Supplementary Informations

Unsymmetrical diimine chelation to M(II) (M = Zn, Cd, Pd): atropisomerism, pi-pi stacking and photoluminescence

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Syntheses, Analytical and Spectral Data of:

($L_{C(Me)3}^{\phi}$)$ZnCl_2$ (1b). It was prepared using 4-tertbutylaniline (300 mg, 2 mmol), pyridine-2-carbaldehyde (214 mg, 2 mmol) and anhydrous zinc chloride (275 mg, 2 mmol). Yield: 562 mg (75% with respect to zinc). MS (ESI positive ion, CH_3CN): *m/z* = 338.84, {**1b**-Cl}$^+$; δ_H(300 MHz; DMSO-d_6; Me_4Si) 8.82 (1 H, d, 6-H), 8.69 (1 H, s, -N=CH), 8.09 (2 H, m, 3-H & 4-H), 7.66 (1 H, t, 5-H), 7.44 (2 H, d,10-H & 14-H), 7.31(2 H, d, 11-H &13-H) and 1.29 (9 H, s, -$C(Me)_3$); Elemental anal. (%) for $C_{16}H_{18}N_2ZnCl_2$: Calcd. C 51.30, H 4.84, N 7.47. Found: C 50.92, H 4.47, N 7.29. IR(KBr)($\nu_{max,}$ cm^{-1}): 2966(vs), 1599(s), 1560(m), 1508(m), 1476(s), 1444(s), 1373(m), 1275(m), 1104(m), 974(m), 838(vs), 766(s), 742(m) and 560(s). UV-Vis: λ_{max} (ε, 10^4 $M^{-1}cm^{-1}$)/nm, CH_3CN, 350(2.58), 246(1.74): CH_2Cl_2, 362(3.99), 249(2.40).

($L_{C(Me)3}^{\phi}$)$ZnBr_2$ (1c). It was prepared using 4-tertbutylaniline (300 mg, 2 mmol), pyridine-2-carbaldehyde (214 mg, 2 mmol) and anhydrous zinc bromide (450mg, 2 mmol). Yield: 740 mg (80% with respect to zinc). MS (ESI positive ion, CH_3CN): *m/z*, 385.04, {**1c**-Br}$^+$; δ_H (300 MHz; DMSO-d_6; Me_4Si) 8.88 (1 H, d, 6-H,), 8.71 (1 H, s, -N=CH), 8.10 (2 H, m, 3-H & 4-H), 7.73 (1 H, t, 5-H,), 7.40 (2 H, d, 10-H & 14-H), 7.25 (2 H, d, 11-H & 13-H) and 1.24 (9 H, s, -$C(Me)_3$); Elemental anal. (%) for $C_{16}H_{18}N_2ZnBr_2$: Calcd. C 41.30, H 3.90, N 6.02. Found: C 40.72, H 3.47, N 5.92. IR(KBr) ($\nu_{max,}$ cm^{-1}): 2963(vs), 1599(s), 1560(m), 1508(m), 1476(s), 1443(s), 1371(m), 1275(s), 1103(m), 972(m), 837(vs), 764(s), 742(m), 651(w), 560(s) and 412(w). UV-Vis: λ_{max} (ε, 10^4 $M^{-1}cm^{-1}$)/nm, CH_3CN, 351(2.50), 242(1.87): CH_2Cl_2, 364(6.42), 247(4.40).

(L_{OH}^{ϕ})$ZnCl_2$ (1d). It was prepared with the pre-isolated $\mathbf{L_{OH}}$ ligand. To a solution of L_{OH} (400 mg, 2 mmol) in methanol (25 ml), anhydrous Zinc chloride (275 mg, 2 mmol) was added and stirred for 20 minutes at room temperature. A dark yellow solution was obtained, which was filtered and the filtrate was allowed to evaporate slowly in air. Within two days

