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Electronic Supplementary Information

Cu(II) and Zn(II) complexes with a poly-functional ligand derived from *o*-vanillin and thiophene. Crystal structure, physicochemical properties, theoretical studies and cytotoxicity assays against human breast cancer cells

María R. Rodríguez [a], Julián Del Plá [a], Lucía M. Balsa [a], Ignacio E. León [a], Oscar E. Piro [b], Gustavo A. Echeverría [b], Javier García-Tojal [c], Reinaldo Pis-Diez [a], Beatriz S. Parajón-Costa [a] and Ana C. González-Baró [a *]

[a] CEQUINOR (CONICET-CCT La Plata, UNLP), Bvd. 120 N°1465, B1900AVV La Plata, Argentina.

[b] IFLP (CONICET-CCT La Plata, UNLP), CC 67, B1900AVV, La Plata, Argentina.

[c] Departamento de Química, UBU, Pza. Misael Bañuelos s/n, E-09001 Burgos, España.

Table S1a. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for complex CuL_2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
C(1)	10900(30)	2050(30)	6149(11)	32(1)
C(2)	11640(16)	1994(10)	7300(8)	57(2)
C(3)	9928(9)	1279(6)	7969(5)	47(1)
C(4)	7688(11)	721(6)	7279(4)	45(1)
C(5)	12335(4)	2671(2)	5169(2)	34(1)
C(6)	9626(4)	2474(2)	3412(2)	33(1)
C(7)	7738(4)	2702(2)	2581(2)	32(1)
C(8)	6572(4)	3784(2)	2854(2)	30(1)
C(9)	4638(4)	3912(2)	1982(2)	34(1)
C(10)	4012(4)	3026(2)	912(2)	43(1)
C(11)	5230(5)	1972(2)	644(2)	49(1)
C(12)	7038(4)	1813(2)	1463(2)	41(1)
C(13)	1910(5)	5274(2)	1448(2)	51(1)
N	10608(3)	3210(2)	4434(2)	31(1)
O(1)	7146(3)	4669(1)	3841(1)	40(1)
O(2)	3571(3)	4968(2)	2331(2)	45(1)
S	7782(2)	1118(2)	5828(1)	50(1)
Cu	10000	5000	5000	30(1)
C(1A)	10800(80)	2010(80)	6080(30)	32(1)
C(2A)	8320(30)	1280(20)	5965(17)	57(4)
C(3A)	7380(40)	740(20)	6935(15)	45(3)
C(4A)	9200(30)	1110(20)	7852(18)	46(3)
SA	12126(13)	2141(8)	7520(6)	47(1)

Table S1b. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for complex ZnL_2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
C(1)	6302(2)	9269(13)	6842(3)	29(1)
C(2)	6659(5)	10224(16)	6478(5)	45(2)
C(3)	7195(3)	8868(11)	6500(4)	40(1)
C(4)	7246(2)	6861(10)	6902(3)	39(1)
C(5)	5709(1)	10223(5)	6949(1)	36(1)
C(6)	4974(1)	7899(5)	6176(1)	33(1)
C(7)	4524(1)	6038(4)	5885(1)	31(1)
C(8)	4272(1)	4309(4)	6253(1)	29(1)
C(9)	3831(1)	2575(5)	5888(1)	33(1)
C(10)	3661(1)	2599(5)	5204(1)	42(1)
C(11)	3914(1)	4335(5)	4850(1)	48(1)
C(12)	4333(1)	6013(5)	5180(1)	44(1)
C(13)	3166(1)	-845(5)	5937(1)	50(1)
N	5235(1)	8266(3)	6795(1)	29(1)
O(1)	4410(1)	4201(3)	6902(1)	39(1)
O(2)	3606(1)	928(3)	6271(1)	45(1)
S	6640(1)	6641(3)	7263(1)	41(1)
Zn	5000	6258(1)	7500	35(1)
C(1A)	6333(12)	9310(60)	6953(18)	29(1)
C(2A)	6566(11)	7020(50)	7128(15)	43(5)
C(3A)	7142(12)	6660(60)	7013(15)	40(4)
C(4A)	7245(15)	8370(60)	6580(20)	39(5)
SA	6696(6)	10680(20)	6407(7)	38(2)

Table S2a. Full bond lengths [Å] and angles [°] for complex CuL_2.

C(1)-C(2)	1.344(11)	C(2)-C(1)-C(5)	132.3(8)
C(1)-C(5)	1.498(5)	C(2)-C(1)-S	107.9(5)
C(1)-S	1.709(8)	C(5)-C(1)-S	119.6(5)
C(2)-C(3)	1.362(10)	C(1)-C(2)-C(3)	119.3(7)
C(3)-C(4)	1.349(5)	C(4)-C(3)-C(2)	109.0(6)
C(4)-S	1.734(4)	C(3)-C(4)-S	112.6(4)
C(5)-N	1.475(2)	N-C(5)-C(1A)	109(3)
C(5)-C(1A)	1.478(12)	N-C(5)-C(1)	111.4(9)
C(6)-N	1.288(2)	N-C(6)-C(7)	127.44(18)
C(6)-C(7)	1.428(3)	C(8)-C(7)-C(12)	119.82(19)
C(7)-C(8)	1.410(3)	C(8)-C(7)-C(6)	121.55(18)
C(7)-C(12)	1.411(3)	C(12)-C(7)-C(6)	118.63(19)
C(8)-O(1)	1.297(2)	O(1)-C(8)-C(7)	124.11(18)
C(8)-C(9)	1.433(3)	O(1)-C(8)-C(9)	118.22(18)
C(9)-O(2)	1.364(2)	C(7)-C(8)-C(9)	117.67(18)
C(9)-C(10)	1.367(3)	O(2)-C(9)-C(10)	125.59(19)
C(10)-C(11)	1.401(3)	O(2)-C(9)-C(8)	113.83(17)
C(11)-C(12)	1.358(3)	C(10)-C(9)-C(8)	120.6(2)
C(13)-O(2)	1.425(2)	C(9)-C(10)-C(11)	120.9(2)
N-Cu	1.9919(16)	C(12)-C(11)-C(10)	119.8(2)
O(1)-Cu	1.8866(13)	C(11)-C(12)-C(7)	121.2(2)
C(1A)-C(2A)	1.35(2)	C(6)-N-C(5)	115.89(17)
C(1A)-SA	1.71(2)	C(6)-N-Cu	123.48(14)
C(2A)-C(3A)	1.360(18)	C(5)-N-Cu	120.59(12)
C(3A)-C(4A)	1.326(14)	C(8)-O(1)-Cu	129.01(13)
C(4A)-SA	1.764(15)	C(9)-O(2)-C(13)	117.33(17)
		C(1)-S-C(4)	91.2(3)
		O(1)-Cu-N	91.25(6)
		O(1)-Cu-N#1	88.75(6)
		C(2A)-C(1A)-C(5)	129.5(19)
		C(2A)-C(1A)-SA	110.1(10)
		C(5)-C(1A)-SA	120.4(16)
		C(1A)-C(2A)-C(3A)	118.1(16)
		C(4A)-C(3A)-C(2A)	108.8(16)
		C(3A)-C(4A)-SA	114.3(15)
		C(1A)-SA-C(4A)	88.6(9)

Symmetry transformation: (#1) -x+2, -y+1, -z+1

Table S2b. Full bond lengths [Å] and angles [°] for complex ZnL_2.

