

Supporting information for

Weak intermolecular hydrogen and halogen-
interactions in an isomorphous series of halogen-
pseudoterpyridine Zn^{II} complexes

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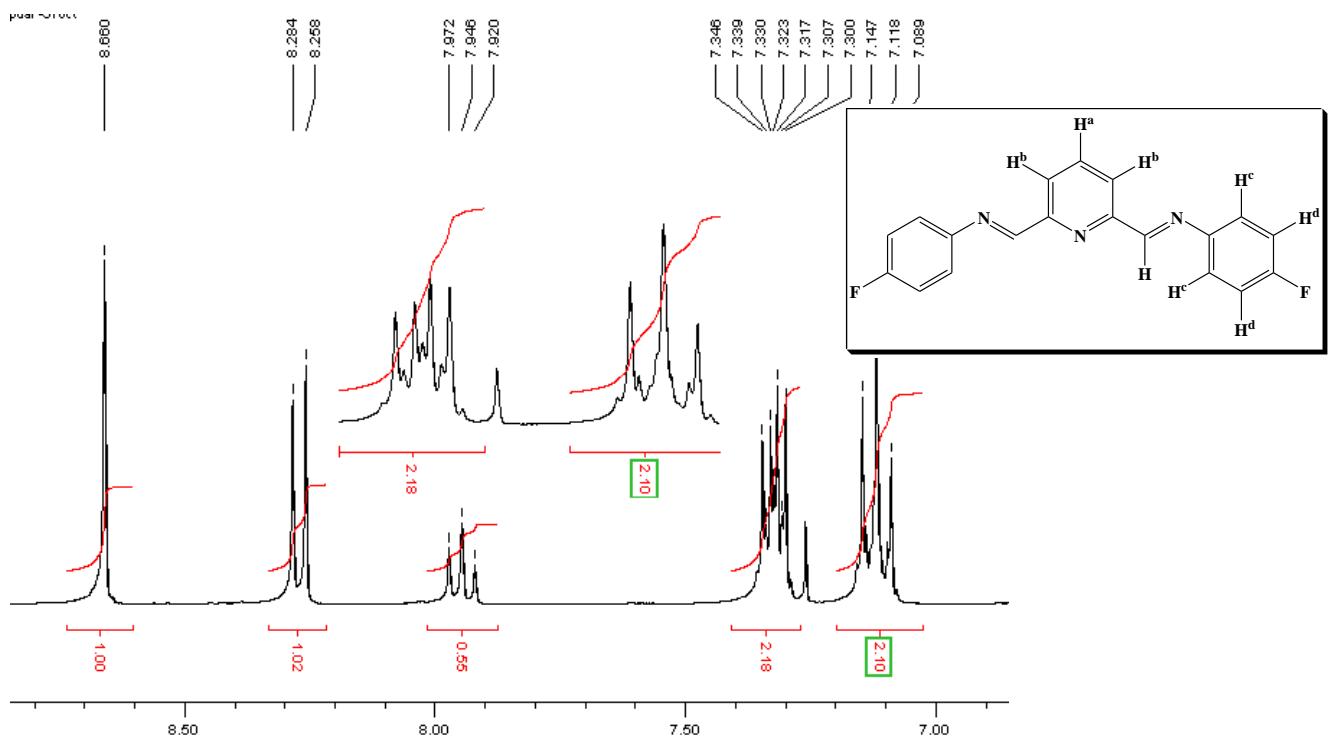


Fig. S1. ¹H-NMR spectrum of L₁₁, 2,6-pyridinedicarboxaldehydebis(*p*-fluorophenylimine)

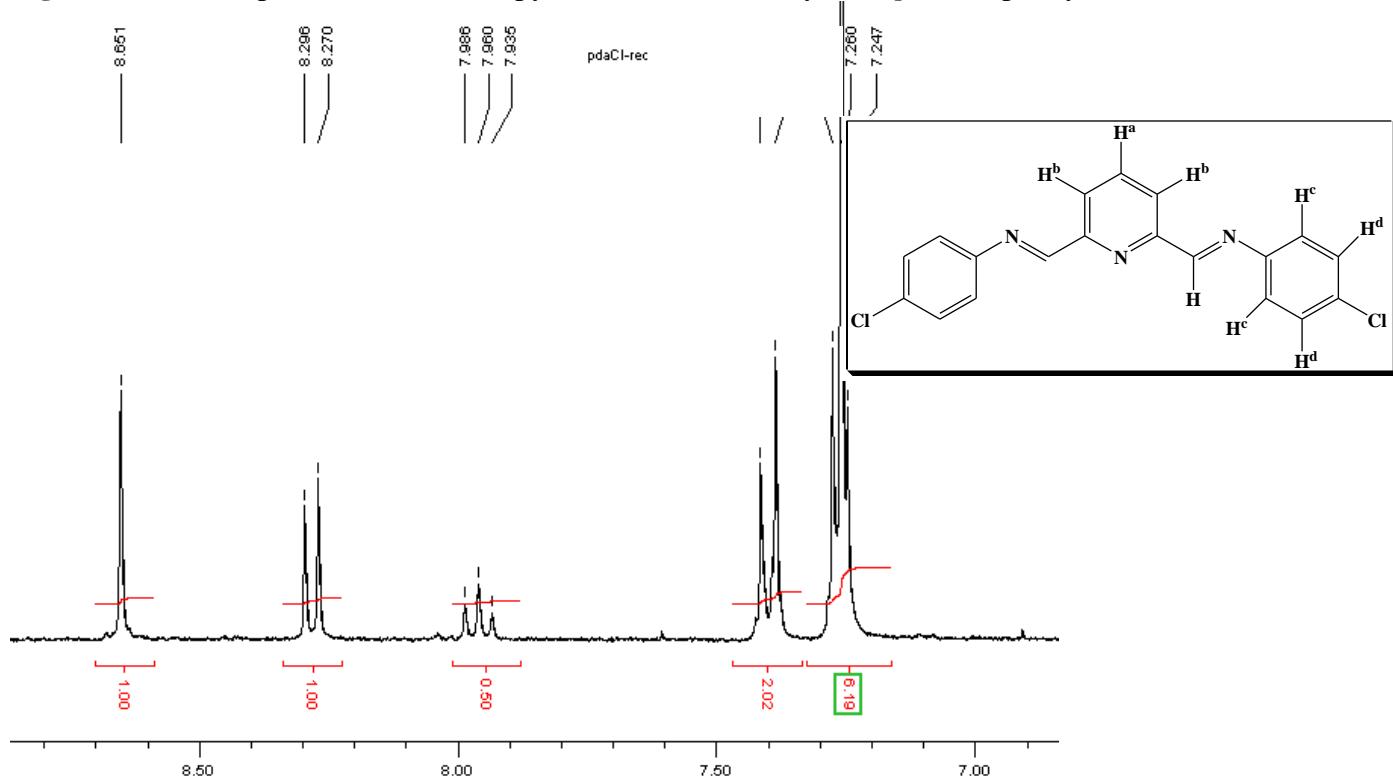


Fig. S2. ¹H-NMR spectrum of L₂₂, 2,6-pyridinedicarboxaldehydebis(*p*-chlorophenylimine)