yellow crystalline compound separated out, which was filtered and dried in air. Yield: 568 mg (85% with respect to zinc). MS (ESI positive ion, CH_3OH): *m/z,* 298.81, {**1d**-Cl}$^+$; δ_H(300 MHz; DMSO-d_6; Me_4Si) 9.79 (s, -OH), 8.86 (1 H, d, 6-H), 8.67 (1 H, s, -N=CH), 8.12 (1 H, t, 4-H,), 8.04 (1 H, d, 3-H), 7.70 (1 H, t, 5-H), 7.26(2 H, d, 10-H & 14-H) and 6.76 (2 H, d, 11-H &13-H); δ_C(300 MHz;DMSO-d_6; Me_4Si) 157.6 (C-6), 156.1(C-7), 149.7 (C-3 & C-4), 140.1, 138.9 (C2 & C-5), 127.5,126 (C-9 & C-12), 123.5 (C-10 & C-14) and 115.7 (C-11 & C-13); Elemental anal. (%) for $C_{12}H_{10}N_2OZnCl_2$: Calcd. C 42.98, H 3.00, N 8.35. Found: C 43.08 H 2.90, N 8.21. IR(KBr)($\nu_{max,}$ cm^{-1}): 3378(vs), 1604(vs), 1515(vs), 1458 (m), 1290(s), 1218(vs), 1174(vs), 842(s) and 535(m). UV-Vis: λ_{max} (ε, 10^4 M^{-1}cm^{-1})/nm, CH_3CN, 369(1.48), 253(1.25): CH_2Cl_2, 377(1.21), 255(0.87).

(L_{OH}^{ϕ})$ZnBr_2$ (1e). It was prepared by the same procedure as for **7** using L_{OH} (400 mg, 2 mmol) in methanol (25 ml) and anhydrous zinc bromide (400 mg, 2 mmol). Within two days yellow crystals of **1e** separated out, which was filtered and dried in air (single crystals for X-ray structure determination were picked out from this product). Yield: 725 mg (85% with respect to zinc). MS (ESI, positive ion, CH_3OH): *m/z,* 342.96, {**1e**-Br}$^+$; δ_H(300 MHz; DMSO-d_6; Me_4Si) 9.80 (1 H, s, -OH), 8.88 (1 H, d, 6-H), 8.68 (1 H, s, -N=CH), 8.15 (1 H, t, 4-H), 8.03 (1 H, d, 3-H), 7.75(1 H, t, 5-H), 7.21 (2 H, d, 10-H & 14-H) and 6.73 (2 H, d,11-H & 13-H); Elemental anal. (%) for $C_{12}H_{10}N_2OZnBr_2$: Calcd. C 33.96, H 2.37, N 6.60. Found: C 33.81, H 1.99, N 6.31. IR(KBr)($\nu_{max,}$ cm^{-1}): 3410(vs), 1601(vs), 1557(s), 1512(vs), 1475 (s), 1272(s), 1211(s), 1176(vs), 841(s), 778(m), 535(m) and 413(m). UV-Vis: λ_{max} (ε, 10^4 M^{-1}cm^{-1})/nm, CH_3CN, 372(0.83), 253(0.66): CH_2Cl_2, 378(1.48), 254(1.26).

(L_{OMe}^{ϕ})$ZnCl_2$ (1f). It was prepared by the general procedure as for **1a** using 4-methoxyaniline (245 mg, 2 mmol), pyridine-2-carbaldehyde and (214 mg, 2 mmol) and anhydrous zinc chloride (275 mg, 2 mmol). Yield: 632 mg (~88% with respect to zinc). MS (ESI positive ion, CH_3CN): *m/z* , 311.02, {**1f**-Cl}$^+$; δ_H(300 MHz; DMSO-d_6; Me_4Si) 8.84 (1 H, d, 6-H), 8.71 (1 H, s, -N=CH), 8.1 (2 H, m, 3-H & 4-H), 7,69 (1 H, t, 5-H), 7.40 (2 H, d, 10-H & 14-H), 6.98 (2 H, d, 11-H & 13-H) and 3.78 (s, 3H, -OMe); δ_C(300 MHz;DMSO-d_6; Me_4Si) 159.1(C-6), 157.2(C-7), 149.7 (C-4 & C-2), 140.5, 139.9 (C-3 & C-5), 127.5, 125.8 (C-9), 123.4 (C-10 & C-14), 115.5 (C-12), 114.4 (C-11 & C-13) and 55.5 (-OMe); Elemental anal. (%) for $C_{13}H_{12}N_2OZnCl_2$: Calcd. C 44.80, H 3.47, N 8.03. Found: C 44.05, H 3.21, N 8.01. IR(KBr)($\nu_{max,}$ cm^{-1}): 1600(vs), 1559(m), 1510(vs), 1449(m), 1312 (m), 1257(vs),

1176(s), 1023(s) 834(s), 782(m) and 539(w). UV-Vis: λ_{max} (ε, 10^4 $M^{-1}cm^{-1}$)/nm, CH_3CN, 371(5.44), 252(4.09): CH_2Cl_2, 382(2.47), 257(1.76).

