Supporting Information

Shedding light on the photophysical properties of Iridium (III) complexes with *N*-heterocyclic carbene ligands from a theoretical viewpoint

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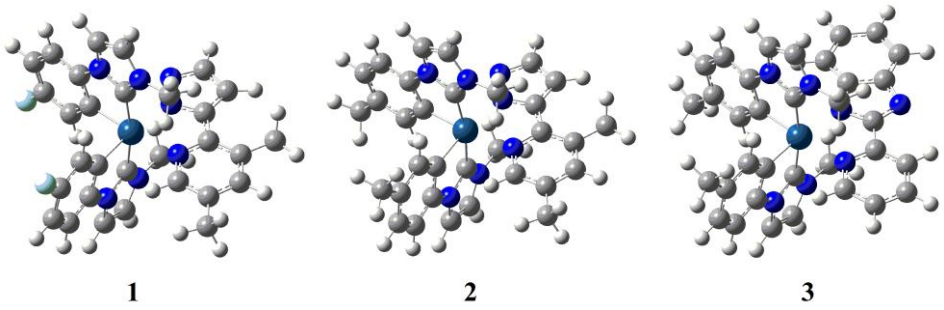


Fig. S1. The optimized structures for complexes **1**-**3** in the ground state.

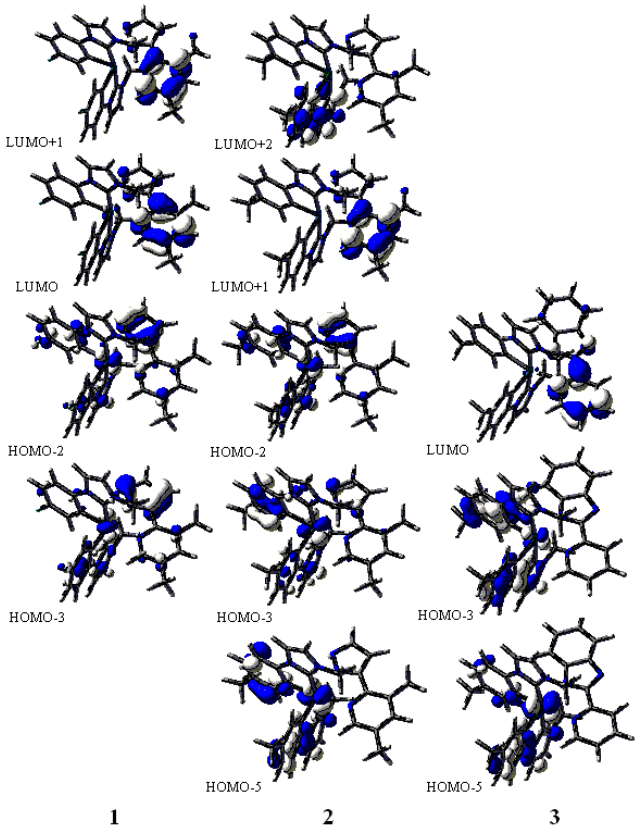


Fig. S2. Diagrams of the related frontier orbitals to the absorption peaks for complexes **1-3** at their optimized S_0 geometry. (Some HOMOs and LUMOs are not shown as they have displayed in the body part of the paper.)

According to Nozaki, when the singlet excited state ($d_{yz}\rightarrow\pi^*$) (denoted as S) couples with the triplet excited state ($d_{xy}\rightarrow\pi^*$) (denoted as T), only the element involving T_y has a nonzero value. The following process will explain how this result comes from.

Usually, the inner product of the angular momentum $\vec{l}$ and the spin of the electron $\vec{s}$ can be represented in the following equation:

$$\vec{l}\cdot\vec{s} = l_x s_x + l_y s_y + l_z s_z = l_z s_z + \frac{1}{2}\left[l_+ s_- + l_- s_+\right]$$