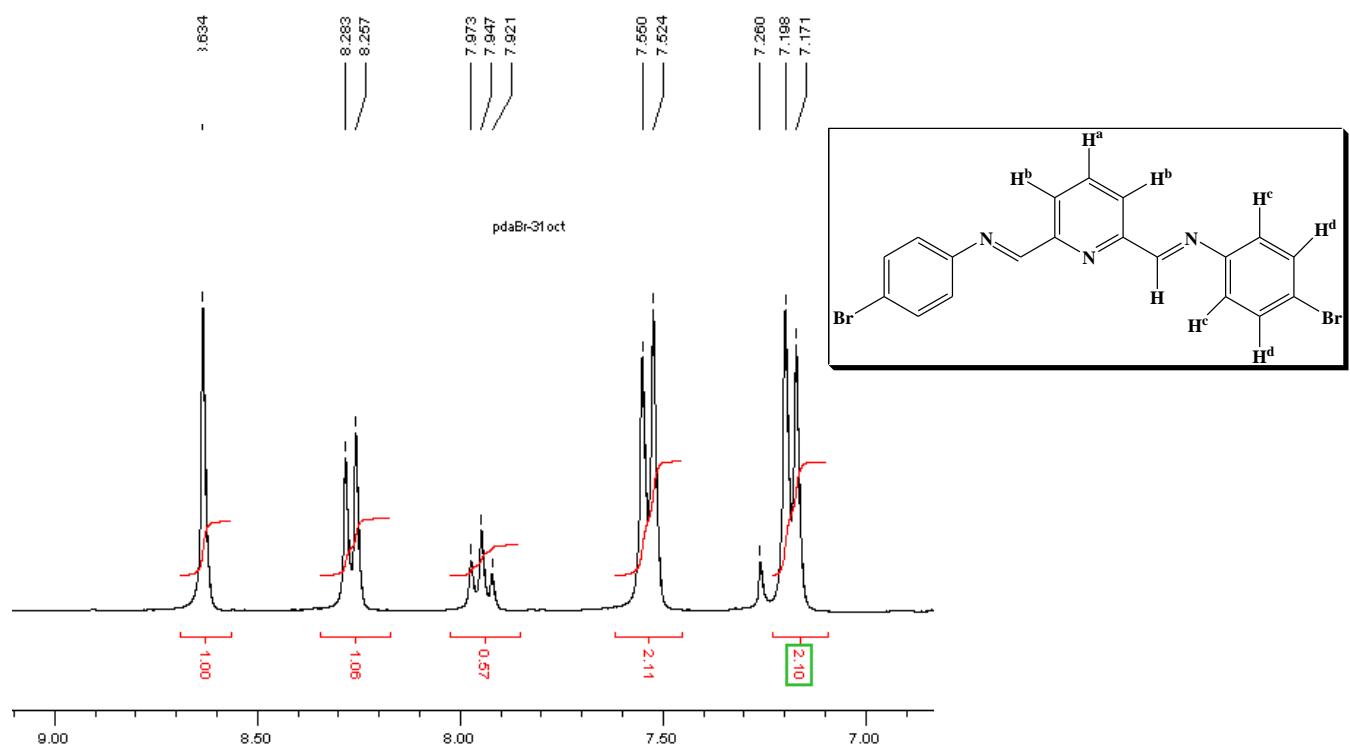


Fig. S3. ¹H-NMR spectrum of **L₃₃**, 2,6-pyridinedicarboxaldehydebis(*p*-bromophenylimine)

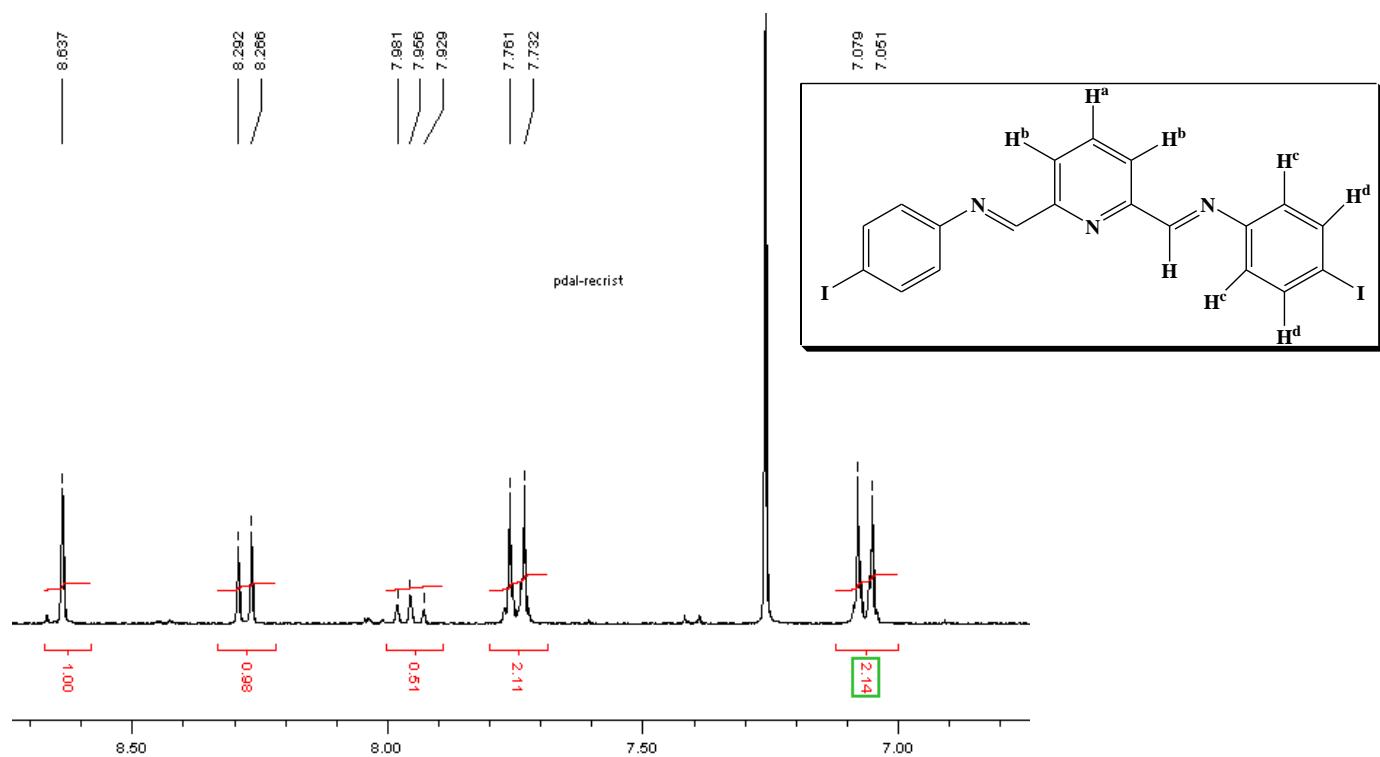


Fig. S4. ¹H-NMR spectrum of **L₄₄**, 2,6-pyridinedicarboxaldehydebis(*p*-iodophenylimine)

