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Electronic Supplementary Information (ESI)

Enhancing the luminescence properties and stability of cationic iridium(III) complexes based on phenyl-benzoimidazole ligand: a combined experimental and theoretical study

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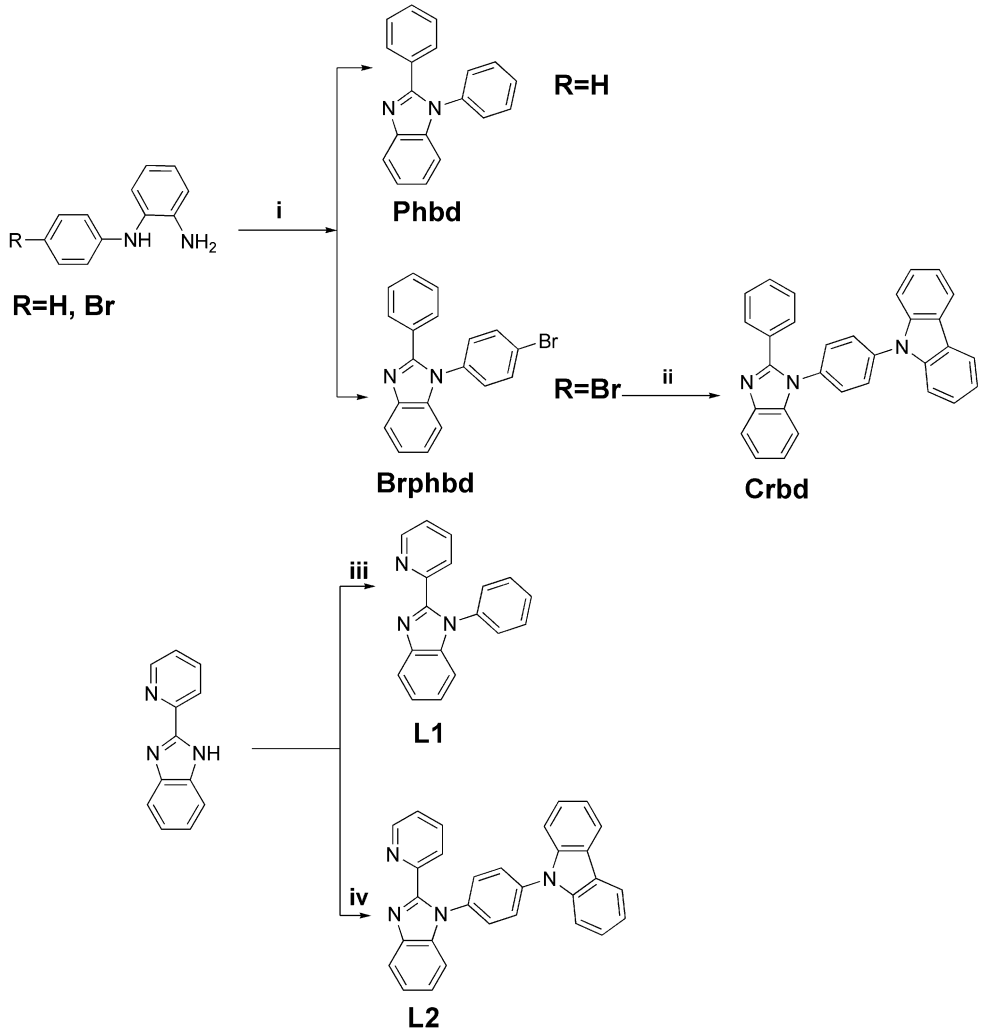
Synthesis and characterization of ligands Phbd, Crbd, L1 and L2

Scheme **S1** shows the general synthesis route of all ligands used in this study. The ^{1}H NMR spectra of them were recorded using a Bruker Avance 500 MHz spectrometer relative to tertramethylsilane as internal standard.



Scheme S1 Synthesis of ligands **Phbd**, **Crbd**, **L1 and L2.** Reagents and conditions: (i) benzaldehyde, acetic acid, 2-ethoxyethanol, reflux; (ii) carbazole, CuI, K_2CO_3, 18-crown-6, DMPU, 190 ^{o}C; (iii) iodobenzene, CuI, Cs_2CO_3, 1,10-Phenanthroline, DMF, reflux; (iv) 9-(4-bromophenyl)-9*H*-carbazole, CuI, K_2CO_3, 18-crown-6, DMPU, 190 ^{o}C.

Synthesis of 1,2-diphenyl-1*H*-benzo[d]imidazole (Phbd)

A mixture of 2-aminodiphenylamine (3.7 g, 20 mmol), benzaldehyde (2.1 g，20 mmol) and acetic acid (10 mL) in 2-ethoxyethanol (15 mL) was stirred and refluxed for 24 h under a N_2 atmosphere. After that, the cooled solution was poured into water, and

extracted with CH_2Cl_2. The organic layer was washed with sodium bicarbonate solution and water for several times. Then, the organic layer was dried over anhydrous $MgSO_4$, filtered and then concentrated. The residue was purified by column chromatography (silica, ethyl acetate/petroleum ether=1:10), and the resulting product was washed with n-hexane to yield a off-white powder **Phbd** (2.5 g, yield: 46%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.90 (d, *J* = 8 Hz, 1H), 7.57 (d, *J* = 7 Hz, 1H), 7.48–7.51 (m, 3H), 7.26–7.36 (m, 8H).

Synthesis of 9-(4-(2-phenyl-1*H*-benzo[d]imidazol-1-yl)phenyl)-9*H*-carbazole (Crbd)

The synthesis of intermediate **Brphbd** was similar to that of ligand **Phbd** except that 2-aminodiphenylamine was replaced by N^1-(4-bromophenyl)benzene-1,2-diamine. A mixture of intermediate **Brphbd** (2.1 g, 6.0 mmol), carbazole (1.1 g, 6.6 mmol), copper(I) iodide (0.11 g, 0.60 mmol), 18-crown-6 (16 mg, 0.06 mmol), K_2CO_3 (1.2 g, 9.0 mmol) and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU, 5 mL) was heated to 190 °C for 24 h under a N_2 atmosphere. After cooling to room temperature (RT), the reaction was quenched with 2 N hydrochloric acid and then the reaction mixture was extracted with CH_2Cl_2. After washing with $NH_3{\cdot}H_2O$ and water, drying over anhydrous Na_2SO_4, and evaporating the solvents, we purified the residue by column chromatography on silica gel using ethyl acetate/petroleum ether =1:10 as eluent to give a white solid (**Crbd**). Yield: 76%. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.18 (d, *J* = 8 Hz, 2H), 7.98 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 8 Hz, 2H), 7.69 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.33–7.50 (m, 12H).