(L_{Cl}^{ϕ})$ZnCl_2$ (1g). It was prepared using 4-chloroaniline (255 mg, 2 mmol), pyridine-2-carbaldehyde (214 mg, 2 mmol) and anhydrous zinc chloride (275 mg, 2mmol). Yield: 562.5 mg (80% with respect to Zinc). MS (ESI positive ion, CH_3CN): *m/z* ,316.92, {**1g**-Cl}$^+$; δ_H(300 MHz; DMSO-d_6; Me_4Si) 8.84 (1 H, d, 6-H), 8.69 (1 H, s, -N=CH), 8.12 (2 H, m, 3-H & 4-H), 7.70 (1 H, d, 5-H), 7.48 (2 H, d, 10-H & 14-H) and 7.40 (2 H, d, 11-H & 13-H); Elemental anal. (%) for $C_{12}H_9N_2ZnCl_3$: Calcd. C 40.86, H 2.57, N 7.93. Found: C, 40.15, H 2.36, N 7.21. IR(KBr)(cm^{-1}): 1594(vs), 1560(m), 1492(vs), 1446(m), 1094(vs), 1024(s), 832(vs), 776(s) and 532(s). UV-Vis: λ_{max} (ε, 10^4 $M^{-1}cm^{-1}$)/nm, CH_3CN, 371(5.44), 252(4.09): CH_2Cl_2, 382(2.47), 257(1.76).

(L_{CH3}^{ϕ})$CdCl_2$ (1h). It was prepared by the general procedure as for **1a** using 4-methylaniline (214 mg, 2 mmol), pyridine-2-carbaldehyde (214 mg, 2 mmol) and anhydrous cadmium chloride (370 mg, 2 mmol). Yield: 600 mg (79% with respect to cadmium). MS (ESI positive ion, CH_3CN); *m/z,* 344.13, {**1h**-Cl}$^+$; δ_H(300 MHz; DMSO-d_6; Me_4Si) 8.89 (d, 1 H, 6-H), 8.81 (1 H, s, -N=CH), 8.16 (1 H, t, 4-H,), 8.09(1 H, d, 3-H), 7.76 (1 H, t, 5-H), 7.45 (2 H, d, 10-H & 14-H), 7.25 (2 H, d, 11-H &13-H) and 2.34 (3 H, s, -Me); Elemental anal. (%) for $C_{13}H_{12}N_2CdCl_2$: Calcd. C 41.14 H 3.18, N 7.36. Found: C 40.82, H 2.67, N 6.98. IR(KBr)($\nu_{max,}$$cm^{-1}$): 1591(s), 1560(s), 1508(s), 1441(m), 1015(s), 818(vs), 782(s) and 540(m)

($L_{C(Me)3}^{\phi}$)$CdCl_2$ (1i). It was prepared by the general procedure as for **1a** using 4-*tert*-butylaniline (300 mg, 2 mmol), pyridine-2-carbaldehyde (214 mg, 2 mmol) and anhydrous cadmium chloride (370 mg, 2 mmol). Yield: 590 mg (70% with respect to cadmium). MS (ESI positive ion, CH_3CN): *m/z, 386.94*, {**1i**-Cl}$^+$; δ_H(300 MHz; DMSO-d_6; Me_4Si) 8.93 (1 H, d, 6-H), 8.86 (1 H, s, -N=CH), 8.23 (1 H, t, 4-H,), 8.07 (1 H, d, 3-H), 7.87 (1 H, t, 5-H), 7.52 (2 H, d, 10-H & 14-H), 7.45 (2 H, d, 11-H &13-H) and 1.30 (9 H, s, -$C(Me)_3$); Elemental anal. (%) for $C_{16}H_{18}N_2CdCl_2$: Calcd. C 45.58, H 4.30, N 6.64. Found: C 45.32, H 4.27, N 6.32. IR(KBr)($\nu_{max,}$ cm^{-1}): 2955(vs), 2863(m), 1596(s), 1560(s), 1508(m), 1438(s), 1373(m), 1016(s), 838(vs), 776(s) and 567(s). UV-Vis: λ_{max} (ε, 10^4 $M^{-1}cm^{-1}$)/nm, CH_3CN, 338(1.49), 287(1.45), 243(1.64): CH_2Cl_2, 354(1.47), 288(1.35), 244(1.64).

