苯胺基团对一类Pt(II)磷光发光材料非辐射跃迁调控的理论研究

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摘要:采用密度泛函(DFT)和含时-密度泛函(TD-DFT)方法研究二苯胺基团对一类Pt(II)配合物(M1~M3)光学性质的调控。通过 与实验合成的分子对比,揭示苯胺基团取代位置和数量对电子结构和光学性质的调控规律。引入苯胺基团可有效地增大金属 和配体的 π 共轭性。逐渐增多苯胺基团导致 M3 分子可以有效地增大吸收光谱的强度和金属到配体的电荷转移(MLCT)占比, 有利于金属对光的吸收和自旋轨道耦合。M1~M3 的发射峰在 602~630 nm,发射光谱归属为³MLCT 和配体之间的电荷转移 (³LLCT)。通过对非辐射跃迁过程,即T₁(³MLCT) → TS → 金属中心三重态³MC(*d*-*d*)的研究,发现当二苯胺取代基团引入位置可 以有效地增大分子内空间位阻时,形成S₀和T₁的系间交叉 MECP能量变得更高,从而抑制了非辐射的概率,有利于发光性能 提高。

关键词:密度泛函理论;激发态;非辐射跃迁过程;金属中心三重态
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Theoretical Study on Regulation of Aniline Moiety on Non-radiative Transition of a Kind of Pt(II) Phosphorescent Materials

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Abstract: A series of efficient red platinum-based emitter with functionalized diphenylamine moiety (M1~M3) were designed and investigated by density functional theory (DFT) and time-dependent DFT (TD-DFT). The effect of different substituent positions on the electronic structures and optical properties were fully explored by compared with the synthesized complex. The introduction of diphenylamine moiety could effectively strengthen the π -conjugation interaction between the metal and ligand. By gradually increasing the amount of diphenylamine moiety, the intensities and the participation of metal-to-ligand charge-transfer (MLCT) for the absorption bands of M3 were enhanced, which are beneficial to collect light energy participation of metals and increase the spin-orbital coupling effect. M1~M3 exhibited red emission with the peak wavelengths at 602~630 nm. These emission spectra are mixtures of ³MLCT and ligand to ligand charge - transfer (³LLCT) character. The possible non - radiative process T₁ (³MLCT) \rightarrow TS \rightarrow triplet metal-centered ³MC (*d-d*) state were deeply investigated, and the results show that the possibility of the non-radiative process will decrease because the surface crossing at a minimum energy crossing point (MECP) between T₁ and S₀ state is difficult to populate when the functionalized diphenylamine moiety is useful to enhance steric hindrance.

Keywords: density functional theory; excited state; non-radiative process; metal-centered triplet state

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0 Introduction

Organometallic complexes of Pt (II) and/or Ir (III) play important roles on the phosphorescent organic light-emitting diodes (PhOLEDs). Due to the strong spin-orbit coupling (SOC) induced by the metal atoms, the singlet and triplet excitions contribute to the emission^[1-4]. For many years, many efforts have been made to synthesize highly efficient and stable materials^[5-8]. However, it is still a crucial task to work out detailed understanding of the deactivation mechanism because of the complicated intersystem crossing (ISC). Nowadays, density functional theory (DFT) and time dependent DFT (TD - DFT) calculations are the most widely used techniques to provide the relationship between structure and optical properties^[9-13]. Especially, a type of efficient Pt(II) emitters is obtained by introducing the diphenylamine functional substitutions (1a~ **1c**) as shown in Fig. 1a^[14]. These primary results show the functionalized diphenylamine moiety can tune the non - radiative process. However, the most important position (R₂ position of carbazole ring, as shown in Fig. 1a), which is closed to biphenyl substitutions, may show greatly influence on reaching triplet metal centered (³MC) state. In particular, once populating in ³MC state, it can return to the local minimum structure on T₁ surface (T1) or non-radiative decay process to S0 state through the minimal energy crossing point (MECP) between T_1 and S_0 state. Therefore, these interesting prospects lead us to investigate this type pf Pt(II) emitters (M1~M3) in order to set a firmer basis and obtain a deeper understanding of its properties.



