C32A	F9A	106.3(9)	F5B	C31B	F4B	82(2)
F8A	C32A	C33A	111.6(10)	F6B	C31B	C30B	129(3)
F8A	C32A	F9A	106.0(11)	F6B	C31B	F4B	103(2)
F9A	C32A	C33A	109.2(7)	F6B	C31B	F5B	101(2)
O5A	C33A	C32A	114.4(8)	C33B	C32B	F7B	104.6(15)
O5A	C33A	C34A	128.3(9)	F8B	C32B	C33B	118.9(18)
C34A	C33A	C32A	116.9(10)	F8B	C32B	F7B	103.0(17)
C33A	C34A	C35A	119.9(14)	F9B	C32B	C33B	123.4(18)
O6A	C35A	C34A	128.6(10)	F9B	C32B	F7B	96.2(13)
O6A	C35A	C36A	110.4(7)	F9B	C32B	F8B	106.1(18)
C34A	C35A	C36A	120.9(10)	O5B	C33B	C32B	123.8(15)
F10A	C36A	C35A	115.9(9)	O5B	C33B	C34B	125.7(18)
F10A	C36A	F11A	105.2(10)	C34B	C33B	C32B	110.2(18)
F10A	C36A	F12A	114.4(7)	C33B	C34B	C35B	123(2)
F11A	C36A	C35A	107.6(6)	O6B	C35B	C27A	110.5(11)
F12A	C36A	C35A	111.6(8)	O6B	C35B	C34B	126.5(18)
F12A	C36A	F11A	100.4(8)	C34B	C35B	C27A	123.0(16)
C3A	O1A	C4A	119.8(3)	C28B	C36B	F1B	126(2)
C12A	O2A	C13A	118.4(3)	C28B	C36B	F2B	115.0(18)
C1A	N1A	Zn1A	122.4(2)	C28B	C36B	F3B	117.7(19)
C1A	N1A	C18A	117.4(3)	F1B	C36B	F2B	102.6(14)
C18A	N1A	Zn1A	120.2(2)	F1B	C36B	F3B	101.3(17)
C10A	N2A	C9A	116.3(3)	F3B	C36B	F2B	86.8(16)
N1A	C1A	C2A	121.3(3)	C3B	O1B	C4B	119.5(3)
N1A	C1A	C12A	122.3(3)	C13B	O2B	C12B	118.2(3)
C2A	C1A	C12A	116.3(3)	C1B	N1B	Zn1B	125.4(3)
C3A	C2A	C1A	120.8(3)	C1B	N1B	C18B	117.1(3)
O1A	C3A	C10A	118.3(3)	C18B	N1B	Zn1B	117.4(2)
C2A	C3A	O1A	118.3(3)	C10B	N2B	C9B	117.1(3)
C2A	C3A	C10A	123.4(3)	N1B	C1B	C2B	120.3(3)

O1A	C4A	C5A	117.8(3)	N1B	C1B	C12B	123.0(3)
O1A	C4A	C9A	119.2(3)	C2B	C1B	C12B	116.8(3)
C9A	C4A	C5A	122.9(3)	C3B	C2B	C1B	120.4(3)
C4A	C5A	C19A	121.7(3)	O1B	C3B	C2B	118.2(3)
C6A	C5A	C4A	115.3(3)	O1B	C3B	C10B	119.3(3)
C6A	C5A	C19A	122.9(3)	C2B	C3B	C10B	122.5(3)
C5A	C6A	C7A	124.5(3)	O1B	C4B	C5B	117.7(3)
C6A	C7A	C23A	119.4(3)	O1B	C4B	C9B	119.1(3)
C8A	C7A	C6A	118.0(3)	C5B	C4B	C9B	123.1(3)
C8A	C7A	C23A	122.6(3)	C4B	C5B	C19B	122.1(3)
C7A	C8A	C9A	120.3(3)	C6B	C5B	C4B	115.1(3)
N2A	C9A	C4A	122.7(3)	C6B	C5B	C19B	122.8(3)
N2A	C9A	C8A	118.3(3)	C5B	C6B	C7B	124.3(3)
C4A	C9A	C8A	118.9(3)	C6B	C7B	C23B	118.7(3)
N2A	C10A	C3A	123.5(3)	C8B	C7B	C6B	117.6(3)
N2A	C10A	C11A	120.8(3)	C8B	C7B	C23B	123.7(3)
C11A	C10A	C3A	115.6(3)	C7B	C8B	C9B	121.2(3)
C12A	C11A	C10A	121.1(3)	N2B	C9B	C4B	122.4(3)
O2A	C12A	C1A	119.3(3)	N2B	C9B	C8B	119.0(3)
C11A	C12A	O2A	118.0(3)	C8B	C9B	C4B	118.7(3)
C11A	C12A	C1A	122.7(3)	N2B	C10B	C3B	122.5(3)
O2A	C13A	C14A	117.0(3)	N2B	C10B	C11B	120.6(3)
O2A	C13A	C18A	121.0(3)	C11B	C10B	C3B	116.9(3)
C18A	C13A	C14A	122.0(3)	C12B	C11B	C10B	120.7(3)
C13A	C14A	C15A	119.1(4)	O2B	C12B	C1B	119.0(3)
C16A	C15A	C14A	118.7(3)	C11B	C12B	O2B	118.2(3)
C15A	C16A	Cl1A	119.4(3)	C11B	C12B	C1B	122.7(3)
C15A	C16A	C17A	122.5(3)	O2B	C13B	C14B	117.6(3)
C17A	C16A	Cl1A	118.1(3)	O2B	C13B	C18B	121.1(3)
C16A	C17A	C18A	118.9(4)	C14B	C13B	C18B	121.3(3)
C13A	C18A	N1A	121.6(3)	C13B	C14B	C15B	120.0(4)
C13A	C18A	C17A	118.7(3)	C16B	C15B	C14B	118.5(4)
C17A	C18A	N1A	119.7(3)	C15B	C16B	Cl1B	119.8(3)
C5A	C19A	C20A	111.0(5)	C17B	C16B	Cl1B	118.0(3)
C21A	C19A	C5A	110.5(5)	C17B	C16B	C15B	122.1(3)
C21A	C19A	C20A	109.4(3)	C16B	C17B	C18B	119.4(4)
C21A	C19A	C22A	106.6(6)	N1B	C18B	C13B	121.6(3)
C22A	C19A	C5A	111.4(3)	N1B	C18B	C17B	119.8(3)
C22A	C19A	C20A	107.7(6)	C17B	C18B	C13B	118.6(4)
C7A	C23A	C26A	107.5(5)	C5B	C19B	C22B	110.1(5)
C24A	C23A	C7A	112.0(3)	C20B	C19B	C5B	109.8(5)
C24A	C23A	C26A	107.5(5)	C20B	C19B	C21B	108.0(6)
C25A	C23A	C7A	110.6(5)	C20B	C19B	C22B	110.7(3)
C25A	C23A	C24A	110.2(5)	C21B	C19B	C5B	110.9(3)

C25A	C23A	C26A	108.8(3)	C21B	C19B	C22B	107.5(6)
F1A	C27A	C28A	115.9(5)	C7B	C23B	C24B	107.8(5)
F1A	C27A	F2A	95.0(5)	C7B	C23B	C26B	111.6(3)
F1A	C27A	F3A	109.9(5)	C25B	C23B	C7B	111.1(5)
F2A	C27A	C28A	114.8(5)	C25B	C23B	C24B	109.3(3)
F2A	C27A	F3A	106.5(5)	C25B	C23B	C26B	109.7(5)
F3A	C27A	C28A	113.1(5)	C26B	C23B	C24B	107.3(5)

Table S4. Bond lengths [Å] and valence angles [rad] for **5d**.

Atom	Atom	Distance, Å		Atom	Atom	Distance, Å	
Zn1	O4	2.0407(11)		C21	C22	1.536(2)	
Zn1	O3	2.0369(11)		C21	C20	1.390(2)	
Zn1	O2	2.0314(11)		C4	C9	1.399(2)	
Zn1	O5	2.0363(11)		C4	C5	1.398(2)	
Zn1	N1	2.0831(12)		C3	C2	1.357(2)	
F5	C22	1.3370(19)		C3	C1	1.427(2)	
F4	C22	1.3355(19)		C2	C1	1.450(2)	
F6	C22	1.3334(18)		C9	C8	1.397(2)	
O1	C4	1.3787(17)		C5	C6	1.398(2)	
O1	C2	1.3532(17)		C5	C10	1.537(2)	
O4	C26	1.2546(19)		C7	C14	1.542(2)	
O3	C21	1.2580(19)		C7	C8	1.380(2)	
F7	C27	1.319(2)		C7	C6	1.401(2)	
O2	C19	1.2551(19)		C14	C16	1.521(2)	
F8	C27	1.331(2)		C14	C17	1.538(2)	
F10	C23	1.3335(19)		C14	C15	1.534(2)	
O5	C24	1.2551(19)		C26	C27	1.542(2)	
F1	C18	1.321(2)		C26	C25	1.390(2)	
F9	C27	1.336(2)		C20	C19	1.389(2)	
F12	C23	1.336(2)		C24	C25	1.392(2)	
F2	C18	1.330(2)		C24	C23	1.538(2)	
F11	C23	1.313(2)		C19	C18	1.536(2)	
F3	C18	1.331(2)		C10	C13	1.538(2)	
N1	C1	1.3257(19)		C10	C12	1.541(3)	
N1	C9	1.4000(18)		C10	C11	1.537(3)	
Atom	Atom	Atom	Angle, °	Atom	Atom	Atom	Angle, °
O4	Zn1	N1	110.95(5)	C15	C14	C17	109.77(16)
O3	Zn1	O4	86.94(4)	F5	C22	C21	113.10(13)
O3	Zn1	N1	101.99(5)	F4	C22	F5	107.42(13)
O2	Zn1	O4	145.35(4)	F4	C22	C21	111.23(12)
O2	Zn1	O3	87.48(4)	F6	C22	F5	107.34(12)
O2	Zn1	O5	84.49(5)	F6	C22	F4	107.44(13)

