The effect of group-substitution on structures and photophysical properties of rhenium(I) tricarbonyl complexes with pyridyltetrazole ligand: A DFT/TDDFT study

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Abstract

A series of rhenium(I) tricarbonyl complexes having a general formula $fac-[Re(CO)_3(L)(R-N^{\wedge}N)]$ ($L = Br$; $N^{\wedge}N =$ tert-butylated pyridyltetrazole; $R = -H$, **1**; $-NO_2$, **2**; $-CN$, **3**; $-OCH_3$, **4**; $-CH_3$, **5**) have been investigated theoretically by density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods. The calculated results reveal that introductions of different groups on R position of $N^{\wedge}N$ ligand can induce changes on electronic structures, photophysical properties and emission quantum yield for these complexes. When the electron-withdrawing groups ($-NO_2$ and $-CN$) are introduced in complex **2** and **3**, the lowest energy absorption and emission bands are red-shifted compared with that of **1**. On the contrary, the introduction of electron-donating group ($-OCH_3$ and $-CH_3$) in complex **4** and **5** cause corresponding blue-shifted. For these complexes, the stronger electron-donating ability of introduced group on $N^{\wedge}N$ ligand is, the larger blue-shifted of the lowest energy absorption and emission bands is. The solvent effect on absorption and emission spectrum indicates that the lowest-energy absorption and emission bands have both red shifts with the decrease of solvent polarity. The electronic affinity (EA), ionization potential (IP) and reorganization energy (λ) results show that complex **4** may be suitable to be used as an emitter in organic light-emitting diodes OLEDs. Meanwhile the emission quantum yield of complex **4** is possibly higher than other complexes.

Keywords: organometallic compounds; photoemission; computer modelling and simulation; electronic structure

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1. Introduction

Phosphorescent organic light-emitting diodes (OLEDs) have attracted an increasing attention due to their potential applications in full-color display, large-area solid-state lighting, flat panel displays as well as flexible screens. These applications are already commercialized in mobile phones and TV sets [1-2]. And red, green and blue light-emitting phosphorescent materials are indispensable for full-color displays and white OLED lighting. Among these phosphorescent materials, the blue counterparts have relatively inferior performance in terms of color purity, luminous efficiency and durability. To obtain higher phosphorescence efficiency, the heavy transition metal with d^6 configuration complexes, such as rhenium(I), osmium(II), iridium(III) and ruthenium(II), were investigated extensively as electron luminescent emitters of OLEDs in experimental and theoretical studies [3-9]. This is due to the heavy-atom-induced strong spin-orbit coupling (SOC) effect, which leads to partially allowed intersystem crossing (ISC) and phosphorescence. Among these metal ion complexes, rhenium(I) complexes with $fac-[Re(CO)_3]^+$ also show the triplet metal-to-ligand charge transfer (3MLCT) excited state can emit molecular phosphorescence for the strong SOC effect. And such complexes have unique chemical stability, strong visible absorption, excited state reactivity, photoredox chemistry and catalytic properties. So they have a wider range of application, such as photocatalytic CO_2 reduction, solar energy conversion, biological labels and probes, imaging microscopy, photoswitches, luminescent metallogels and signaling [10-16].

The $fac-[Re(N^{\wedge}N)(CO)_3(L)]^{n+}$ complexes are the most popular Re(I) complexes for their luminescent properties [17-22], where $N^{\wedge}N$ ligand represents a neutral diimine ligand, such as 1,10-phenanthroline(phen) or 2,2'-bipyridine(bipy), L is an ancillary ligand and $n = 0$ or 1 depending on the anionic or neutral charge of L ligand. And rich variety of researches have successfully proven that properties of transition metal complexes are varied by the introduction of differently functional groups, such as electron-donating groups ($-NH_2$, $-OCH_3$, $-CH_3$) or -withdrawing groups ($-F$, $-Cl$, $-CN$, $-NO_2$) [23-27]. Recently, the photophysical properties of mononuclear and dinuclear tricarbonyl rhenium(I) tetrazolato complexes and the indirect influence of the tetrazolato ancillary ligand in governing the relative energy of the 3MLCT [$5d(Re) \rightarrow \pi^*(diimine)$] excited states via stabilization or destabilization of 5d orbitals of Re have been researched by Wright et al. [28-29]. As a continuation of the work, $fac-[Re(CO)_3(L)(N^{\wedge}N)]$ ($L = Cl$ or Br ; $N^{\wedge}N =$ tert-butylated pyridyltetrazole) were

successfully synthesized [30]. The photophysical and electrochemical properties of these species were also investigated and corroborated by computational calculations. However, theoretical studies on the effects of substituted groups attached N[^]N ligand in these Re(I) complexes are absence.