Fig.1 (a) Schematic structures with atomic labeling for metal-ligand bond of studied complexes M1~M3 and referenced complexes 1, 1a~1c^[14]; (b) Optimized structures of M1~M3 in ground states

1 Computational method

In this work, the hybrid density functional, PBE0, was employed for all calculations using the program package in Gaussian 09 program package^[15]. The geometry optimizations of the ground-state (S_0) and lowest-lying triplet excited state (T_1) were calculated using restricted and unrestricted DFT with hybrid - type Perdew - Burke - Ernzerh of exchange correlation functional (PBE0)^[16-17]. The effective core potential (ECP) basis sets of the Stuttgart group (SDD)^[18-19] and 6-31G (d) basis set was used for Pt(II) and non-metal atoms, respectively. Frequencies calculations were calculated at the same level to ensure that they were minimums on

the potential energy surface. The stability calculations were performed for all these optimized geometries to confirm these wavefunctions were stable. Based on these optimized S_0 and T_1 geometries, the absorption and emission spectra of the investigated complexes were calculated by TDDFT/PBE0 and TDDFT/PBE38 in a CH₂Cl₂ solution, respectively. The ³MC states were computed by UPBE0 method. The transition state (TS) geometries between T_1 and ³MC state were searched. The connection of T_1 and ³MC state through the TS was confirmed by the intrinsic reaction coordinate (IRC) calculation. The minimal energy crossing points (MECP) for T_1/S_0 surface crossing were calculated by sobMECP program^[20-21], which is modified version of Harvey's MECP program and is performed with the Gaussian 09 program. Frequency calculations were run at the same level of theory and the absence of imaginary frequencies ascertained the nature of these points as minima.

2 **Results and discussion**

2.1 Ground state structures and lowest-lying triplet state

The molecular structures of complexes M1~M3 are depicted in Fig. 1. The optimized geometries of these complexes in S_0 and T_1 state are collected in Table 1. As shown in Table 1, the N1—Pt—N2 and N1—Pt—C2 bond angles of M1 in S_0 state were 100.35° and 166.28°, respectively, while its N1—N2— C2—C1 angle was 14.95°. The N1—Pt—N2, N1— Pt—C2, as well as N1—N2—C2—C1 bond angles of M2 and M3 are similar with those of M1. Clearly, all the complexes adopt distorted square-planar coordination geometries around the metal center, which are similar with the referenced complexes 1 and $1a\sim1c^{[14]}$. Compared with the synthesized molecule 1, the introduction of diphenylamine moiety can effectively strengthen the π -conjugation interaction between the metal and ligand, and thus the metal bond lengths are shortened. Especially, the Pt—N1 and Pt—C1 bond of **M2** and **M3** were decreased by *ca*. 0.002 nm and *ca*. 0.004 nm, respectively, compared with complex $1^{[14]}$. On going from S₀ state to T₁ state, the large structural modifications of these complexes happened on the same ligand. The Pt—N1 and Pt—C1 bonds of **M2** and **M3** were shortened by *ca*. 0.004 nm and *ca*. 0.006 nm, while the Pt—N1 and Pt—C1 of **M1** were decreased by *ca*. 0.005 nm and *ca*. 0.002 nm, respectively. The strengthened metal-ligand interaction may raise the probability of charge transfer from the metal to the ligand, which will be further discussed in Section 2.2.

The spin density of T_1 state of studied complexes is shown in Fig. 2. For M1~M3, the electron density was mainly located at the metal center and ligands, thus T_1 state of these complexes is MLCT characteristic. T_1 state with MLCT character is useful to tune spinorbit coupling and therefore facilitates the ISC. Besides, a distinguish contribution from the diphenylamine moiety have been detected on M2 and M3, indicating that the photophysical properties can be well tuned by diphenylamine moiety.

	M1		M2		M3	
	S_0	T_1	S_0	T_1	S_0	T_1
Pt—N1	0.214	0.209	0.212	0.208	0.212	0.208
Pt—C1	0.195	0.193	0.199	0.193	0.199	0.193
Pt—N2	0.214	0.215	0.214	0.215	0.214	0.214
Pt—C2	0.199	0.199	0.195	0.199	0.195	0.199
N1—Pt—N2	100.35	98.93	100.18	99.33	100.27	98.89
N1—Pt—C2	166.28	167.39	165.63	168.09	165.71	166.50
N1—N2—C2—C1	14.95	13.55	14.28	12.82	14.22	14.74

 Table 1
 Selected optimized electron geometries (bond length (nm), bond angle (°), dihedral angles (°)) of M1~M3 at S₀ and T₁ states



Fig.2 Spin density in the lowest-lying triplet states for M1~M3

2.2 Absorption wavelength and emission spectra

The calculated absorption wavelength $(\lambda, \text{ nm})$, transition energy (E, eV), oscillator strengths (f), dominant configurations, and transition assignments of main absorption spectra are collected in Table 2. The simulated absorption spectra of these complexes are depicted in Fig. 3, together with the absorption spectrum of synthesized compound $\mathbf{1}^{[8]}$. To analyze nature of these excitations, the molecular orbital composition and the characteristics of Pt*d* orbitals are shown in Fig.4.