Where $l_+ = l_x + il_y$, $l_- = l_x - il_y$. Then, considering the spatial orbital firstly, there will be:[1]

$$\begin{aligned}
&\left\langle d_{yz}\left|h_{so}\right|d_{xy}\right\rangle = \left\langle d_{yz}\left|l_x + l_y + l_z\right|d_{xy}\right\rangle = \left\langle d_{yz}\left|l_z + \frac{1}{2}(l_+ + l_-)\right|d_{xy}\right\rangle \\
&= \left\langle d_{yz}\left|l_z\right|d_{xy}\right\rangle + \frac{1}{2}(\left\langle d_{yz}\left|l_+\right|d_{xy}\right\rangle + \left\langle d_{yz}\left|l_-\right|d_{xy}\right\rangle) \\
&= \left\langle d_{yz}, -2i(d_{x^2-y^2})\right\rangle + \left\langle d_{yz}\left|l_x\right|d_{xy}\right\rangle + \left\langle d_{yz}\left|l_y\right|d_{xy}\right\rangle \\
&= \left\langle d_{yz}, -2i(d_{x^2-y^2})\right\rangle + \left\langle d_{yz}, id_{xz}\right\rangle + \left\langle d_{yz}, d_{yz}\right\rangle
\end{aligned}$$

Thus, only the matrix element involving the angular momentum of y orientation has a nonzero value. Hence, it is reasonable to take T_y into account in the above mentioned coupling procedure.

The spin functions of the singlet or triplet ones along with the x, y, z coordinate can be written as: $\left|S\right\rangle = \frac{1}{\sqrt{2}}\left|\alpha\beta - \beta\alpha\right\rangle$, $\left|T_X\right\rangle = \frac{1}{\sqrt{2}}\left|\beta\beta - \alpha\alpha\right\rangle$, $\left|T_Y\right\rangle = \frac{i}{\sqrt{2}}\left|\beta\beta + \alpha\alpha\right\rangle$, $\left|T_Z\right\rangle = \frac{1}{\sqrt{2}}\left|\alpha\beta + \beta\alpha\right\rangle$, respectively.[2]

Based on the theory above, considering the spatial orbital and spin coupling together, the complete result will be:[3]

$$\begin{aligned}
&\left\langle T_y\left|h_{so}\right|S\right\rangle = \zeta\left\langle \frac{i}{\sqrt{2}}C_{d_{yz}}(d_{yz}^{\beta} + d_{yz}^{\alpha})\left|\vec{l}\cdot\vec{s}\right|\frac{1}{\sqrt{2}}C_{d_{xy}}(d_{xy}^{\alpha} - d_{xy}^{\beta})\right\rangle \\
&= \frac{i}{2}\zeta C_{d_{yz}}C_{d_{xy}}
\end{aligned}$$

The calculated soc matrix elements are listed in **Table S1.**

Table S1. SOC matrix elements between the $^3(d_k\pi^*)$ and $^1(d_l\pi^*)$ states.[1, 3-5]

	$^1(d_{xz}\pi^*)$	$^1(d_{yz}\pi^*)$	$^1(d_{xy}\pi^*)$
$^3(d_{xz}\pi^*)$	0	$-\frac{i}{2}C_{xz}C_{yz}$	$\frac{i}{2}C_{xz}C_{xy}$
$^3(d_{yz}\pi^*)$	$\frac{i}{2}C_{yz}C_{xz}$	0	$-\frac{i}{2}C_{yz}C_{xy}$
$^3(d_{xy}\pi^*)$	$-\frac{i}{2}C_{xy}C_{xz}$	$\frac{i}{2}C_{xy}C_{yz}$	0

Table S2. Electronic transitions of **1** calculated at optimized T_1 geometry by TDDFT in CH_2Cl_2 solution. The solvent effect is modeled by the PCM method.[a]

S_n/T_m	Energy (cm^{-1})	λ (nm)	Major contribution[b]

T_1	18543	539	H→L(0.71)，H-1→L(0.49)，H-2→L(-0.38)
T_2	24745	404	H→L(0.37)，H-2→L(0.71)，H-4→L(-0.38)
S_1	25410	393	H→L(0.98)
S_2	27460	364	H-1→L(0.96)
S_3	29485	339	H-2→L(0.96)
S_4	31100	321	H-3→L(0.91)
S_5	33082	302	H→L+1(0.75)，H→L+2(0.40)，H→L+4（-0.31）

[a] Only the triplet excited states below the first singlet excited states are listed.