With the aforementioned in mind, on the basis of the synthesized *fac*-[Re(CO)₃(L)(R-N[^]N)] (L = Br; N[^]N = tert-butylated pyridyltetrazole) complex **1**, the introduction of differently substituted groups (-NO₂, **2**; -CN, **3**; -OCH₃, **4**; -CH₃, **5**) on R position of N[^]N ligand have been designed theoretically in this work. They have been investigated by density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods. Comparison of ground-state geometries, electronic structures, spectral properties, electronic affinity (EA), ionization potential (IP), reorganization energy (λ) and emission quantum yield (Φ) of five complexes were carried out. The main goal of theoretical investigations is to understand the relationship between different groups and structure, photophysical properties, emission quantum yield. Moreover, the theoretical study may offer guidelines on the applications of these complexes in white OLED lighting in future.

2. Computational methodology

The singlet ground state (S₀) and lowest lying triplet excited state (T₁) geometries of **1-5** were optimized by DFT [31] with restricted and unrestricted PBE1PBE, which is a hybrid Hartree-Fock/density functional model approach based on the Perdew–Burke–Erzenrhof (PBE) functional [32-34], where the HF/DFT exchange ratio is fixed a priori to 1/4. The LANL2DZ basis set [35-37] was applied for Re atom together with 6-31G(d) basis set [38-40] for other atoms. Vibrational frequency calculations, in which there is absence of imaginary frequency for all configurations, confirm that they are minimum point on the potential energy surface.

To explain the rationality of the method and basis set, complex **1** was selected to calculate structure parameters, the lowest energy absorption and emission bands with different functionals together with experimental data in Table S1 and Table S2 (Supporting material). Compared with the experimental values, the PBE1PBE functional has the best performance. Meanwhile, the same characters of complex **1** were obtained by LANL2DZ/6-31G(d) and other larger basis sets with PBE1PBE functional in Table S3 and Table S4. It can be found that LANL2DZ/6-31G(d) was adopted for satisfied results and saved computational resources, which also was used for further calculations.

Additionally, on the basis of the optimized S₀ and T₁ equilibrium geometries, absorption and emission spectral properties were investigated by TDDFT [41-43] with the polarized continuum model

(PCM) [44-45] in dichloromethane (CH_2Cl_2) media. The calculated electronic density plots for the frontier molecular orbitals were presented by Gauss View 3.09 software. All the calculations were carried out with Gaussian 09 software package [46].

3. Results and discussion

3.1 The optimized geometries in the ground and lowest triplet states

Schematic structures of the investigated rhenium(I) tricarbonyl complexes and the optimized ground-state geometries are presented in Fig.1 and Fig.2 respectively. Meanwhile, the selected bond lengths and angles of complexes **1-5** in optimized ground state (S_0) and the lowest triplet state (T_1), as well as the experimental data of complex **1** in ground state are collected in Table 1.

(Fig.1)

(Fig.2)

(Table 1)

It can be seen from Fig.1 and Fig.2 that these studied Re(I) complexes have an analogous octahedral coordination around rhenium atom with bromine atom, $\text{N}^{\wedge}\text{N}$ ligand and three carbonyl ligands in a *facial* configuration. Table 1 shows that the bond lengths and angles in complexes **1-5** display typical features of Re(I) tricarbonyl diimine complexes[23-27]. The optimized bond lengths and angles of **1** are in satisfactory agreement with the experimental values based upon crystallographic data from the literature [30]. The slight deviations between calculated and experimental values are probably from the fact that theoretical calculations refer to gas phase but experiment results are from the close-packed crystal lattice. And effects of chemical environment are not considered in the calculations.

Table 1 also shows that different groups attached on R position of $\text{N}^{\wedge}\text{N}$ ligand don't give rise to obvious variations for bond lengths and angles of complexes **1-5** in S_0 state. There is a typical angle (about 90°) among three CO ligands in the *fac*- $\text{Re}(\text{CO})_3$ unit for all the researched complexes. And the axial Re-C bond distance is shorter than the equatorial Re-C bond distances in each complex. This may be attributed to different ligand-to-metal back bonding abilities at different positions, which is that the axial CO opposite Br atom. Therefore, the introduction of different groups on $\text{N}^{\wedge}\text{N}$ ligand takes a minor effect on their geometric structures in S_0 state.

The calculated geometrical parameters of **1-5** in T_1 state are also given in Table 1. It indicates that the introduction of different groups on $\text{N}^{\wedge}\text{N}$ ligand gives rise to a small effect on their geometric structures in T_1 state. However, the bond lengths and bond angles of **1-5** in T_1 state have obvious

changes compared with those in S_0 state. Specifically, the bond lengths of Re-Br, Re-N are contracted while the bond lengths of Re-C have the opposite trend. This manifests that the interaction between Re(I) and $N^{\wedge}N$ ligand is strengthened, while the interactions between Re(I) and three CO ligands are weakened in T_1 state. Therefore, $N^{\wedge}N$ ligand may have a greater effect on frontier molecular orbitals (FMOs) of these complexes in T_1 state. And the different strengths between Re(I) and $N^{\wedge}N$ ligand or CO ligands will lead to different electron transition characters. However, there are no laws in the changes of bonds angles for **1-5** in this state.