Synthesis of 1-phenyl-2-(pyridin-2-yl)-1*H*-benzo[d]imidazole (L1)

A mixture of 2-(pyridin-2-yl)-1*H*-benzo[d]imidazole (1.5 g, 7.7 mmol), iodobenzene (2.5 g, 12 mmol) 1,10-phenanthroline (0.86 g, 4.8 mmol), copper(I) iodide (0.48 g, 2.5 mmol), and cesium carbonate (3.7 g, 11 mmol) was dissolved in 40 mL dimethylformamide (DMF). The mixture was stirred vigorously for 10 min at RT and subsequently refluxed under a N_2 atmosphere for another 18 h. After cooling to RT, the solvent was removed under vacuum and the residue was extracted with CH_2Cl_2

(200 mL). The product was then obtained by column chromatography on silica gel with dichloromethane/ethyl acetate (4:1) as the eluent to yield a white solid (71%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.41 (dd, *J* = 5 Hz, 1H), 8.04 (d, *J* = 8 Hz, 1H), 7.93 (d, *J* = 8 Hz, 1H), 7.72–7.76 (m, 1H), 7.45–7.51 (m, 3H), 7.21–7.38 (m, 6H).

Synthesis of 9-(4-(2-(pyridin-2-yl)-1*H*-benzo[d]imidazol-1-yl)phenyl)-9*H*-carbazole (L2)

A mixture of 2-(pyridin-2-yl)-1*H*-benzo[d]imidazole (0.43 g, 2.2 mmol), 9-(4-bromophenyl)-9*H*-carbazole (0.64 g, 2.0 mmol), copper(I) iodide (0.38 g, 0.2 mmol), 18-crown-6 (52 mg, 0.2 mmol), K_2CO_3 (0.41 g, 3.0 mmol) and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU, 5 mL) was heated to 190 °C for 24 h under a N_2 atmosphere. After cooling to RT, the reaction was quenched with 2 N hydrochloric acid and then the reaction mixture was extracted with CH_2Cl_2. After washing with $NH_3 \cdot H_2O$ and water, drying over anhydrous Na_2SO_4, and evaporating the solvents, we purified the residue by column chromatography on silica gel using ethyl acetate/petroleum ether =8:3 as eluent to give a white solid (**L2**). Yield: 53%. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.47 (d, *J* = 4 Hz, 1H), 8.26 (d, *J* = 8 Hz, 1H), 7.19 (d, *J* = 8 Hz, 2H), 7.97 (d, *J* = 8 Hz, 1H), 7.81–7.85 (m, 1H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.25–7.58 (m, 12H).

Characterization of the chloro-bridged dimers $[Ir(Phbd)_2Cl]_2$ and $[Ir(Crbd)_2Cl]_2$

Characterization of $[Ir(Phbd)_2Cl]_2$

^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ: major set, 8.97 (d, *J* = 7.5 Hz, 2H), 8.79 (d, *J* = 7.5 Hz, 2H), 7.95 (s, 2H), 7.79–7.89 (m, 12H), 7.63–7.67 (m, 6H), 7.43–7.54 (m, 8H), 7.16–7.17 (m, 4H), 6.55–6.66 (m, 10H), 6.40–6.43 (m, 4H), 5.94–5.96 (m, 2H). MALDI-TOF (m/z) 1532.3.

Characterization of $[Ir(Crbd)_2Cl]_2$

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ: major set, 8.75 (d, *J* = 8.5 Hz, 2H), 8.17–8.22 (m, 10H), 8.08 (d, *J* = 2.5 Hz, 2H), 8.06 (d, *J* = 2.5 Hz, 2H), 7.86–7.88 (m, 4H), 7.59–7.69 (m, 10H), 7.51–7.54 (m, 10H), 7.36–7.40 (m, 16H), 7.03–7.06 (m, 4H),

6.93–6.96 (m, 6H), 6.75–6.77 (m, 6H), 6.48–6.57 (m, 6H), 6.30 (d, J = 8.5 Hz, 2H).

MALDI-TOF (m/z) 2193.3.

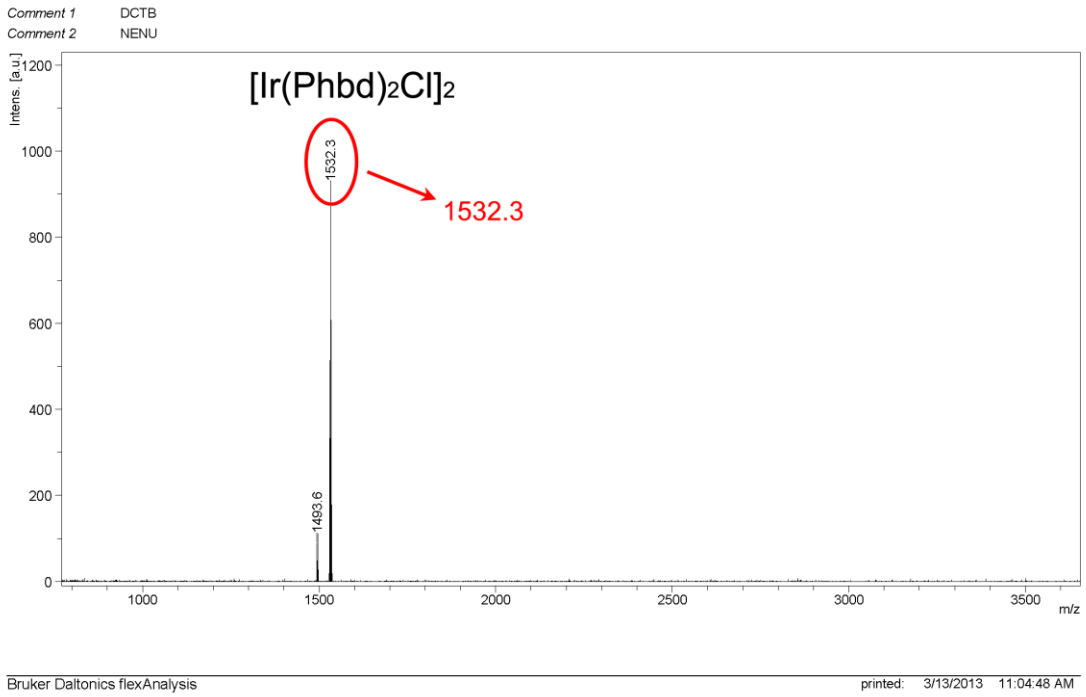


Fig. S1 Copy of the MALDI-TOF MS spectrum for $[Ir(Phbd)_2Cl]_2$.

