Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Theoretical study substituent effect controlling the radiative and nonradiative decay processes of platinum (II) complexes

Wei Shen,[a,b] Wenting Zhang,[b] and Chaoyuan Zhu*[a]

[a] *Institute of Molecular Science, Department of Applied Chemistry and Center for Interdisciplinary Molecular Science, National Chiao-Tung University, Hsinchu 30050, Taiwan*

[b] *School of Chemistry and Chemical Engineering, Southwest University, Chongqing, P.R. China*

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Table S1. Selected bond lengths at S0 optimized geometry for complex **1** by using different functional (6-31g*) in PCM model as well as experimental data.

	Pt-N	Pt-C	Pt-O1	Pt-O2	Average relative error
Exp	1.981	1.961	2.068	1.992	
TPSSh	2.014	1.981	2.119	2.024	0.017
Relative Error	0.016	0.010	0.025	0.016	
B3LYP	2.024	1.987	2.141	2.039	0.024
Relative Error	0.022	0.013	0.036	0.024	
PBE0	2.003	1.970	2.116	2.019	0.013
Relative Error	0.011	0.005	0.023	0.013	
BMK	2.007	1.980	2.129	2.060	0.022
Relative Error	0.013	0.010	0.030	0.034	
BHandHLYP	2.023	1.982	2.121	2.025	0.019
Relative Error	0.021	0.011	0.026	0.017	
CAM-B3LYP	2.018	1.980	2.119	2.023	0.017
Relative Error	0.019	0.009	0.025	0.016	

We have chosen several DFT method according to component of HF in DFT, including TPSSh(HF 10%), B3LYP (HF 20%), PBE0 (HF 25%), BMK (HF 42%) and BHandHLYP (HF 50%). The long-range DFT (CAM-B3LYP) also be considered.

Table S2. The energies and the energy differences calculated by different functionals in PCM model as well as experimental data for complex **1**

	Exp	TPSSh	B3LYP	PBE0	BMK	BHandHLYP	CAM-B3LYP
S_0		-1178.623	-1178.599	-1177.333	-1177.285	-1177.777	-1177.927
T_1		-1178.535	-1178.508	-1177.240	-1177.186	-1177.681	-1177.830
$\Delta E_{T1\text{-}S0}$		2.40	2.48	2.52	2.70	2.62	2.65
Wavelength	485.0	517.2	499.3	492.5	458.7	473.8	467.9

Table S3. The energies and the energy differences calculated by PBE0 at different basis set in PCM model as well as experimental data for complex **1.**

		6-31g*	6-31+g*	6-31g**	6-311g*
S0		-1177.333	-1177.359	-1177.359	-1177.553
T1		-1177.240	-1177.268	-1177.280	-1177.461
$\Delta E_{T1\text{-}S0}$		2.52	2.49	2.15	2.50
Wavelength	485.0	492.5	498.9	576.6	496.2

Table S4. Transition dipole moments μ(S_n) (Debye) for S_0–S_n transitions, singlet–triplet splitting energies ΔE(S_n–T_1) (eV) and the SOC matrix elements $\langle T_1|\hat{H}_{SOC}|S_n\rangle$ (cm^{-1}) for complex **1** at its optimized T_1 geometry calculated by B3LYP and M06 functionals.

B3LYP				M06			
S_n	μ(S_n)	ΔE(S_n–T_1)	$\langle T_1\| H_{SOC}\| S_n\rangle$	S_n	μ(S_n)	ΔE(S_n–T_1)	$\langle T_1\| H_{SOC}\| S_n\rangle$
S_1	1.71	0.608	27.694	S_1	1.84	0.753	53.440
S_2	1.83	1.029	359.848	S_2	0.39	1.107	684.134
S_3	0.35	1.035	796.842	S_3	1.86	1.290	325.005
S_4	1.36	1.518	1.937	S_4	1.20	1.739	33.844
S_5	0.80	1.653	99.214	S_5	1.92	1.903	60.543
S_6	0.00	1.708	614.017	S_6	1.81	1.977	39.540
S_7	2.07	1.775	16.395	S_7	0.00	2.066	473.078
S_8	0.04	1.911	19.125	S_8	0.05	2.085	77.043
S_9	1.52	1.912	10.014	S_9	0.76	2.183	232.323
S_{10}	0.61	1.924	291.650	S_{10}	1.23	2.190	15.006