O2	Zn1	N1	103.66(5)	F6	C22	C21	110.06(13)
O5	Zn1	O4	87.08(4)	O4	C26	C27	114.26(14)
O5	Zn1	O3	156.26(5)	O4	C26	C25	128.75(15)
O5	Zn1	N1	101.61(5)	C25	C26	C27	116.95(14)
C2	O1	C4	120.08(11)	C19	C20	C21	121.13(14)
C26	O4	Zn1	127.23(10)	O5	C24	C25	128.14(15)
C21	O3	Zn1	126.39(10)	O5	C24	C23	113.88(14)
C19	O2	Zn1	126.81(10)	C25	C24	C23	117.92(14)
C24	O5	Zn1	127.83(11)	C7	C8	C9	120.78(13)
C1	N1	Zn1	122.31(10)	C5	C6	C7	123.56(14)
C1	N1	C9	118.19(12)	O2	C19	C20	128.49(14)
C9	N1	Zn1	119.49(9)	O2	C19	C18	112.79(14)
O3	C21	C22	113.20(13)	C20	C19	C18	118.69(14)
O3	C21	C20	128.28(15)	F7	C27	F8	107.83(15)
C20	C21	C22	118.50(14)	F7	C27	F9	107.64(14)
O1	C4	C9	119.23(13)	F7	C27	C26	112.52(13)
O1	C4	C5	118.02(13)	F8	C27	F9	106.27(14)
C5	C4	C9	122.72(13)	F8	C27	C26	110.14(13)
C2	C3	C1	120.24(13)	F9	C27	C26	112.15(14)
O1	C2	C3	117.23(13)	C5	C10	C13	111.39(13)
O1	C2	C1	119.51(13)	C5	C10	C12	109.65(14)
C3	C2	C1	123.26(13)	C5	C10	C11	109.73(14)
N1	C1	C3	122.18(13)	C13	C10	C12	107.33(15)
N1	C1	C2	121.32(13)	C11	C10	C13	107.55(14)
C3	C1	C2	116.50(13)	C11	C10	C12	111.17(15)
C4	C9	N1	121.61(13)	C26	C25	C24	120.88(14)
C8	C9	N1	119.44(13)	F10	C23	F12	106.33(14)
C8	C9	C4	118.89(13)	F10	C23	C24	112.23(14)
C4	C5	C6	115.69(13)	F12	C23	C24	109.70(13)
C4	C5	C10	122.12(13)	F11	C23	F10	108.59(15)
C6	C5	C10	122.18(13)	F11	C23	F12	107.59(15)
C8	C7	C14	119.67(13)	F11	C23	C24	112.14(14)
C8	C7	C6	118.35(14)	F1	C18	F2	107.82(15)
C6	C7	C14	121.74(13)	F1	C18	F3	107.49(16)
C16	C14	C7	112.45(13)	F1	C18	C19	111.36(14)
C16	C14	C17	109.47(14)	F2	C18	F3	106.96(15)
C16	C14	C15	109.00(15)	F2	C18	C19	113.03(15)
C17	C14	C7	105.79(13)	F3	C18	C19	109.94(14)
C15	C14	C7	110.31(13)				

2. UV/vis and emission spectra

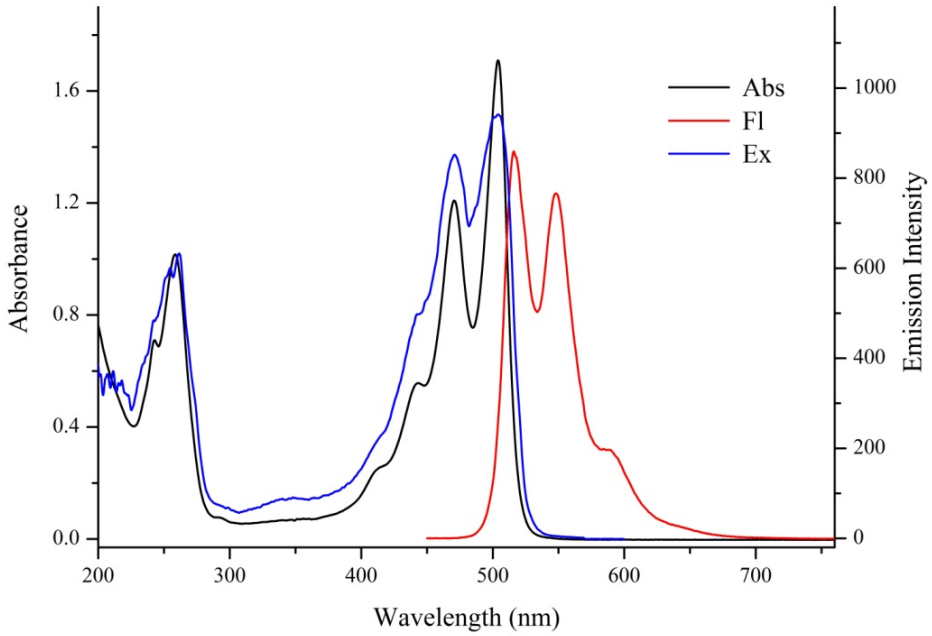


Figure S3. UV/vis, fluorescence emission (λ_{ex} = 365 nm) and fluorescence excitation (λ_{obs} = 610 nm) spectra of compound **1a** (heptane, $C = 1 \cdot 10^{-4}$ M, l = 0.2 cm, T = 293 K).

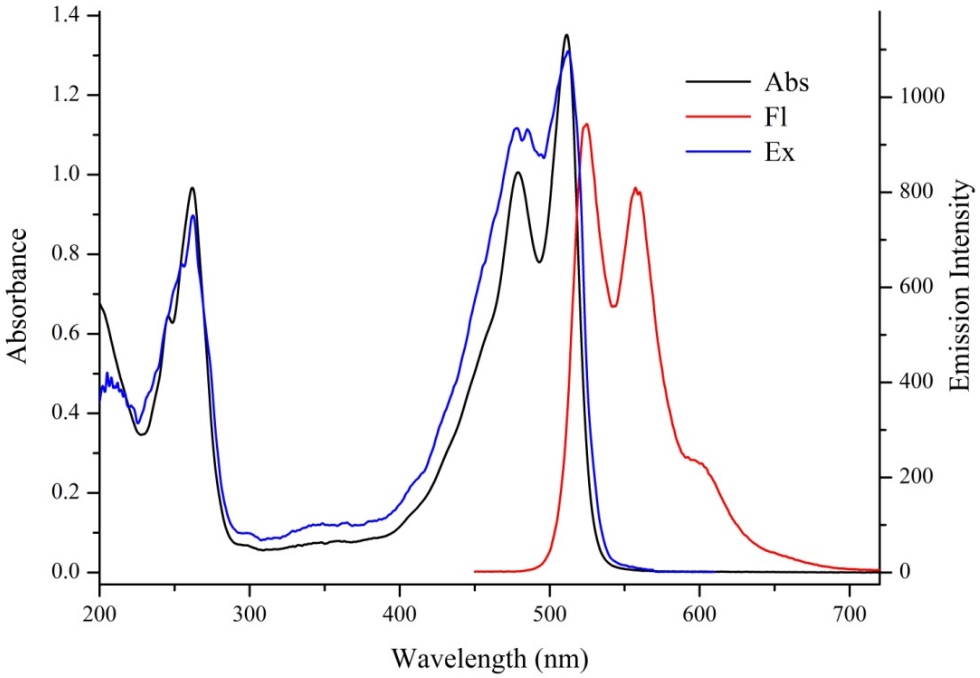


Figure S4. UV/vis and fluorescence emission (λ_{ex} = 365 nm) and fluorescence excitation (λ_{obs} = 620 nm) spectra of compound **1b** (heptane, $C = 1 \cdot 10^{-4}$ M, l = 0.2 cm, T = 293 K).

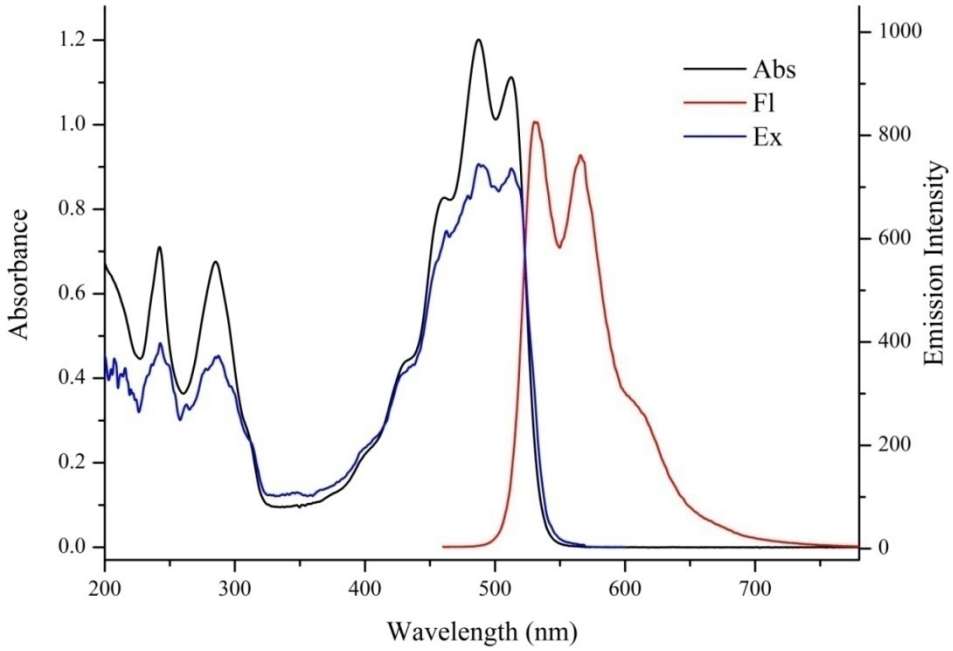


Figure S5. UV/vis and fluorescence emission (λ_{ex} = 365 nm) and fluorescence excitation (λ_{obs} = 640 nm) spectra of ligand **1c** (heptane, $C = 1 \cdot 10^{-4}$ M, l = 0.2 cm, T = 293 K).