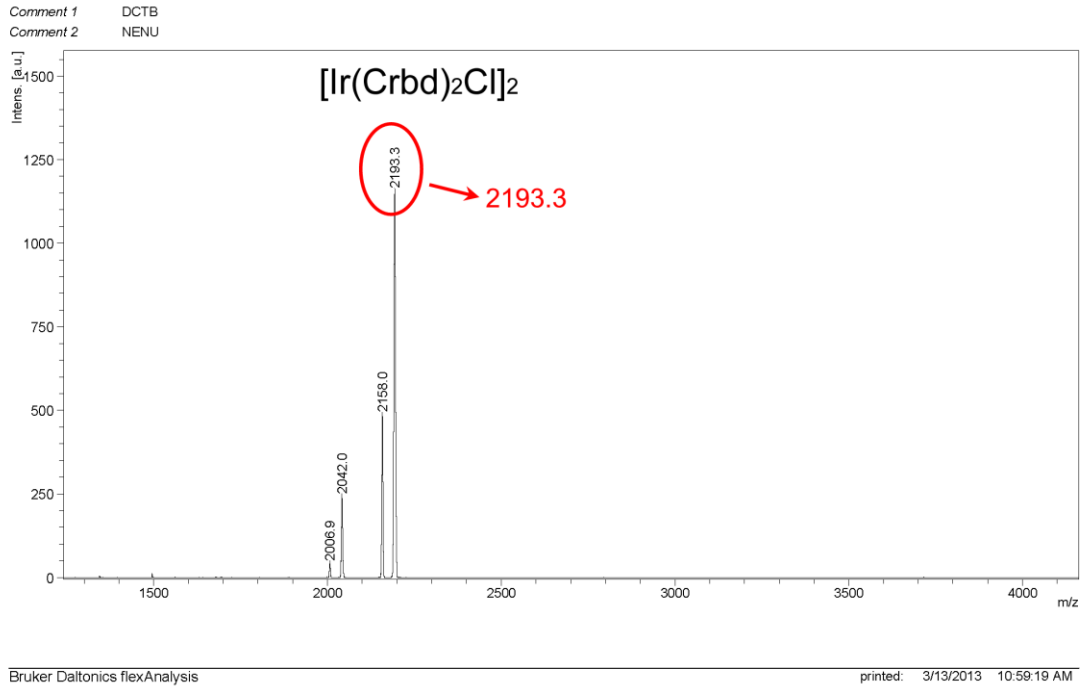


Fig. S2 Copy of the MALDI-TOF MS spectrum for $[Ir(Crbd)_2Cl]_2$.

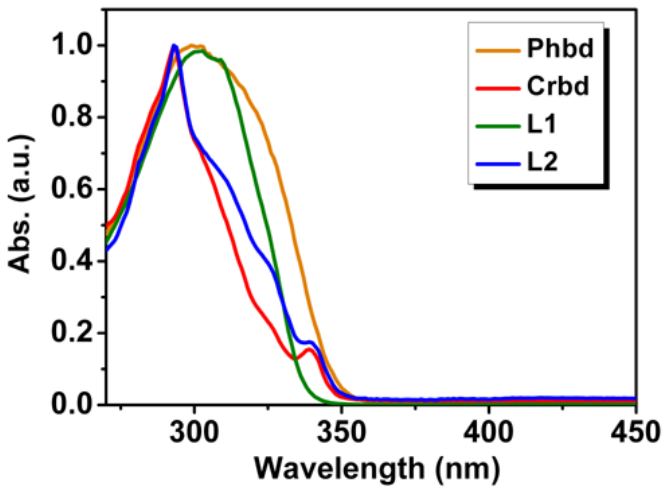


Fig. S3 Absorption spectra of the ligands used in this work in CH_2Cl_2 solvent at room temperature.

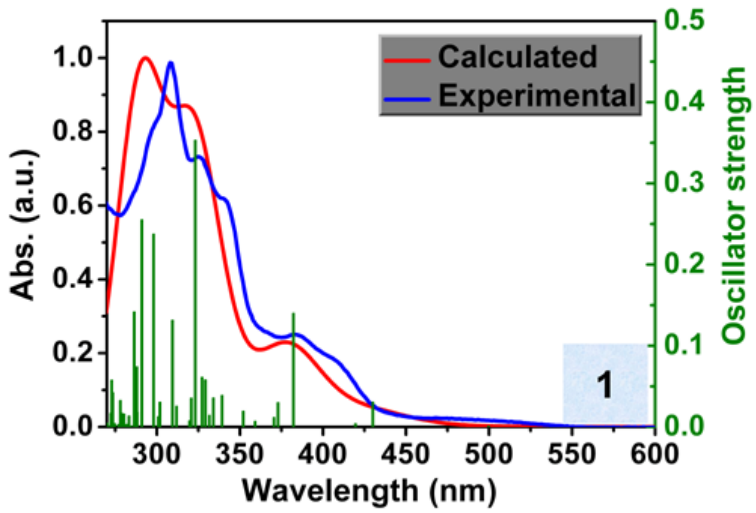


Fig. S4 Simulated and experimental absorption spectra of complex **1** in CH_2Cl_2 solvent.

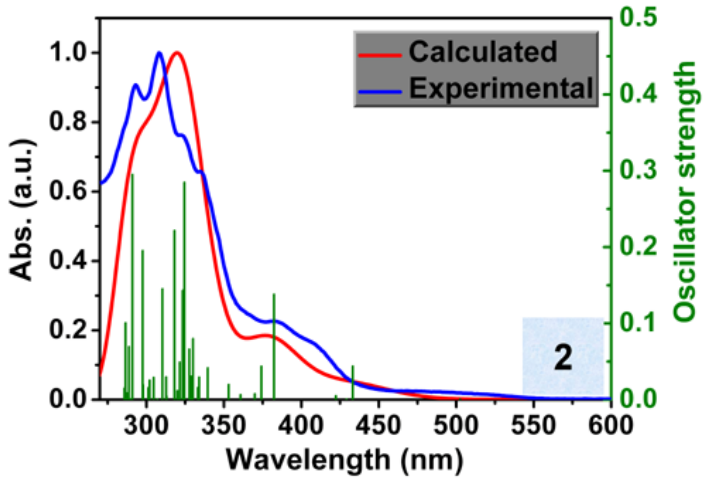


Fig. S5 Simulated and experimental absorption spectra of complex **1** in CH_2Cl_2 solvent.