3.2 Frontier Molecular Orbitals

It is well known that optical properties of complexes are related to FMOs, especially the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The main FMO compositions, energy levels and main bond type of **1-5** are listed in Tables S5-S9. The contour plots of HOMO (H) and LUMO (L) of **1-5** are shown in Fig.3 and the main FMO energy levels are plotted in Fig.4.

(Fig.3)

(Fig.4)

From Tables S5-S9, it can be found that HOMOs of complexes **1-5** mainly consist of rhenium atom d orbital [d(Re)], bromine atom p orbital [p(Br)] and three CO ligands π orbitals [π (CO)], while LUMOs predominantly contribute from $N^{\wedge}N$ ligand π^* antibonding orbitals. The distributions of HOMO-1 and LUMO+1 are similar to those of HOMO and LUMO, respectively. The introductions of different groups on $N^{\wedge}N$ ligand have little effect on FMOs compositions and it also can be clearly seen from Fig.3.

According to Tables S5-S9 and Fig.4, when different groups were introduced on R position of $N^{\wedge}N$ ligand, energy levels of HOMOs present small changes. But energy levels of LUMOs have obvious variation. The introductions of electron-withdrawing group ($R = -NO_2$, **2**; $-CN$, **3**) can decrease the energy level of LUMO (E_{LUMO}), while the introductions of electron-donating group ($R = -OCH_3$, **4**; $-CH_3$, **5**) make the E_{LUMO} increasing. The energy level order is $E_{LUMO(4)} (-1.97 \text{ eV}) > E_{LUMO(5)} (-2.11 \text{ eV}) > E_{LUMO(1)} (-2.19 \text{ eV}) > E_{LUMO(3)} (-2.91 \text{ eV}) > E_{LUMO(2)} (-3.36 \text{ eV})$. The rising trend of E_{LUMO} is in line with the increasing of donating abilities of the introduced groups. Therefore, energy gaps of complexes **1-5** decreases in the order **4** > **5** > **1** > **3** > **2** (seeing Fig.4). The energies of HOMO and LUMO are related to hole- and electron-injection abilities of complexes, which will be discussed in

detail in latter section.

3.3 Absorption Spectra

With the optimized ground-state geometries as the starting point, TDDFT/PBE1PBE method with PCM in CH₂Cl₂ media was used to calculate absorption spectra of the five complexes. To understand the transition behavior, the relevant energies/wavelengths, oscillator strengths, dominant orbital excitations with configuration interaction (CI) coefficients and their assignments as well as experimental values of **1** are summarized in Table 2. The corresponding simulated ultraviolet visible (UV-vis) absorption spectra of **1-5** are sketched in Fig.5.

(Table 2)

(Fig.5)

For complex **1**, the calculated lowest-lying energy absorption (λ_{max}) is at 394 nm, which is assigned to electronic transition from HOMO(H) to LUMO(L). According to Table S5, HOMO is contributed by [d(Re)+p(Br)+ π (CO)], while LUMO predominantly are located on $\pi^*(\text{N}^{\wedge}\text{N})$. So the electronic transition can be described as [d(Re)+p(Br) + π (CO)] $\rightarrow$ [$\pi^*(\text{N}^{\wedge}\text{N})$] with MLCT(metal to ligand charge transfer)/XLCT(halogen to ligand charge transfer)/LLCT(ligand to ligand charge transfer). The moderately intense band is at 377 nm, which is in agreement with the experimental value (358 nm) with a deviation of less than 20 nm. Similarly, the transition of this band is from HOMO-1 (H-1) to LUMO with character of MLCT/XLCT/LLCT. And the strong absorption at 281 nm is from H-4 $\rightarrow$ L with XLCT character, which is also in good agreement with the experimental value (268 nm) with a deviation of 13 nm. Therefore this calculation method is the accuracy and reliability to explain absorption spectra characteristics.