C(1)-C(2)	1.342(9)	C(2)-C(1)-C(5)	130.1(6)
C(1)-C(5)	1.503(4)	C(2)-C(1)-S	110.0(4)
C(1)-S	1.727(5)	C(5)-C(1)-S	119.8(3)
C(2)-C(3)	1.403(10)	C(1)-C(2)-C(3)	115.2(6)
C(3)-C(4)	1.346(5)	C(4)-C(3)-C(2)	111.5(5)
C(4)-S	1.727(4)	C(3)-C(4)-S	111.9(4)
C(5)-N	1.474(3)	N-C(5)-C(1A)	113.9(16)
C(5)-C(1A)	1.492(14)	N-C(5)-C(1)	110.8(4)
C(6)-N	1.288(3)	N-C(6)-C(7)	128.3(2)
C(6)-C(7)	1.442(3)	C(8)-C(7)-C(12)	119.8(2)
C(7)-C(8)	1.409(3)	C(8)-C(7)-C(6)	124.34(19)
C(7)-C(12)	1.419(3)	C(12)-C(7)-C(6)	115.8(2)
C(8)-O(1)	1.307(2)	O(1)-C(8)-C(7)	124.6(2)
C(8)-C(9)	1.431(3)	O(1)-C(8)-C(9)	118.0(2)
C(9)-O(2)	1.371(3)	C(7)-C(8)-C(9)	117.37(19)
C(9)-C(10)	1.375(3)	O(2)-C(9)-C(10)	124.1(2)
C(10)-C(11)	1.396(4)	O(2)-C(9)-C(8)	114.78(18)
C(11)-C(12)	1.357(4)	C(10)-C(9)-C(8)	121.1(2)
C(13)-O(2)	1.420(3)	C(9)-C(10)-C(11)	120.5(2)
N-Zn	1.9971(18)	C(12)-C(11)-C(10)	120.0(2)
O(1)-Zn	1.9211(15)	C(11)-C(12)-C(7)	121.2(2)
C(1A)-C(2A)	1.35(2)	C(6)-N-C(5)	116.60(19)
C(1A)-SA	1.73(2)	C(6)-N-Zn	120.90(16)
C(2A)-C(3A)	1.398(19)	C(5)-N-Zn	122.49(14)
C(3A)-C(4A)	1.343(17)	C(8)-O(1)-Zn	125.94(15)
C(4A)-SA	1.722(18)	C(9)-O(2)-C(13)	117.45(18)
		C(1)-S-C(4)	91.3(2)
		O(1)-Zn-O(1)#1	110.23(10)
		O(1)-Zn-N	95.88(7)
		O(1)-Zn-N#1	120.81(7)
		N-Zn-N#1	114.99(10)
		C(2A)-C(1A)-C(5)	127(2)
		C(2A)-C(1A)-SA	110.2(14)
		C(5)-C(1A)-SA	117.8(15)
		C(1A)-C(2A)-C(3A)	113.3(18)
		C(4A)-C(3A)-C(2A)	110(2)
		C(3A)-C(4A)-SA	113.0(18)
		C(1A)-SA-C(4A)	89.8(11)

Symmetry transformation: (#1) -x+1, y, -z+3/2.

Table S3a. Anisotropic displacement parameters ($Å^2 \times 10^3$) for CuL_2. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	34(2)	29(2)	35(2)	5(2)	-2(1)	14(1)
C(2)	39(3)	54(3)	66(5)	-6(3)	-17(3)	3(3)
C(3)	51(3)	51(3)	42(2)	12(2)	-6(2)	16(3)
C(4)	48(3)	46(2)	46(3)	23(3)	10(2)	9(2)
C(5)	34(1)	33(1)	39(1)	6(1)	-3(1)	14(1)
C(6)	37(1)	29(1)	35(1)	6(1)	5(1)	10(1)
C(7)	34(1)	31(1)	29(1)	6(1)	1(1)	4(1)
C(8)	29(1)	32(1)	27(1)	7(1)	-1(1)	2(1)
C(9)	30(1)	36(1)	34(1)	11(1)	-1(1)	2(1)
C(10)	39(1)	54(1)	33(1)	9(1)	-8(1)	3(1)
C(11)	54(2)	50(1)	32(1)	-6(1)	-7(1)	3(1)
C(12)	49(1)	37(1)	36(1)	2(1)	1(1)	9(1)
C(13)	43(1)	61(2)	56(2)	25(1)	-9(1)	14(1)
N	32(1)	32(1)	30(1)	7(1)	-2(1)	9(1)
O(1)	42(1)	40(1)	38(1)	-4(1)	-13(1)	17(1)
O(2)	43(1)	47(1)	46(1)	8(1)	-14(1)	16(1)
S	34(1)	57(1)	56(1)	16(1)	-6(1)	-2(1)
Cu	33(1)	29(1)	29(1)	4(1)	-5(1)	9(1)
C(1A)	35(2)	29(2)	34(2)	5(2)	-2(1)	14(1)
C(2A)	45(3)	80(7)	42(3)	27(4)	-10(2)	-6(3)
C(3A)	39(3)	57(6)	41(4)	20(4)	-4(2)	9(3)
C(4A)	38(3)	64(7)	39(3)	19(4)	-3(2)	12(4)

Table S3b. Anisotropic displacement parameters ($Å^2 \times 10^3$) for ZnL_2. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	34(1)	28(1)	21(3)	-6(2)	0(2)	-4(1)
C(2)	57(4)	32(4)	40(4)	-1(2)	4(3)	-8(3)
C(3)	39(2)	43(4)	38(3)	-8(2)	11(2)	-14(2)
C(4)	30(2)	49(3)	38(3)	-3(2)	10(2)	6(2)
C(5)	37(1)	32(1)	38(1)	-4(1)	6(1)	1(1)
C(6)	37(1)	33(1)	29(1)	3(1)	11(1)	2(1)
C(7)	33(1)	32(1)	26(1)	-1(1)	3(1)	1(1)
C(8)	29(1)	31(1)	27(1)	-1(1)	4(1)	5(1)
C(9)	36(1)	31(1)	32(1)	-1(1)	7(1)	0(1)
C(10)	48(1)	39(2)	32(1)	-7(1)	0(1)	-7(1)
C(11)	64(2)	54(2)	21(1)	-2(1)	1(1)	-9(2)
C(12)	58(2)	46(2)	26(1)	2(1)	8(1)	-8(1)
C(13)	49(2)	45(2)	59(2)	-10(1)	17(1)	-15(1)
N	29(1)	29(1)	29(1)	-2(1)	5(1)	3(1)
O(1)	49(1)	44(1)	22(1)	1(1)	5(1)	-11(1)
O(2)	53(1)	44(1)	38(1)	-3(1)	9(1)	-18(1)
S	41(1)	39(1)	44(1)	9(1)	11(1)	8(1)
Zn	39(1)	40(1)	22(1)	0	3(1)	0
C(1A)	34(2)	28(2)	21(3)	-6(2)	0(2)	-4(1)
C(2A)	48(6)	35(3)	49(11)	7(5)	19(7)	6(4)
C(3A)	45(5)	36(5)	40(8)	5(5)	14(5)	5(4)
C(4A)	44(5)	35(6)	38(9)	2(6)	12(6)	3(5)

Table S4a. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for complex CuL_2.