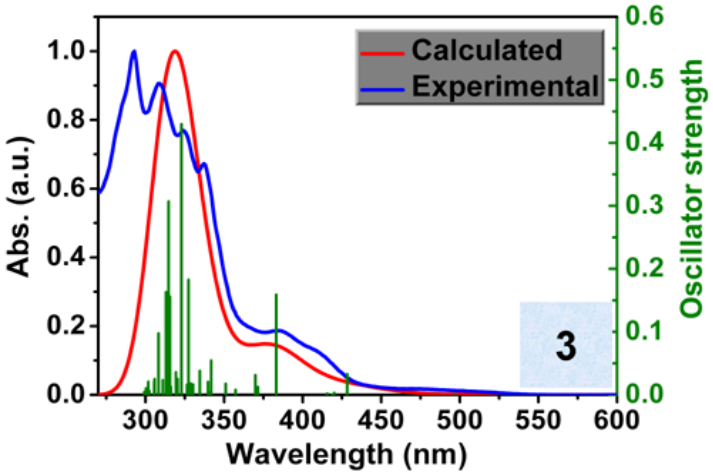


Fig. S6 Simulated and experimental absorption spectra of complex **1** in CH_2Cl_2 solvent.

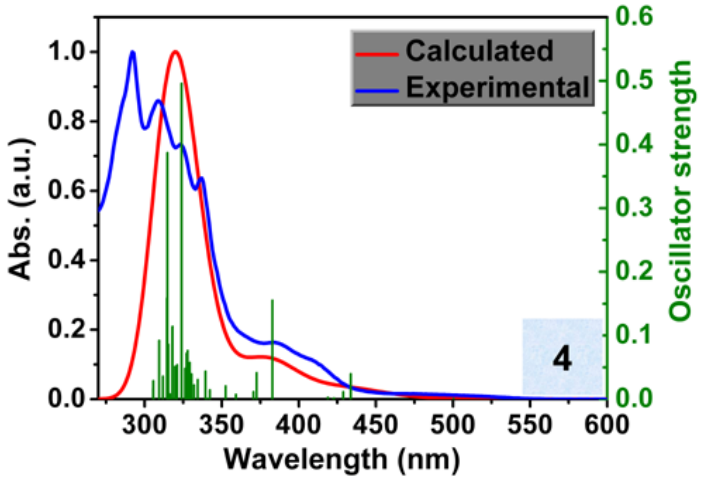


Fig. S7 Simulated and experimental absorption spectra of complex **1** in CH_2Cl_2 solvent.

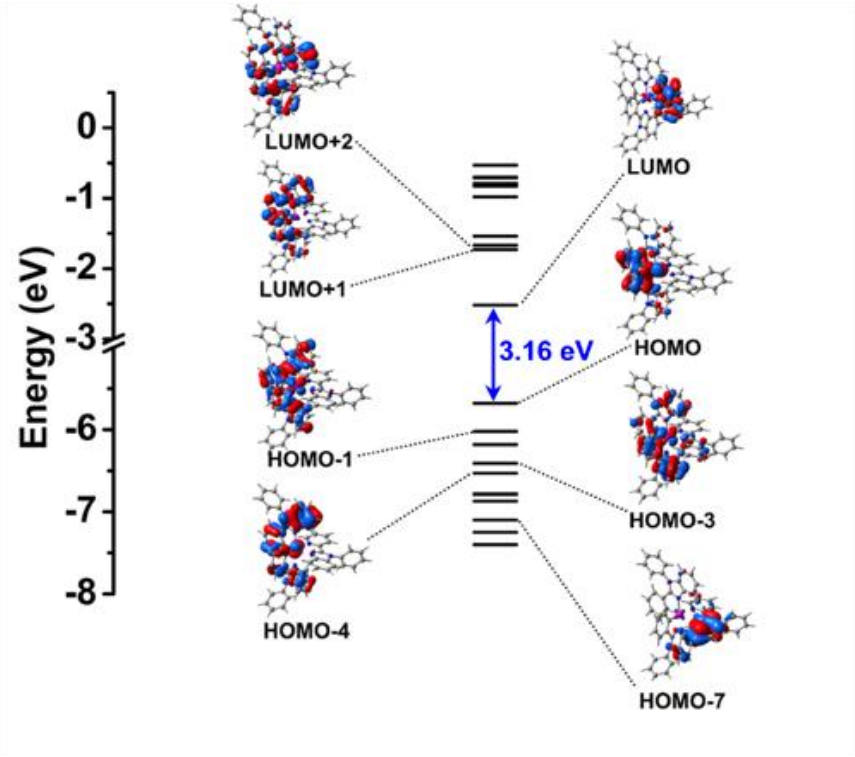


Fig. S8 Frontier molecular orbitals involved in crucial electronic excitations of complex **1** calculated by TD-DFT/6-31G*/LANL2DZ.

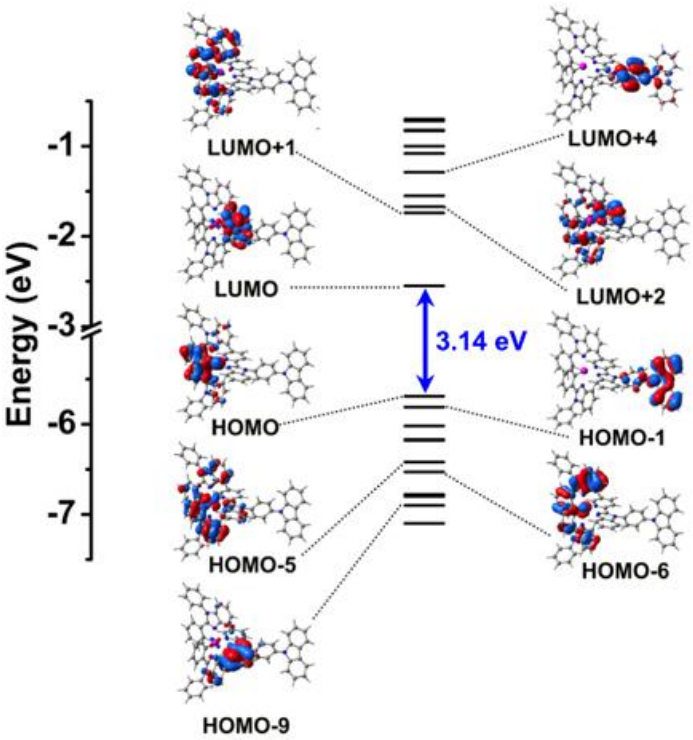


Fig. S9 Frontier molecular orbitals involved in crucial electronic excitations of complex **2** calculated by TD-DFT/6-31G*/LANL2DZ.