As depicted in Fig.3, complex M2 displayed intense high-energy absorption band (230~300 nm)

	λ / nm	E/eV	£	M : C .:		
		- ,	J	Main configuration	Assignment	Contribution of MLCT / %
				M1		
S_1	483.8	2.56	0.036 1	H−1→L(0.68)	LLCT	0
S_2	442.7	2.80	0.487 5	H→L(0.68)	MLCT/LLCT	8.6
S_{19}	303.4	4.09	0.252 4	H→L+6(0.46)	MLCT/LLCT	4.32
				$H-1 \rightarrow L+5(0.37)$		
S_{28}	281.4	4.41	0.299 5	H−3→L+2(0.45)	MLCT/LLCT	7.84
				$H-1 \rightarrow L+7(-0.29)$		
				H−5→L+2(−0.26)		
				M2		
S_1	496.9	2.50	0.090 4	H→L(0.69)	MLCT/LLCT	5.86
S_{17}	305.3	4.06	0.323 2	H−6→L(0.39)	MLCT/LLCT	15.1
				H−2→L+3(0.36)		
S_{29}	277.8	4.46	0.341 4	H→L+9(0.47)	MLCT/LLCT	7.49
				M3		
S_1	494.5	2.51	0.088 8	H→L(0.64)	MLCT/LLCT	6.28
\mathbf{S}_2	449.8	2.76	0.311 2	H−1→L(0.58)	LLCT	0
S_{18}	312.5	3.97	0.203 9	H−5→L(0.35)	MLCT/LLCT	19.75
				H−3→L+2 (0.25)		
				H−2→L+2 (0.29)		
				H→L+5 (0.24)		
S_{22}	305.4	4.06	0.219 2	H−6→L (0.42)	MLCT/LLCT	6.99
				H−3→L+3 (−0.38)		
(10^4) (a) (10^4) (10^4) (10^4) (10^4) (10^4) (10^4) (10^4)	A		M1 M2 M3	7×10^{4} (b) 6×10^{4} (c) 6×10^{4} (b) $(1-100 \cdot 1)^{1/9}$ (c) $(1-100 \cdot 1)^{1/9}$ (c) $(1-100 \cdot 1)^{1/9}$ (c) 3×10^{4} (c) 2×10^{4} (c) 1×10^{4} (c) 1×10^{4} (c) $(1-100 \cdot 1)^{1/9}$	300 200 100 0 560 580 600 620 Wavelength / nm	640 RT 77 K

Table 2 Adsorption spectrum calculation results of M1~M3

Inset: T1 absorption transition, reproduced with permission from Ref.^[8]

Fig.3 (a) Simulated absorption spectra for M1~M3 in CH₂Cl₂ solution; (b) Absorption spectrum (left) of synthesized compound 1 measured in CH₂Cl₂ at room temperature and emission spectra (right) measured in CH₂Cl₂ at room temperature (solid line) and in 2-methyl-THF at 77 K (dash-dot line)



Fig.4 Calculated components of Ptd for the main transition orbitals

and weaker band in the region of 450~550 nm, which can display similar curves to the absorption spectrum of experimental molecule 1^[14]. Especially, the absorption spectra of M1 and M3 were slightly blue-shifted and the absorption intensity were greatly enhanced. Therefore, the possibility of the intersystem crossing (ISC) from the singlet and triplet state may be well tuned by the introduction of diphenylamine groups. As listed in Table 2, the first strong absorption peak of M1 was at 442.7 nm. The dominant orbital transition is HOMO \rightarrow LUMO. Because of the large contribution of Ptd (10.7% d_{x}), the absorption peak of **M1** at 442.7 nm was 8.6% MLCT character. The largest absorption peak of M1 at 281.4 nm (S₂₈ state, 7.84%MLCT) shared a similar transition character with that of synthesized 1 at 294 nm (S_{18} state) with 9.6% MLCT. For M2, the largest absorption peaks were located at 305.3 and 277.8 nm. According to Table 2 and Fig.4, the peaks at 305.3 nm (15.1%) and 277.8 nm (7.49%) possessed large amounts of MLCT character. Clearly, introducing the diphenylamine at the R₂ position is more suitable for enhancing the light energy collection and singlet triplet transitions than at R_1 position. Besides, for M3, the distinguishable absorption peaks around 312.5 and 305.4 nm possessed 19.75% and 6.99% MLCT character, respectively. Obviously, the participation of MLCT in the absorption spectra can be increased by gradually increasing the amount of diphenylamine moiety. The increased amount of MLCT might be efficient to collect light energy participation of metals and increase the spin-orbital coupling effect. Meanwhile, the intensities of the absorption bands of M3 were much larger than those of **M1**, which may result in high intensity for the triplet excited states through the ISC procedure, and hence increasing the phosphorescence efficiency, which is consistent with the analyses of molecular geometry.