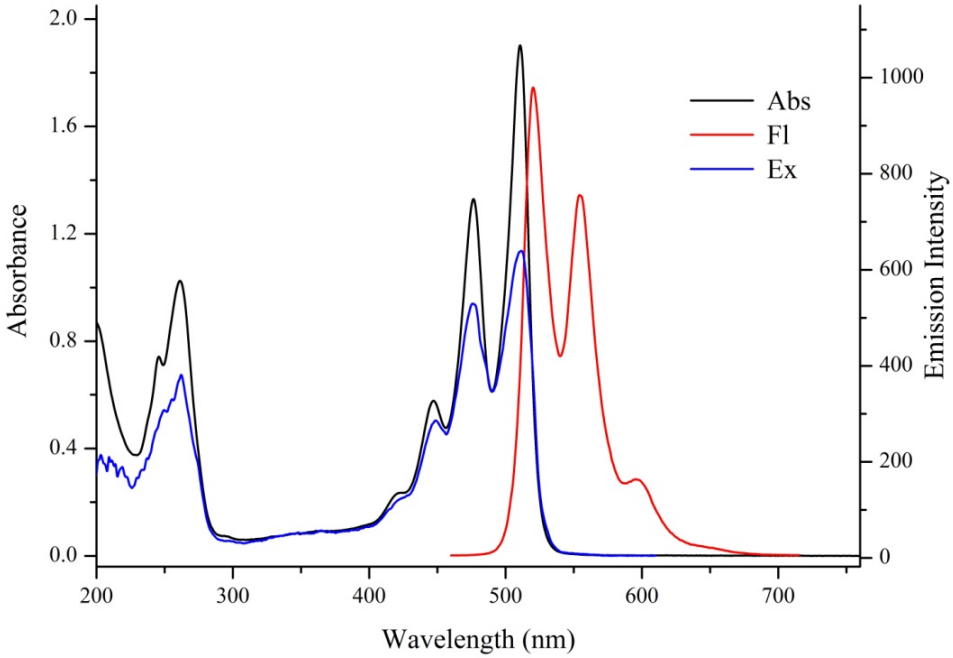


Figure S6. UV/vis and fluorescence emission (λ_{ex} = 365 nm) and fluorescence excitation (λ_{obs} = 620 nm) spectra of compound **1d** (heptane, $C = 1 \cdot 10^{-4}$ M, l = 0.2 cm, T = 293 K).

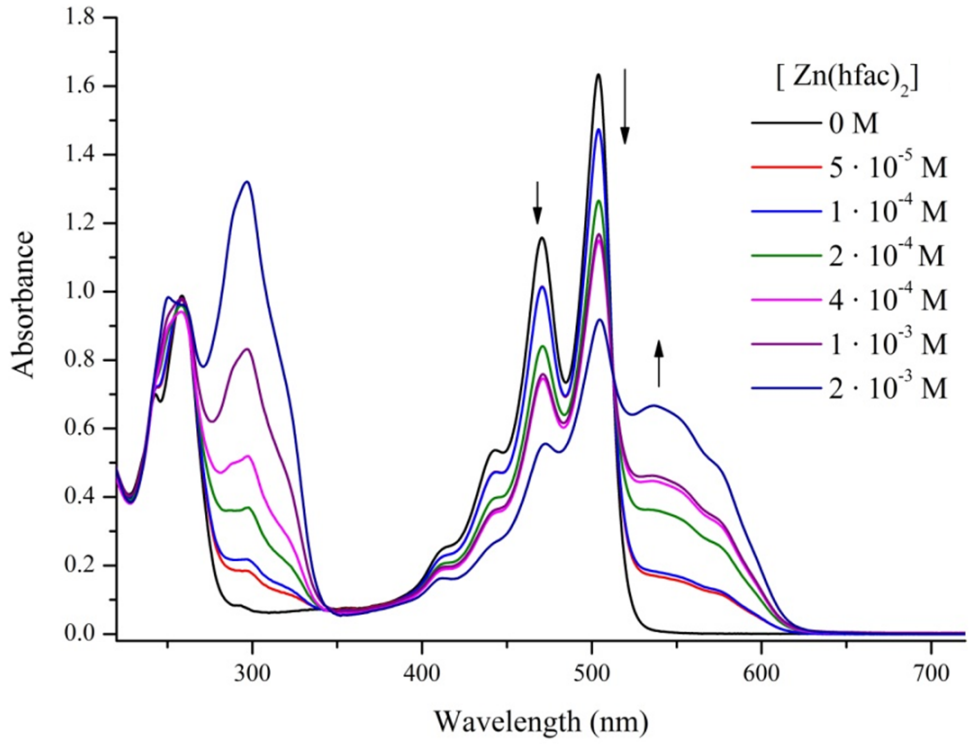


Figure S7. Changes in the UV-Vis spectrum of a heptane solution of **1a** ($C = 1 \cdot 10^{-4}$ M, $l = 0.2$ cm, $T = 293$ K) under increasing $Zn(hfac)_2$ concentration.

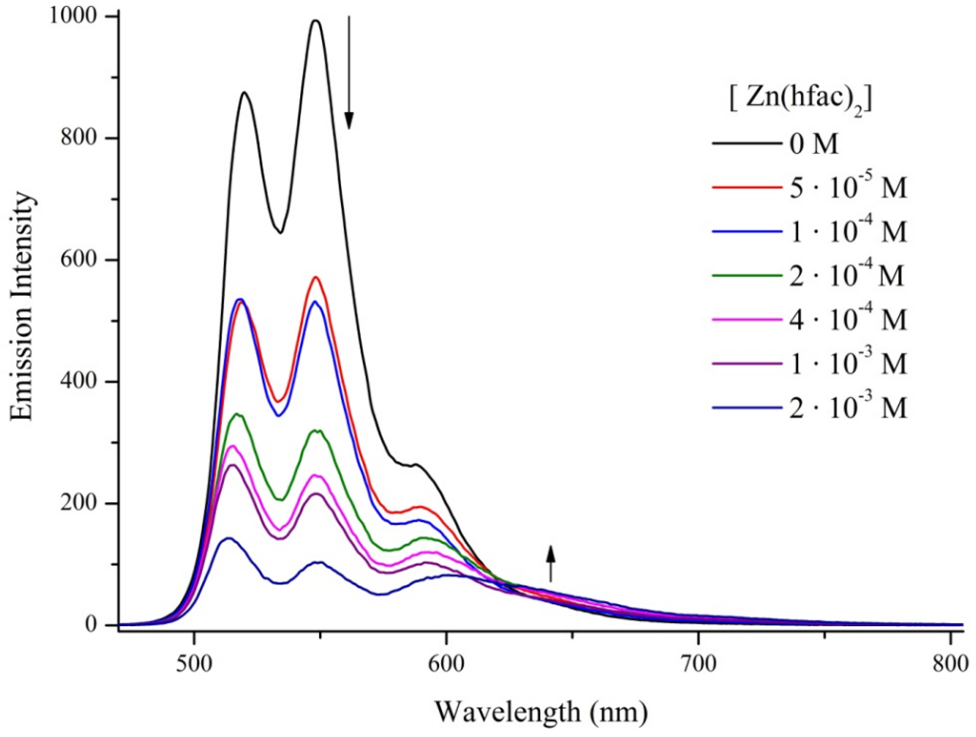


Figure S8. Changes in the Fluorescence spectrum ($\lambda_{ex} = 410$ nm) of a heptane solution of **1a** under increasing $Zn(hfac)_2$ concentration.

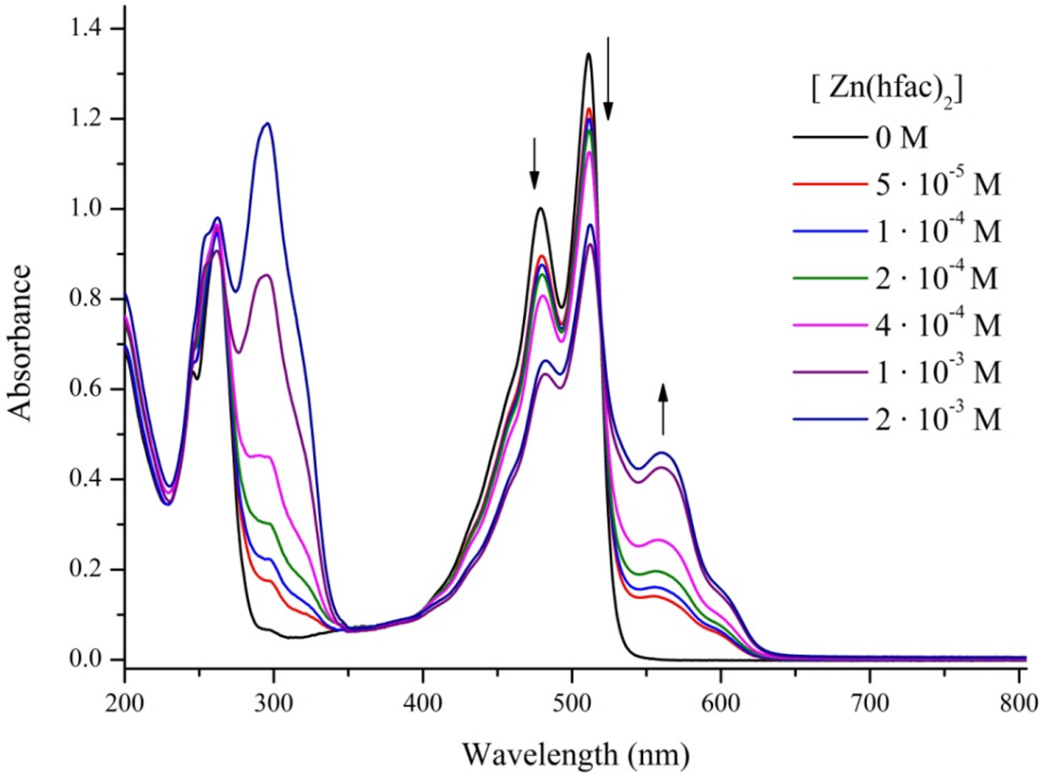


Figure S9. Changes in the UV-Vis spectrum of a heptane solution of **1b** ($C = 1 \cdot 10^{-4}$ M, $l = 0.2$ cm, $T = 293$ K) under increasing $Zn(hfac)_2$ concentration.