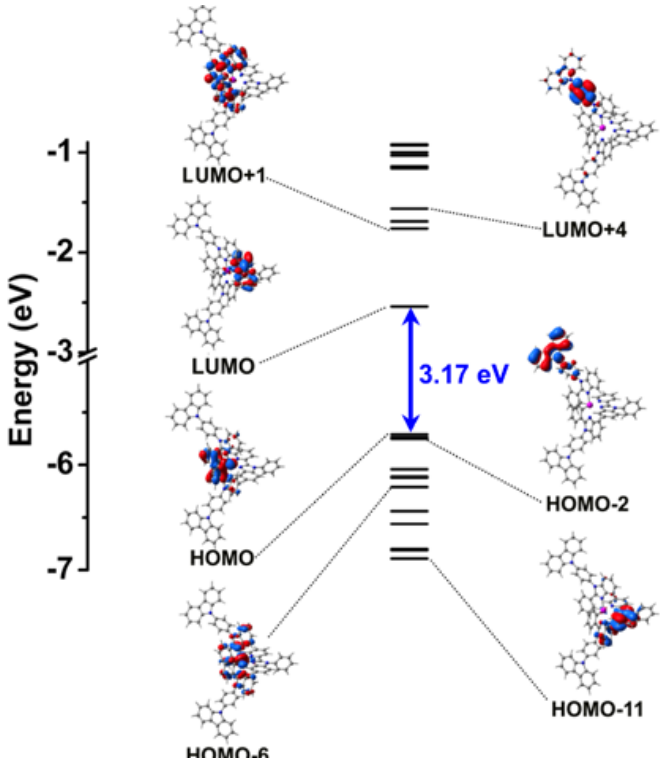


Fig. S10 Frontier molecular orbitals involved in crucial electronic excitations of

complex **3** calculated by TD-DFT/6-31G*/LANL2DZ.

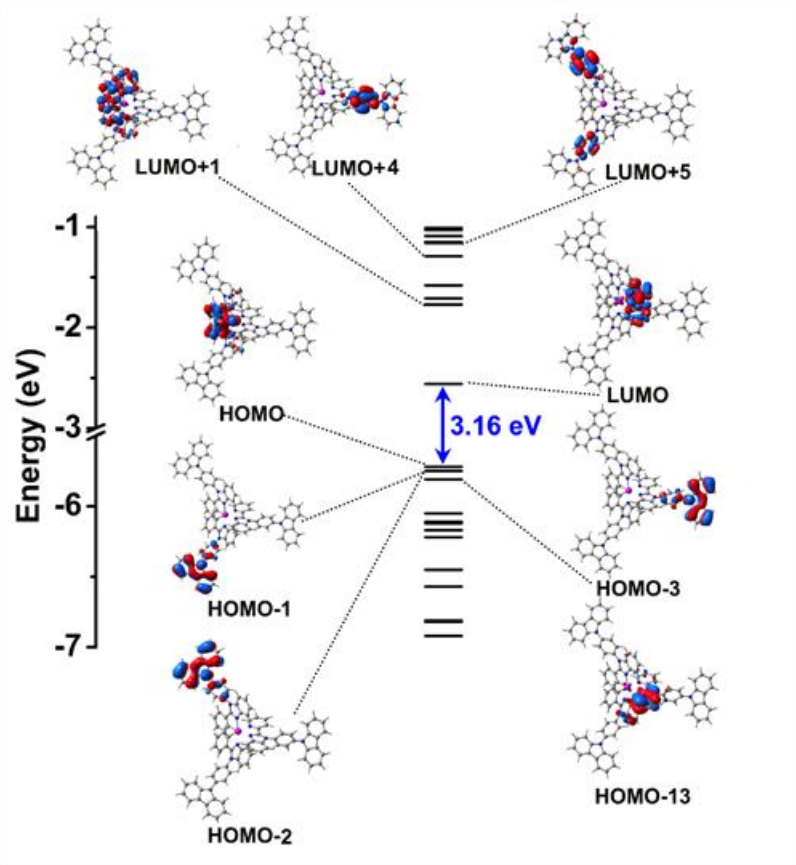


Fig. S11 Frontier molecular orbitals involved in crucial electronic excitations of complex **11** calculated by TD-DFT/6-31G*/LANL2DZ.

Table S1 Calculated excited energies, dominant orbital excitations, and oscillator strength of complex **1** in CH_2Cl_2 solution from TD-DFT calculation.

Excited state	Wavelength (nm)	Oscillator strength	Major contributions
S_1	499.7	0.0009	H-0->L+0(+98%)
S_2	430.1	0.0304	H-1->L+0(+92%)
S_3	419.6	0.0038	H-2->L+0(+91%)
S_4	382.3	0.1398	H-0->L+1(+97%)
S_5	373	0.0298	H-3->L+0(+88%)
S_6	370.6	0.0114	H-0->L+2(+90%)
S_7	359.2	0.0068	H-4->L+0(+95%)
S_8	352.1	0.0192	H-0->L+3(+92%)
S_9	339.3	0.0387	H-1->L+1(+80%)
S_{10}	334.1	0.0357	H-1->L+2(+73%)
S_{11}	331.7	0.0142	H-5->L+0(+95%)
S_{12}	329.3	0.0578	H-6->L+0(+71%)
S_{13}	327.3	0.061	H-2->L+1(+59%)
S_{14}	323.2	0.3531	H-7->L+0(+72%)
S_{15}	320.8	0.0353	H-1->L+3(+52%) H-2->L+2(+33%)
S_{16}	319.7	0.0073	H-2->L+2(+47%) H-1->L+3(36%)
S_{17}	311.9	0.0253	H-8->L+0(+53%) H-2->L+3(+38%)
S_{18}	309.5	0.1312	H-2->L+3(+52%) H-8->L+0(30%)
S_{19}	301.9	0.0301	H-3->L+1(+73%)
S_{20}	300.9	0.0123	H-9->L+0(+79%)
S_{21}	298.1	0.2373	H-3->L+2(+88%)
S_{22}	291	0.255	H-4->L+1(+81%)
S_{23}	288.3	0.0179	H-0->L+4(+84%)
S_{24}	288.1	0.0739	H-3->L+3(+79%)
S_{25}	286.5	0.1415	H-4->L+2(+83%)
S_{26}	284.5	0.0009	H-0->L+5(+78%)
S_{27}	283.3	0.0132	H-0->L+6(+78%)
S_{28}	282.0	0.0029	H-14->L+0(+75%)
S_{29}	280.3	0.0157	H-5->L+1(+57%)
S_{30}	279.1	0.0163	H-10->L+0(+54%)
S_{31}	278.6	0.0168	H-4->L+3(+51%)
S_{32}	278.1	0.0325	H-0->L+8(+37%)
S_{33}	277.1	0.0028	H-16->L+0(+67%)
S_{34}	274.7	0.0038	H-0->L+7(+95%)
S_{35}	273.6	0.042	H-0->L+9(+60%)
S_{36}	272.9	0.0576	H-5->L+2(+50%)
S_{37}	272.7	0.0054	H-11->L+0(+65%)
S_{38}	272.4	0.0167	H-6->L+1(+53%)
S_{39}	271.3	0.0002	H-12->L+0(+90%)
S_{40}	270.2	0.0044	H-0->L+10(+76%)

Table S2 Calculated excited energies, dominant orbital excitations, and oscillator strength of complex **2** in CH_2Cl_2 solution from TD-DFT calculation.