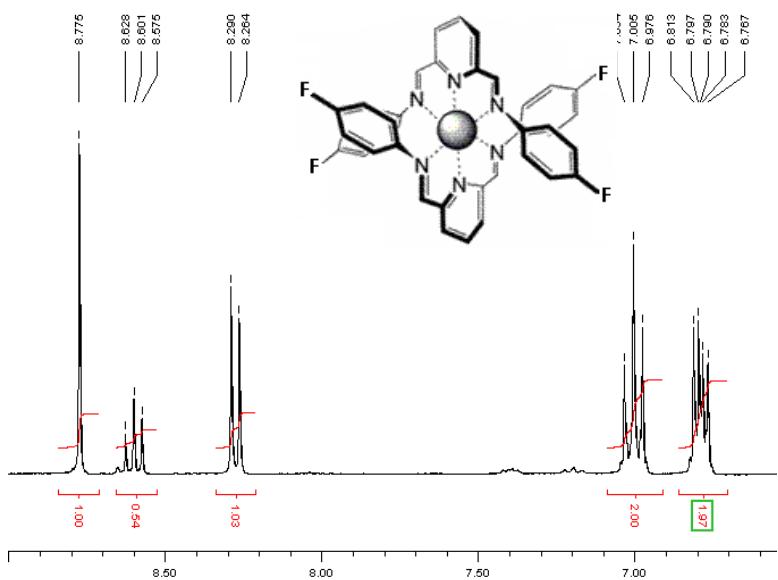


Fig. S5. ^1H -NMR spectrum of $[\text{Zn}(\text{L}_{11})_2]^{2+}$

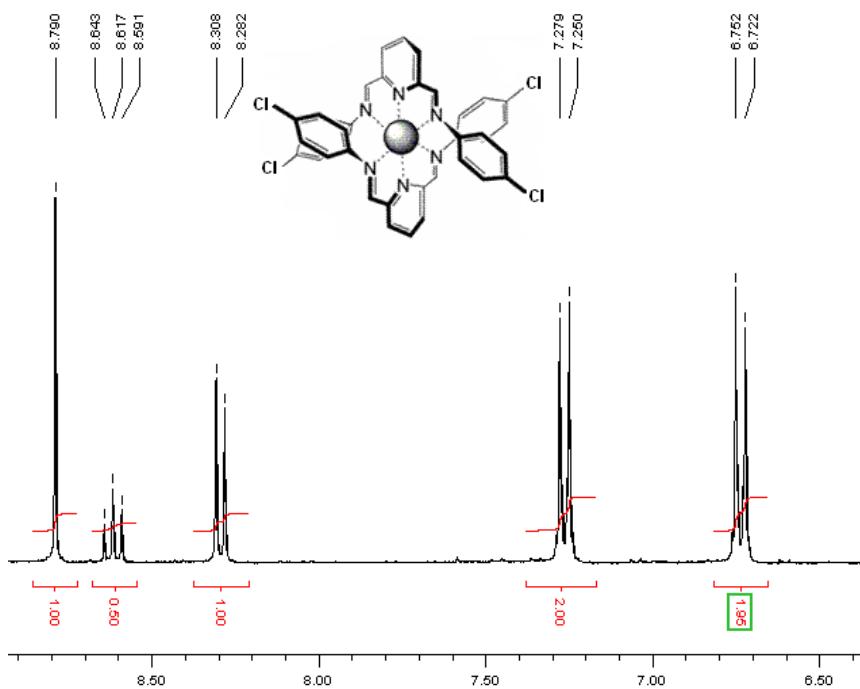


Fig. S6. ^1H -NMR spectrum of $[\text{Zn}(\text{L}_{22})_2]^{2+}$

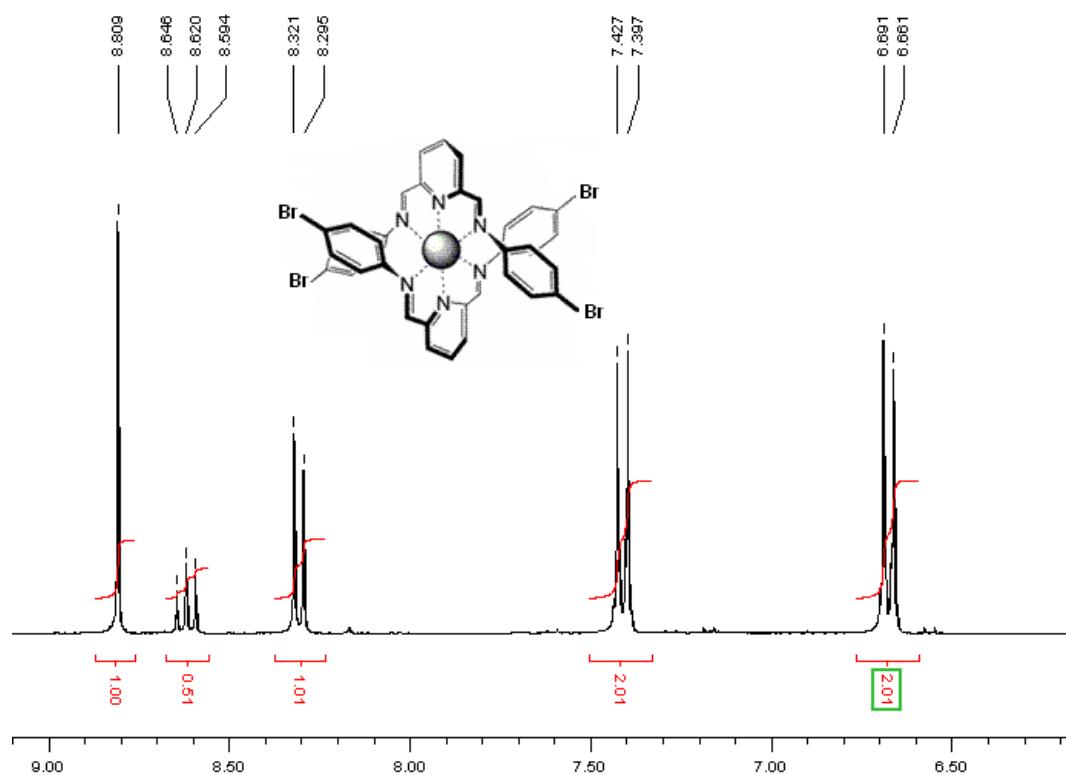


Fig. S7. ^1H -NMR spectrum of $[\text{Zn}(\text{L}_{33})_2]^{2+}$

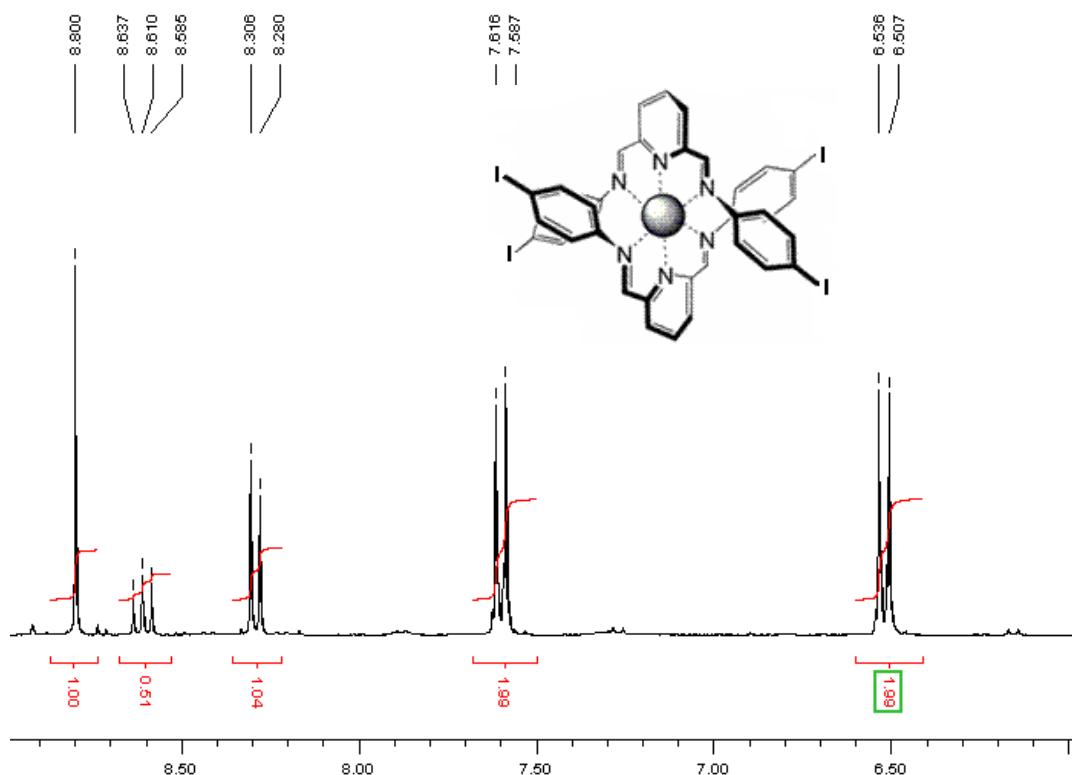