The emission energies and wavelength, transition characters are listed in Table 3. The calculated phosphorescent spectrum of **M1** was 631.6 nm, demonstrat-

	λ / nm	Main configuration	Orbital contribution	Assignment
M1	631.6	$0.50L \rightarrow H$	$12.2\% d_{xz}$ +84.2% π (ligand) \rightarrow 95.6% π *(ligand)	³ MLCT/ ³ LLCT
		$-0.30 L \rightarrow H-2$	$16.5\% d_{y_z}$ +76.2% π (ligand) \rightarrow 95.6% π *(ligand)	
M2	615.6	$0.54L \rightarrow H$	$8.9\% d_{_{y_2}}$ +89.3% π (ligand) \rightarrow 95.8% π *(ligand)	³ MLCT/ ³ LLCT
		$0.24L \rightarrow H-1$	$7.4\%d_{_{y2}}$ +88.2% π (ligand) \rightarrow 95.8% π *(ligand)	
		$-0.23L \rightarrow H-2$	$15.3\% d_{_{yz}}$ +82.9% π (ligand) \rightarrow 95.8% π *(ligand)	
M3	602.7	$0.47L \rightarrow H$	$4.9\%d_{xz}$ + $4.7\%d_{yz}$ + $88.7\%\pi(\text{ligand}) \rightarrow 95.8\%\pi^*(\text{ligand})$	³ MLCT/ ³ LLCT
		$0.30L \rightarrow H-1$	$98.5\%\pi(\text{ligand}) \rightarrow 95.8\%\pi^*(\text{ligand})$	
1 ^[14]	626			

Table 3 Phosphorescence emission spectrum calculation results of M1~M3

ing that it is potential candidates for red emitting materials. Different from the referenced molecules (1a~1c) and M1, the calculated phosphorescent spectrum of complexes M2 (615.6 nm) and M3 (602.7 nm) were blue-shifted, which is caused by that the internal occupied orbitals are dominant transition orbitals, and the energy gaps of transition orbitals increased. In addition, due to the significant contribution of Ptd orbital in the transition orbital, the phosphorescence spectra of these compounds can be described as ³MLCT/³LLCT character. As well accepted, the contribution of ³MLCT in T₁ state will be beneficial to enhance the SOC and transition probability. The calculation results show that the introduction of the diphenylamine moiety at different position could influence the emission spectra, which can provide useful information for further designing highly efficient emitters.

2.3 Deactivation pathway

As described in the introduction, ³MC excited state acts as a very efficient activated non-radiative channel for the deactivation to S_0 state, due to the presence of MECP between S_0 and ³MC potential energy surface. In view of this, we attempt to optimize ³MC state by increasing the metal-ligand bond lengths. The optimized geometries of the TS state between T_1 state and ³MC state as well as T_1 state are also shown in Fig. 5. The calculated IRCs for $T_1 \rightarrow {}^3MC$ pathways of studied complexes are shown in Fig. 6, together with the spin density distributions.

For M1, the metal-ligand bond length Pt-N1 of ³MC state was largely stretched (0.444 nm), which was much larger than those of complex 1 and $1a^{[14]}$. Coupled with the dissociation bond length, M1 showed large out of plane on the 4-phenylpyridine ligand. The intermolecular dihedral angle θ_1 between the carbazole and biphenyl moiety increased from 4.2° (T₁) to 144.0° (³MC₁), as shown in Fig. 5. And the Pt—N1 bond increased by 0.151 nm from TS_1 to T_1 state. Coupled with the large geometry conformation, the energy barrier from T_1 to ³MC state was 147.0 kJ·mol⁻¹ for M1. And the MECP state of M1 was 67.0 kJ·mol⁻¹ higher than that of ³MC, which was similar with that of 1^[14]. The spin densities of TS, ³MC, and MECP state for these complexes with the typical feature of the large population at Pt atoms. Thus, the nonradiative deactivation pathway can be assigned to T_1 (MLCT/ $\pi \rightarrow \pi^*$) \rightarrow TS $(d-d) \rightarrow {}^{3}MC (d-d) \rightarrow MECP (d-d)$. Clearly, the introduction of diphenylamine moiety at R₁ position plays small effect on tuning the non-radiative decay process.