Excited state	Wavelength (nm)	Oscillator strength	Major contributions
S_1	502.4	0.0004	H-0->L+0(+99%)
S_2	433.2	0.0438	H-2->L+0(+68%)
			H-1->L+0(+24%)
S_3	429.1	0.0005	H-1->L+0(+75%)
			H-2->L+0(21%)
S_4	422.3	0.005	H-4->L+0(+89%)
S_5	382.4	0.138	H-0->L+1(+97%)
S_6	375.3	0	H-3->L+0(+100%)
S_7	374.2	0.0436	H-5->L+0(+92%)
S_8	370	0.0075	H-0->L+2(+92%)
S_9	360.8	0.0063	H-6->L+0(+94%)
S_{10}	353.1	0.0196	H-0->L+3(+91%)
S_{11}	339.6	0.0416	H-2->L+1(+80%)
S_{12}	334.1	0.0293	H-2->L+2(+67%)
S_{13}	333.2	0.0157	H-7->L+0(+94%)
S_{14}	330.1	0.0799	H-8->L+0(+70%)
S_{15}	328.8	0.0305	H-1->L+2(+62%)
S_{16}	327.7	0.0662	H-4->L+1(+50%)
S_{17}	324.5	0.2847	H-1->L+1(+41%)
			H-9->L+0(27%)
S_{18}	323.4	0.1431	H-1->L+1(+51%)
			H-9->L+0(+27%)
S_{19}	321.5	0.049	H-2->L+3(+71%)
S_{20}	320	0.0116	H-4->L+2(+66%)
S_{21}	318.1	0.2216	H-1->L+4(+74%)
S_{22}	313	0.0043	H-1->L+3(+71%)
S_{23}	312.7	0.0296	H-10->L+0(+45%)
			H-4->L+3(+43%)
S_{24}	310.3	0.145	H-4->L+3(+46%)
			H-10->L+0(33%)
S_{25}	307.1	0.0006	H-0->L+4(+98%)
S_{26}	304.7	0.029	H-1->L+5(+93%)
S_{27}	302.1	0.0254	H-5->L+1(+53%)
			H-12->L+0(36%)
S_{28}	301.2	0.0155	H-12->L+0(+58%)
			H-5->L+1(+34%)
S_{29}	297.9	0.0193	H-1->L+6(+79%)
S_{30}	297.6	0.1951	H-5->L+2(+74%)
S_{31}	296.4	0	H-3->L+2(+73%)
S_{32}	294.6	0	H-3->L+1(+88%)
S_{33}	291	0.2949	H-6->L+1(+86%)
S_{34}	289.5	0.0007	H-3->L+4(+92%)
S_{35}	288.7	0.0693	H-5->L+3(+77%)
S_{36}	287.3	0.0087	H-0->L+6(+89%)
S_{37}	286.5	0.1004	H-6->L+2(+72%)
S_{38}	286.4	0.0092	H-11->L+0(+90%)
S_{39}	285.8	0.0148	H-2->L+4(+87%)
S_{40}	285.1	0	H-3->L+3(+82%)

Table S3 Calculated excited energies, dominant orbital excitations, and oscillator strength of complex **3** in CH_2Cl_2 solution from TD-DFT calculation.

Excited state	Wavelength (nm)	Oscillator strength	Major contributions
S_1	496.7	0.0005	H-0->L+0(+98%)
S_2	428.4	0.033	H-3->L+0(+88%)
S_3	420.1	0.0032	H-1->L+0(+59%)
			H-6->L+0(23%)
S_4	418.6	0.0002	H-2->L+0(+82%)
S_5	415.5	0.0021	H-6->L+0(+66%)
			H-1->L+0(+21%)
S_6	383.2	0.1591	H-0->L+1(+96%)
S_7	371.5	0.0127	H-0->L+2(+51%)
			H-7->L+0(41%)
S_8	369.9	0.0313	H-7->L+0(+52%)
			H-0->L+2(+44%)
S_9	369.8	0.0001	H-4->L+0(+100%)
S_{10}	369.4	0	H-5->L+0(+100%)
S_{11}	357.3	0.008	H-8->L+0(+94%)
S_{12}	351.1	0.0175	H-0->L+3(+92%)
S_{13}	341.8	0.0546	H-1->L+1(+53%)
S_{14}	341.5	0.0047	H-2->L+1(+77%)
S_{15}	339.8	0.0206	H-3->L+1(+69%)
S_{16}	334.6	0.038	H-3->L+2(+71%)
S_{17}	330.3	0.0164	H-10->L+0(+52%)
			H-9->L+0(43%)
S_{18}	328.8	0.0181	H-6->L+1(+27%)
			H-10->L+0(24%)
S_{19}	328.1	0.015	H-1->L+2(+52%)
S_{20}	327.4	0.1827	H-6->L+1(+27%)
S_{21}	326.4	0.016	H-2->L+2(+78%)
S_{22}	322.9	0.4296	H-11->L+0(+73%)
S_{23}	320.5	0.0253	H-3->L+3(+57%)
			H-6->L+2(+27%)
S_{24}	319.4	0.0361	H-6->L+2(+51%)
			H-3->L+3(27%)
S_{25}	316.2	0.0127	H-2->L+3(+91%)
S_{26}	315.6	0.156	H-1->L+3(+53%)
			H-1->L+5(30%)
S_{27}	314.7	0.3071	H-2->L+4(+81%)
S_{28}	313.1	0.1632	H-1->L+5(+55%)
			H-1->L+3(+34%)
S_{29}	311	0.0235	H-12->L+0(+60%)
			H-6->L+3(28%)
S_{30}	308.3	0.0977	H-6->L+3(+59%)
S_{31}	305.8	0.0251	H-1->L+7(+93%)
S_{32}	305.6	0.0208	H-2->L+6(+93%)
S_{33}	305.4	0.0001	H-5->L+1(+89%)
S_{34}	305.3	0.0001	H-4->L+1(+77%)
S_{35}	302.5	0.0061	H-0->L+4(+53%)
S_{36}	301.8	0.0209	H-7->L+1(+47%)
			H-0->L+4(+33%)
S_{37}	301.4	0.0065	H-0->L+5(+62%)
S_{38}	300.3	0.0104	H-15->L+0(+87%)
S_{39}	299.2	0.0043	H-1->L+10(+83%)
S_{40}	299.2	0.0033	H-2->L+9(+84%)

Table S4 Calculated excited energies, dominant orbital excitations, and oscillator strength of complex **4** in CH_2Cl_2 solution from TD-DFT calculation.