Atom	x	y	z	U(eq)
H(2)	13302	2437	7634	68
H(3)	10251	1190	8773	57
H(4)	6249	181	7551	54
H(5AA)	13799	3373	5541	41
H(5AB)	13025	2018	4639	41
H(5BC)	13748	3376	5583	41
H(5BD)	13092	2045	4640	41
H(6)	10213	1707	3189	40
H(10)	2761	3126	353	51
H(11)	4802	1381	-91	58
H(12)	7828	1107	1284	50
H(13A)	2856	5427	738	77
H(13B)	1336	6050	1790	77
H(13C)	419	4551	1220	77
H(2A)	7293	1153	5245	69
H(3A)	5729	194	6952	54
H(4A)	8948	845	8605	55

Table S4b. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for complex ZnL_2.

Atom	x	y	z	U(eq)
H(2)	6559	11681	6230	54
H(3)	7479	9301	6266	48
H(4)	7568	5728	6976	47
H(5AA)	5771	10748	7407	43
H(5AB)	5575	11666	6666	43
H(5BC)	5720	10928	7381	43
H(5BD)	5597	11554	6623	43
H(6)	5091	8971	5878	39
H(10)	3374	1450	4976	50
H(11)	3796	4342	4388	58
H(12)	4499	7166	4940	52
H(13A)	2804	14	5699	76
H(13B)	3068	-1961	6256	76
H(13C)	3331	-1786	5630	76
H(2A)	6364	5790	7307	51
H(3A)	7416	5412	7207	48
H(4A)	7578	8322	6397	46

Table S5a.Hydrogen bonds for complex CuL_2 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(5)-H(5A)...O(1)#1	0.97	2.23	2.792(5)	115.5

Symmetry transformation: (#1) -x+2, -y+1, -z+1

Table S5b.Hydrogen bonds for complex ZnL_2 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(4)-H(4)...S#2	0.93	2.99	3.858(5)	156.1
C(5)-H(5A)...O(1)#3	0.97	2.43	3.264(5)	144.0

Symmetry transformations: (#2) -x+3/2, y-1/2, -z+3/2; (#3) -x+1, y+1, -z+3/2.

Table S6. Vibrational spectra of [Cu(oVATPNH2)$_2$] and [Zn(oVATPNH2)$_2$]. Assignment and comparison with the free ligand data (wavenumbers in cm^{-1}).

oVATPNH2 (a)				Cu(oVATPNH2)$_2$				Zn(oVATPNH2)$_2$			
IR.	**Raman**	**Calc**	**Assignment**	**IR**	**Raman**	**Calc.**	**Assignment**	**IR**	**Raman**	**Calc**	**Assignment**
3003 vw	3005 w	3153	ν O-H								
2923 sh	2928 m	3045	ν_{as} CH_2	2907 w	2913 vw	3140/3118	ν_{as} CH_2	2903 m		3079	ν_{as} CH_2
1631 vs	1635 vs	1685	ν C=N	1618 vs	1624 s	1665/1659	ν C=N	1615 vs	1628 s	1660/1651	ν C=N
1583 sh	1587 m	1660	ν ring (oVA)	1599 m	1602 sh		ν ring (oVA)			1642	νring (oVA)
		1618	+ δ O-H	1545 m	1546 m	1640/1639		1544 m	1546 m	1640	
1462 vs	1472 m	1505	δ_{as} CH_3	1476 s	1478 vs	1506/1505	δ_{as} CH_3	1467 s	1467 s	1504	δ_{as} CH_3
	1440 m	1493	δ_{as} CH_3	1447m	1437 s	1494/1491	δ_{as} CH_3	1441 s	1445 vs	1492	δ_{as} CH_3
1415 m,b		1480	δ CH_2	1405 w	1404 sh	1489/1484	δ CH_2	1407 m	1420 sh	1491/1474	δ CH_2 + δ_s CH_3
		1460	δ O-H + δ_s CH_3 + δ C-H(oVA)			1472	ν coord. ring +δ CH_2 + δ_s CH_3			1465/1461	ν coord. ring + δ CH_2 + δ_s CH_3
1361 m	1365 w	1370	δ O-H + ν ring (oHVA)	1363 m	1373 m	1462/1464	ν ring (oVA + Tph)+δs CH_2	1353 w,b	1360 s	.1393/1394	ν ring (oVA + Tph) +
					1370 sh	1440/1433	δ CH (ArCH)				δ C-H (Ar-CH) + ρ_w CH_2
				1357 sh	1360 sh	1398/1393	ρ_w CH_2 + δ CH (Tph)				
							+ δ C-H (Ar-CH)				
1333 m-w	1337 s	1355	ρ_w CH_2	1342 m		1359	ρ_w CH_2	1337 m		1350	ρ_w CH_2
1313 m		1315	ν C-O (ArOH)	1319 w	1323 w	1377/1366	ν C-O (Ar-O)	1325 sh	1327 m	.1375/1373	ν C-O (Ar-O)
			+ δ C-H (oVA)				+ δ C-H (oVA)				+ δ C-H (oVA)
							+ ρ_w CH_2				+ ρ_w CH_2
1269 s		1286	δ C-H (Tph)			1302/1292	δ CH-(Tph) + ρ_r CH_2			1394/1289	δ CH-(Tph)
			+ ρ_r CH_2								+ ρ_r CH_2
1255 vs	1258 vw	1282	ν C-OCH_3	1245 s	1245 sh	1269/1267	ν C-OCH_3 + δ CH (oVa)	1241 s	1246 sh	1271	ν C-OCH_3
			+ δ C-H (oVA)								+ δ CH (oVa)
1242 sh	1229 m	1168	ν C-CH_2	1225 s,b	1225 m-w	1165/1158	ν C-CH_2	1212 s,b	1215 m	1166	ν C-CH_2
1081 m-s	1088 m	1129	ν O-CH_3	1082 w	1079 w	1139/1136	ν O-CH_3 + δ CH (oVa)	1080 m	1082 w	1139	ν O-CH_3 +δ CH (oVa)
			+ δ ring (oVA)	1075 w			δ ring (oVa)			1107	δ ring (oVa)
853 mw	856 vw	842	γ C-H (Tph)	864 w	866 w	868	γ C-H (Tph)	855 m	860 vw	841	γC-H (Tph)
				849 sh	857 sh	857					
832 ms,b	838 w	851	γ O-H								
750 mw	757 w	762	ν S-CH	750 sh	754 w	763	ν S-CH + δring(oVa)	746 sh	751 w	753	ν S-CH +
			+ δ C-C-C(CH_2)			753/752	ν S-CH				δ ring(oVa)
736 s	735 m	740	γ C-H (oVA)	734 m		745/744	γ C-H (oVA)	736 m		745	γ C-H (oVA)
725 s		742	δ ring (oVA)	703 m		762	δ ring (oVa)	715 m		764/ 762	δ ring [oVA + Tph]
								695 sh			
615 vw	620 m	627	δ ring [oVA + Tph]	614 vw	607 w	627/621	δ ring [oVA + Tph]	611 w	604 w	621	δ ring [oVA + Tph]
						605	δ coord ring	602 sh		601	δ coord ring
				489 vw		565	ν_{as} O-Cu-O			568	ν_{as} O-Zn-O
					471 w			477 vvw			
				475 vw		559	ν_s O-Cu-O			563	ν_s O-Zn-O
				453 vw	454 sh	420	ν_{as} N-Cu-N	458 vw	461 vw	461	ν_{as} N-Zn-N
				429 vw		401	ν_s N-Cu-N	443 vw	441 sh	455	ν_s N-Zn-N
					408 vw	370	γ coord. ring	408 vw		411	γ coord. ring