The electronegativity and conjugation effect of substituents

The HOMO,LUMO, natural bond charge and dipole moment, as well as the electronegativity of these electron-withdrawing substituents are calculated and the corresponding results are summarized in Table S4. Many researchers have demonstrated that introducing the electron-withdrawing units is an effective way to obtain highly-efficient blue-emitting OLED emitters. As is well known, the electron-withdrawing capabilities of substituents could be evaluated by the electronegativity ($\boldsymbol{\chi}$), which can be calculated by the average value of the HOMO and LUMO energies: $\boldsymbol{\chi} = -(\boldsymbol{E}_{\mathbf{HOMO}} + \boldsymbol{E}_{\mathbf{LUMO}})/\mathbf{2}$.[1]Meanwhile, considering conjugation effect, we calculated the NBO charge and dipole moment of Pt complex. The values of $\boldsymbol{\chi}$ are arranged in the following order: -$CF_2CF_2CF_3$ (3.92) <-*o*-carborane(4.48) <-CN(4.65) <-NO_2 (5.49) <-SF_5 (6.05). While, the sequence of NBO charge does not agree with $\boldsymbol{\chi}$. The biggest $\boldsymbol{\chi}$ (-SF_5) even possess the positive NBO charge. The dipole moment of those compounds, which show the degree of conjugation to a certain extent, are listed in this order: -$CF_2CF_2CF_3$ (6.09) <-SF_5 (7.66) <-CN(8.52) <-NO_2 (8.74) <-*o*-carborane(9.69). Those three sequences indicate that (1) substituent group effect includes electronegativity and conjugation effect, and (2) two kinds of effect in different groups is different degree. Taken together, *o*-carborane group have strongest conjugation effect and -NO_2 have strongest electronegativity effect.

Table S5. The energies of HOMO, LUMO and electronegativity (χ) of substituents saturated with hydrogen, as well as NBO charge and dipole moment of studied complexes

	o-carborane	CN	NO_2	$CF_2CF_2CF_3$	SF_5
HOMO[a]	-8.88	-10.14	-9.07	-9.71	-11.32
LUMO	-0.07	0.84	-1.91	1.87	-0.78
χ	4.48	4.65	5.49	3.92	6.05
NBO Charge	-0.11	-0.04	-0.29	-0.01	0.10
Dipole moment	9.69	8.52	8.74	6.09	7.66

[a] HOMO and LUMO only obtain from substituents saturated with hydrogen, NBO charge and Dipole moment include whole Pt complex.

1. Zhan, C.-G.; Nichols, J. A.; Dixon, D. A., Ionization Potential, Electron Affinity, Electronegativity, Hardness, and Electron Excitation Energy: Molecular Properties from Density Functional Theory Orbital Energies. *The Journal of Physical Chemistry A* **2003**, *107*, 4184-4195.