Table 2 clearly shows that the lowest energy and moderately intense absorption bands of complexes **2-5** have same transition character as corresponding absorption bands of complex **1**. But the strong absorption bands of **2** and **3** are obviously different from that of **1**. Specifically, for **2**, the strongest absorption band at 343 nm is from H-4 $\rightarrow$ L with MLCT/XLCT character, along with a new absorption band at 298 nm, whose transition character is H-5 $\rightarrow$ L with having the mixed XLCT/LLCT. For complex **3**, the strong absorption band at 318 nm is also from H-4 $\rightarrow$ L with MLCT/XLCT, along with a stronger absorption band at 254 nm. Its transition character is H-4 $\rightarrow$ L+1 with MLCT mixing XLCT. Moreover, for complexes **4** and **5**, the strong absorption bands are small different from bands of **1**. The transition character of strong absorption band is H-3 $\rightarrow$ L with having the mixed character of

XLCT/ILCT in **4**, while this absorption band of **5** is assigned to H-3→L and H-4→L excitations with mixing MLCT/XLCT/LLCT.

From Fig.5, it can intuitively be seen that the calculated absorption bands for **1-5** have almost identical profiles but positions of absorption bands are different obviously. The lower energy absorption bands of **1-5** follow this order, **2**(461 nm) > **3**(438 nm) > **1**(378 nm) > **5**(371 nm) > **4**(358 nm). The order is same as variation rules of energy gap discussed above. It indicated that the introductions of electron-withdrawing group on N[^]N ligand (complexes **2** and **3**) make absorption bands are red-shifted. On the contrary, electron-donating substituents introduced on N[^]N ligand in **4** and **5** lead to the blue shift.

3.4 Phosphorescence Spectra

On the basis of optimized T₁ structures, the emission spectra of complexes **1-5** were calculated by TDDFT/PBE1PBE level with PCM in CH₂Cl₂ media. The lowest-energies/wavelengths, dominant transitions with larger CI coefficients and their assignments, together with experimental values of **1** are summarized in Table 3. Meanwhile, main compositions of FMOs of complexes **1-5** in excited state are also listed in Table 4 to discuss the transition properties of emission conveniently. For clarity, contour plots of HOMO and LUMO are shown in Fig.6 and main FMOs energy levels are plotted in Fig.7.

(Table 3)

(Table 4)

(Fig.6)

(Fig.7)

For complex **1**, the lowest-energy emission band is 588 nm (seeing Table 3), which has a small deviation with the experimental datum (568 nm). It indicates that this calculation method is accurate and reliable to explain the emission spectra characteristics. And Table 3 shows that the lowest-energy emissions of **1-5** mainly originate from LUMO to HOMO transition. According to Table 4, it also can be seen that LUMOs are mainly localized on $\pi^*(N^{\wedge}N)$ orbital for all the complexes, while HOMOs are primarily on $[d(Re)]$, $[p(Br)]$ and $[\pi(CO)]$. To intuitively understand emission transition, the plots of HOMO and LUMO mainly related to emissions of **1-5** are presented in Fig.6.

In addition, the calculated lowest-energy emission bands of the studied complexes decreases in this order **2** (886 nm) > **3** (730 nm) > **1** (588 nm) > **5** (585 nm) > **4** (566 nm), which is related to the variation trend of HOMO-LUMO energy gaps (Fig.7). For complexes **1-5**, HOMO energy levels are

similar to each other, but LUMO energy levels present obvious variation. The introduction of $-\text{NO}_2$ (complex **2**) and $-\text{CN}$ in complex **3** on R position of $\text{N}^{\wedge}\text{N}$ ligand can decrease the E_{LUMO} , while introductions of $-\text{OCH}_3$ in complex **4** and $-\text{CH}_3$ in complex **5** make E_{LUMO} increasing. So the introductions of $-\text{NO}_2$ and $-\text{CN}$ lead to the lowest energy emissions bands red-shifted, relative to **1**, while the introductions of $-\text{OCH}_3$ and $-\text{CH}_3$ can cause corresponding blue shift. Therefore, for such complexes, the stronger donating electron ability of introduced group on $\text{N}^{\wedge}\text{N}$ ligand is, the larger blue-shifted of the lowest energy emission band is.

3.5 Solvent Effect on Absorption and Emission Spectra

The different polarity of solvents can cause diverse excitation energies. For the lowest-energy absorption and emission wavelengths of the studied complexes, different solvent effects are assessed using PCM method, as shown in Table 5. Both the lowest-energy absorption and emission bands have red-shifted with the decrease of solvent polarity for these complexes. Compared with the experiment, it is very easy for theoretical calculations to change solvents and this is another advantage of theoretical calculations. We hope that this change rule will provide available guidance for experiments.