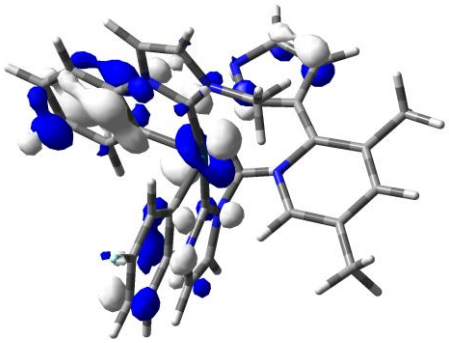
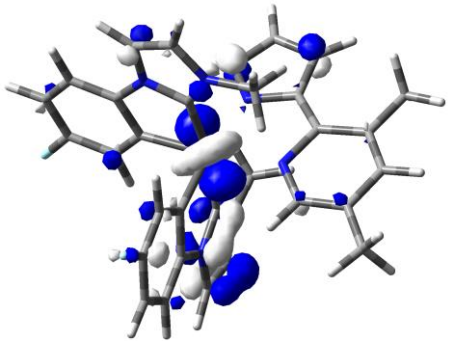
[b] the values in the parentheses are the CI coefficients (a_i) of a particular transition. Only the abs of CI coefficients >0.20 are displayed.

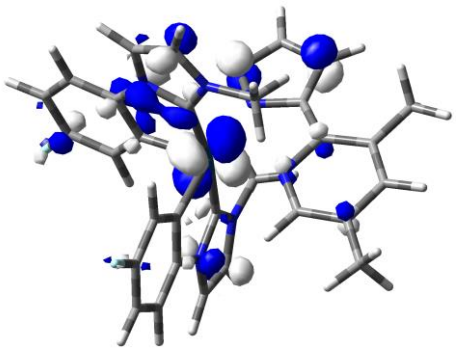
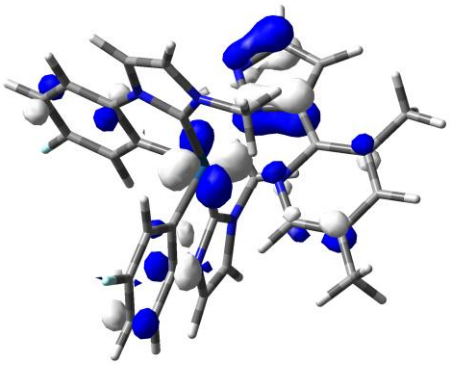
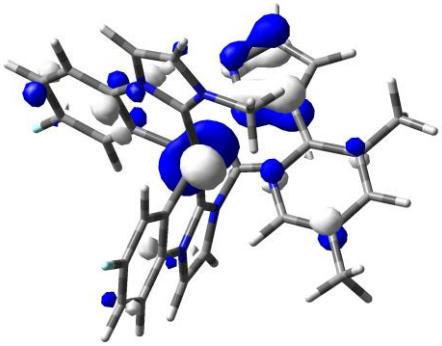
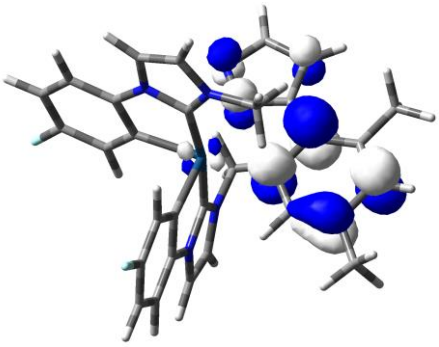
Table S3. The Calculated transition dipole moment (unit: a.u.) from the ground state to the singlet excited state together with the oscillator strengths.[a]