Fig. S8. ^1H -NMR spectrum of $[\text{Zn}(\text{L}_{44})_2]^{2+}$

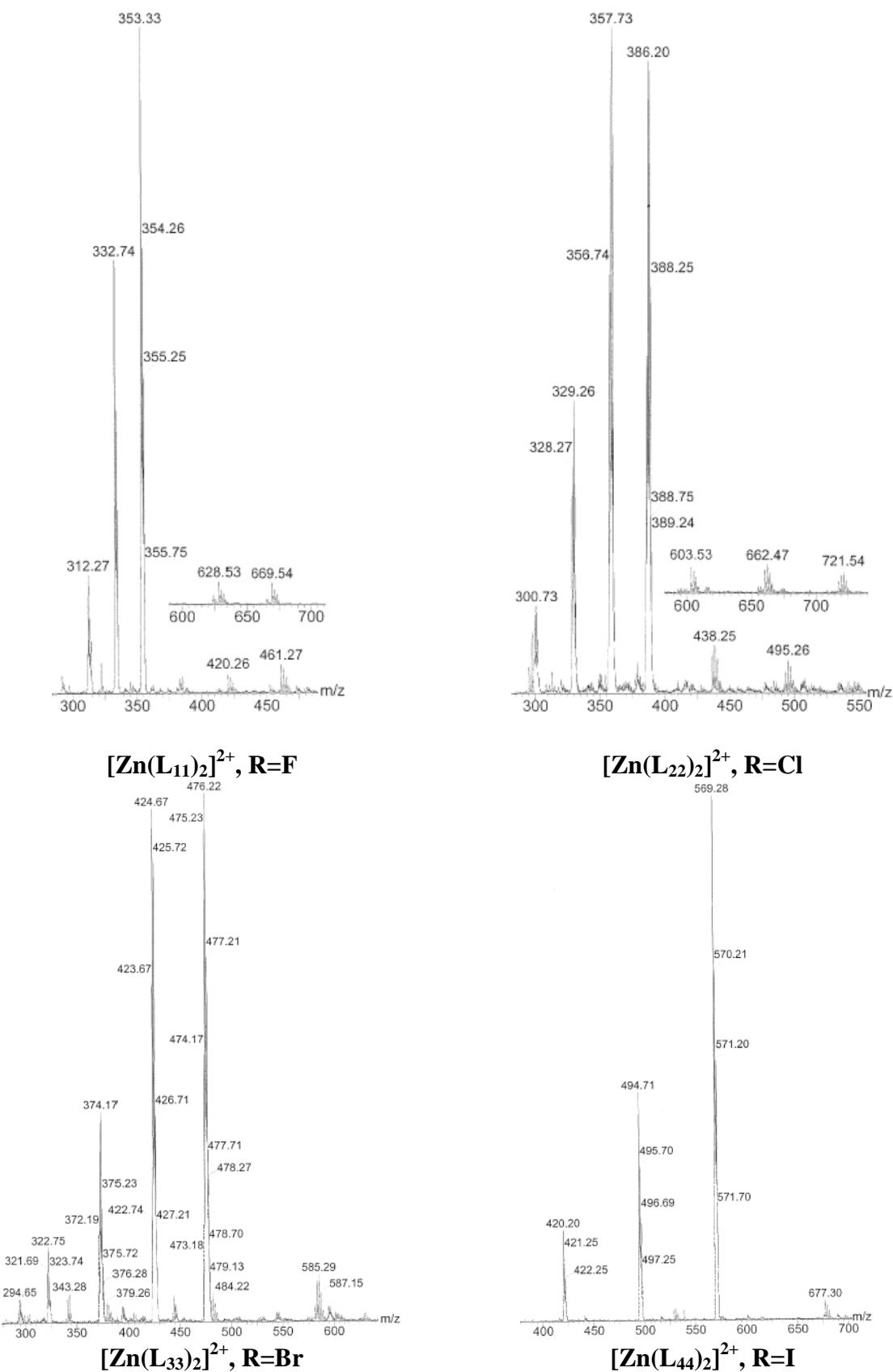


Fig. S9. Fragments of mass spectra (ESI+) for $[Zn(L_i)_2]^{2+}$, $i=1-4$, R=F, Cl, Br, I

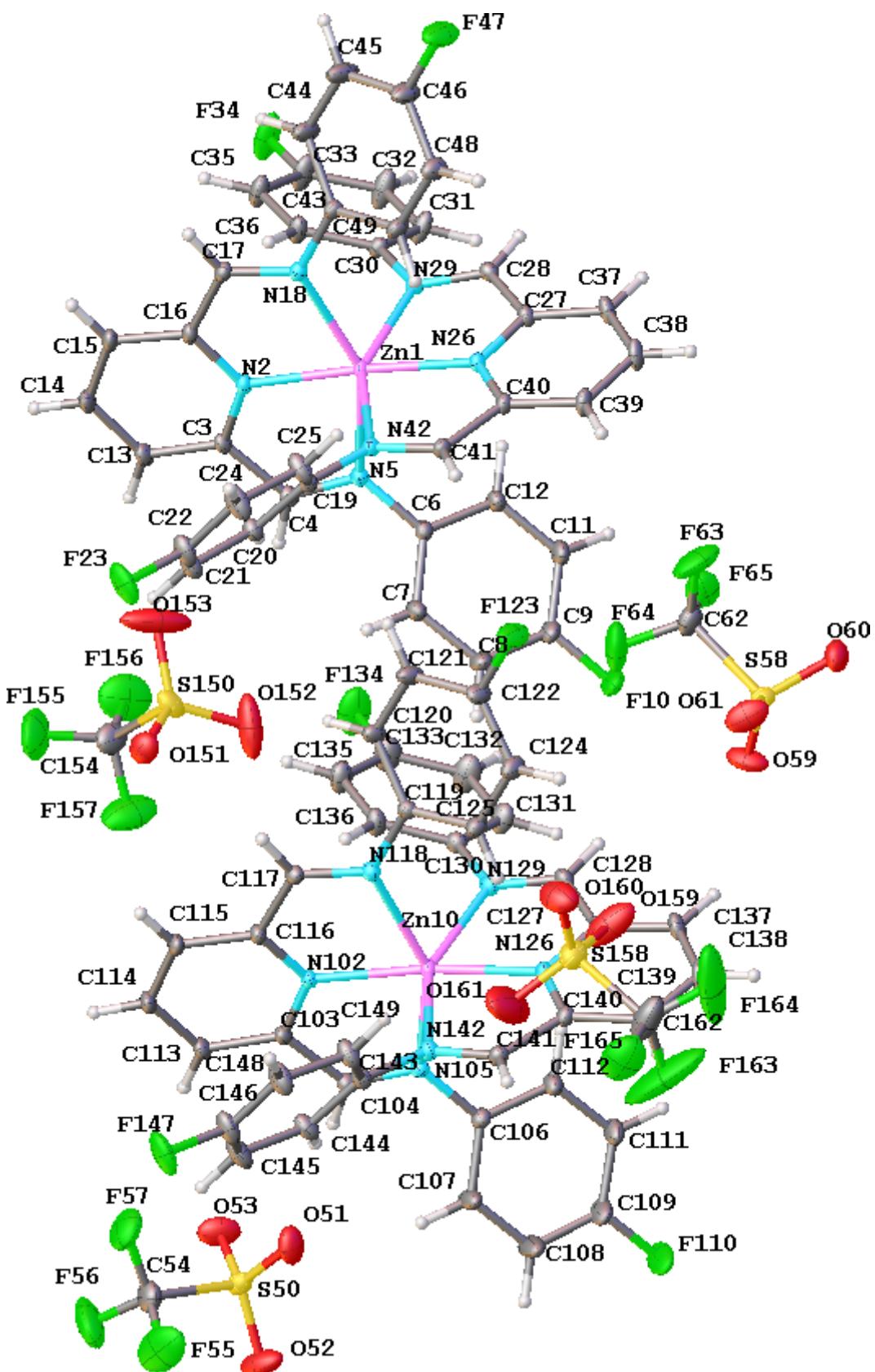


Fig. S10. Molecular structure of $[Zn(L_{11})_2](CF_3SO_3)_2$ with displacement ellipsoids drawn at the 30% probability level.