(Table 5)

3.6 Electronic affinity (EA), ionization potential (IP) and reorganization energy (λ)

The electronic affinity (EA) and ionization potential (IP) are important for device performances of OLED materials [47-49]. And a larger EA/smaller IP suggests that it facilitates injection electrons/holes into the emitting materials from electron/hole transporting layers, thus the turn-on voltage would be lower and the performances of those devices also would be better. **To the best of our knowledge, the reorganization energy (λ) can be used to evaluate charge transfer rate and balance between holes and electrons in some approximate way.** We present DFT calculated vertical and adiabatic of EA and IP (EA_v , EA_a , IP_v , IP_a), electron extraction potential (EEP), hole extraction potential (HEP), electron transport reorganization energy ($\lambda_{\text{electron}}$), hole transport reorganization energy (λ_{hole}) and the difference between λ_{hole} and $\lambda_{\text{electron}}$ for five complexes in Table 6. The details for these definitions can be acquired from our previous works [50].

(Table 6)

Table 6 clearly shows that EA values and IP values of **1-5** decrease in the order **2** > **3** > **1** > **5** > **4**, which is consistent with the trend of HOMO energy level. In comparison with **1**, complexes **2** and **3** have larger EA values, which are easier to inject electrons into emitting materials from electron

transporting layers. The electron injection abilities of such complexes are enhanced. The hole injection abilities for **4** and **5** are easier compared with other complexes, which may be relative to a relatively higher HOMO energy levels. So the introductions of electron-withdrawing groups on N[^]N ligand facilitates the electron injection, while introduced electron-donating groups facilitates the hole injection. And the involved complexes have greater *HEP* values than *EEP*. Here a large *HEP* signifies that the hole transfer favors the adiabatic process [51].

On the basis of the Marcus/Hush model [52-54], the charge transfer rate (*k*) can be estimated by the following formula:

$$k = (\pi / \lambda k_b T)^{1/2} (V^2 / \hbar) e^{(-\lambda / 4 k_b T)} = A e^{(-\lambda / 4 k_b T)} \quad (1)$$

where k_b is the Boltzmann constant, T is the temperature, λ is the reorganization energy and V is the coupling matrix element between ions and molecules, which is dictated by the overlap of orbitals. Due to the limited intermolecular charge transfer range in solid state, the mobility of charges dominantly relates to the reorganization energy λ for OLED materials [54]. Generally, λ is determined by the internal reorganization energy (λ_i) in molecular but it is affected by the external reorganization energy (λ_e) in solvent polarization of medium. In OLEDs, λ_i is a determinant factor as a result of the limited intermolecular charge transfer range in solid-state devices. Therefore, the effect from λ_e is negligible. A low λ value is imperative for an efficient charge transport process from eq (1). The $\lambda_{electron}$ and λ_{hole} can be expressed as follows: [55]

$$\lambda_{electron} = EEP - EA_v \quad (2)$$

$$\lambda_{hole} = IP_v - HEP \quad (3)$$

As shown in Table 6, it can be found that all of these complexes possess lower $\lambda_{electron}$ in comparison of λ_{hole} , which reveal that electron transporting performance is slightly better than hole transporting performance. This means that all of these complexes can be used as electron transporting materials. And **3** has the best electron transfer ability because of the smallest $\lambda_{electron}$ among these complexes, while **1** and **5** have better hole transfer abilities with the smaller λ_{hole} . Moreover, it can also be seen that **4** has a relatively small difference between $\lambda_{electron}$ and λ_{hole} , which can improve the charge transfer balance and further enhance the device performance of OLEDs. So **4** is more suitable to be used as an emitter in OLEDs. The analysis results above present that the different substituted groups on N[^]N ligand of these complexes can influence charge transfer rates of electrons and holes. In this case,

we hope that theoretical investigations can guide experiment to develop novel and efficient materials of OLEDs.

3.7 The emission quantum yield in CH₂Cl₂ media

The emission quantum yield (Φ) can be affected by the competition between radiative and nonradiative decay rate (k_r and k_{nr}) constants, which can be generally formulated as:

$$\Phi = k_r \tau_{em} = k_r / (k_r + k_{nr}) \quad (4)$$

where τ_{em} is the emission decay time. It can be seen that a large k_r and a small k_{nr} are required to increase the value of Φ . The k_r and k_{nr} are expressed as [56-57]:

$$k_r \approx \gamma \langle \Psi_{S_1} | H_{S_0} | \Psi_{T_1} \rangle^2 \mu_{S_1}^2 / (\Delta E_{S_1-T_1})^2, \gamma = 16\pi^3 10^6 n^3 E_{T_1}^3 / 3h\epsilon_0 \quad (5)$$

$$k_{nr} = \alpha e^{(-\beta E_{T_1})} \quad (6)$$

where α and β are constant, μ_{S_1} is the transition electric dipole moment from S_0 to S_1 , $\Delta E_{S_1-T_1}$ is the energy gap between S_1 and T_1 states, E_{T_1} is the energy of lowest triplet excited state for phosphorescence, n , h and ϵ_0 are the refractive index, Planck's constant and the permittivity in vacuum, respectively. So the variation of Φ can be qualitatively researched from these above formulas. According to Eq. (5) and Eq. (6), when E_{T_1} value increase, k_r may increase and k_{nr} may decrease. The corresponding data are collected in Table 7. It can be seen that **4** has the largest E_{T_1} (2.19 eV), which may increase the value of Φ .