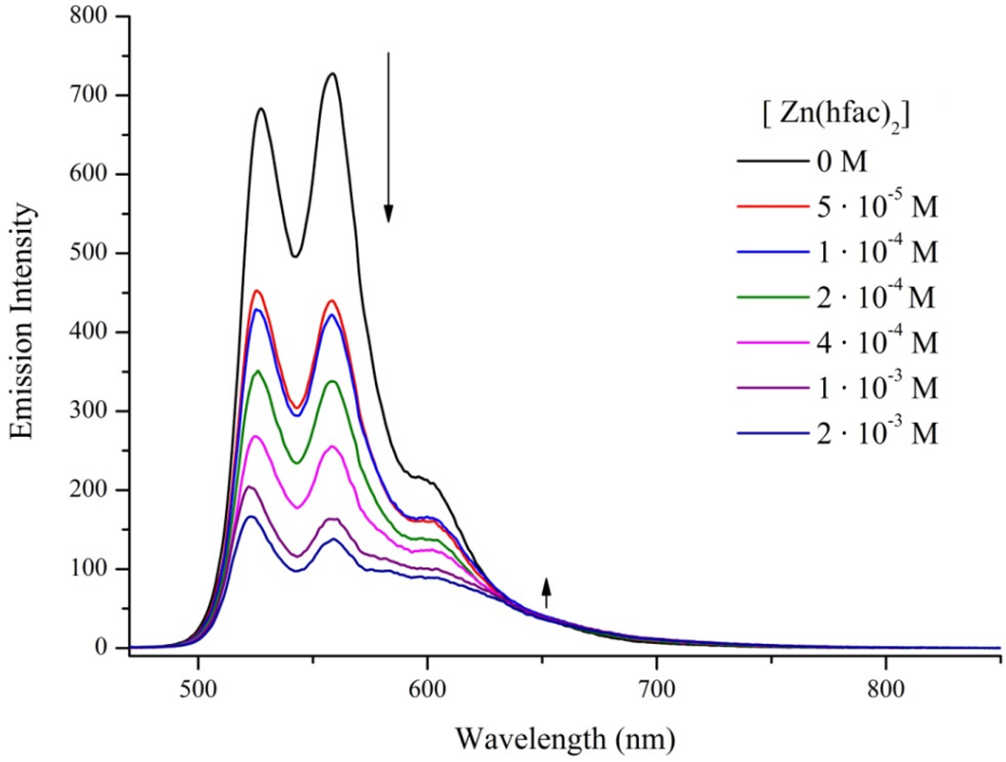


Figure S10. Changes in the Fluorescence spectrum ($\lambda_{ex} = 410$ nm) of a heptane solution of **1b** under increasing $Zn(hfac)_2$ concentration.

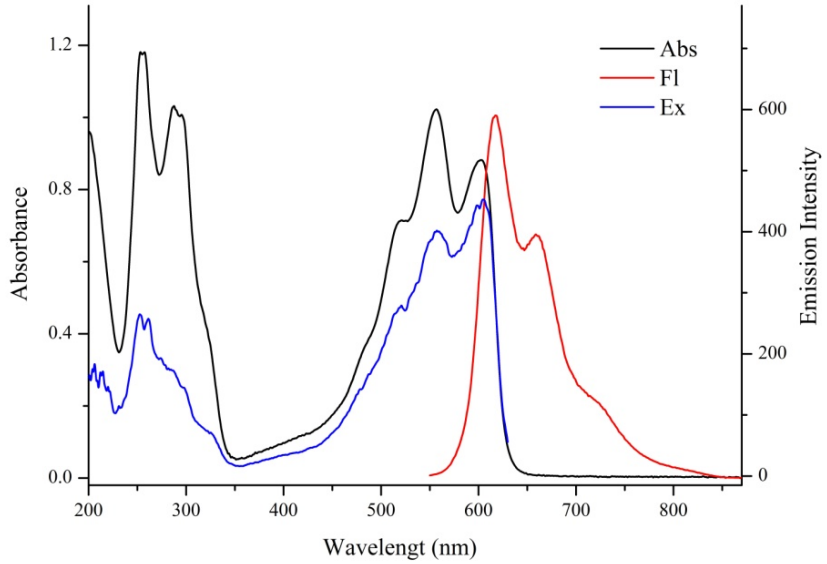


Figure S11. UV/vis and fluorescence emission (λ_{ex} = 540 nm) and fluorescence excitation (λ_{obs} = 650 nm) spectra of complex **5d** (heptane, $C = 1 \cdot 10^{-4}$ M, l = 0.2 cm, T = 293 K).

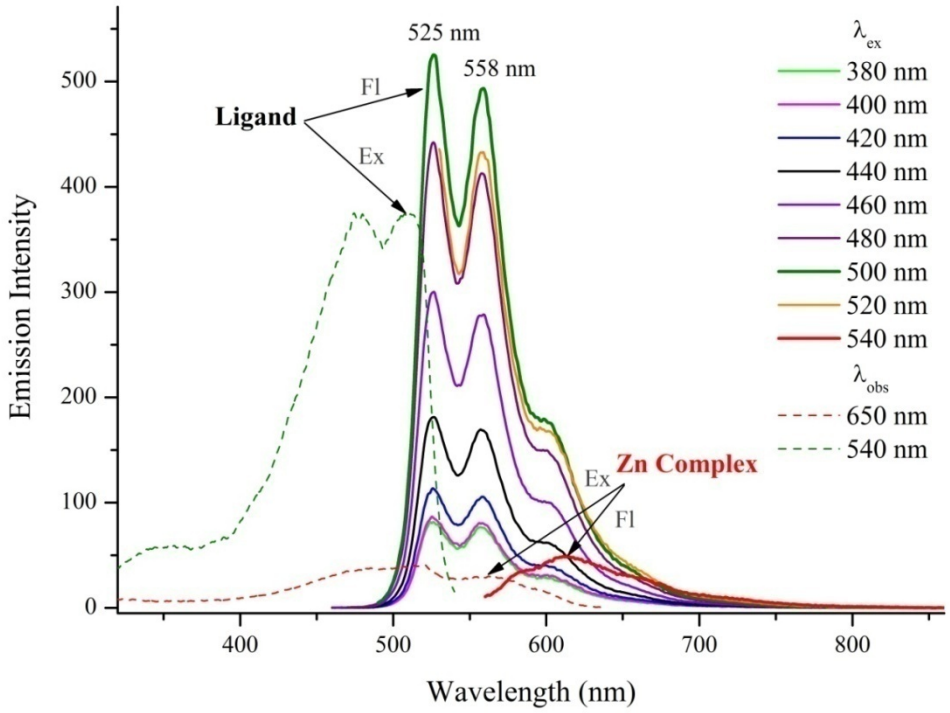


Figure S12. Changes in the fluorescence emission (*solid lines*) spectrum of compound $Zn(hfacac)_2(TPDO\text{-}Cl)_2$ **4b·TPDO** (heptane, $C = 1 \cdot 10^{-5}$ M, l = 1cm, T = 293 K) under increasing wavelength of excitation light and fluorescence excitation spectra (*dashed*) of ligand (λ_{obs} = 540 nm) and of complex (λ_{obs} = 650 nm).

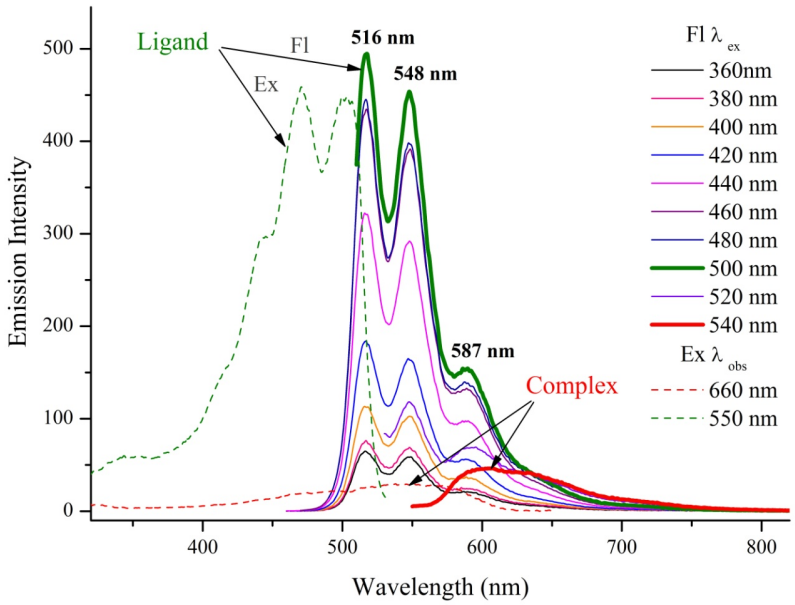


Fig. S13. Changes in the fluorescence emission (*solid lines*) spectrum of a complex $Zn(hfac)_2$-$TPDO)_2$ **4a·TPDO** (heptane, $C = 1 \cdot 10^{-5}$ M, $T = 293$ K) under increasing wavelength of the exciting light and the fluorescence excitation spectra (*dashed*) of the ligand ($\lambda_{obs} = 550$ nm) and the complex ($\lambda_{obs} = 660$ nm).

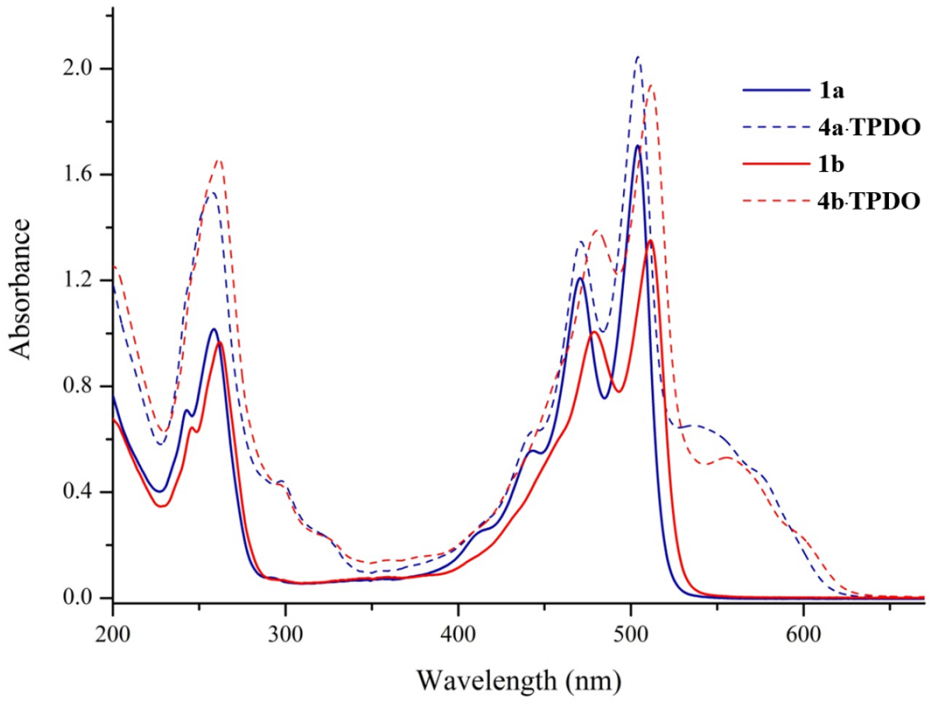


Fig. S14. UV/vis spectra of compounds **1a,b** (*solid lines*) and compounds **4a·TPDO, 4b·TPDO** (*dashed*) (heptane, $C = 1 \cdot 10^{-4}$ M, $l = 0.2$ cm, $T = 293$ K).