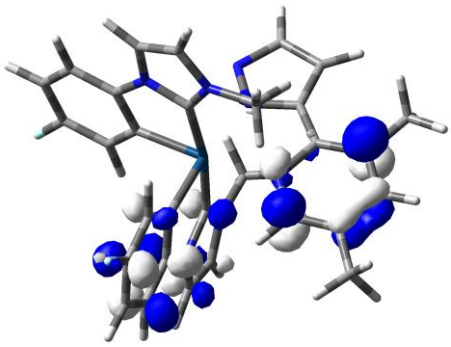
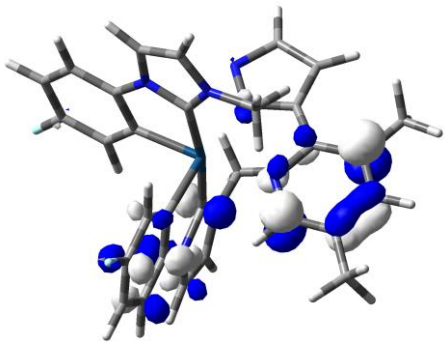
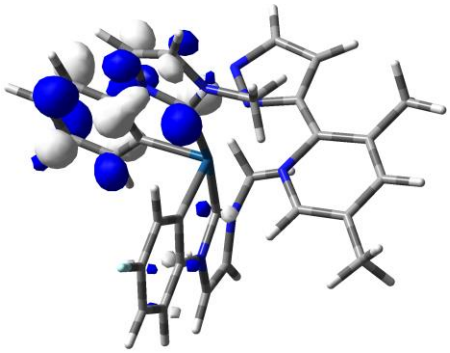
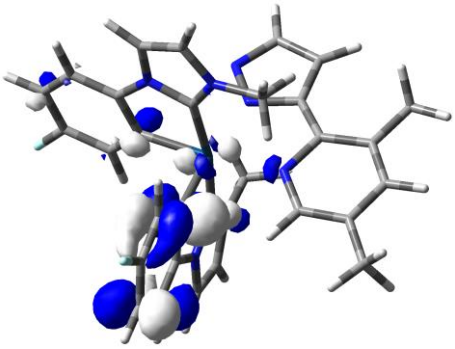
State	X	Y	Z	*f*
S_1	-0.3831	0.6091	0.0705	0.0403
S_2	-0.8662	0.5987	0.0353	0.0926
S_3	-0.5351	-1.0390	-0.1475	0.1243
S_4	0.5266	-0.9062	-0.1891	0.1071
S_5	0.2207	-0.2672	-0.3967	0.0279

a: Oscillator strengths and transition dipole moment are some intrinsic characteristics of the excited states, here we use the larger one obtained in the TDDFT calculation on respective S_0 and T_1 geometry for the following calculation of the radiative decay rates.

Table S4. MO surface and orbital contributions of **1** at optimized T_1 geometry.

MO	MO surface	Nature(c_d[a])
HOMO-4		d_{xz}(0.3187)
HOMO-3		d_{yz}(-0.3575)

HOMO-2		d_{xz}(-0.4242)
HOMO-1		d_{xy}(-0.3067)
HOMO		d_{yz}(-0.3927)
LUMO		π_1*

LUMO+1		π_2*
LUMO+2		π_3*
LUMO+3		π_4*
LUMO+4		π_5*

[a] Only those with $|c_d|>0.3$ are given in **Table S4.**

Table S5. SOC matrix elements $<T_1^{\alpha}|H_{soc}|S_n>$ (cm^{-1}) of **1** calculated at the optimized T_1 geometry. The calculated radiative decay rate constant (k_n/s^{-1}) is also shown in the **Table S5**.

					$E(T_1)$=18543 cm^{-1}				
S_n	$<T_1^x\|H_{soc}\|S_n>$	$<T_1^y\|H_{soc}\|S_n>$	$<T_1^z\|H_{soc}\|S_n>$	$\Delta E(T_1^x)$	$\Delta E(T_1^y)$	$\Delta E(T_1^z)$	$k_n^x/8.478x10^{-30}C \cdot m$	$k_n^y/8.478x10^{-30}C \cdot m$	$k_n^z/8.478x10^{-30}C \cdot m$
S_1		128.85	137.48		-2.418	-2.752		0.0114289	0.0014114
S_2	-105.82	-181.41		-1.256	-3.691		0.010279	-0.01218	
S_3	-137.17		250.91	-1.720		-5.754	0.006708		-0.003382

S_4	108.80	116.09		-0.943	-1.073		-0.007852	-0.001748
S_5								
k_r^{α}			-2.976	-7.052	-9.579	10767.44	2761.4107	516.0841
k_r							4681.6465	

The blank represents that there is no nonzero coupling value at the specified coupling states.

Table S6. Electronic transitions of **2** calculated at optimized T_1 geometry by TDDFT in CH_2Cl_2 solution. The solvent effect is modeled by the PCM method.[a]

S_n/T_m	Energy (cm^{-1})	λ (nm)	Major contributions[b]
T_1	18559	539	H→L(0.54)，H-1→L(0.58)，H-2→L(-0.47)
T_2	24285	412	H→L(0.40)，H-1→L(0.40)，H-2→L(0.61)，H-4→L(0.44)
S_1	24375	410	H→L(0.99)
S_2	26666	375	H-1→L(0.96)
S_3	26900	347	H-2→L(0.95)
S_4	30593	327	H-3→L(0.89)
S_5	32200	311	H→L+2(-0.44)，H→L+1(0.68)，H-4→L(-0.45)

[a] Only the triplet excited states below the first singlet excited states are listed.