(a) Data extracted from ref 19. vs: very strong, s: strong, m: medium, w: weak, vw: very weak, b: broad, sh: shoulder: Tph: thiophene

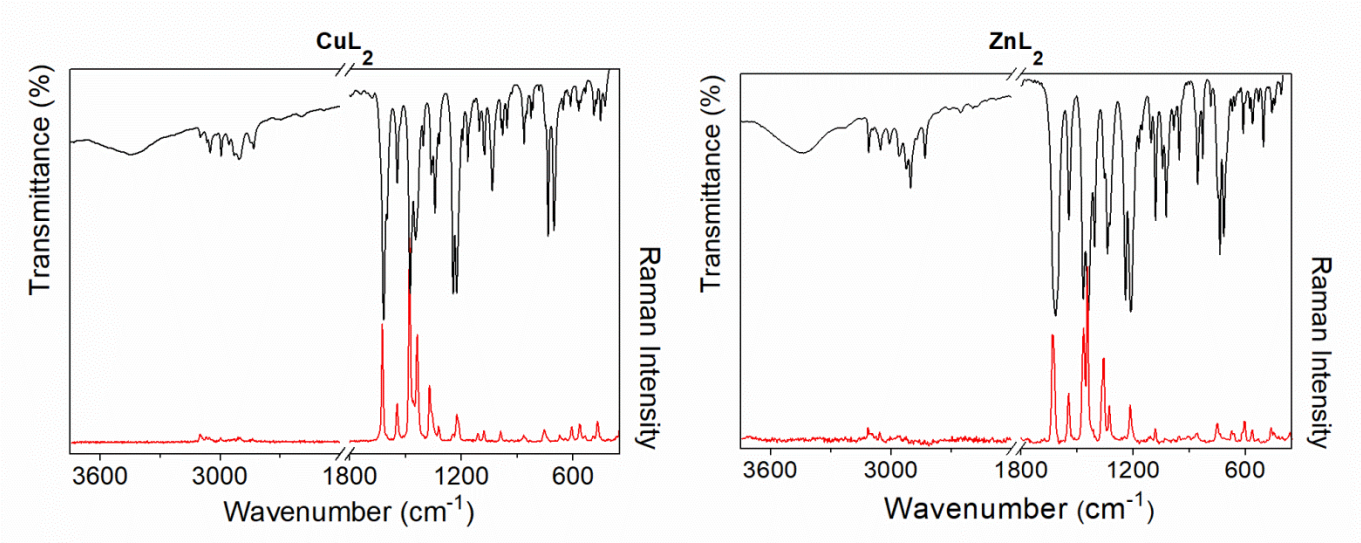

Figure S1. IR (top) and Raman (bottom) spectra of both complexes in the 3700-400 cm^{-1} spectral region.

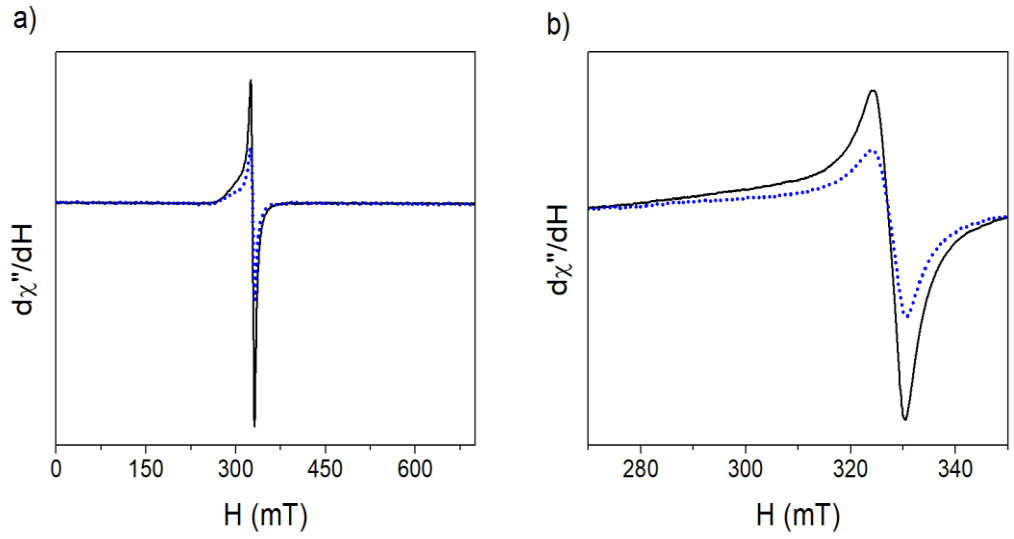

Figure S2. EPR spectra of $[Cu(oVATPNH2)_2]$ (**I**) at different temperatures: 150 K (solid line) and 298 K (dotted line). **a)** 0 – 700 mT region; **b)** 250 – 350 mT region. Experimental details: modulation amplitude 0.1 mT, time constant 40.96 ms, conversion time 327.68 ms, gain 1 10^3 (short ranges) or 1 10^4 (long 0 – 700 mT ranges) and power 20 mW. Microwavefrequencies: 9.4258 (298 K), 9.4261 (250 K), 9.4273 (150 K), 9.4281 (298 K), 9.4285 GHz (150 K)

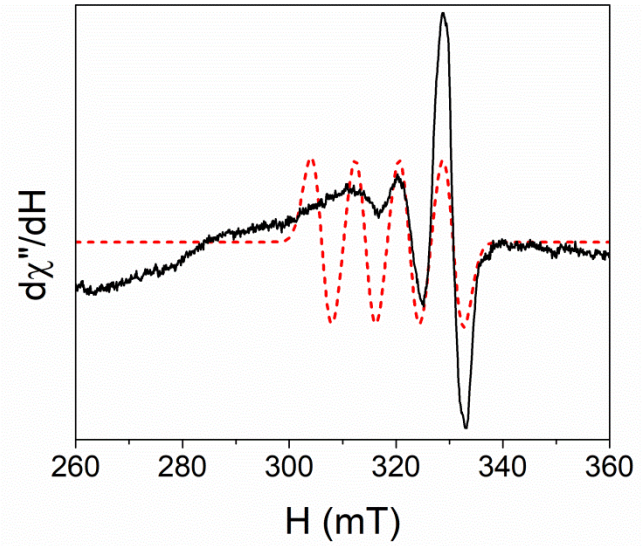

Figure S3. EPR spectrum of of an approximately 5 10^{-4} M solutionof [Cu(oVATPNH2)$_2$] at RT (black line) together with the best fit (red line). Experimental details: modulation frequency = 100 kHz, modulation amplitude = 0.5 mT, time constant = 81.92 ms, conversion time = 327.68 ms, gain = 6,3 x 104, power = 20.0 mW, microwave frequency = 9.4239 GHz. Fitting parameters: Gaussian-type signal, giso = 2.115, Aiso = 8.2 mT (185.8 10−4 cm−1) (linewidth H = 4.0 mT).