3. DFT study

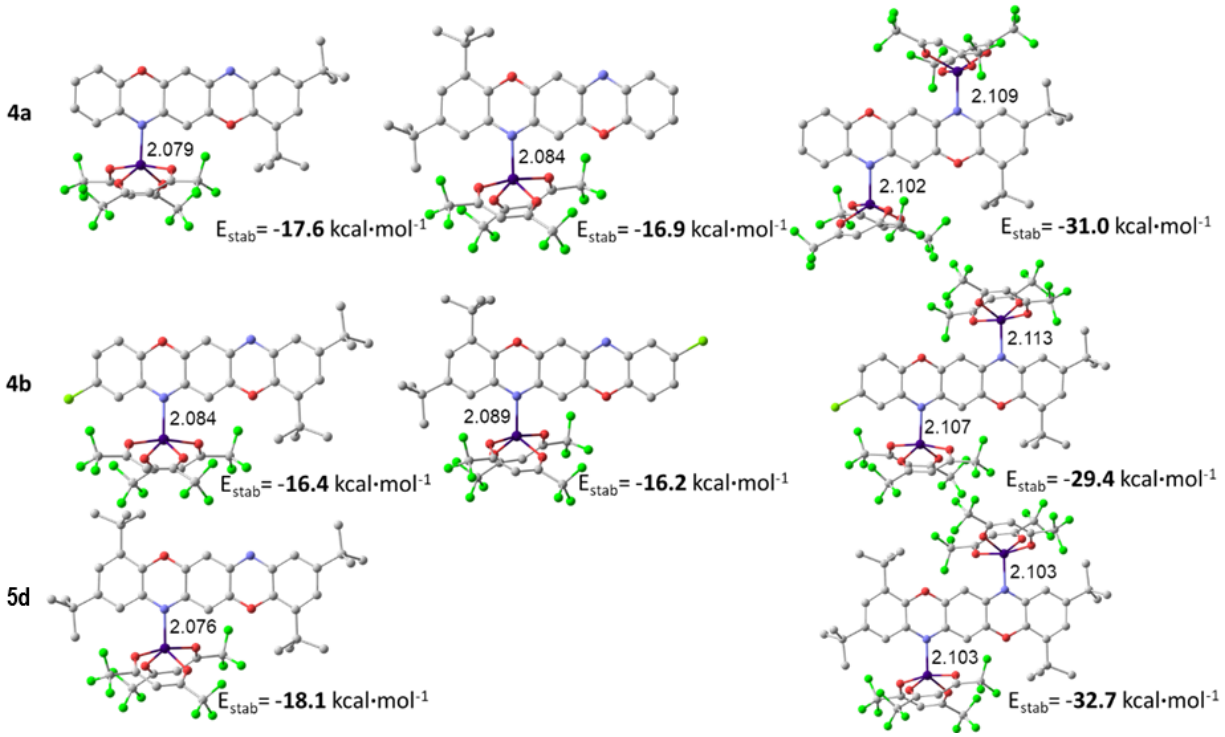


Fig. S15. Stabilization energies (with respect to dissociation into the ligand and $Zn(hfac)_2$) and selected geometrical parameters of complexes **4** and **5** as calculated by DFT(B3LYP)6-311++G(d,p)) method.

4. Cyclic voltammetry

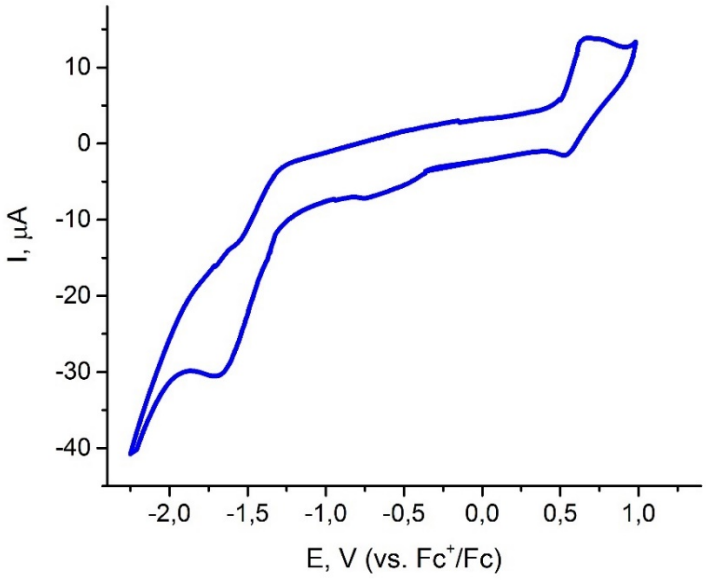
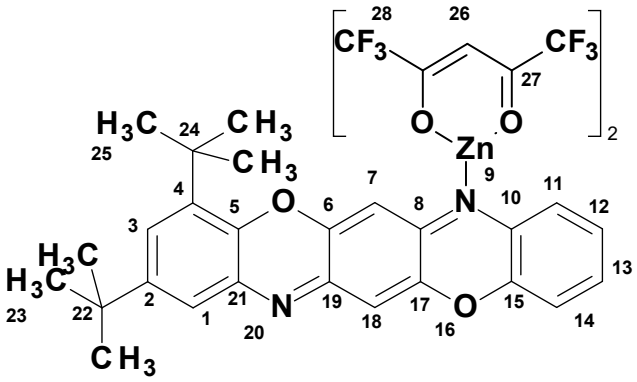


Fig. S16. Cyclic voltammogram of **5d** in dichloromethane solution (C = 5 mM) at 300 K. $TBAPF_6$ supporting electrolyte (C = 0.1 M); 0.05 V/s; GC working electrode. The redox potential data are referenced to the Fc^+/Fc, couple.

5. ^{1}H, ^{13}C NMR spectra.

NMR spectra of (2,4-di-(tert-butyl)-benzo[5,6][1,4]oxazine[2,3-b]phenoxazine)-bis-(1,1,1,5,5,5-hexafluoro-pentane-2,4-dioate) Zn (II) **4a**



	Nuclear	1	2	3	4	5	6	7	8	10	11	12	13	14
	^{1}H	7.64		7.35				6.58			7.55	6.79	6.74	6.64
4a	$J_{1H\text{-}1H}$	2.3		2.3							7.8	7.8	7.8	7.8
	$^{13}C/^{15}N$	125.11	137.65	126.26	148.98	142.24	152.97	107.53	148.92	135.98	129.21	126.28	130.30	116.78
	$J_{13C\text{-}19F}$													

	Nuclear	15	17	18	19	21	22	23	24	25	26	27	28
	^{1}H			6.65				1.41		1.27	6.16		
4a	$J_{1H\text{-}1H}$												
	$^{13}C/^{15}N$	145.82	151.59	106.58	149.42	136.37	35.74	30.99	36.08	32.23	91.34	181.76	118.87
	$J_{13C\text{-}19F}$											34.9	285.3

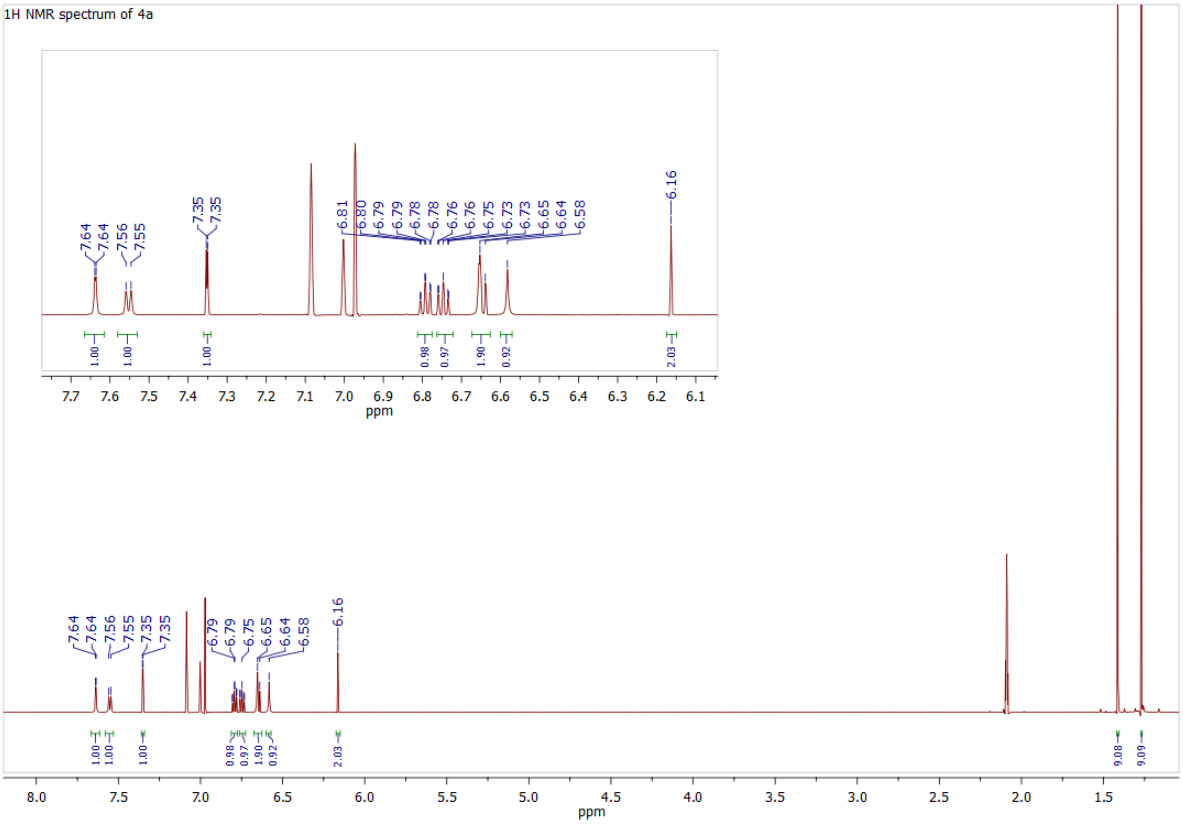


Fig. S17. ^{1}H NMR spectrum of **4a**.