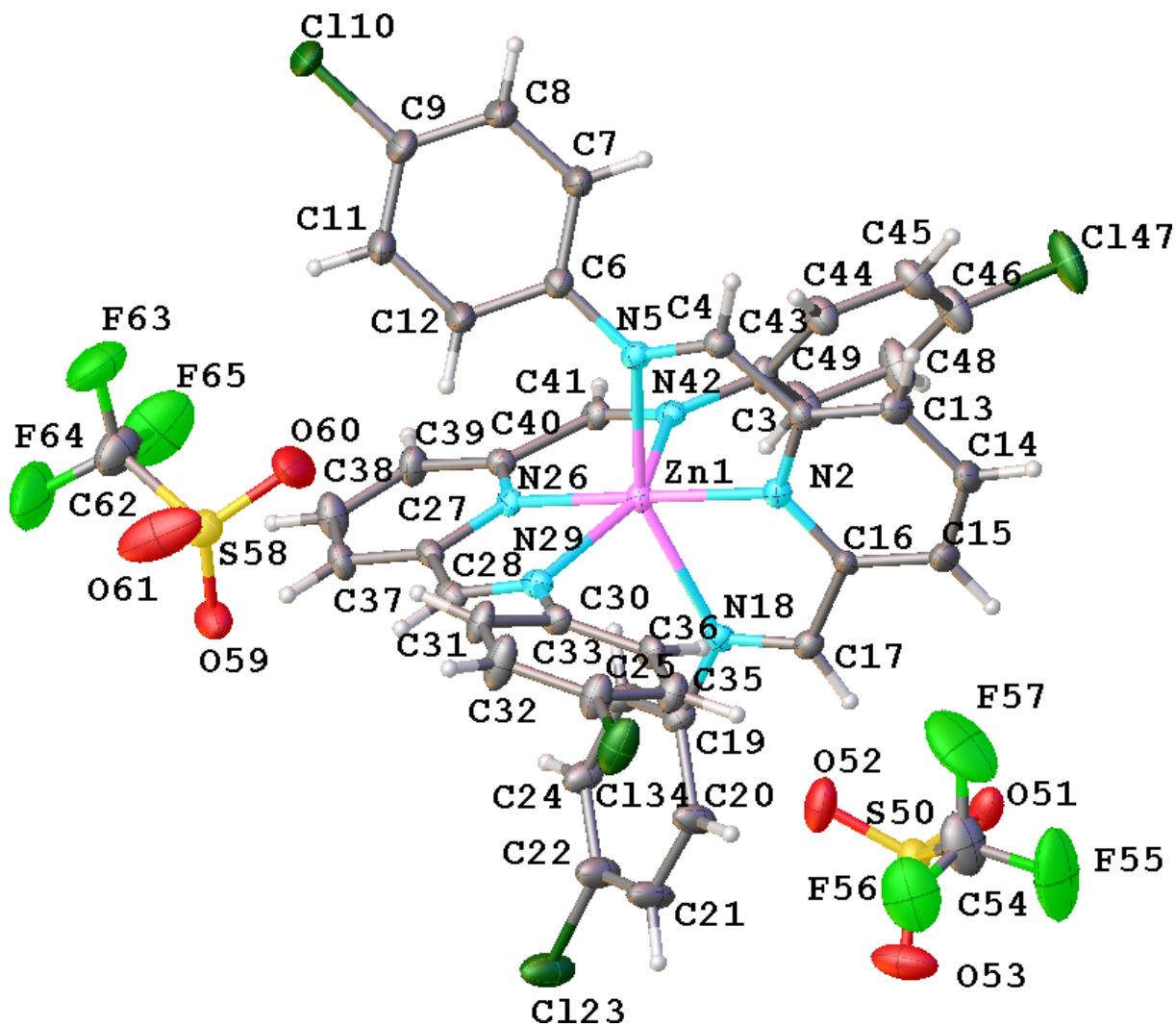


Fig. S11. Molecular structure of $[Zn(L_{22})_2](CF_3SO_3)_2$ with displacement ellipsoids drawn at the 30% probability level.

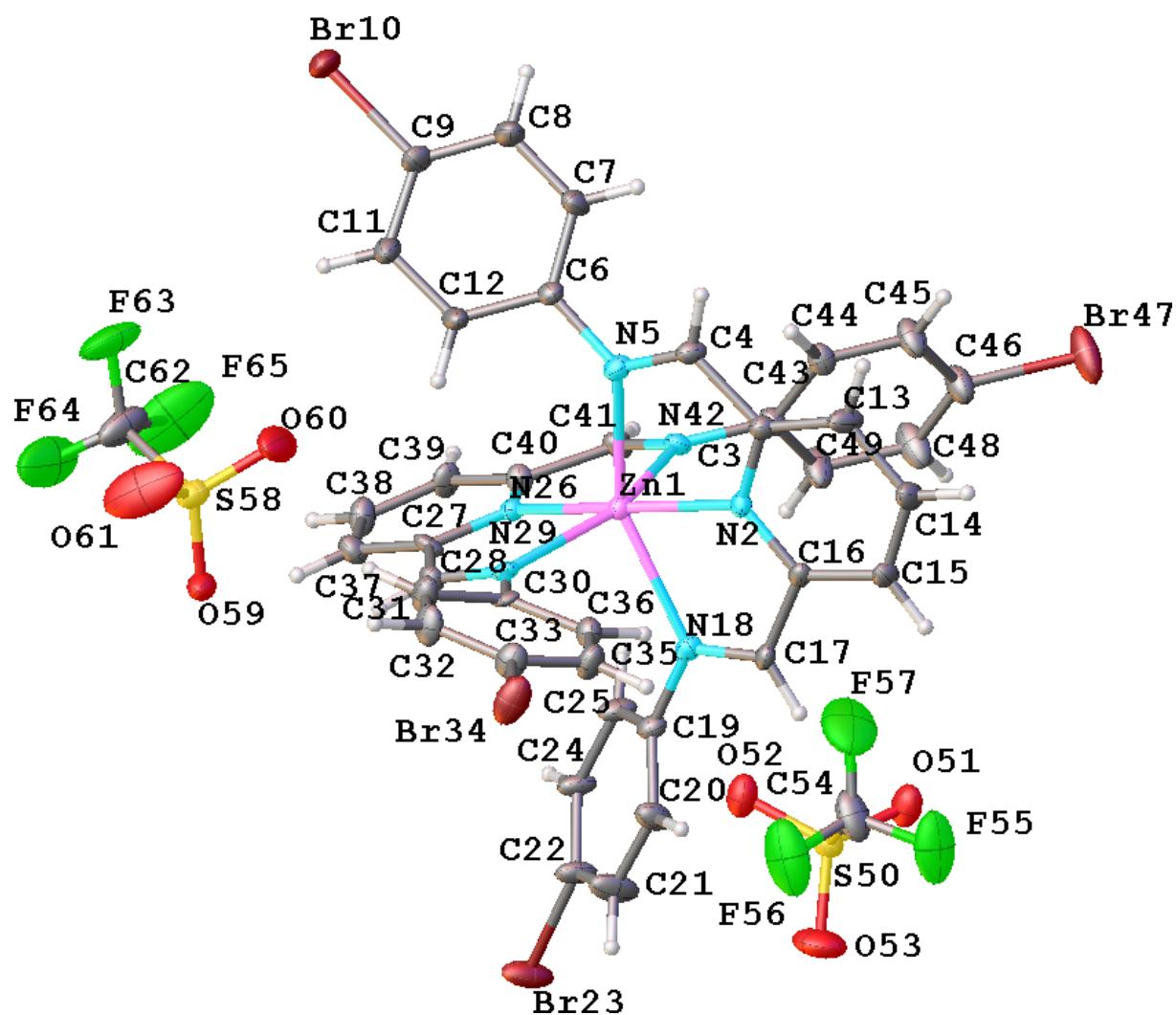


Fig. S12. Molecular structure of $[Zn(L_{33})_2](CF_3SO_3)_2$ with displacement ellipsoids drawn at the 30% probability level.