(Table 7)

It is also well known that the heavy atom participation can increase spin-orbit coupling (SOC) effects and intersystem crossing (ISC) [58]. Chantal et al. have also researched the rationalization of the influence of the metal center on the photophysical/photochemical properties of the $M(R)(CO)_3(\alpha\text{-diimine})$ complexes with $R = H$, methyl, or ethyl, and $M = Mn, Re$ [59]. The SOC effect can be elucidated mainly from the following two aspects. One is the contribution of MLCT (3MLCT) in T_1 state [60]. A larger 3MLCT can enhance SOC, which can result in a drastic decrease of radiative lifetime and avoid nonradiative process [61-62], which is good for increasing k_r . The second aspect is the energy gap between S_1 and T_1 states ($\Delta E_{S_1-T_1}$) [63-66]. The $S_1 \rightarrow T_1$ intersystem crossing plays a significant role in phosphorescent process. The ISC rate decreases exponentially as $\Delta E_{S_1-T_1}$ increases [67]. The minimal $\Delta E_{S_1-T_1}$ will enhance ISC rate and transition moment, which could increase k_r . And according to Eq. (5), a smaller $\Delta E_{S_1-T_1}$ and a higher μ_{S_1} will also lead to a larger k_r . From the discussion

above, a larger $^3\text{MLCT}$, a lower $\Delta E_{\text{SI-TI}}$ and a higher μ_{SI} can cause a larger k_r , which will increase the emission quantum yield.

Table 7 shows that complex **4** has the largest $^3\text{MLCT}$ value (34.31%), the smallest value of $\Delta E_{\text{SI-TI}}$ (0.35 V) and a higher μ_{SI} (2.58 D) in five complexes, which may make it have a larger Φ than that of other complexes. So the designed complex **4** is possible to be a good candidate for phosphorescent materials among these studied complexes. However, because Φ is the competition between k_r and k_{nr} , other factors also may play an important role for a high quantum yield.

4. Conclusion

In this paper, a series of rhenium (I) tricarbonyl complexes containing pyridyltetrazole ligand with different substituted groups ($-\text{NO}_2$, $-\text{CN}$, $-\text{OCH}_3$ and $-\text{CH}_3$) have been investigated by DFT/TDDFT methods. Specifically, the ground-state geometries, the lowest-lying triplet excited state, electronic structures, absorption spectra, emission spectra, solvent effect, electronic affinity, ionization potential, reorganization energy and emission quantum yield of the complexes were studied.

The calculated results suggest that, for these complexes, the introductions of different groups on R position of $\text{N}^{\wedge}\text{N}$ ligand have significant influence on electronic structures and photophysical properties, such as absorption and emission spectra, charge injection and transfer abilities and emission quantum yield. On the basis of FMOs analysis, for complexes **1-5**, HOMO energy levels have small changes, but LUMO energy levels present obvious variation. Specifically, introductions of electron-withdrawing groups ($-\text{NO}_2$ and $-\text{CN}$) can decrease the energy level of LUMO resulting in narrower energy gap, which lead to red-shifted of the lowest energy absorption and emission bands in comparison with that of **1**. On the contrary, introductions of electron-donating group ($-\text{OCH}_3$ and $-\text{CH}_3$) can make the energy level of LUMO increasing, which cause the corresponding blue-shifted. Therefore, for such complexes, the stronger donating electron ability of introduced group on $\text{N}^{\wedge}\text{N}$ ligand is, the larger blue-shifted of the lowest energy absorption and emission bands is. The different groups substitution on $\text{N}^{\wedge}\text{N}$ ligand may also be an efficient approach of tuning emitting color for **1**.

The solvent effect on absorption and emission spectra indicates that the lowest-energy absorption and emission bands have red-shift with the decrease of solvent polarity for these complexes. From EA, IP and λ results, we also can conclude that these complexes can be used as electron transporting materials. Moreover, the difference between $\lambda_{\text{electron}}$ and λ_{hole} of **4** is the smallest among these complexes, enhancing the device performance of OLEDs further. Therefore, **4** is more suitable to be used as an

emitter in the OLEDs. Moreover, complex **4** may have a higher emission quantum yield, which is possible to be a good candidate for phosphorescent materials among these studied complexes. Lastly, we hope that theoretical investigations can provide useful information in design and synthesis of novel and high-efficiency OLEDs materials.