(L_{OH}^{ϕ})$CdCl_2$ (1j). It was prepared by the procedure as described for **7** using a solution of

L_{OH} (400 mg, 2 mmol) in methanol (25 ml) and anhydrous cadmium chloride (370 mg, 2 mmol). Yield: 685 mg (90% with respect to cadmium). MS (ESI positive ion, CH_3OH): *m/z,* 346.04 {**1j**-Cl}$^+$; δ_H(300 MHz; DMSO-d_6; Me_4Si) 9.84 (1 H, s, -OH), 8.94 (1 H, d, 6-H), 8.75 (1 H, s, -N=CH), 8.19 (1 H, t, 4-H), 7.99 (1 H, d, 3-H), 7.79 (1 H, t, 5-H), 7.42 (2 H, d, 10-H & 14-H) and 6.75 (2 H, d, 11-H &13-H); δ_C(300 MHz;DMSO-d_6; Me_4Si) 157.9 (C-6), 155.4 (C-7), 150.1(C-4), 147.7 (C-3), 140.6, 138.6(C-2, C-5), 128.7, 128.1 (C-9, C-12), 124.1(C-10, C-14) and 115.6 (C-11, C-13); Elemental anal. (%) for $C_{12}H_{10}N_2OCdCl_2$: Calcd. C 37.78, H 2.64, N 7.34. Found: C 37.01, H 2.35, N 7.12. IR(KBr)($\nu_{max,}$ cm^{-1}): 3285(vs), 1624(m), 1602(vs), 1560(m), 1514(vs), 1440(m), 1321 (m), 1287(s), 1216(vs), 1171(vs), 841(s), 783(m) and 538(m). UV-Vis: λ_{max} (ε,10^4 M^{-1} cm^{-1})/nm, CH_3CN, 357(1.09), 284(0.78), 248(1.07).

(L_{OMe}^{ϕ})$CdCl_2$ (1k). It was prepared by the procedure as for **1a** using 4-methoxyaniline (245 mg, 2 mmol), pyridine-2-carbaldehyde (214 mg, 2 mmol) and anhydrous cadmium chloride (370 mg, 2 mmol). Yield: 710 mg (90% with respect to cadmium). MS (ESI positive ion, CH_3OH): *m/z,* 360.69 {**1k**-Cl}$^+$; δ_H(300 MHz; DMSO-d_6; Me_4Si) 8.90 (1 H, d, 6-H), 8.82 (1 H, s, -N=CH), 8.19 (1 H, t, 4-H), 8.06 (1 H, d, 3-H), 7.77 (1 H, t, 5-H), 7.58 (2 H, d, 10-H & 14-H), 6.99 (2 H, d, 11-H &13-H) and 3.79(3 H, s, -OMe); δ_C(300 MHz;DMSO-d_6; Me_4Si) 159.3 (C-6), 156.6 (C-7), 150.1 (C-4), 148.3 (C-3), 140.3 (C2 & C-5), 128.1, 127.9(C-9 & C-12), 123.9 (C-10 & C-14), 114.3 (C-11 & C-13) and 55.5 (-OMe); Elemental anal. (%) for $C_{13}H_{12}N_2OCdCl_2$: Calcd. C 39.47, H 3.06, N 7.08. Found: C 39.05, H 2.21, N 7.01. IR(KBr)($\nu_{max,}$ cm^{-1}): 3448(m), 1598(s), 1508(vs), 1307 (m), 1259(vs), 1026(m), 847(w) and 776(w). UV-Vis: λ_{max} (ε, 10^4 M^{-1} cm^{-1})/nm, CH_3CN, 362(3.08), 284(1.95), 249(3.04).