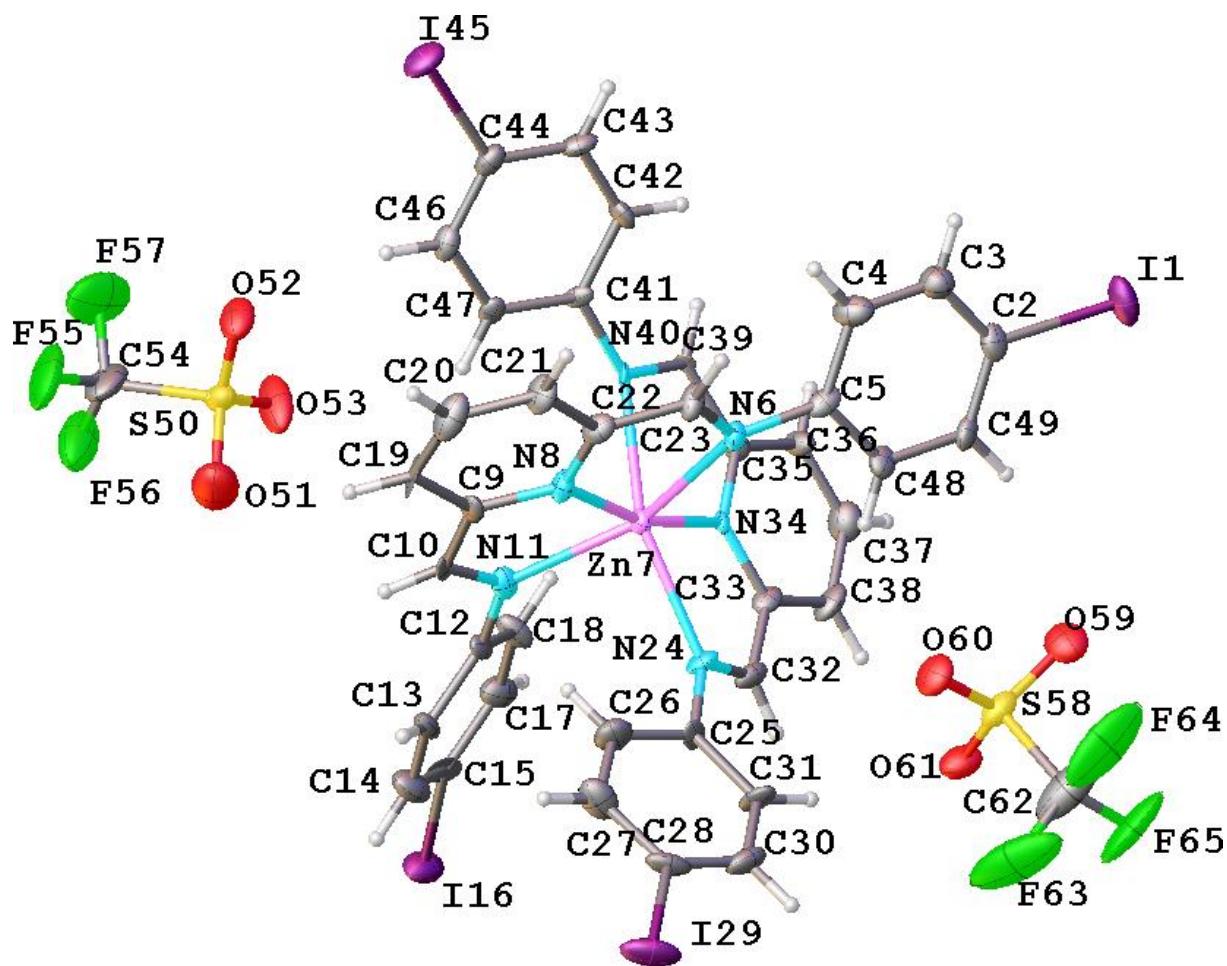


Fig. S13. Molecular structure of $[Zn(L_{44})_2](CF_3SO_3)_2$ with displacement ellipsoids drawn at the 30% probability level.

Table S1. Crystallographic data for $[\text{Zn}(\text{L}_{ii})_2](\text{CF}_3\text{SO}_3)_2$ complexes, $i=1-4$, X=F, Cl, Br,

	$[\text{Zn}(\text{L}_{11})_2](\text{CF}_3\text{SO}_3)_2$	$[\text{Zn}(\text{L}_{22})_2](\text{CF}_3\text{SO}_3)_2$	$[\text{Zn}(\text{L}_{33})_2](\text{CF}_3\text{SO}_3)_2$	$[\text{Zn}(\text{L}_{44})_2](\text{CF}_3\text{SO}_3)_2$
Chemsum	$\text{C}_{40}\text{H}_{26}\text{F}_{10}\text{N}_6\text{O}_6\text{S}_2\text{Zn}$	$\text{C}_{40}\text{H}_{26}\text{Cl}_4\text{F}_6\text{N}_6\text{O}_6\text{S}_2\text{Zn}$	$\text{C}_{40}\text{H}_{26}\text{Br}_4\text{F}_6\text{N}_6\text{O}_6\text{S}_2\text{Zn}$	$\text{C}_{40}\text{H}_{26}\text{I}_4\text{N}_6\text{O}_6\text{S}_2\text{Zn}$
SG	$P-1$	$P-1$	$P-1$	$P-1$
a (Å)	10.0901(2)	10.2008(6)	10.2631(6)	13.3328(9)
b (Å)	20.3099(5)	10.2790(7)	10.4481(8)	14.3957(9)
c (Å)	22.3120(4)	21.6355(14)	22.1315(17)	14.6008(9)
α (°)	65.5992(19)	93.942(5)	83.959(6)	95.972(5)
β (°)	88.3686(15)	91.113(5)	88.508(5)	110.040(6)
γ (°)	89.7419(17)	90.349(5)	89.483(5)	99.907(5)
V (Å ³)	4162.14(16)	2262.7(3)	2359.1(3)	2552.9(3)
Z	4	2	2	2
size (mm ³)	0.350x0.400x0.450	0.110x0.200x0.270	0.050x0.250x0.250	0.016x0.080x0.330
ρ (gcm ⁻³)	1.606	1.573	1.759	1.870
N_{reftot}	141022	36933	39589	34206
N_{refls}	34206	26870	15623	26890
R_{int}	0.025	*	*	0.118
N_{par}	1171	588	588	586
R_1	0.0528	0.1104	0.0919	0.0964
wR_2	0.0544	0.0974	0.0928	0.0828
GOF	1.0552	0.9796	1.1200	1.0049

*Twinned structures: only values available for reflections groups belonging to

different domains of overlapping reflections.