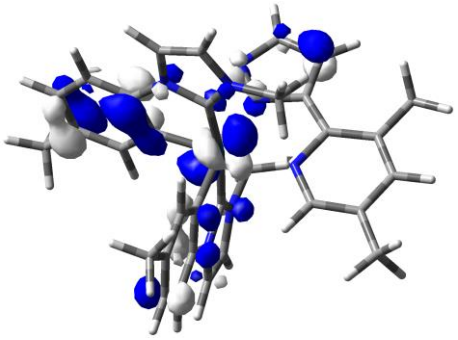
[b] the values in the parentheses are the CI coefficients(a_i) of a particular transition. Only the abs of CI coefficients >0.20 are displayed.

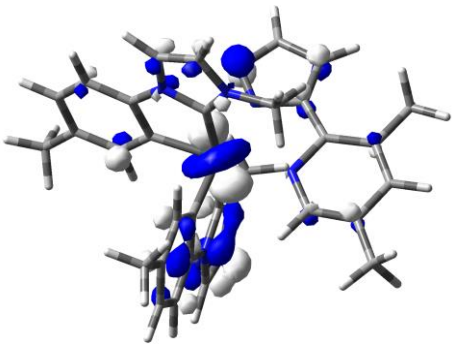
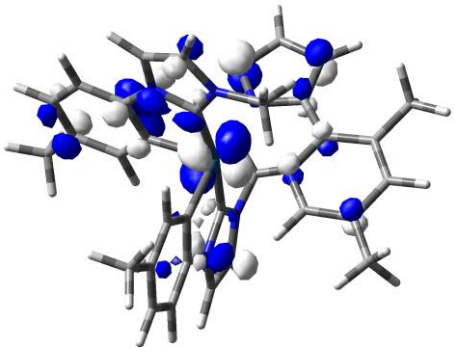
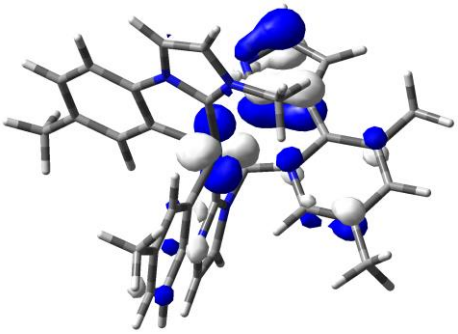
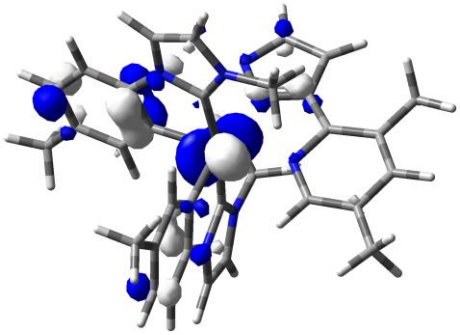
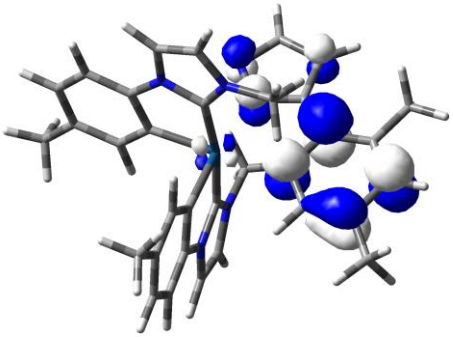
Table S7. The Calculated transition dipole moment (unit: a.u.) from the ground state to the excited state together with the oscillator strengths.[a]