Coordinates of Optimozed Geometries

$(1b)_2$ unit in gas-phase:

Z-Matrix Orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	30	7.042629	9.340805	1.545793
2	7	6.819199	9.891523	-0.562517
3	6	5.531833	10.135801	-0.896641
4	6	5.152873	10.434975	-2.208835
5	6	6.140608	10.500342	-3.192714
6	6	7.468944	10.266385	-2.837253
7	6	7.762888	9.959248	-1.505552
8	6	4.542201	10.103202	0.190114
9	7	4.900504	9.821285	1.393951
10	6	3.960197	9.791484	2.453827
11	6	2.618479	9.427422	2.269983
12	6	1.740557	9.440183	3.355094
13	6	2.156736	9.813718	4.644089
14	6	3.512438	10.159589	4.803169
15	6	4.407354	10.139804	3.738059
16	6	1.203807	9.859663	5.851176
17	6	-0.230477	9.428284	5.486700
18	6	1.724857	8.913691	6.961150
19	6	1.146082	11.307175	6.400250
20	1	4.105695	10.592093	-2.446005
21	1	5.873738	10.728339	-4.220575
22	1	8.267764	10.312896	-3.570355
23	1	8.781308	9.763181	-1.181582
24	1	3.512251	10.349322	-0.067055
25	1	2.261739	9.107289	1.294382
26	1	0.711669	9.148038	3.175924
27	1	3.887636	10.454434	5.778815
28	1	5.444734	10.428717	3.886703
29	1	-0.267816	8.396106	5.117451
30	1	-0.867008	9.481056	6.377551
31	1	-0.675573	10.080858	4.726404
32	1	1.052840	8.941212	7.827973
33	1	1.775743	7.878106	6.603554
34	1	2.724471	9.197635	7.306857
35	1	0.472915	11.357466	7.265278
36	1	0.773320	12.001735	5.638211

37	1	2.130855	11.661380	6.723247
38	30	2.210874	5.902287	-1.545802
39	7	2.434295	5.351532	0.562499
40	6	3.721659	5.107246	0.896625
41	6	4.100611	4.808040	2.208814
42	6	3.112870	4.742650	3.192685
43	6	1.784537	4.976616	2.837222
44	6	1.490600	5.283784	1.505527
45	6	4.711298	5.139873	-0.190123
46	7	4.353002	5.421818	-1.393956
47	6	5.293317	5.451650	-2.453824
48	6	6.635034	5.815700	-2.269959
49	6	7.512964	5.802975	-3.355064
50	6	7.096792	5.429492	-4.644076
51	6	5.741090	5.083629	-4.803177
52	6	4.846167	5.103376	-3.738072
53	6	8.049727	5.383598	-5.851160
54	6	9.484013	5.814944	-5.486653
55	6	7.528693	6.329635	-6.961087
56	6	8.107442	3.936115	-6.400311
57	1	5.147788	4.650916	2.445987
58	1	3.379735	4.514628	4.220542
59	1	0.985712	4.930087	3.570319
60	1	0.472182	5.479859	1.181556
61	1	5.741246	4.893747	0.067047
62	1	6.991769	6.135799	-1.294344
63	1	8.541852	6.095108	-3.175876
64	1	5.365896	4.788823	-5.778836
65	1	3.808788	4.814470	-3.886733
66	1	9.521361	6.847102	-5.117351
67	1	10.120550	5.762211	-6.377502
68	1	9.929098	5.162327	-4.726387
69	1	8.200713	6.302153	-7.827908
70	1	7.477816	7.365202	-6.603435
71	1	6.529076	6.045720	-7.306811
72	1	8.780617	3.885863	-7.265335
73	1	8.480189	3.241511	-5.638305
74	1	7.122668	3.581938	-6.723335
75	17	7.335734	7.120126	1.562393
76	17	8.202434	10.844071	2.734339
77	17	1.917741	8.122963	-1.562374
78	17	1.051094	4.399027	-2.734380