For **M2**, because the large steric hindrance limited torsion of biphenyl moiety, the Pt—N1 bond length of $T_{1.2}$ (MLCT/*d*-*d*) state was 0.398 nm, which was shortened *ca*. 0.05 nm relative to ${}^{3}MC_{1}$ (*d*-*d*) state of **M1**. Therefore, the conjugation interaction between the metal center and ligand were still strong, and thus $T_{1.2}$ state still belonged to ${}^{3}MLCT$ character. The process of T_{1} (MLCT/ $\pi \rightarrow \pi^{*}$) \rightarrow TS₁ (*d*-*d*) \rightarrow $T_{1.2}$ (MLCT/*d*-*d*) needed to overcome a large energy barrier of 143.6 kJ·mol⁻¹.



Fig.5 Optimized geometries of T1, TS, MC, MECP states for M1~M3



Fig.6 Energy levels of reaction path leading from triplet excited state T1 state to MECP state

Next, starting from T_{1-2} state, the Pt—N2 bond was broken as well as the dihedral θ_2 between pyridine and carbazole rotated from T_{1-2} to 3MC_1 . The TS₂ connecting both T_{1-2} and 3MC_1 were optimized. The metal-ligand bonds Pt—N1 in TS₂ and 3MC_1 became larger by 0.022 and 0.026 nm than those in T_{1-2} state of **M2**, respectively, while Pt—N2 of **M2** in TS₂ and 3MC_1 became 0.033 and 0.138 nm relative to T_{1-2} state. The activation barrier of the reaction $T_{1-2} \rightarrow TS_2 \rightarrow {}^3MC_1$ of **M2** was 101.7 kJ·mol⁻¹. Besides, the MECP of **M2** was 60.7 kJ·mol⁻¹, higher than that of 3MC_1 and thus the nonradiative deactivation channels of **M2** became much difficult.

Similar with **M2**, the nonradiative deactivation channels of **M3** followed two steps: one was T_1 (MLCT/ $\pi \rightarrow \pi^*$) \rightarrow TS₁ (*d*-*d*) \rightarrow T₁₋₂ (MLCT/*d*-*d*) with 144.9 kJ·mol⁻¹ energy barrier; the other one was T_{1-2} (MLCT/*d* -*d*) \rightarrow TS₂ (*d*-*d*) \rightarrow ³MC₁ (*d*-*d*) with 102.2 kJ·mol⁻¹. For the first step, the Pt—N1 bond length of T₁ state for M3 was elongated and the intermolecular dihedral angle θ_1 was rotated. T₁₋₂ Thus, T₁ distortion opened up the first deactivation channel, which appeared for state of **M3**. T₁₋₂ state was connected to ³MC₁ state via a TS₂ state. The MECP of **M3** was found in 59.5 kJ·mol⁻¹ above ³MC₁ minimum. Furthermore, the energy gap between T_1 and MECP of M2 and M3 were *ca*. 206.7 kJ·mol⁻¹, which were much higher than that of M1 (192.0 kJ·mol⁻¹). Thus, the high energy of MECP state of M2 and M3 makes its T_1 state more stable; a deactivation pathway via the MECP state could be difficult. Moreover, the introduction of phenylamine moiety at R_2 position could result in difficult nonradiative decay and possible increase of the quantum efficiency.

3 Conclusions

A detailed theoretical study on Pt(II) cyclometalated complexes with diphenylamine group were carried out by DFT and TDDFT methods. The absorption spectra and emission spectra of these complexes are significantly affected by the diphenylamine substituents and their positions. The potential energy profiles for the nonradiative decay from T₁ of studied complexes were explored to reveal the effect of nonradiative decay on phosphorescence. The calculated results show that the deactivation process is via MECP state. **M2** and **M3** have much higher energy of MECP state and larger energy barrier through the process of T₁ (MLCT/ $\pi \rightarrow \pi^*$) \rightarrow TS₁ (*d*-*d*) \rightarrow T₁₋₂ (MLCT/*d*-*d*) \rightarrow TS₂ (*d*-*d*) \rightarrow ³MC₁ (*d*-*d*) than that of **M1**. Thus, a deactivation pathway of **M2** and **M3** via the MECP state could be difficult. So, the introduction of phenylamine moiety at R_2 position could result in difficult nonradiative decay and possible increase of the quantum efficiency, which sheds light on a better understanding of the excited-state behavior of this type of Pt emitters.

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