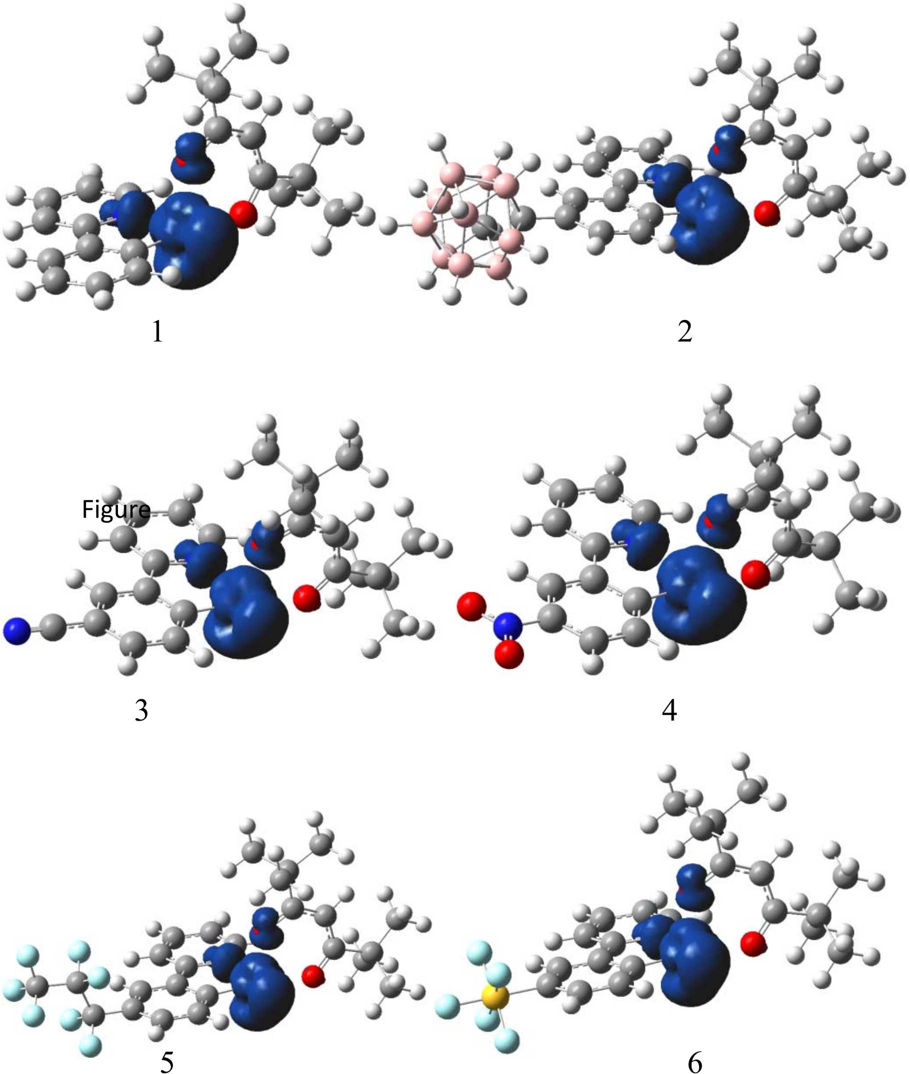


Fig. 1S. The spin densities of ^{3}MC state for complexes 1-6 (isovalue = 0.005).