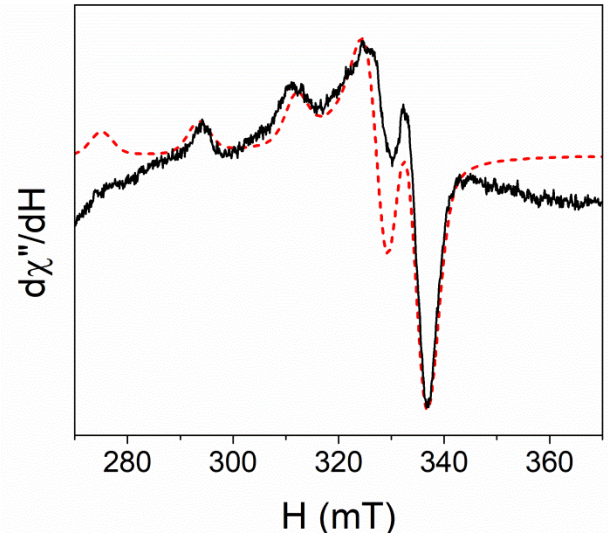

Figure S4. EPR spectrum of an approximately 5 10^{-4} M solution of [Cu(oVATPNH2)$_2$] in a (1:1) (DMSO:ethanol) mixture of solvents at 150 K (black line) together with the best fit (red line). Experimental details: modulation frequency = 100 kHz, modulation amplitude = 0.5 mT, time constant =81.92 ms, conversion time = 327.68 ms, gain = 6,3 x 104, power = 2.0 mW, microwave frequency = 9.4255 GHz. Fitting parameters: (a) 50 % Gaussian/Lorentzian-type signal, $g_{||}$ = 2.224; $A_{||}$ = 18.5 mT (192.1 10−4 cm−1) (linewidth $H_{||}$ = 4.0 mT), $g_{\perp}$ = 2.055 (linewidth $H_{\perp}$ = 5.0 mT).

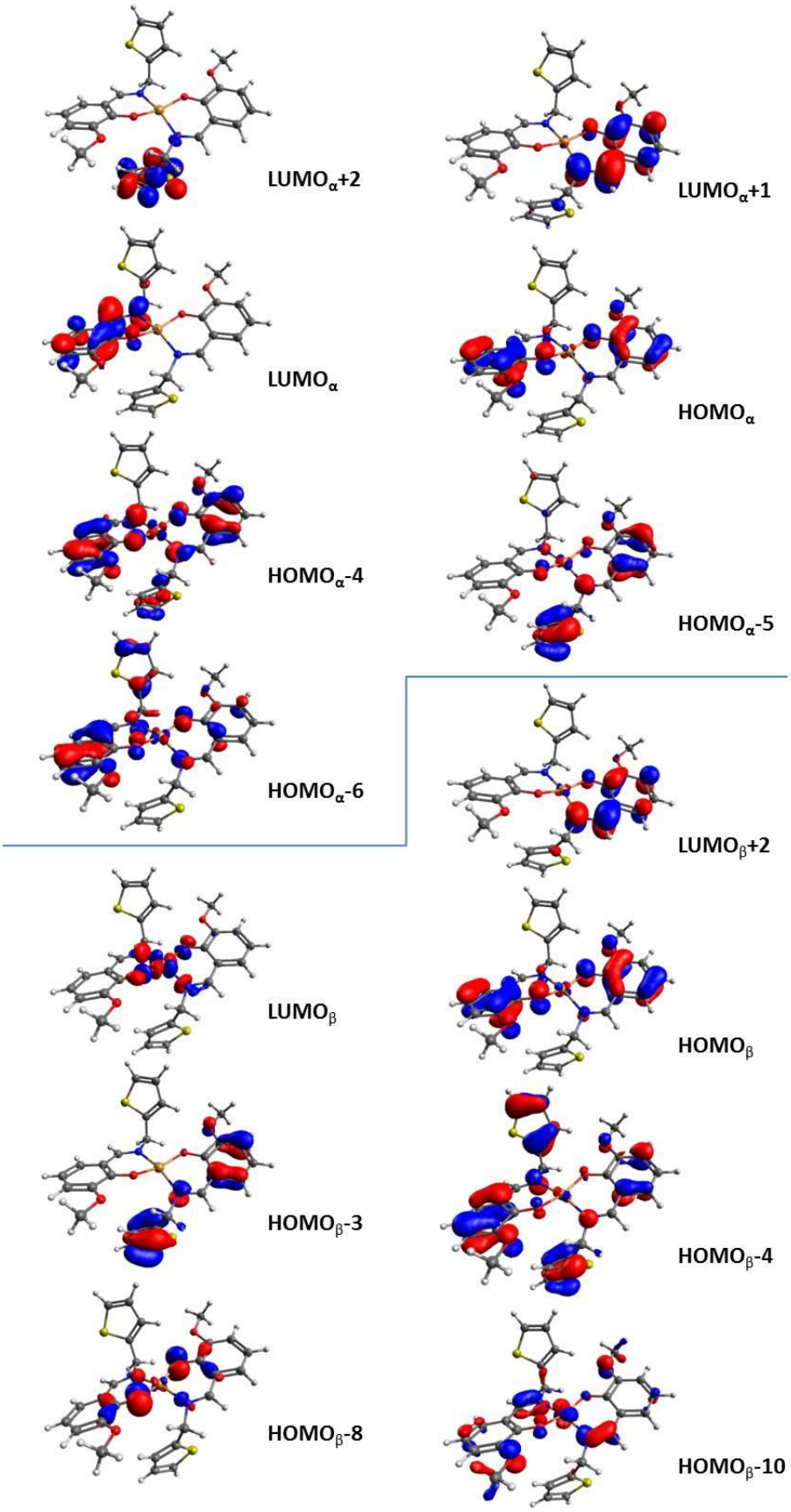

Figure S5. Molecular orbitals involved in the electronic transitions of [Cu(oVATPNH2)$_2$] (**CuL$_2$**).