Excited state	Wavelength (nm)	Oscillator strength	Major contributions
S_1	500.3	0.0007	H-0->L+0(+98%)
S_2	433.7	0.0397	H-3->L+0(+75%)
			H-4->L+0(22%)
S_3	428.8	0.0113	H-4->L+0(+69%)
			H-3->L+0(+24%)
S_4	422.8	0.0014	H-2->L+0(+82%)
S_5	422.3	0.0001	H-1->L+0(+97%)
S_6	418.9	0.0027	H-8->L+0(+77%)
S_7	382.9	0.1552	H-0->L+1(+96%)
S_8	377	0	H-7->L+0(+100%)
S_9	372.7	0.0413	H-9->L+0(+84%)
S_{10}	372.4	0	H-5->L+0(+100%)
S_{11}	372.4	0	H-6->L+0(+100%)
S_{12}	370.6	0.0116	H-0->L+2(+86%)
S_{13}	359.2	0.0074	H-10->L+0(+94%)
S_{14}	352.5	0.0206	H-0->L+3(+91%)
S_{15}	342.3	0.0144	H-2->L+1(+82%)
S_{16}	340.7	0.0009	H-1->L+1(+65%)
			H-1->L+2(+26%)
S_{17}	339.5	0.0436	H-4->L+1(+79%)
S_{18}	334.4	0.0307	H-4->L+2(+67%)
S_{19}	332.1	0.022	H-11->L+0(+96%)
S_{20}	330.4	0.0393	H-3->L+2(+62%)
			H-3->L+3(+22%)
S_{21}	329.3	0.0574	H-12->L+0(+68%)
S_{22}	328.3	0.0253	H-1->L+2(+61%)
			H-1->L+1(26%)
S_{23}	327.9	0.0763	H-2->L+2(+43%)
			H-8->L+1(22%)
S_{24}	327.2	0.0717	H-2->L+2(+44%)
			H-8->L+1(+24%)
S_{25}	326.3	0.048	H-3->L+1(+90%)
S_{26}	324	0.4959	H-13->L+0(+48%)
S_{27}	321.1	0.0538	H-4->L+3(+67%)
S_{28}	319.8	0.0513	H-8->L+2(+63%)
S_{29}	318.1	0.1141	H-3->L+4(+42%)
			H-2->L+3(+37%)
S_{30}	318	0.1129	H-2->L+3(+52%)
			H-3->L+4(26%)
S_{31}	316.4	0.0079	H-1->L+3(+88%)
S_{32}	315.4	0.0858	H-3->L+3(+60%)
S_{33}	314.8	0.3871	H-2->L+5(+37%)
			H-2->L+6(+20%)
S_{34}	314.5	0.1587	H-1->L+6(+47%)
			H-2->L+5(+26%)
S_{35}	311.9	0.0358	H-14->L+0(+54%)
			H-8->L+3(+31%)
S_{36}	309.4	0.092	H-8->L+3(+55%)
			H-14->L+0(24%)
S_{37}	306	0.0001	H-6->L+1(+89%)
S_{38}	305.7	0.0287	H-2->L+8(+72%)
S_{39}	305.6	0.0174	H-1->L+9(+72%)
S_{40}	305.6	0.0002	H-0->L+4(+97%)

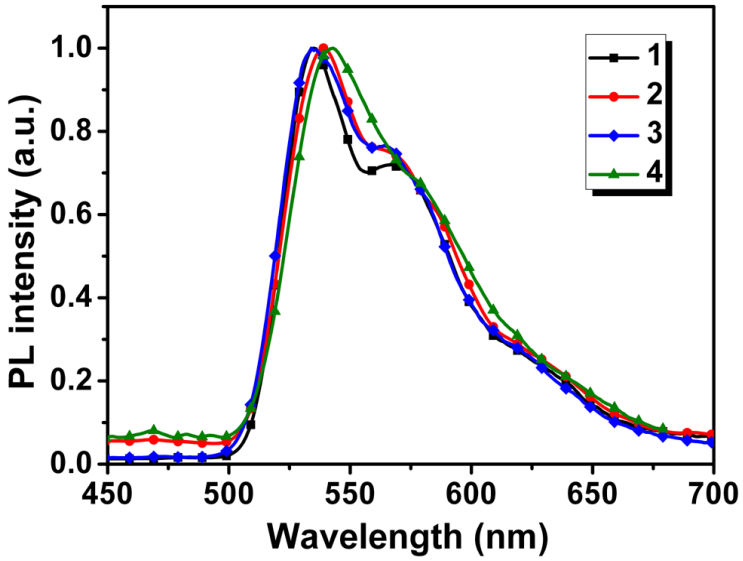


Fig. S12 Emission spectra of complexes **1-4** in CH_2Cl_2 solvent at 77 K.

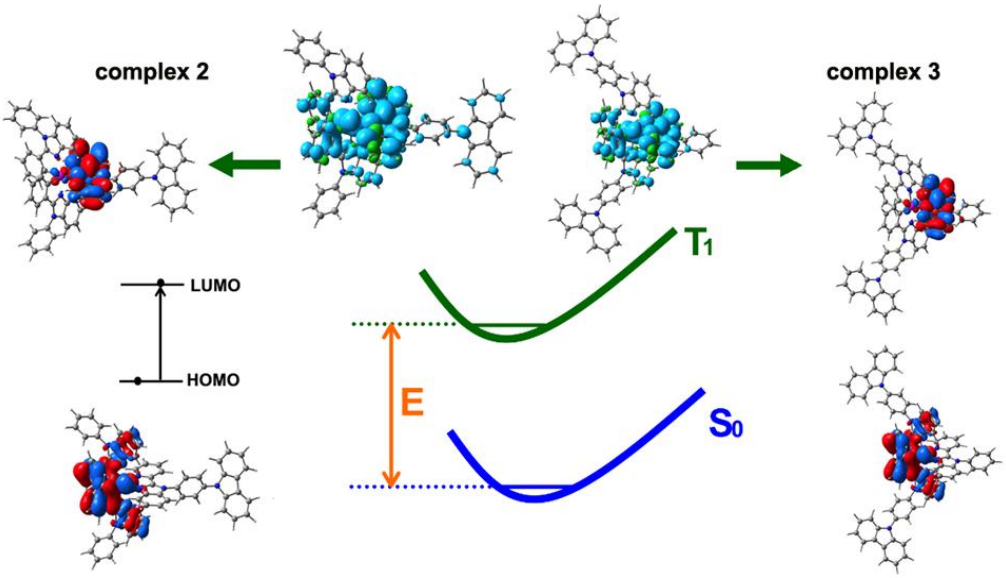


Fig. S13 The spin density and electron density distribution calculated for the optimized lowest lying triplet states (T_1) of complexes **2** and **3**. The energy difference E computed between the S_0 and T_1 states of complexes **2** and **3** is 2.24 eV and 2.23 eV, respectively.