Table S2: Rms-differences (Å) between the halogen stripped $[Zn(L_{ii})_2]^{II}$ moieties

	$[Zn(L_{22})_2](CF_3SO_3)_2$	$[Zn(L_{33})_2](CF_3SO_3)_2$	$[Zn(L_{44})_2](CF_3SO_3)_2$
$[Zn(L_{11})_2]^{II}$ -I	0.15	0.19	0.72
$[Zn(L_{11})_2]^{II}$ -II	0.26	0.22	0.75
$[Zn(L_{22})_2]^{II}$		0.09	0.74
$[Zn(L_{33})_2]^{II}$			0.69

Note: the $[Zn(L_{11})_2](CF_3SO_3)_2$ structure contains 2 independent $[Zn(L_{11})_2]^{II}$ moieties in the asymmetric part of the unit cell, labelled $[Zn(L_{11})_2]^{II}$ -I and $[Zn(L_{11})_2]^{II}$ -II

Table S3: Rms-differences and powder x-ray diffraction similarity indices between the crystal packing in $[Zn(L_{11})_2](CF_3SO_3)_2$, $[Zn(L_{22})_2](CF_3SO_3)_2$ and $[Zn(L_{33})_2](CF_3SO_3)_2$ for clusters of at maximum 15 units.

	Rms difference (Å)	Powder similarity index
$[Zn(L_{11})_2]^{II}$ - $[Zn(L_{22})_2]^{II}$	0.68 [12]	0.97
$[Zn(L_{11})_2]^{II}$ - $[Zn(L_{33})_2]^{II}$	0.97 [15]	0.95
$[Zn(L_{22})_2]^{II}$ - $[Zn(L_{33})_2]^{II}$	0.31 [15]	0.99

Note: the number in squared parentheses in the rms difference columns refers to the number of units that was taken into account in the calculations. The maximum tolerances were 20% for the bond distances and 20 degrees for the bond angles in order to be considered to be equal. With the triflate anion included, the maximal cluster size which remains within the specified tolerances goes down to 9.

Table S4. Distances and angles C-H...Hal in compounds $[Zn(L_{ii})_2]^{\text{II}}$, i=1-4, X = F, Cl, Br,**I involving intermolecular $[Zn(L_{ii})_2]^{\text{II}}$ moieties**

CH...Hal	$d(\text{H} \cdots \text{Hal})$	d_{norm}	$\angle \text{CH} \cdots \text{Ha}$
$[Zn(L_{11})_2]^{\text{II}} (\mathbf{r}_{\text{H}} + \mathbf{r}_{\text{F}} = 2.67 \text{ \AA})$			
C4H41...F23 ⁱ	2.828(2)	1.060	116.31(5)
C11H111...F65 ⁱⁱ	2.792(3)	1.046	138.82(6)
C13H131...F147 ⁱⁱⁱ	2.591(2)	0.970	122.64(6)
C14H141...F34 ^{iv}	2.649(3)	0.992	125.16(6)
C14H141...F147 ⁱⁱⁱ	2.731(3)	1.023	118.45(5)
C15H151...F34 ^{iv}	2.700(2)	1.011	122.25(6)
C15H151...F55 ⁱⁱⁱ	2.663(3)	0.997	149.02(6)
C37H371...F10 ⁱⁱ	2.906(2)	1.088	113.05(5)
C38H381...F10 ⁱⁱ	2.537(2)	0.950	128.94(6)
C38H381...F123 ^v	2.664(2)	0.998	120.95(5)
C39H391...F63	2.719(2)	1.018	118.94(6)
C39H391...F123 ^v	2.620(2)	0.981	122.20(6)
C104H1041...F147 ⁱ	2.691(2)	1.008	122.31(5)
C113H1131...F23 ^{vi}	2.759(2)	1.033	124.38(5)
C114H1141...F23 ^{vi}	2.744(3)	1.028	125.86(5)
C114H1141...F134 ^{vii}	2.735(2)	1.024	140.04(6)
C128H1281...F10	2.730(2)	1.022	134.16(4)
C135H1351...F157 ^{vii}	2.881(3)	1.079	114.47(7)
C137H1371...F165 ⁱ	2.878(3)	1.078	104.38(6)
C138H1381...F47 ^v	2.534(3)	0.949	131.74(6)
C138H1381...F110 ^{viii}	2.517(3)	0.942	138.22(8)
C139H1391...F47 ^v	2.920(2)	1.094	113.40(6)
C139H1391...F163	2.890(4)	1.082	149.42(7)
C139H1391...F163 ^{ix}	2.897(4)	1.085	96.28(8)
C141H1411...F47 ^x	2.781(2)	1.042	118.02(5)
C145H1451...F57	2.801(3)	1.049	146.11(6)

[Zn(L₂₂)₂]^{II} (r_H+r_{Cl}=2.95 Å)			
C4H41...Cl47 ^{xi}	3.024(5)	1.025	124.92(10)
C13H131...C147 ⁱⁱ	3.025(6)	1.025	132.21(12)
C14H141...Cl34 ^{ix}	2.995(6)	1.015	133.42(12)
C17H171...Cl34 ⁱ	2.793(5)	0.947	143.81(11)
C28H281...Cl10 ^x	2.949(5)	1.000	143.12(10)
C38H381...Cl10 ⁱⁱⁱ	2.967(6)	1.006	142.62(13)
C38H381...Cl23 ^{xii}	3.198(7)	1.084	121.89(11)
C39H391...Cl23 ^{xii}	3.029(6)	1.027	129.62(12)
C41H411...Cl23 ^{xiii}	2.909(5)	0.986	128.93(11)
[Zn(L₃₃)₂]^{II} (r_H+r_{Br}=3.05 Å)			
C4H41...Br47 ⁱ	3.005(6)	0.985	126.02(12)
C13H131...Br47 ^{xiv}	3.128(7)	1.026	132.29(13)
C14H141...Br34 ^v	3.176(8)	1.041	134.00(14)
C17H171...Br34 ^{xi}	2.882(6)	0.945	146.76(12)
C28H281...Br10 ^{xiii}	3.025(6)	0.991	148.92(12)
C38H381...Br10 ⁱⁱⁱ	3.173(7)	1.040	141.88(14)
C39H391...Br23 ^{xv}	3.226(7)	1.058	133.44(13)
C41H411...Br23 ^x	3.106(7)	1.018	125.95(13)
[Zn(L₄₄)₂]^{II} (r_H+r_I=3.18 Å)			
C17H171...I45 ^{viii}	3.300(14)	1.036	131.1(3)
C43H431...I16 ^x	3.348(14)	1.047	131.3(2)
C32H321...I29 ^{xvi}	3.194(12)	1.004	121.3(2)

Symmetry codes: (i) x+1,y,z; (ii) 2-x,1-y,1-z; (iii) 1-x,1-y,-z ; (iv) 2-x,2-y,1-z ; (v) 1-x,1-y,1-z ; (vi) 1-x,-y,-z ; (vii) 2-x,1-y,-z ; (viii) 2-x,-y,1-z ; (ix) 1-x,-y,1-z ; (x) x,-1+y,z ; (xi) -1+x,y,z ; (xii) 2-x,-y,-z ; (xiii) x,1+y,z ; (xiv) -x,-y,1-z ; (xv) -x,1-y,-z ; (xvi) 2-x,1-y,2-z ; (xvii) -1+x,-1+y,z ; (xviii) -1+x,1+y,z ; (xix) 1+x,y,1+z ; (xx) 2-x,-y,2-z

Table S5. Distances and angles C-Hal₁...Hal₂-C in compounds [Zn(L_{ii})₂]^{II}, i=1-4, X = F, Cl,**Br, I**