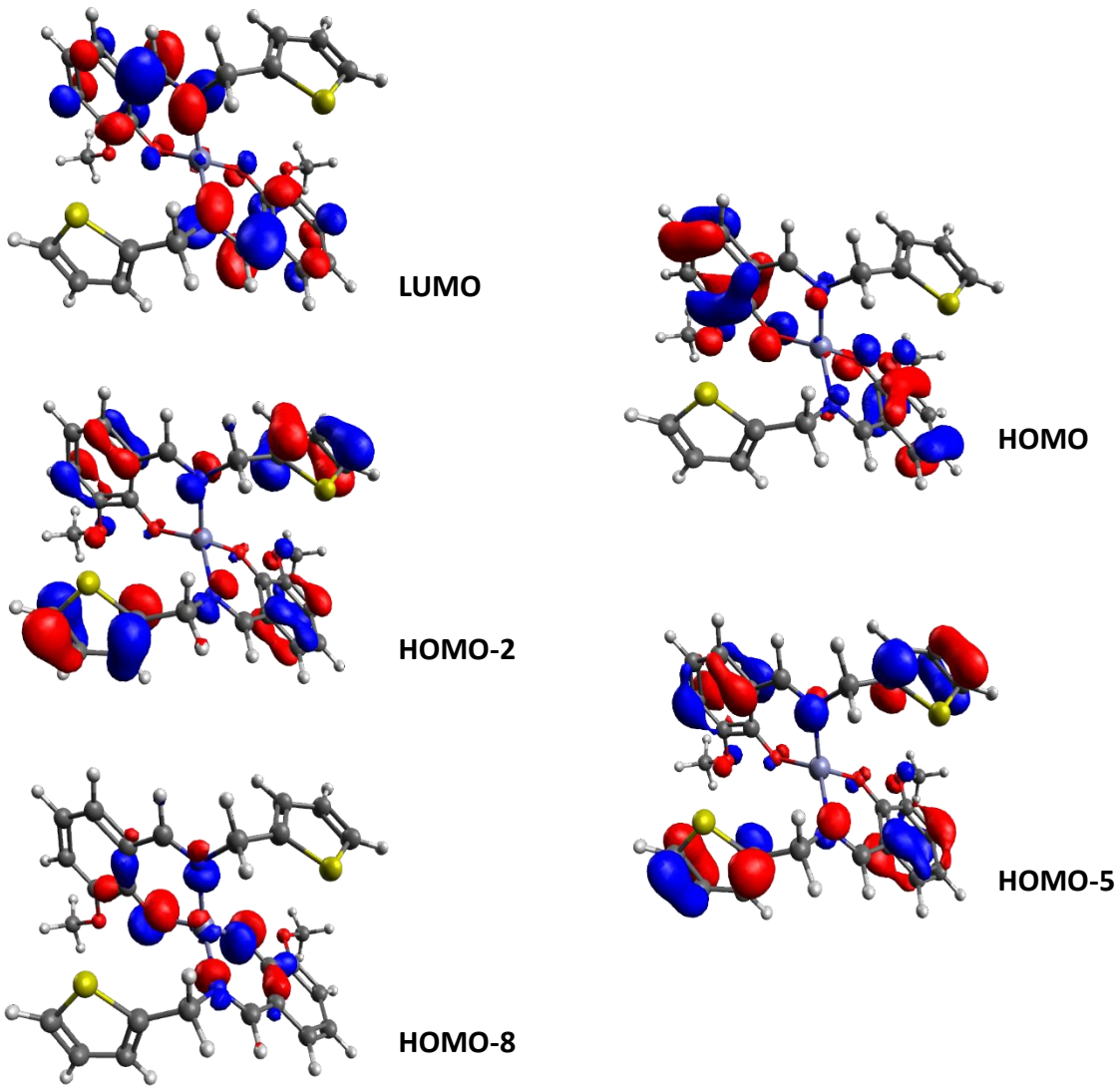

Figure S6. Molecular orbitals involved in the electronic transitions of [Zn(oVATPNH2)$_2$] (**ZnL$_2$**)

OMS description

Complex CuL$_2$: It can be seen in Figure S2 that the HOMO$_\alpha$ – 5 of is mainly localized on one oVATPNH2 ligand, whereas the HOMO$_\alpha$ – 6 is localized on the other oVATPNH2 ligand. In both cases, a small contribution from the metal ion is observed. The HOMO$_\alpha$ – 4 is located in the two oVA fragments and on one TPNH2 fragment, with contributions from the N atom of the second TPNH2 fragment and from the metal ion. The HOMO$_\alpha$ is strongly localized on both oVA fragments with a minor contribution from the Cu(II) ion. The LUMO$_\alpha$ is located in one oVA fragment and on the N atom of the TPNH2 fragment of the same ligand. The LUMO$_\alpha$ + 1 is

similar to the $LUMO_{\alpha}$ but it is located in the other ligand. The $LUMO_{\alpha}$ + 2 is located in one TPNH2 fragment. The $HOMO_{\beta}$ – 10 is localized on all the O atoms, the C=N double bond and the Cu(II) ion. The $HOMO_{\beta}$ – 8 is located in the O atom of the coordination sphere and the N atom, with a minor contribution from the metal ion. The $HOMO_{\beta}$ – 4 is localized on the two ligands, whereas $HOMO_{\beta}$ – 3 is predominantly located in one ligand only. The $HOMO_{\beta}$ is mainly located in the two o-VA rings and in the four O atoms. The three MO's also present a small contribution from the metal ion. The $LUMO_{\beta}$ is localized on the Cu(II) ion and on the four atoms bound to it. The $LUMO_{\beta}$ + 2 is mainly located in the oVA ring, the O atom of the coordination sphere and the N atom of one ligand only..

Complex ZnL_2: Figure S5 shows that the HOMO – 8 is located in the metal ion and in the atoms bound to it. The HOMO – 5 and the HOMO – 2 exhibits almost the same localization pattern, which involves the two ligands. The HOMO and the LUMO present very similar localization patterns, although the first one is bonding and the second one is anti-bonding in character. They are located in the two oVA rings, the four O atoms and the N atoms of the TPNH2 fragments.