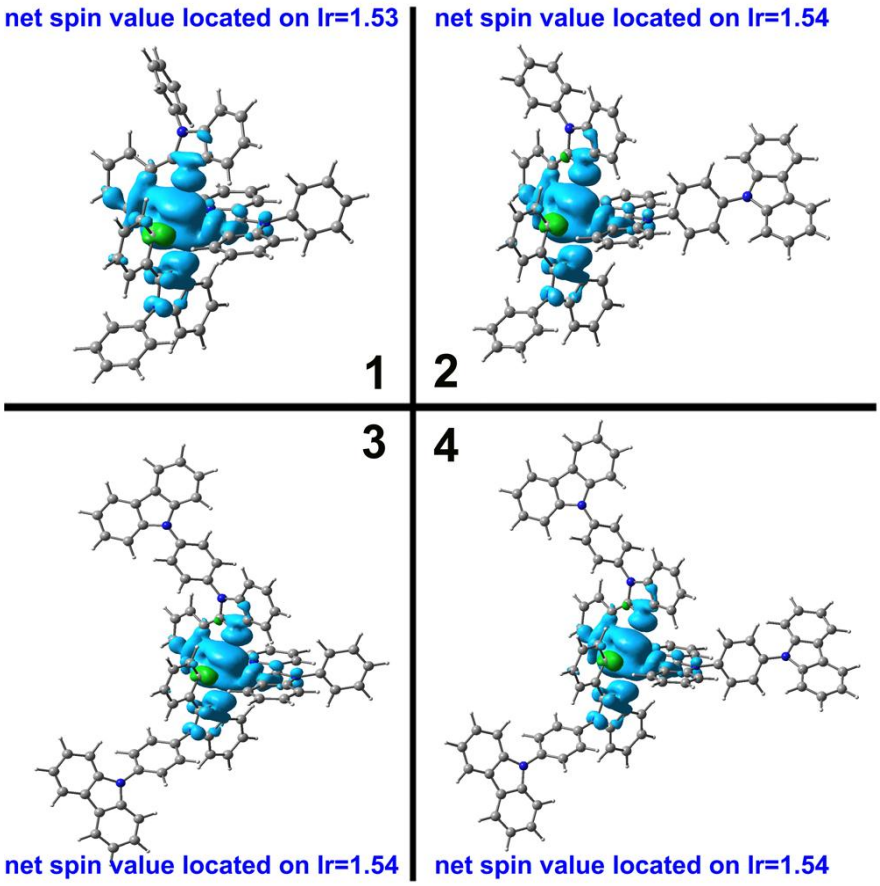


Fig. S14 Spin density distribution calculated for optimized metal-centered states (^{3}MC) of complexes **1**-**4**.

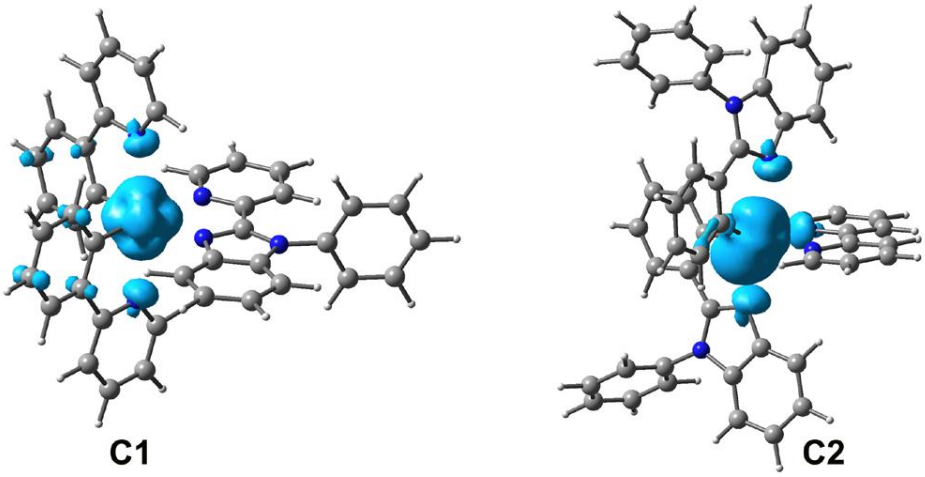


Fig. S15 Spin density distribution calculated for optimized metal-centered states (^{3}MC) of complexes **C1** and **C2**.

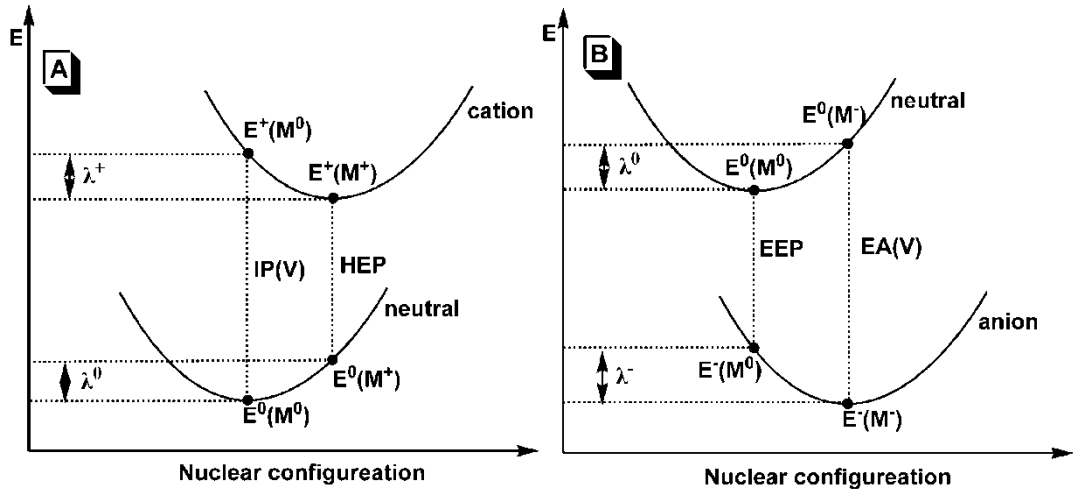


Fig. S16 Sketch of the potential energy surface for neutral, cation and anion species. HEP is the energy difference between neutral molecule and cation using the cationic geometric structure and EEP is the energy difference between neutral molecule and anion using the anionic geometric structure.