1b in methanol solvent:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-4.043190	-0.722717	0.790776
2	6	-2.681634	-0.845917	1.072052
3	6	-1.982543	0.272984	1.508305
4	6	-2.661662	1.482949	1.650328
5	6	-4.019413	1.527829	1.348206
6	7	-4.694777	0.435023	0.923328
7	1	-0.921070	0.209852	1.736413
8	1	-4.624776	-1.576480	0.447744
9	1	-2.192379	-1.807884	0.946811
10	1	-2.152058	2.381865	1.989672
11	6	-8.142165	3.925434	1.616333
12	6	-6.787385	4.007564	1.284983
13	6	-6.232029	5.259403	0.998335
14	6	-7.018508	6.403219	1.082046
15	6	-8.372818	6.348919	1.452052
16	6	-8.913979	5.079601	1.707701
17	1	-8.588190	2.959577	1.829147
18	1	-5.196030	5.343263	0.679537
19	1	-6.555754	7.350586	0.832469
20	1	-9.956616	4.968493	1.977786
21	7	-6.038694	2.804409	1.220163
22	1	-4.231587	3.658451	1.820285
23	6	-4.781500	2.775260	1.482165
24	30	-6.764615	0.866120	0.592477
25	17	-7.417090	0.851678	-1.629054
26	17	-8.163417	-0.159103	2.129204
27	6	-9.240212	7.625855	1.491507
28	6	-8.431735	8.837765	2.020099
29	1	-7.603843	9.100053	1.356632
30	1	-9.086658	9.710890	2.087222
31	1	-8.024544	8.640847	3.016450
32	6	-10.479107	7.445948	2.402365
33	1	-11.151315	6.667093	2.033310
34	1	-10.188183	7.193158	3.426517
35	1	-11.046438	8.380314	2.432055
36	6	-9.718154	7.929323	0.048566
37	1	-10.331770	8.836485	0.038813
38	1	-8.867605	8.084626	-0.621986
39	1	-10.319129	7.104911	-0.347056

1f in methanol solvent:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.546572	1.549464	0.438483
2	6	-2.926345	1.378606	-0.796601
3	6	-2.214582	2.445365	-1.343683
4	6	-2.148188	3.643756	-0.642218
5	6	-2.797028	3.739595	0.589192
6	7	-3.476518	2.718243	1.117025
7	1	-1.720029	2.338188	-2.306311
8	1	-3.004010	0.425121	-1.313914
9	1	-1.604703	4.500221	-1.031408
10	1	-2.768657	4.660793	1.168271
11	6	-4.311399	0.460327	1.054565
12	1	-4.359178	-0.482555	0.502765
13	7	-4.903120	0.631523	2.183650
14	6	-5.604681	-0.409368	2.834401
15	6	-5.289922	-1.762916	2.667919
16	6	-6.645240	-0.055704	3.708240
17	6	-6.013102	-2.748139	3.333068
18	1	-4.454617	-2.064519	2.041172
19	6	-7.377805	-1.029424	4.363248
20	1	-6.898603	0.989121	3.852872
21	6	-7.069019	-2.385662	4.179920
22	1	-5.729787	-3.784408	3.192529
23	1	-8.193647	-0.758179	5.027912
24	8	-7.835481	-3.267134	4.872962
25	30	-4.565927	2.626306	2.951924
26	6	-7.576710	-4.668268	4.733826
27	1	-8.311287	-5.166586	5.363629
28	1	-7.704275	-4.989692	3.696000
29	1	-6.568767	-4.917285	5.078609
30	17	-6.453121	3.972161	2.975533
31	17	-3.247971	2.611839	4.856924

$1f^{+}$ in gas-phase

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.081671	1.613602	-0.425516
2	6	-2.946070	2.448644	-1.131697
3	6	-4.317888	2.348540	-0.899027
4	6	-4.769604	1.424877	0.031830
5	6	-3.836192	0.625903	0.704030
6	7	-2.527737	0.713796	0.482364
7	1	-5.013650	2.982754	-1.434523
8	1	-2.552737	3.160567	-1.847432
9	1	-5.824107	1.312777	0.249374
10	1	-4.159859	-0.101120	1.440335
11	6	-0.638621	1.693220	-0.642958
12	1	-0.278408	2.445822	-1.347421
13	7	0.174569	0.945297	0.011290
14	6	1.525168	0.828252	-0.177484
15	6	2.353594	0.797555	0.986664
16	6	2.098678	0.644586	-1.466674
17	6	3.708790	0.646050	0.869840
18	1	1.877437	0.890165	1.957907
19	6	3.449716	0.484989	-1.588595
20	1	1.457249	0.604518	-2.338242
21	6	4.280553	0.483782	-0.422368
22	1	4.328087	0.629977	1.755999
23	1	3.925574	0.342284	-2.550842
24	8	5.559634	0.306672	-0.656665
25	30	-0.983613	-0.538914	1.413007
26	6	6.535704	0.247856	0.416137
27	1	7.487305	0.092952	-0.082958
28	1	6.542826	1.190884	0.964170
29	1	6.310614	-0.591855	1.074739
30	17	-0.720053	-2.351042	0.123762
31	17	-0.338230	0.255763	3.409797