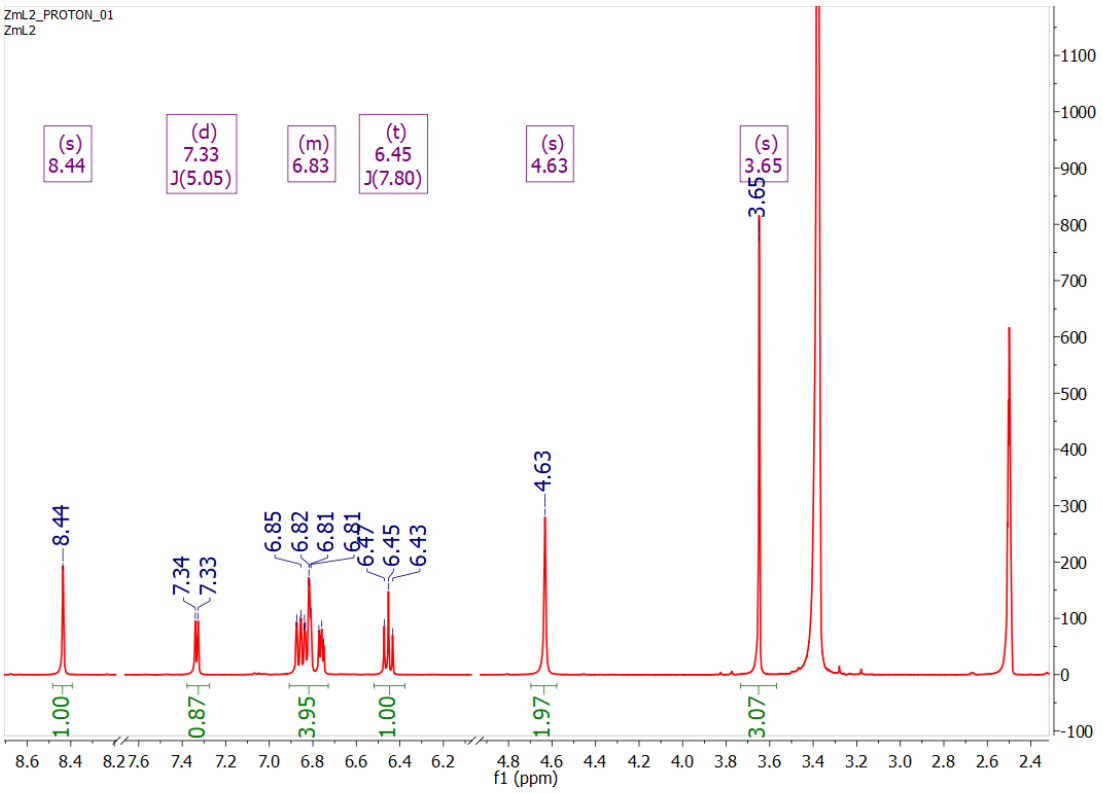

Figure S7. ^{1}H NMR spectrum recorded for ZnL_2 in CD_3SOCD_3 at 25 ^{0}C.

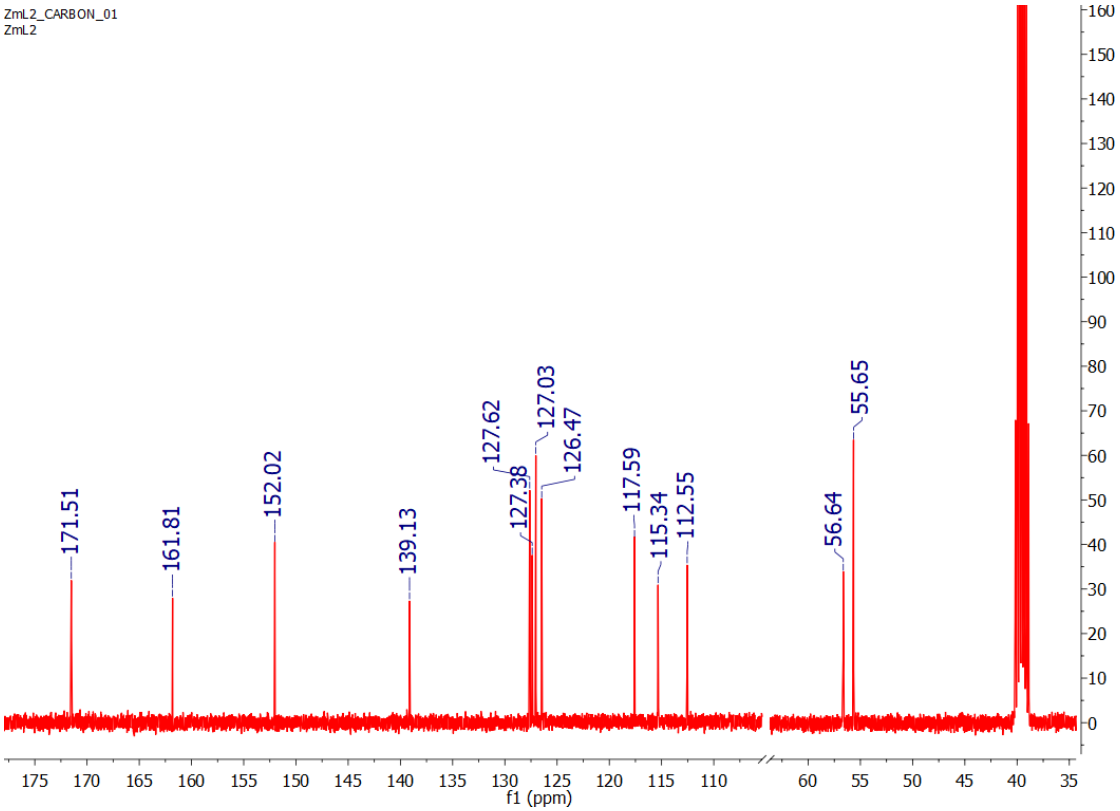

Figure S8. ^{13}C NMR spectrum recorded for ZnL_2 in CD_3SOCD_3 at 25 ^{0}C.