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Figure Captions:

Fig.1 The structures of the investigated Re(I) tricarbonyl complexes having a general formula $fac-[ReBr(CO)_3(R-N^{\wedge}N)]$

Fig.2 The optimized geometries of **1-5** in the ground state

Fig.3 The contour plots of HOMO and LUMO of the investigated complexes

Fig.4 The main FMO energy levels of **1-5**

Fig.5 The simulated UV-vis absorption spectra of **1-5**

Fig.6 The contour plots of HOMO and LUMO of **1-5** in the excited state

Fig.7 The main FMOs energy levels of the investigated complexes in the excited state

Table Captions:

Table 1 The selected bond lengths and angles of **1-5** in the optimized ground and lowest triple states geometries and experimental data of **1**

Table 2 The calculated energies/wavelengths, the oscillator strengths, the dominant orbital excitations with configuration interaction (CI) and their assignments of the all complexes and experimental values of **1**

Table 3 The calculated energies/wavelengths, the dominant orbital excitations with configuration interaction (CI) and their assignments of the all complexes and experimental band values of **1**

Table 4 The main FMO compositions and energy levels of complexes **1-5** in the excited state

Table 5 The lowest-energy absorption and emission wavelengths of the studied complexes in the different polarities solvents

Table 6 The calculated vertical and adiabatic of EA and IP (EA_v , EA_a , IP_v , IP_a in eV), electron extraction potential (EEP in eV), hole extraction potential (HEP in eV), electron transport ($\lambda_{electron}$ in eV), hole transport (λ_{hole} in eV) and the difference between λ_{hole} and $\lambda_{electron}$ of **1-5**

Table 7 The computed emitting energy (E_{T1} /eV), the contribution of 3MLCT in T_1 state ($^3MLCT/\%$) and the energy gaps between S_1 and T_1 states (ΔE_{S1-T1} /eV), together with the transition electric dipole moment in the $S_0 \rightarrow S_1$ transition (μ_{s1} /Debye)

Figure1

Figure2

Figure3

Figure4

Figure5

Figure6

Figure7

Table 1 The selected bond lengths and angles of **1-5** in the optimized ground and lowest triple states geometries and experimental data of **1**

		1		2		3		4		5	
	Exptl.*	S ₀	T ₁	S ₀	T ₁	S ₀	T ₁	S ₀	T ₁	S ₀	T ₁
Bond lengths (Å)											
Re-Br	2.629	2.622	2.542	2.618	2.528	2.619	2.535	2.623	2.550	2.623	2.545
Re-C1	1.924	1.914	1.929	1.915	1.930	1.915	1.929	1.912	1.929	1.913	1.929
Re-C2	1.915	1.918	1.980	1.922	1.977	1.921	1.978	1.917	1.979	1.918	1.980
Re-C3	1.900	1.908	1.950	1.911	1.956	1.911	1.954	1.907	1.947	1.908	1.950
Re-N1	2.140	2.158	2.131	2.155	2.141	2.156	2.139	2.160	2.126	2.158	2.131
Re-N2	2.216	2.217	2.109	2.204	2.122	2.207	2.113	2.220	2.105	2.216	2.105
Bond angles (°)											
C2-Re-C3	89.38	91.44	88.33	91.36	88.28	91.31	88.24	91.48	88.26	91.46	88.34
N1-Re-C3	97.86	94.42	95.08	94.58	95.02	94.49	95.01	94.25	95.22	94.53	94.93
N2-Re-C3	95.00	94.28	88.43	94.85	88.26	94.82	88.49	94.11	89.41	94.28	88.75
C2-Re-Br	92.41	91.15	86.47	90.73	87.01	90.77	86.64	91.29	85.54	91.12	86.10

*From **Ref.** [30]

Table 2 The calculated energies/wavelengths, the oscillator strengths, the dominant orbital excitations with configuration interaction (CI) and their assignments of the all complexes and experimental values of **1**

Complex	E (eV/nm)	Oscillator	Transition	CI	Assign	λ_{exp}^* (nm)
1	3.14/394	0.0033	H→L	0.6975	MLCT/XLCT/LLCT	
	3.29/377	0.0531	H-1→L	0.6995	MLCT/XLCT/LLCT	358
	4.41/281	0.0822	H-4→L	0.6270	XLCT	268
2	2.28/543	0.0054	H→L	0.6880	MLCT/XLCT/LLCT	
	2.44/509	0.0632	H-1→L	0.6896	MLCT/XLCT/LLCT	
	3.61/343	0.1536	H-4→L	0.6864	MLCT/XLCT	
	4.17/298	0.0667	H-5→L	0.5876	XLCT/LLCT	
3	2.59/479	0.0053	H→L	0.6934	MLCT/XLCT/LLCT	
	2.75/450	0.0716	H-1→L	0.6932	MLCT/XLCT/LLCT	
	3.90/318	0.1485	H-4→L	0.6743	MLCT/XLCT	
	4.89/254	0.1571	H-4→L+1	0.5767	MLCT/XLCT	
4	3.33/372	0.0058	H→L	0.6921	MLCT/XLCT/LLCT	
	3.46/358	0.0545	H-1→L	0.6965	MLCT/XLCT/LLCT	
	4.44/279	0.0834	H-3→L	0.6384	XLCT/ILCT	
5	3.20/387	0.0045	H→L	0.6963	MLCT/XLCT/LLCT	
	3.34/371	0.0581	H-1→L	0.6988	MLCT/XLCT/LLCT	
	4.43/280	0.1116	H-3→L	0.4676	MLCT/XLCT/ILCT	
			H-4→L	0.4540	MLCT/XLCT/ILCT	