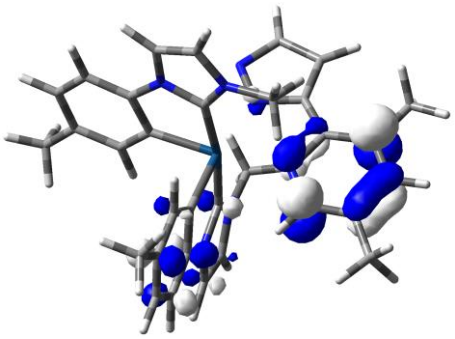
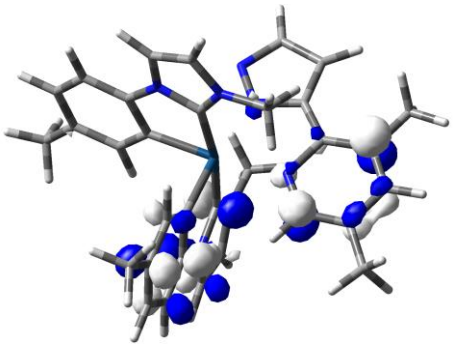
State	X	Y	Z	*f*
S_1	-0.1813	0.4161	0.0196	0.0153
S_2	-0.8815	0.5989	-0.0214	0.0920
S_3	-0.6111	-0.8854	-0.0581	0.1017
S_4	-0.5403	1.0666	0.1091	0.1339
S_5	-0.0392	0.4607	0.4750	0.0430

a: Oscillator strengths and transition dipole moment are some intrinsic characteristics of the excited states, here we use the larger one obtained in the TDDFT calculation on respective S_0 and T_1 geometry for the following calculation of the radiative decay rates.

Table S8. MO surface and orbital contributions of **2** at optimized T_1 geometry.

MO	MO surface	Nature(c_d[a])
HOMO-4		d_{xz}(-0.3542)

HOMO-3		d_{yz}(0.3558)
HOMO-2		d_{xz}(-0.4075)
HOMO-1		d_{yz}(-0.3112)
HOMO		d_{yz}(-0.3417) d_{xy}(0.3733)
LUMO		π_1*

LU MO+1		π_2*
LUMO+2		π_3*

[a] Only those with $|c_d|$>0.3 are given in **Table S8.**

Table S9. SOC matrix elements $<T_1^{\alpha}|H_{soc}|S_n>$ (cm^{-1}) of **2** calculated at the optimized T_1 geometry. The calculated radiative decay rate constant (k_n/s^{-1}) is also shown in the **Table S9**.

				E(T_1)=18559 cm^{-1}					
S_n	$<T_1^x\|H_{soc}\|S_n>$	$<T_1^y\|H_{soc}\|S_n>$	$<T_1^z\|H_{soc}\|S_n>$	$\Delta E(T_1^x)$	$\Delta E(T_1^y)$	$\Delta E(T_1^z)$	k_n^x/8.478x10^{-30}C • m	k_n^y/8.478x10^{-30}C • m	k_n^z//8.478x10^{-30}C • m
S_1	155.67	147.70	142.49	-4.167	-3.751	-3.491	-0.00485	0.0105669	0.0004802
S_2		-132.98	126.06		-2.181	-1.960		-0.009823	-0.000333
S_3	171.57		311.37	-3.529		-11.623	-0.01019		-0.001757
S_4		140.86	-133.53		-1.649	-1.482		0.012485	-0.001211
S_5	-71.23		-129.27	-0.372		-1.225	0.000205		-0.004501
k_r^{α}				-8.068	-7.581	-19.781	8231.553	6547.1485	2005.6726
k_r								5594.7913	

The blank represents that there is no nonzero coupling value at the specified coupling states.

Table S10. Electronic transitions of **3** calculated at optimized T_1 geometry by TDDFT in CH_2Cl_2 solution. The solvent effect is modeled by the PCM method.[a]

S_n/T_m	Energy (cm^{-1})	λ (nm)	Major contribution[b]
T_1	16259	615	H→L(0.91)，H-1→L(-0.31)
T_2	20257	494	H-2→L(0.45)，H-3→L(0.72)
S_1	21051	475	H→L(0.98)
S_2	23128	432	H-1→L(0.98)
S_3	26421	378	H-2→L(0.92)，H-4→L(-0.28)
S_4	28463	351	H→L+1(-0.44)，H-2→L(0.31)，H-3→L(-0.57)，H-4→L(0.59)
S_5	28562	350	H→L+1(0.83)，H-3→L(-0.52)

[a] Only the triplet excited states below the first singlet excited states are listed.