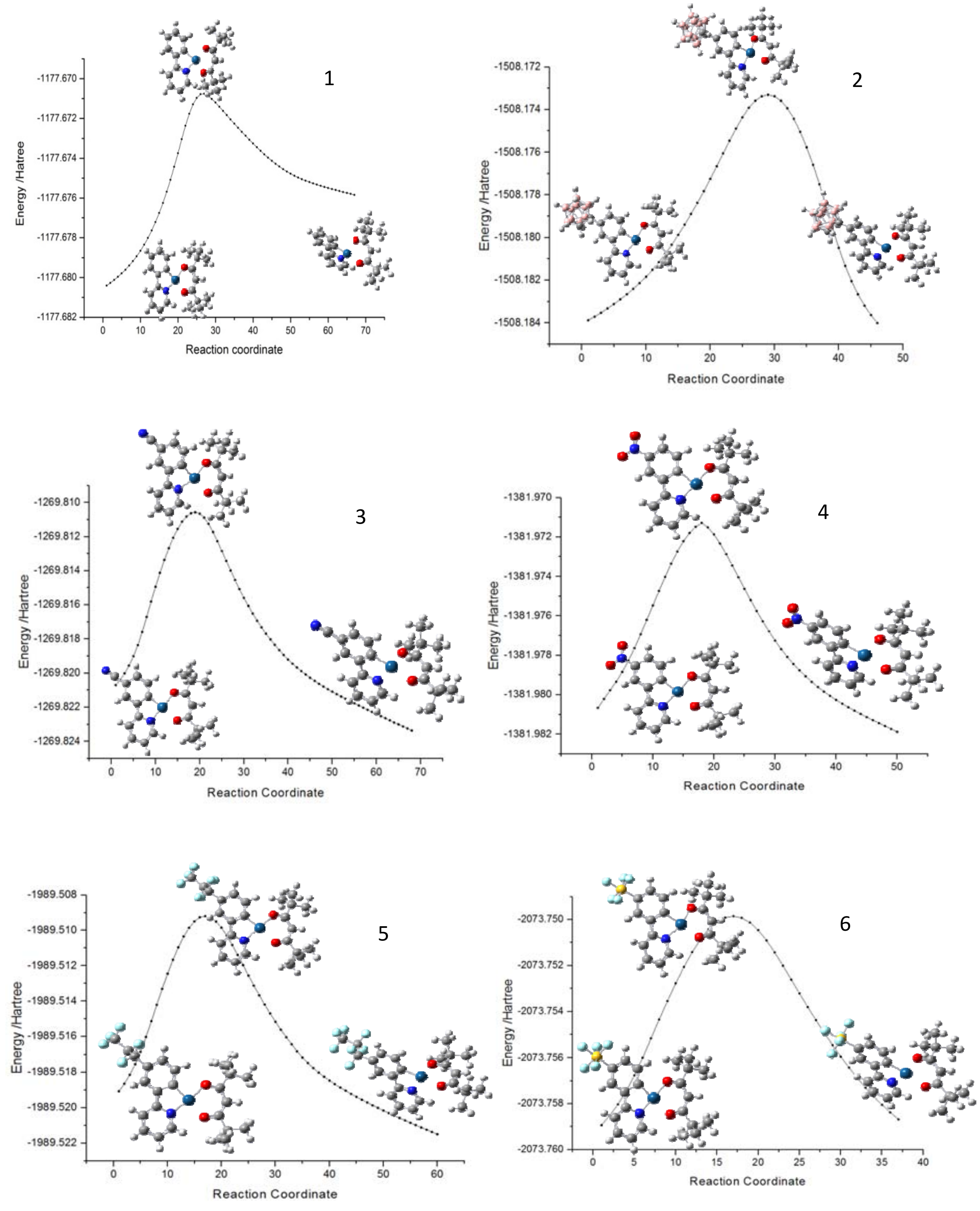
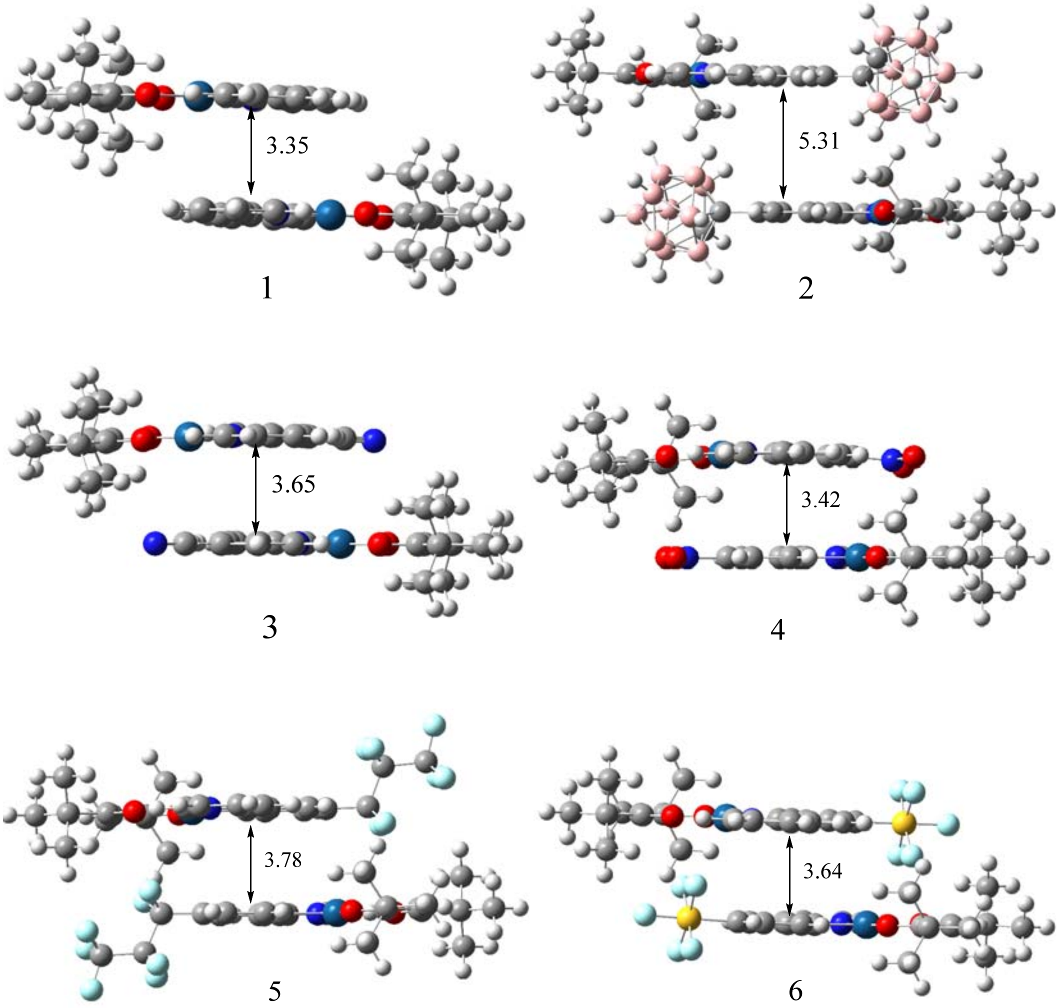


Fig. 2S. The intrinsic reaction coordinates of transition state.



1 2 3 4 5 6

Fig 3S. The π-π stacking distance of head-tail dimer.