* From **Ref.** [30]

Table 3 The calculated energies/wavelengths, the dominant orbital excitations with configuration interaction (CI) and their assignments of the all complexes and experimental band values of **1**

Complex	E(eV/nm)	Transition	CI	Assignment	λ_{exp}^* (nm)
1	2.11/588	L→H	0.6763(91%)	³ MLCT/ ³ XLCT/ ³ LLCT	568
2	1.40/886	L→H	0.6878(95%)	³ MLCT/ ³ XLCT/ ³ LLCT	
3	1.70/730	L→H	0.6847(94%)	³ MLCT/ ³ XLCT/ ³ LLCT	
4	2.19/566	L→H	0.6783(92%)	³ MLCT/ ³ XLCT/ ³ LLCT	
5	2.12/585	L→H	0.6738(91%)	³ MLCT/ ³ XLCT/ ³ LLCT	

* From **Ref.** [30]

Table 4 The main FMO compositions and energy levels of complexes **1-5** in excited state

Orbital	Energy (eV)	Contribution (%)			
		Re	Br	CO	N^N
1					
L	-2.5032	4.59	2.67	5.30	84.69
H	-5.8711	39.67	32.65	16.07	8.56
2					
L	-3.6064	5.47	1.67	4.31	85.33
H	-6.1045	36.95	35.50	14.70	10.23
3					
L	-3.1005	6.15	2.53	6.14	82.17
H	-6.0449	37.89	34.53	14.80	9.77
4					
L	-2.3740	3.13	2.23	3.88	87.50
H	-5.7716	40.42	29.61	16.50	10.85
5					
L	-2.4551	4.22	2.54	5.01	85.09
H	-5.8292	39.99	31.37	16.03	9.18

Table 5 The lowest-energy absorption and emission wavelengths of the studied complexes in the different polarities solvents

Solvent		C ₇ H ₈	CH ₂ Cl ₂	CH ₃ COCH ₃	CH ₃ OH
Polarity		2.4	3.4	5.4	6.6
Absorption (nm)	1	435	394	386	383
	2	610	543	528	524
	3	533	479	466	463
	4	407	372	364	362
	5	427	387	379	376
Emission (nm)	1	655	588	574	570
	2	1005	886	858	850
	3	819	730	710	705
	4	626	566	553	550
	5	650	585	571	568

Table 6 The calculated vertical and adiabatic of EA and IP (EA_v , EA_a , IP_v , IP_a in eV), electron extraction potential (EEP in eV), hole extraction potential (HEP in eV), electron transport ($\lambda_{electron}$ in eV), hole transport (λ_{hole} in eV) and the difference between λ_{hole} and $\lambda_{electron}$ of **1-5**

Complex	EA_v	EA_a	EEP	λ_e	IP_v	IP_a	HEP	λ_h	$\lambda_h-\lambda_e$
1	0.917	1.140	1.363	0.446	7.271	7.031	6.776	0.495	0.049
2	2.062	2.298	2.530	0.468	7.553	7.320	7.056	0.497	0.029
3	1.746	1.907	2.062	0.316	7.513	7.281	7.026	0.487	0.171
4	0.688	0.968	1.240	0.552	7.132	6.873	6.574	0.558	0.006
5	0.862	1.099	1.319	0.457	7.192	6.952	6.697	0.495	0.038

Table 7 The computed emitting energy (E_{Tl} /eV), the contribution of $^3\text{MLCT}$ in T_1 state ($^3\text{MLCT}/\%$) and the energy gap between S_1 and T_1 states (ΔE_{S1-T1} /eV), together with the transition electric dipole moment in the $S_0 \rightarrow S_1$ transition (μ_{s1} /Debye)

Complex	E_{Tl}	$^3\text{MLCT}$	ΔE_{S1-T1}	μ_{s1}
1	2.11	31.92	0.38	2.24
2	1.40	29.91	0.42	1.89
3	1.70	29.84	0.45	2.17
4	2.19	34.31	0.35	2.58
5	2.12	32.55	0.39	2.50