1f⁻ in gas-phase

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.952153	1.721790	-0.114322
2	6	-2.685488	2.942572	-0.180629
3	6	-4.062591	2.924853	-0.133716
4	6	-4.740623	1.683435	-0.022567
5	6	-3.970317	0.527438	0.032651
6	7	-2.631382	0.521781	-0.011280
7	1	-4.624069	3.854798	-0.182003
8	1	-2.139276	3.878699	-0.265562
9	1	-5.822847	1.625025	0.018931
10	1	-4.441110	-0.449589	0.118048
11	6	-0.536295	1.675641	-0.158071
12	1	-0.000033	2.618679	-0.267615
13	7	0.118927	0.506934	-0.135017
14	6	1.510106	0.457943	-0.121744
15	6	2.340587	1.511702	0.312385
16	6	2.145450	-0.730002	-0.559167
17	6	3.737137	1.398695	0.294730
18	1	1.899611	2.421477	0.706997
19	6	3.527300	-0.845716	-0.578654
20	1	1.527521	-1.553144	-0.907320
21	6	4.337676	0.219625	-0.154573
22	1	4.332950	2.232002	0.651687
23	1	4.001891	-1.759500	-0.923661
24	8	5.702150	0.004447	-0.213360
25	30	-1.252187	-1.124545	0.061106
26	6	6.554553	1.038877	0.234578
27	1	7.574509	0.667804	0.109586
28	1	6.429284	1.956018	-0.359092
29	1	6.383988	1.275802	1.294587
30	17	-1.303051	-2.494138	-1.816719
31	17	-1.335167	-2.130249	2.148628

2a in methanol solvent:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.310821	-2.802547	0.417263
2	6	-0.739736	-1.619121	-0.801550
3	6	-0.560200	-2.674540	-1.687669
4	6	-1.300695	-3.842614	-1.495262
5	6	-2.187827	-3.907439	-0.428982
6	1	-2.998489	-2.817223	1.265186
7	1	0.147054	-2.580215	-2.513306
8	1	-1.181867	-4.688190	-2.174238
9	1	-2.787100	-4.798409	-0.240713
10	7	-1.604121	-1.685870	0.235903
11	6	0.011230	-0.363124	-0.956635
12	7	-0.158664	0.608212	-0.142022
13	6	0.757308	4.038737	-1.236284
14	6	1.984413	4.204445	-0.599367
15	6	2.509740	3.174782	0.176950
16	6	1.823215	1.966286	0.333182
17	6	0.588660	1.826074	-0.322590
18	1	0.346930	4.846369	-1.844583
19	1	2.533190	5.140868	-0.707300
20	1	3.471284	3.306294	0.675886
21	30	-1.621704	0.140105	1.390381
22	17	-0.748687	-0.160203	3.513482
23	17	-3.635976	1.263458	1.190144
24	6	0.033582	2.848597	-1.110010
25	1	0.718316	-0.295400	-1.795959
26	6	-1.292841	2.673899	-1.808602
27	1	-1.244449	1.898771	-2.585417
28	1	-1.595084	3.607987	-2.293071
29	1	-2.085897	2.380521	-1.109724
30	6	2.402085	0.852487	1.171316
31	1	1.705718	0.527646	1.954400
32	1	2.640293	-0.031856	0.564926
33	1	3.327841	1.180561	1.654907