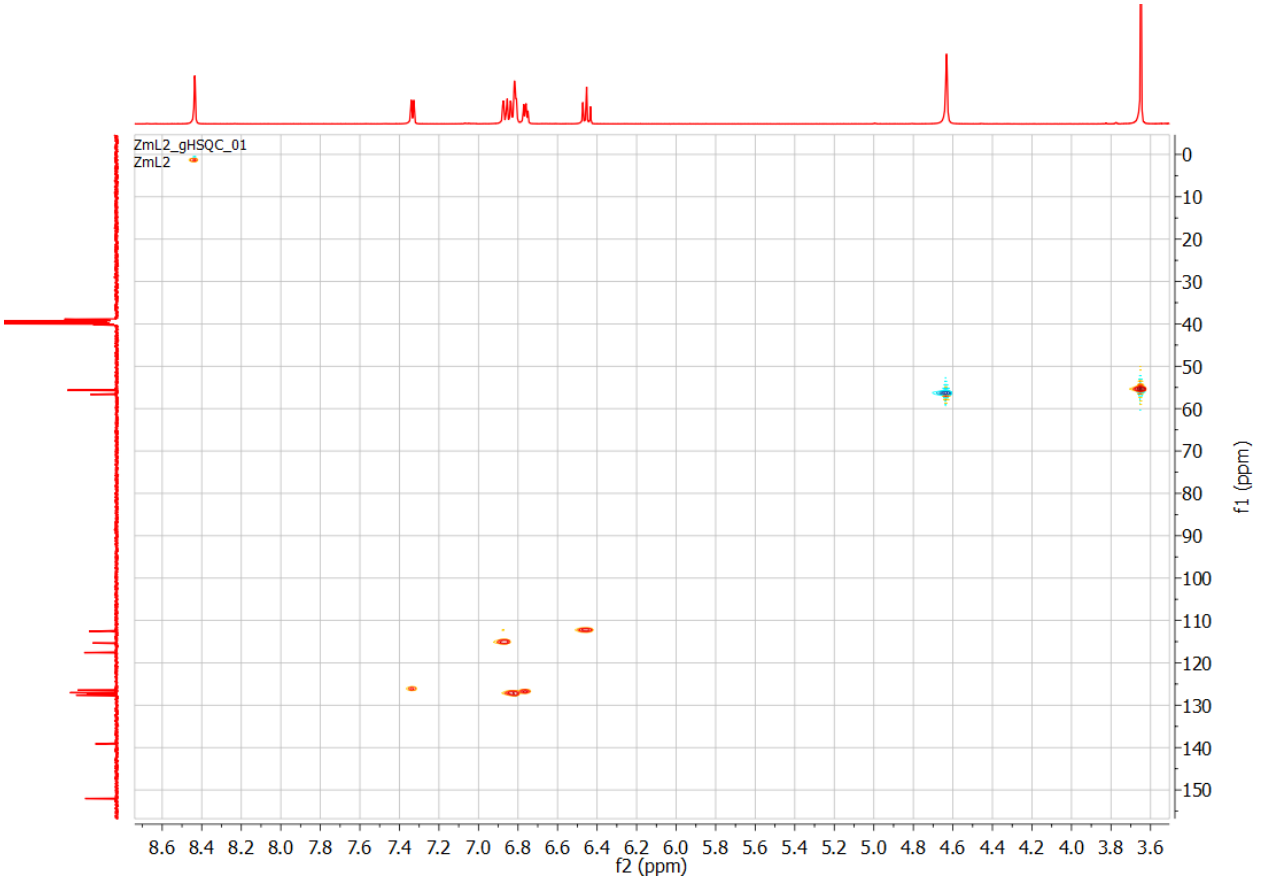

Figure S9. 2D NMR ^{1}H-^{13}C HSQC spectrum for ZnL_2 in CD_3SOCD_3 at 25 ^{0}C.

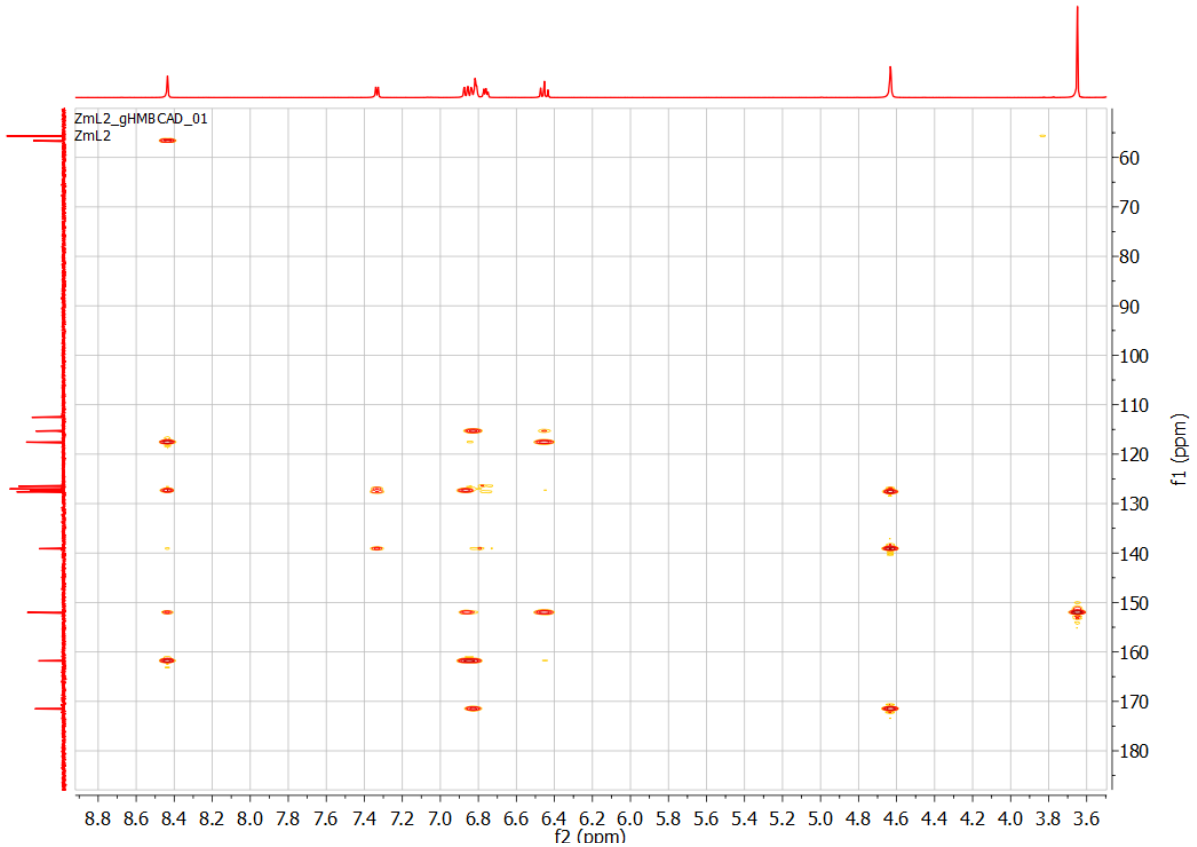

Figure S10. 2D NMR ^{1}H-^{13}C HMBC spectrum for ZnL_2 in CD_3SOCD_3 at 25 ^{0}C

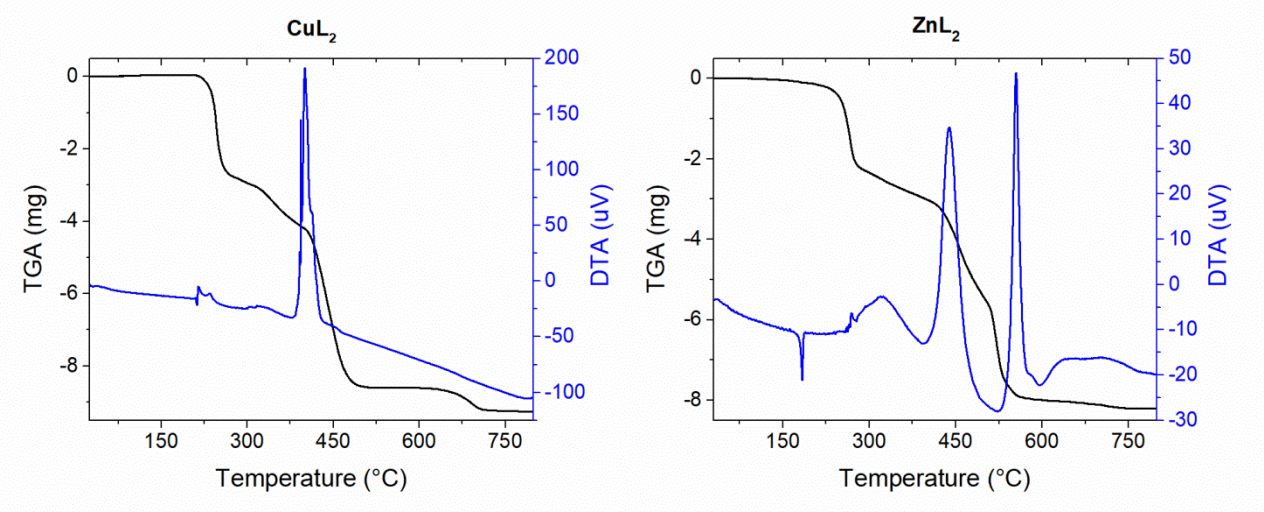

Figure S11. Thermal analysis of the solid complexes [Cu(oVATPNH2)$_2$] (**CuL$_2$**) and [Zn(oVATPNH2)$_2$] (**ZnL$_2$**)