C-Hal ₁ ...Hal ₂ -C	<i>d</i> (Hal ₁ ...Hal ₂)	<i>d</i> _{norm}	∠C-Hal ₁ ...Hal ₂	∠Hal ₁ ...Hal ₂ -C
[Zn(L₁₁)₂]^{II} ($\mathbf{r}_F+r_F=2.94 \text{ \AA}$)				
C9F10...F65C62	3.022(3)	1.028	88.69(12)	110.21(15)
C33F34...F55C54 ^{xvii}	3.084(3)	1.049	165.66(19)	150.5(3)
C62F63...F123C122 ^v	2.885(2)	0.981	164.3(2)	170.29(12)
C62F64...F123C122	3.196(3)	1.087	119.83(19)	74.18(13)
C146F147...F155C154 ^{vi}	3.188(4)	1.084	78.99(15)	105.4(2)
[Zn(L₂₂)₂]^{II} ($\mathbf{r}_F+r_{Cl}=3.22 \text{ \AA}$)				
C54F56...Cl47C46 ^{xvii}	3.302(6)	1.025	159.6(5)	168.6(3)
C54F57...Cl34C33 ^{ix}	3.355(7)	1.042	123.9(6)	85.8(3)
C62F63...Cl23C22 ^{xviii}	3.441(6)	1.069	158.0(5)	165.1(3)
C62F65...Cl10C9 ⁱⁱⁱ	3.469(8)	1.077	124.0(7)	94.0(3)
[Zn(L₃₃)₂]^{II} ($\mathbf{r}_F+r_{Br}=3.32 \text{ \AA}$)				
C54F56...Br47C46 ⁱⁱⁱ	3.320(6)	1.000	165.3(6)	158.5(3)
C54F57...Br34C33 ^v	3.489(8)	1.051	120.0(7)	88.9(3)
C62F63...Br23C22 ^{xviii}	3.336(6)	1.005	162.4(6)	160.8(3)
C62F65...Br10C9 ^{vi}	3.533(10)	1.064	129.5(9)	103.0(3)

Notes: symmetry codes as in Table S4.

Table S6. Distances and angles C-Hal...O in compounds $[Zn(L_{ii})_2]^{\text{II}}$ i=1-4, X = F, Cl, Br,**I**

C-Hal...O	$d(\text{Hal...O})$	d_{norm}	$\angle \text{C-Hal...O}$
$[Zn(L_{22})_2]^{\text{II}} (r_{\text{Cl}}+r_{\text{O}}=3.27 \text{ \AA})$			
C9Cl10...O59 ^{xiii}	3.286(5)	1.005	159.5(2)
C33Cl34...O51 ^{xi}	3.154(5)	0.965	160.1(2)
$[Zn(L_{33})_2]^{\text{II}} (r_{\text{Br}}+r_{\text{O}}=3.37 \text{ \AA})$			
C9Br10...O59 ^x	3.247(5)	0.963	159.4(3)
C33Br34...O51 ⁱ	3.174(6)	0.942	157.0(3)
$[Zn(L_{44})_2]^{\text{II}} (r_{\text{F}}+r_{\text{Br}}=3.50 \text{ \AA})$			
C15I16...O53 ^{xix}	3.182(11)	0.909	175.8(5)

Notes: symmetry codes as in Table S4.

Table S7. Distances and angles C-H...O in compounds $[Zn(L_{ii})_2]^{\text{II}}$ i=1-4, X = F, Cl, Br, I

C-Hal...O	$d(\text{Hal...O})$	d_{norm}	$\angle \text{C-Hal...O}$
$[Zn(L_{11})_2]^{\text{II}} (r_H+r_O=2.72 \text{ \AA})$			
C7H71...O152	2.555(3)	0.939	151.13(8)
C12H121...O60 ⁱⁱ	2.542(3)	0.935	143.60(6)
C25H251...O60 ^v	2.378(2)	0.874	153.23(7)
C31H311...O60 ⁱⁱ	2.569(3)	0.944	146.86(6)
C37H371...O59 ⁱⁱ	2.543(2)	0.934	141.21(6)
C44H441...O51 ^{xiii}	2.351(3)	0.864	159.66(7)
C107H1071...O51	2.488(3)	0.914	161.36(7)
C115H1151...O151 ⁱⁱⁱ	2.584(2)	0.950	126.11(6)
C120H1201...O152	2.544(3)	0.935	151.14(8)
C128H1281...O160 ⁱ	2.406(3)	0.885	142.07(7)
C144H1441...O51	2.498(3)	0.918	147.27(6)
C149H1491...O161	2.500(3)	0.919	146.68(9)
$[Zn(L_{22})_2]^{\text{II}} (r_H+r_O=2.72 \text{ \AA})$			
C7H71...O52 ^{xiii}	2.577(8)	0.947	157.33(16)
C12H121...O60	2.602(9)	0.956	124.38(18)
C14H141...O51 ^{xiv}	2.715(8)	0.998	117.22(16)
C20H201...O52	2.583(8)	0.950	159.65(18)
C25H251...O61 ^{xi}	2.621(9)	0.964	127.8(2)
C28H281...O59	2.532(6)	0.931	140.05(17)
C31H311...O60	2.550(8)	0.938	157.8(2)
C44H441...O53 ^{xiii}	2.585(8)	0.950	130.61(18)
C49H491...O60 ⁱ	2.597(9)	0.952	155.3(2)
$[Zn(L_{33})_2]^{\text{II}} (r_H+r_O=2.72 \text{ \AA})$			
C7H71...O52 ^x	2.566(9)	0.943	153.5(2)

C12H121...O60	2.550(11)	0.938	128.0(2)
C14H141...O51 ^{xiv}	2.607(9)	0.958	123.0(2)
C20H201...O52	2.565(10)	0.943	157.2(2)
C25H251...O61 ^{xi}	2.542(12)	0.935	130.5(3)
C28H281...O59	2.550(8)	0.938	139.59(19)
C31H311...O60	2.632(11)	0.968	151.7(2)
C44H441...O53 ^x	2.620(10)	0.963	129.1(2)
C49H491...O60 ^{xi}	2.732(14)	1.00	147.7(3)
[Zn(L₄₄)₂]^H (r_H+r_O=2.72 Å)			
C20H201...O59 ^{xi}	2.372(17)	0.860	163.1(5)
C21H211...O59 ^{xx}	2.434(19)	0.890	163.5(4)
C23H231...O60 ^{xx}	2.504(16)	0.922	178.2(3)
C31H311...O60	2.558(19)	0.941	127.9(4)
C36H361...O52 ^{viii}	2.52(2)	0.922	164.4(4)
C37H371...O52 ^{xi}	2.435(16)	0.893	138.2(5)
C39H391...O53 ^{viii}	2.541(18)	0.934	169.1(4)
C46H461...O52	2.364(17)	0.875	156.3(4)
C48H481...O60	2.439(16)	0.900	137.0(4)

Notes: symmetry codes as in Table S4.

Table S8. Intermolecular CH...π interactions (below 3Å)

CH...ring	$d(\text{H} \cdots \text{Cg})$	d_{perp}	γ	$\angle \text{CH} \cdots \text{Cg}$
[Zn(L₁₁)₂]^{II}				
C108H1081...C30-C36 ^x	2.84	2.62	22.69	138
C132H1321...C130C136 ⁱ	2.64	2.55	15.02	165
C32H321...C43-C49	2.86	2.64	22.89	152
[Zn(L₂₂)₂]^{II}				
C8H81...C30-C36 ^{xiii}	2.75	2.59	19.28	151
[Zn(L₃₃)₂]^{II}				
C8H81...C30-C36 ^{xiii}	2.91	2.74	19.59	159
[Zn(L₄₄)₂]^{II}				
C3H31...C25-C31 ^{xx}	2.93	2.89	9.53	134

Notes: symmetry codes as in Table S4. Cg is the center of gravity of the ring; d_{perp} is the perpendicular distance from H to the plane formed by the ring; γ is the angle between the vector H...Cg and the normal of the ring

Fig. S14: Non-covalent interactions in the structure of $[\text{Zn}(\text{L}_{22})_2](\text{CF}_3\text{SO}_3)_2$ as calculated by *Jmol*. The figure is integrated as 3D content in this pdf-file. The molecule can be manipulated with the mouse, just by holding the left mouse button down on the molecule and shifting it gently. By holding the right mouse button down on the molecule and shifting the cursor up and down, the molecule can be zoomed in and zoomed out. There are more options accessible with a right-click on the molecule. Adobe Reader 7.0 or better is needed.