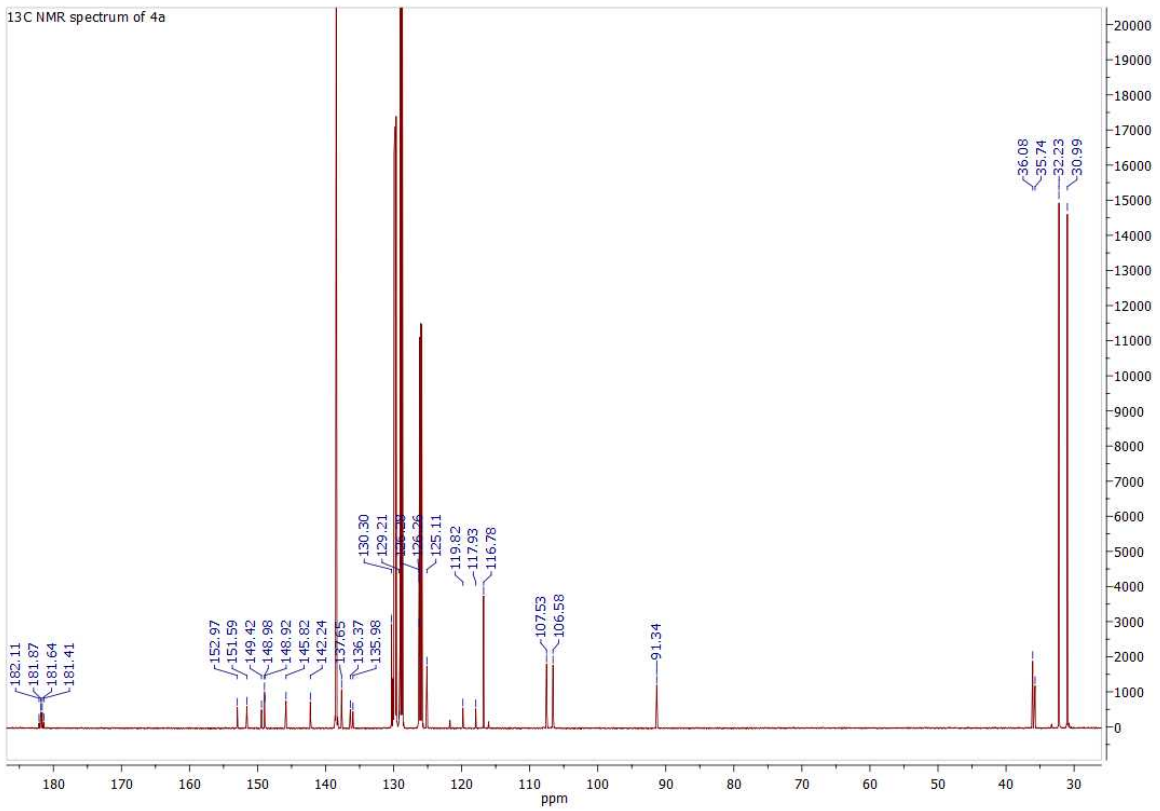
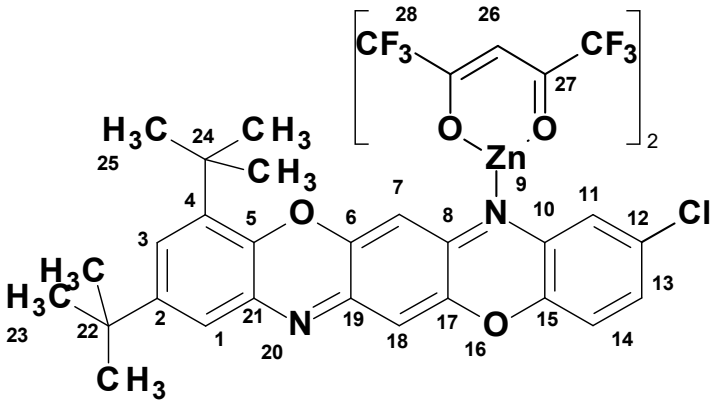


Fig. S18. ^{13}C NMR spectrum of **4a**.

NMR spectra of (2,4-di-(tert-butyl)-9-chlorobenzo[5,6][1,4]oxazine[2,3-b]phenoxazine)-bis-(1,1,1,5,5,5-hexafluoro-pentane-2,4-dioate) Zn (II) **4b**



4b	Nuclear	1	2	3	4	5	6	7	8	10	11	12	13	14
	^{1}H	7.67		7.40				6.50			7.54		6.36	6.68
	$J_{1H\text{-}1H}$	2.2		2.2							2.4		8.7;2.4	8.7
	$^{13}C/^{15}N$	125.16	137.53	126.38	149.37	142.22	153.49	106.71	149.65	131.30	128.69	136.25	130.14	117.65
	$J_{13C\text{-}19F}$													

4b	Nuclear	15	17	18	19	21	22	23	24	25	26	27	28
	^{1}H			6.58				1.40		1.27	6.15		
	$J_{1H\text{-}1H}$												
	$^{13}C/^{15}N$	144.21	151.55	107.44	148.97	137.25	36.15	30.98	36.08	32.24	91.33	181.61	118.87
	$J_{13C\text{-}19F}$											35.1	286.1

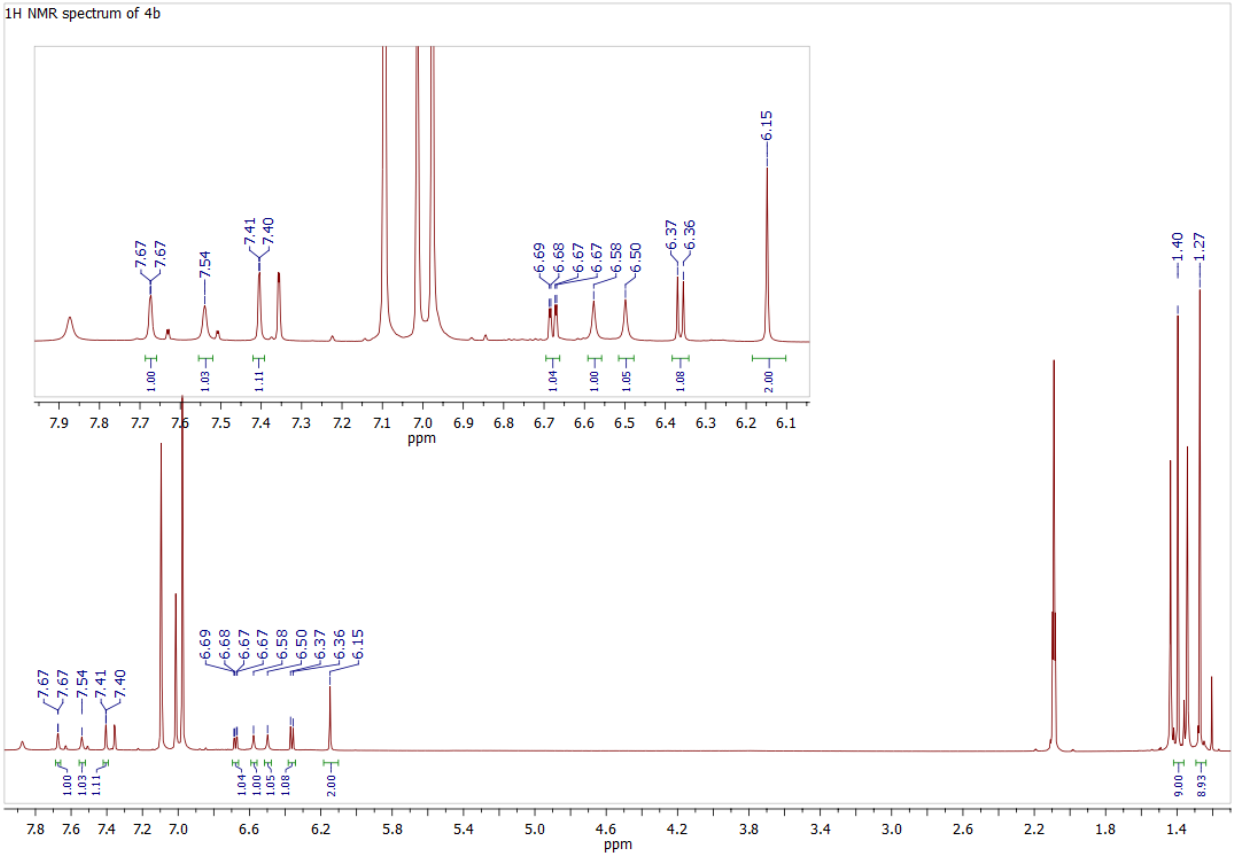


Fig. S19. ^{1}H NMR spectrum of **4b·TPDO**.