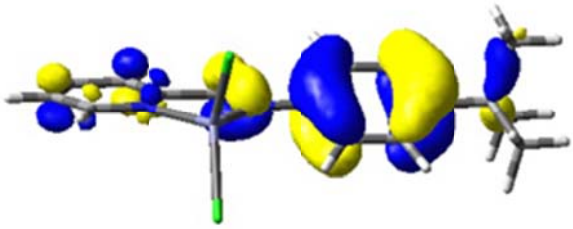
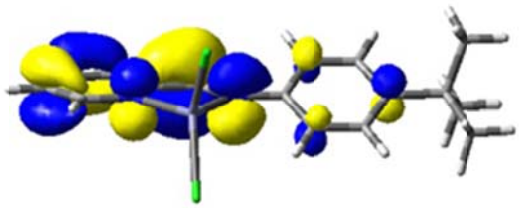
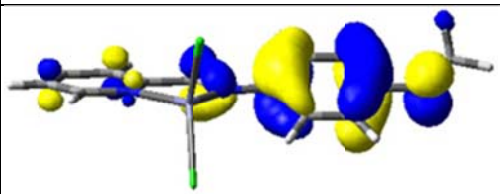
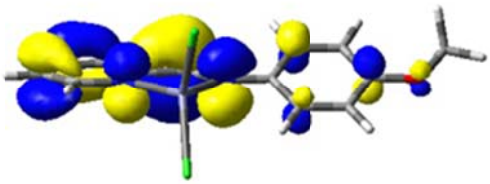
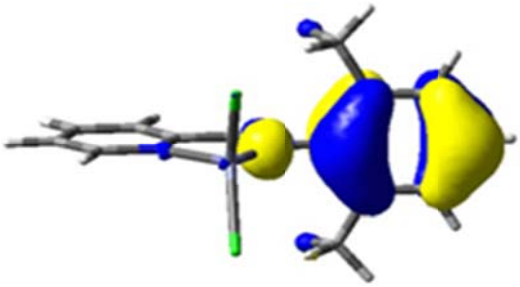
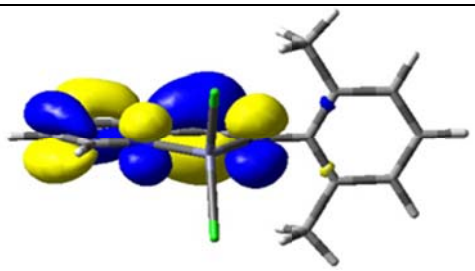
3 in methanol solvent:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-4.887972	-0.808234	-0.888342
2	6	-3.905975	-1.099006	-1.840424
3	6	-3.423852	-0.069025	-2.648874
4	6	-3.939042	1.216431	-2.480753
5	6	-4.917887	1.439834	-1.507830
6	7	-5.379321	0.450610	-0.732954
7	1	-2.661038	-0.268539	-3.395813
8	1	-3.533035	-2.114098	-1.938666
9	1	-3.594670	2.046731	-3.088749
10	1	-5.354046	2.416814	-1.322174
11	6	-5.468495	-1.818240	-0.018662
12	1	-5.142514	-2.854067	-0.118523
13	7	-6.390077	-1.488236	0.831436
14	6	-6.919137	-2.480251	1.696703
15	6	-8.304062	-2.546699	1.906143
16	6	-6.074784	-3.403129	2.340064
17	6	-8.837384	-3.549436	2.709863
18	1	-8.952946	-1.819028	1.435503
19	6	-6.604896	-4.390864	3.161991
20	1	-4.996790	-3.316545	2.234864
21	6	-7.992270	-4.470356	3.342911
22	1	-9.913814	-3.601341	2.859544
23	1	-5.961006	-5.090709	3.685158
24	8	-8.457737	-5.460774	4.158560
25	1	-9.421157	-5.392281	4.254123
26	46	-6.792028	0.600883	0.805381
27	17	-8.279822	0.631986	2.583029
28	17	-7.011861	2.903084	0.559299

Calculated bond distances (Å) and angles (˚) of 1b, 1f, 2a and 3 in methanol solvent

	1b (M=Zn, X=Cl)	**1f** (M=Zn, X=Cl)	**2a** (M=Zn, X=Cl)	**3** (M=Pd, X=Cl)
M(1)-N(1)	2.139	2.136	2.160	2.094
M(1)-N(8)	2.164	2.164	2.169	2.128
M(1)-X(1)	2.316	2.316	2.315	2.326
M(1)-X(2)	2.317	2.318	2.315	2.318
N(1)- C(2)	1.353	1.353	1.352	1.360
N(8)-C(7)	1.285	1.286	1.279	1.296
C(2) -C(7)	1.467	1.466	1.457	1.454
N(1)-M(1)-N(8)	79.12	79.29	78.43	79.11
N(1)-M(1)-Cl(2)	113.19	113.51	112.17	175.74
N(8)-M(1)-Cl(1)	111.74	112.02	111.77	172.36
Cl(1)-M(1)-Cl(2)	117.65	117.29	118.06	90.41
ϕ	29.58	27.53	90.83	43.44

Computed isodensity surfaces of HOMOs and LUMOs of 1b, 1f, 2a and 3

	HOMO	LUMO
1b		
1f		
2a		
3