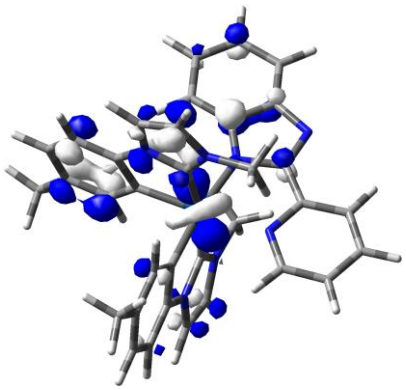
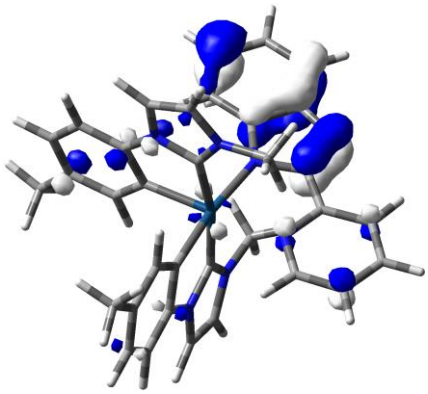
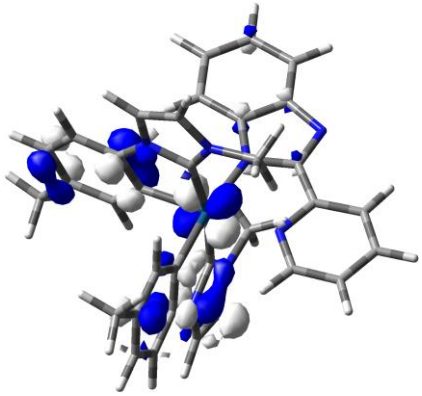
[b] the values in the parentheses are the CI coefficients(a_i) of a particular transition. Only the abs of CI coefficients >0.20 are displayed.

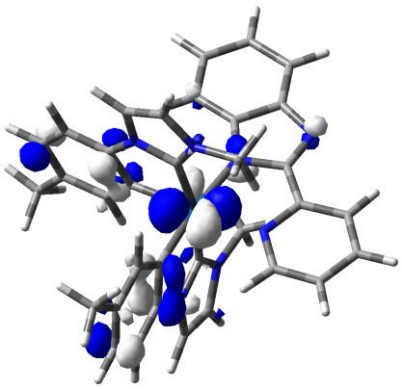
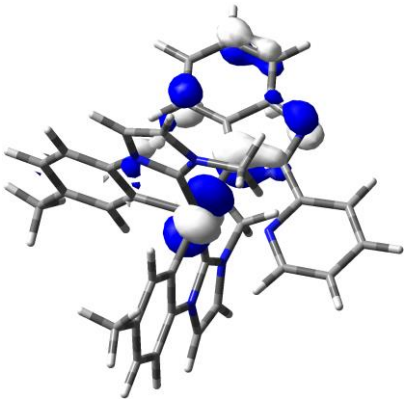
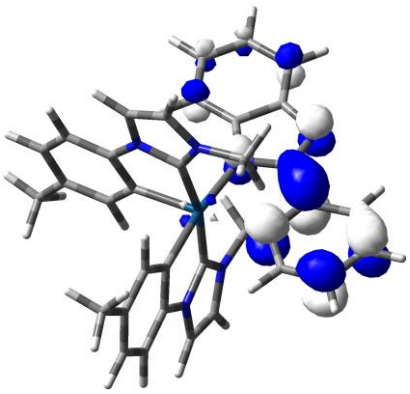
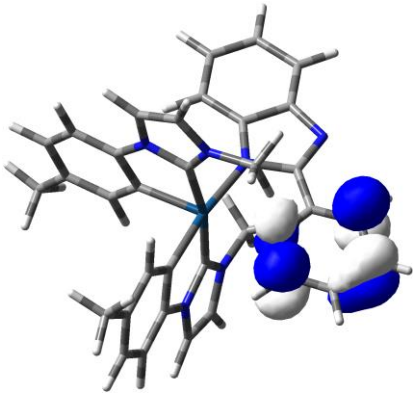
Table S11. The Calculated transition dipole moment (unit: a.u.) from the ground state to the excited state together with the oscillator strengths.[a]

State	X	Y	Z	*f*
S_1	0.0986	0.2267	0.0052	0.0046
S_2	0.2526	-0.8037	-0.0141	0.0573
S_3	1.5167	0.4464	-0.0003	0.2202
S_4	-0.0847	0.0802	-0.0836	0.0019
S_5	-1.3003	-1.1096	0.0552	0.2692

a: Oscillator strengths and transition dipole moment are some intrinsic characteristics of the excited states, here we use the larger one obtained in the TDDFT calculation on respective S_0 and T_1 geometry for the following calculation of the radiative decay rates.