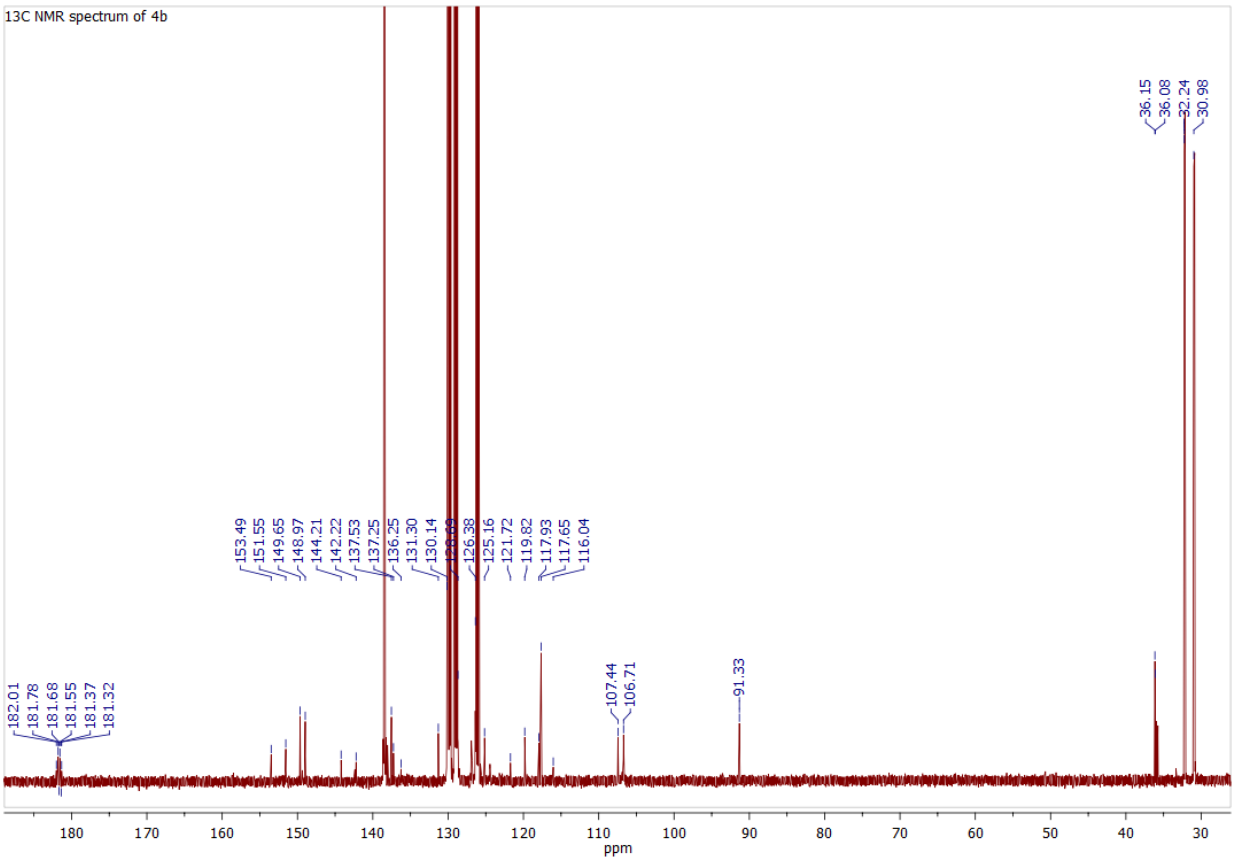
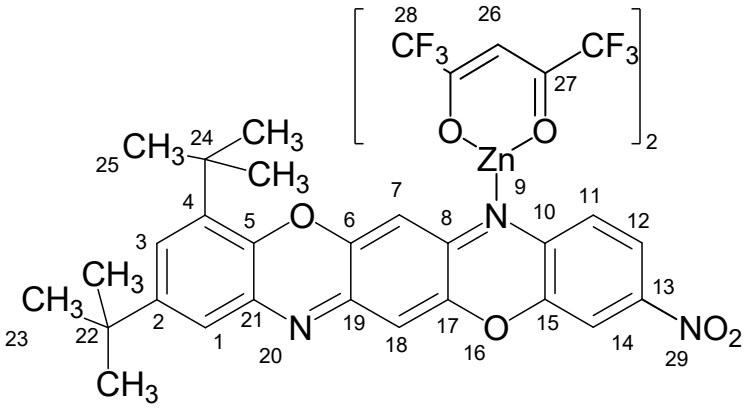


Fig. S20. ^{13}C NMR spectrum of **4b·TPDO**.

NMR spectra of (2,4-di-(tert-butyl)-10-nitrobenzo[5,6][1,4]oxazine[2,3-b]phenoxazine)-bis-(1,1,1,5,5,5-hexafluoro-pentane-2,4-dioate) Zn (II) **4c**



	Nuclear	1	2	3	4	5	6	7	8	9(^{15}N)	10	11	12	13	14
	^{1}H	7.81		7.41				6.55				6.23	7.49		8.32
4c	J_{1H-1H}	2.4		2.4								8.8	8.8;2.6		2.6
	^{13}C/^{15}N	124.89	138.01	127.66	149.86	142.33	153.54	106.92	148.53	366.43	135.56	117.11	125.12	149.01	124.18
	$J_{13C-19F}$														

	Nuclear	15	17	18	19	20(^{15}N)	21	22	23	24	25	26	27	28	29(^{15}N)
	^{1}H			6.78					1.38		1.31	6.16			
4c	J_{1H-1H}														
	^{13}C/^{15}N	146.28	151.26	108.04	149.32		135.15	35.92	30.89	36.14	32.12	91.51	181.80	118.83	364.58
	$J_{13C-19F}$												35.1	285.4	

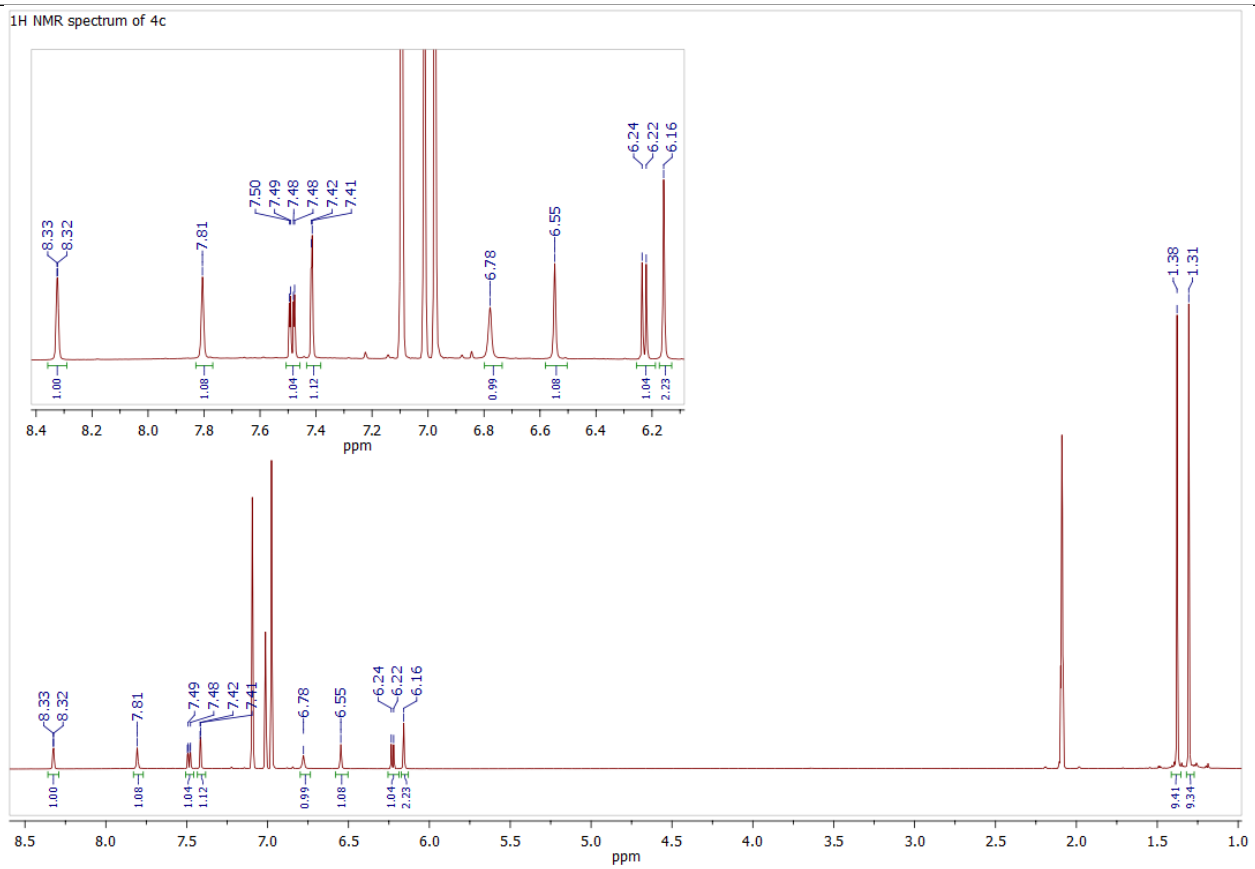


Fig. S21. ^{1}H NMR spectrum of **4c**.

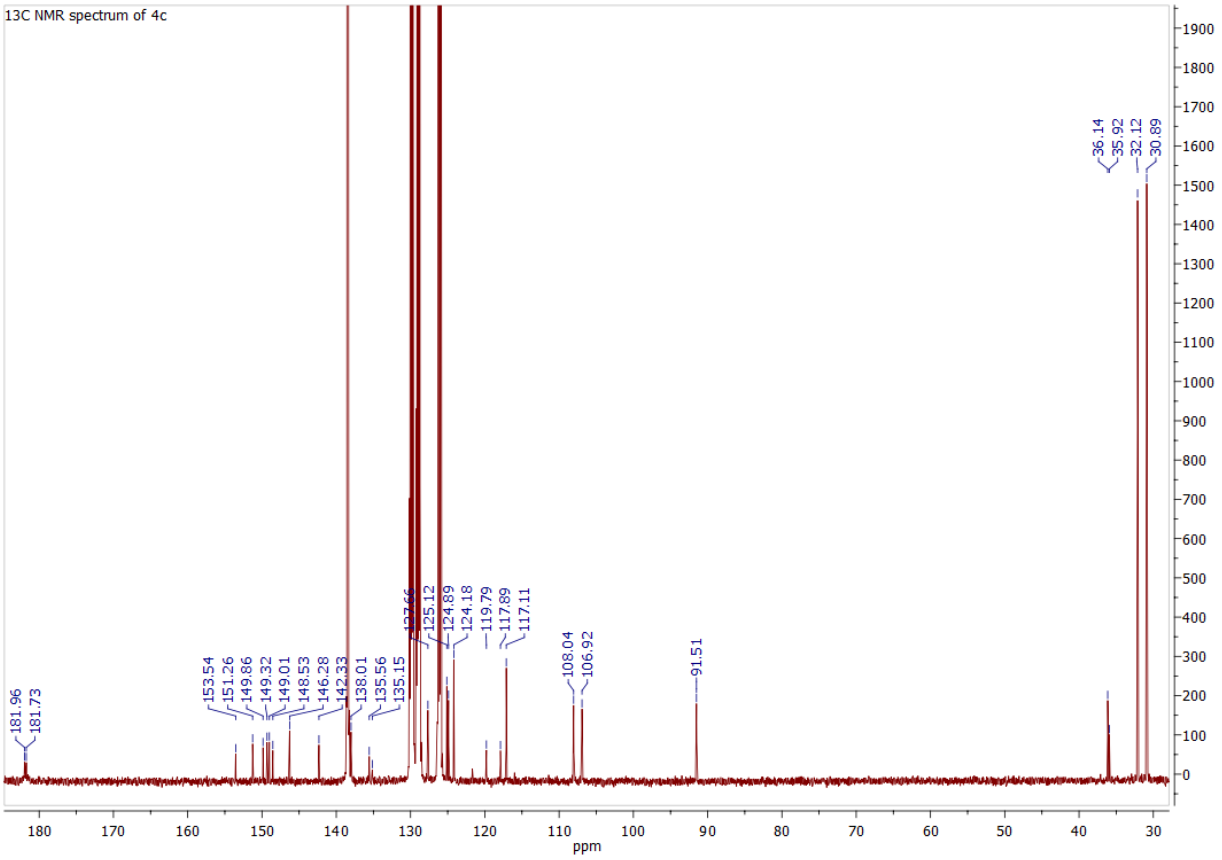
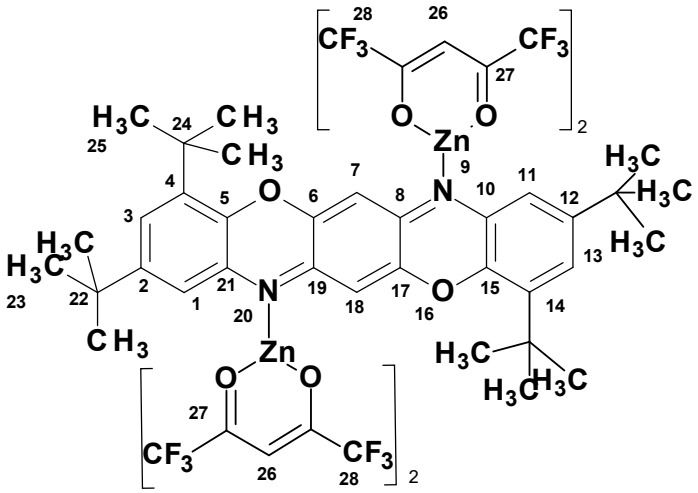


Fig. S22. ^{13}C NMR spectrum of **4c**.

NMR spectra of (2,4,9,11-tetra-(tert-butyl)-benzo[5,6][1,4]oxazine[2,3-b]phenoxazine)-bis-(bis-(1,1,1,5,5,5-hexafluoro-pentane-2,4-dioate)Zn(II)) **5d**.



	Nuclear	1	2	3	4	5	6	7	19	22	23	24	25	26	27	28
5d	^{1}H	7.98		7.44				7.19			1.44		1.37	6.13		
	$J_{1H\text{-}1H}$	1.68		1.68												
	$^{13}C/^{15}N$	124.11	138.25	127.75	149.81	142.43	151.03	106.84	150.33	36.08	30.79	36.20	32.08	91.31	181.71	118.84
	$J_{13C\text{-}19F}$														35.3	284.7

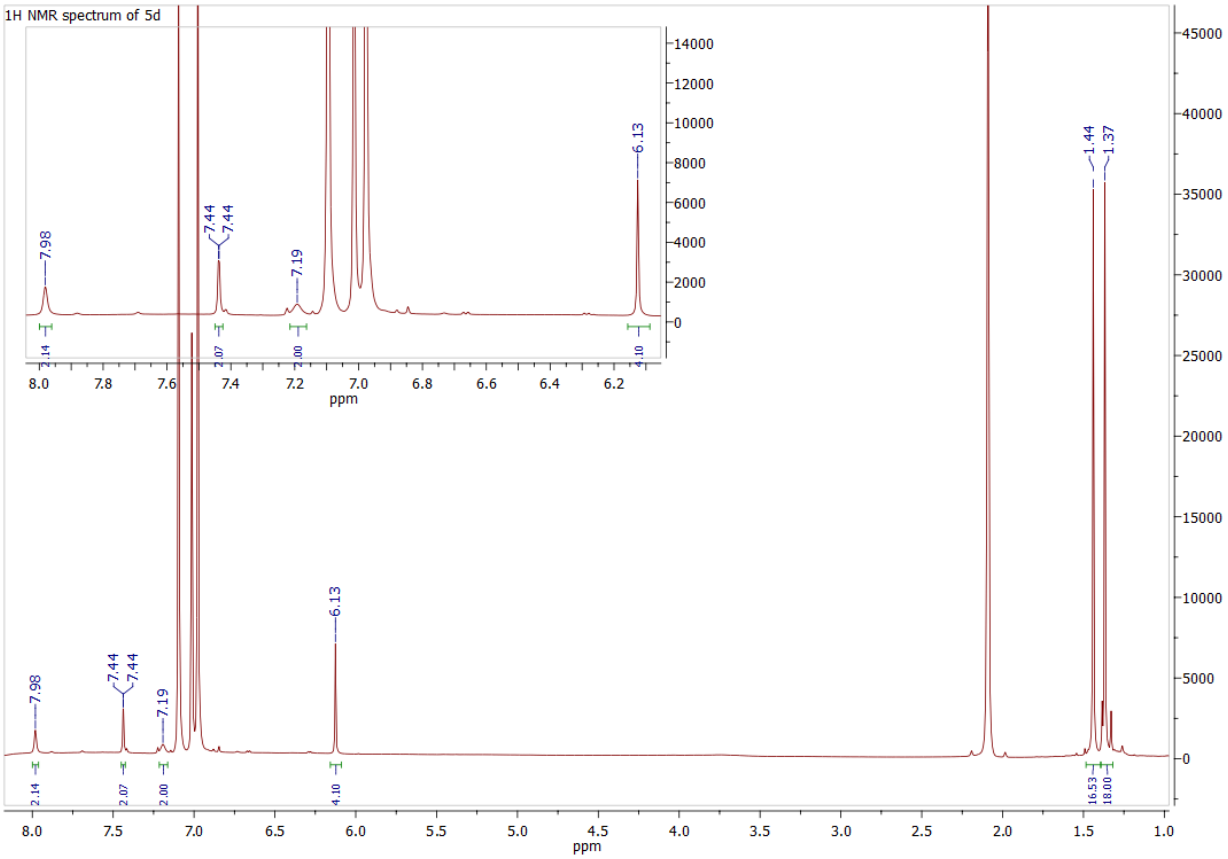


Fig. S23. [1]H NMR spectrum of **5d**.

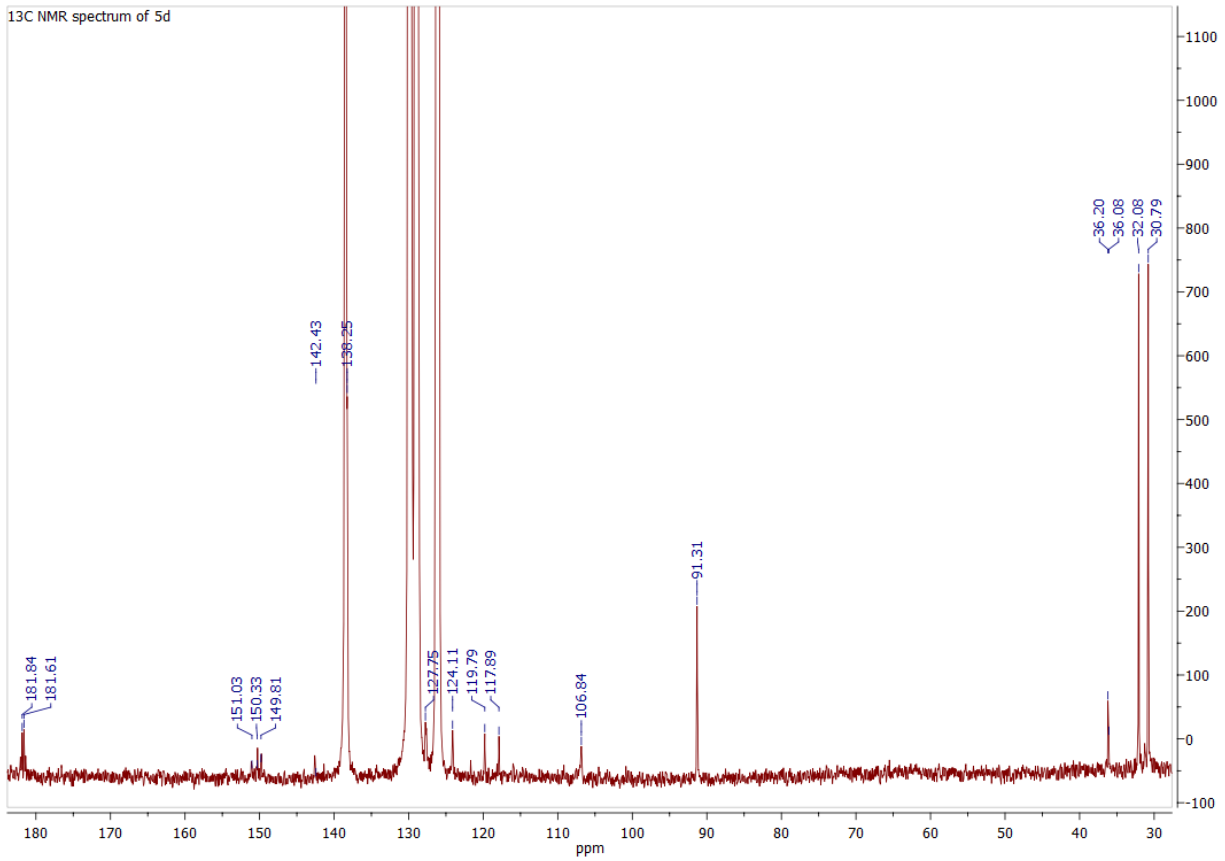


Fig. S24. [13]C NMR spectrum of **5d**.