Table S12. MO surface and orbital contributions of **3** at optimized T_1 geometry.

MO	MO surface	Nature(c_d[a])
HOMO-4		π_1
HOMO-3		π_2
HOMO-2		d_{yz}(0.3793)

HOMO-1		d_{xy}(0.5248)
HOMO		d_{xz}(0.5091)
LUMO		π_3*
LUMO+1		π_4*

[a] Only those with $|c_d|>0.3$ are given in **Table S12.**

Table S13. SOC matrix elements $<T_m^{\alpha}|H_{soc}|S_n>$ (cm^{-1}) of **3** calculated at the optimized T_1 geometry. The calculated radiative decay rate constant (k_n/s^{-1}) is also shown in the **Table S13**.

$E(T_1)$=16259 cm^{-1}

S_n	$<T_1^x\|H_{soc}\|S_n>$	$<T_1^y\|H_{soc}\|S_n>$	$<T_1^z\|H_{soc}\|S_n>$	$\Delta E(T_1^x)$	$\Delta E(T_1^y)$	$\Delta E(T_1^z)$	$k_n^x/8.478x10^{-30}C \cdot m$	$k_n^y/8.478x10^{-30}C \cdot m$	$k_n^z/8.478x10^{-30}C \cdot m$
S_1	179.67			-6.737			0.003696		
S_2	522.67			-39.771			0.019219		
S_3		-126.07	-355.86		-1.564	-12.462		-0.005538	0.00001051
S_4		-42.68	-120.46		-0.149	-1.189		-0.00028	0.0008251
S_5									
k_r^{α}				-46.508	-1.713	-13.651	19595.75	1263.1755	26.056437
k_r								6961.6603	

The blank represents that there is no nonzero coupling value at the specified coupling states.

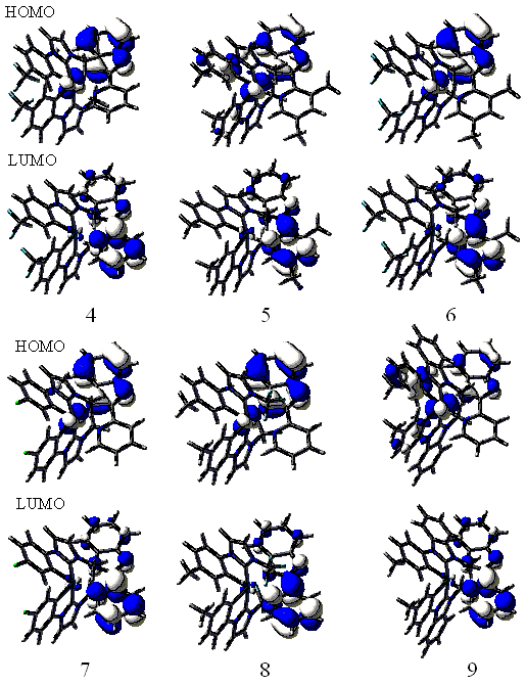


Fig. S3. Diagrams of the related frontier orbitals for complexes **4-9** with different substituents at their optimized S_0 geometry respectively.

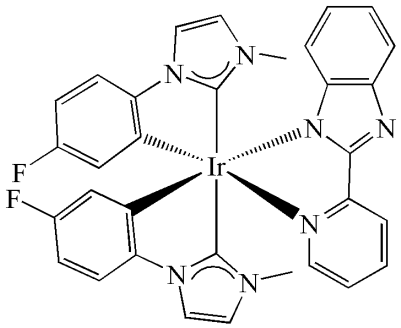


Fig. S4. Molecular graph for complex with F as the substituent at R_1 sites.

Table S14. Calculated frontier molecular orbital energy levels and the energy gap for complex with F as the substituent at R_1 site based on optimized S_0 geometry.

HOMO	LUMO	Energy gap
-5.52	-1.64	3.89

Table S15. NBO analysis for N-C bond between carbene ring and the substituents on it of complexes **3** and **8**.

Complexes	Occupancy	Bond orbital type	Contributions
3	1.9894	BD(1)	64.26%N

			35.74%C
8	1.9878	BD(1)	63.55%N
			36.45%C
	1.6322	BD(2)	97.48%N
			2.52%C

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