Effect of Substituents on Electronic Structure and Photophysical Properties of Re(I)(CO)₃Cl(R-2, 2’-Bipyridine) Complex: DFT/TDDFT Study

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Abstract: The electronic structure, absorption and emission spectra, as well as phosphorescence efficiency of Re(I) tricarbonyl complexes of a general formula fac-[Re(I)(CO)₃(L)(R-N^N)](L = Cl; N^N = 2, 2’-bipyridine; R = -H, 1; -NO₂, 2; -PhNO₂, 3; -NH₂, 4; -TPA (triphenylamine), 5) were investigated by using density functional theory (DFT) and time dependents density functional theory (TDDFT) methods. The calculated results reveal that introductions of the Electron withdrawing group (EWG) and Electron donating group (EDG) on the R position of 2, 2’-bipyridine ligand. When EWG (-NO₂ and -PhNO₂) are introduced into complex 2 and 3, the lowest energy absorption and emission bands are red shifted compared with that of complex 1. On the contrary, the introduction of the EDG (-NH₂ and -TPA) in complex 4 and 5 cause corresponding blue shifted. The solvent effect on absorption and emission spectrum indicates that the lowest energy absorption and emission bands have red shifts with the decrease of solvent polarity. The electronic affinity (EA), ionization potential (IP) and reorganization energy (λ) results show that complex 5 is suitable to be used as an emitter in phosphorescence organic light emitting diodes (PHOLEDs). Meanwhile the emission quantum yield of complex 5 is possibly higher than that of other complexes.

Keywords: Electronic Structure, Internal Quantum Efficiency, Luminescence, Phosphorescence and Photophysical Properties

1. Introduction

Organic light emitting diodes (OLEDs) are solid state electronic devices which emit light in response to the applied electric current. Among different types of OLEDs, PHOLEDs are the classes of OLED that use the principle of phosphorescence to offer four times the internal efficiency of conventional fluorescent OLEDs. Light emitting organic materials has phosphorescent materials which serve as recombination centers for electrons and holes to produce the electronic excited states are mainly captivating. Because, they harvest light from both singlet and triplet excitons and enabling the devices with close to 100% internal quantum efficiency [1]. However, exploration of novel materials including emitting materials and host materials is crucial to push the performance of the PHOLEDs [2]. PHOLEDs have attracted worldwide attention over the past decades due to their unique features and huge potential for flat panel, flexible display, energy saving solid state lighting and virtual reality [3].

The highly efficient PHOLEDs can be designed from the 3rd row d⁶ transition metal complexes with appropriate organic ligand because, existence of transition metal in complex exhibit strong spin orbit coupling (SOC) which substantially accelerates singlet to triplet intersystem crossing ISC [4-6]. Selection of organic ligand allows different electronic transitions occurring between different energy states associated with metal atom is important to design highly efficient luminescent complexes [7-9]. The specific photophysical properties of bidentate hetero-aromatic
diamine ligand complexes with third row d⁶ transition metal ions such as Re(I), Ru(II) and Os(II) are significant. Among them Re(I) tricarbonyl complexes with substituted 2, 2’-bipyridine ligand attached rhenium often show intense and long lived luminescence. 2, 2’-bipyridine is a bidentate ligand with powerful binding abilities towards Re(I) metal ion. It can be easily modified by the introduction of different substituent groups at its different positions. Introduction of electron with drawing group (EDG) or electron withdrawing group (EWG) substituent is useful to tune the energy level of electron withdrawing substituent groups at its different positions. Intr oduction of long lived luminescence. 2, 2’-bipyridine is a bide ntate ligand to provide high efficiency PHOLED ions such as Re(I), Ru(II) and Os(II) are significant. Among them Re(I) tricarbonyl complexes with substituted 2, 2’-bipyridine ligand attached rhenium often show intense and long lived luminescence. 2, 2’-bipyridine is a bidentate ligand with powerful binding abilities towards Re(I) metal ion. It can be easily modified by the introduction of different substituent groups at its different positions. Introduction of electron with drawing group (EDG) or electron withdrawing group (EWG) substituent is useful to tune the energy level of electron withdrawing substituent groups at its different positions. Intr oduction of long lived luminescence. 2, 2’-bipyridine is a bide ntate ligand to provide high efficiency PHOLED...
The optimized parameters of complex 1 are in good agreement with the experimental values based upon crystallographic data taken from literature [34]. It gives positive indication on the reliability of the theoretical method. The slight deviations between calculated and experimental values are due to the fact that the effects of crystal packing and chemical environment. The effects of both crystal packing and chemical environment are not considered in theoretical calculations. Theoretical calculations refer to gas phase but experimental results are from the close packed crystal lattice. The substitution of the R position of 2, 2'-bipyridine ligand by different EWG and EDG give rise to negligible changes for the bond lengths and bond angles in 1 - 5 complexes in S₀ state as it is shown in Table 1. There is a typical angle about 90° among three CO ligands in the fac-Re(CO)₃⁺ unit for all studied complexes. And the axial Re-C bond distance is shorter than the equatorial Re-C bond distances in each complex.
This is attributed to different ligand to metal back bonding ability which is that the axial CO opposite to Cl atom. Therefore, the introduction of R = -H, 1; -NO₂, 2; -PhNO₂, 3; -NH₂, 4 and -TPA, 5 groups on the R position of 2, 2'-bipyridine ligand takes a minor effect on their geometric structures in S₀ state.

The calculated geometrical parameters of 1 - 5 complexes in the triplet state (T₁) are also given in Table 1. It also reveals that the introduction of different substituent groups on the R position of 2, 2'-bipyridine ligand gives rise to a little effect on their geometric structures in T₁ state. However, the bond lengths and bond angles of 1 - 5 complexes in T₁ state have obvious changes compared with those in S₀ state.

Specifically, the bond lengths of Re-N, Re-Cl are contracted while the bond lengths of Re-C was relaxed. This shows that the interaction between Re(I) and 2, 2'-bipyridine ligand is strengthened, while the interactions between Re(I) and three CO ligands are weakened in T₁ state. Therefore, 2, 2'-bipyridine ligand have a greater effect on FMOs of these complexes in T₁ state. The different strengths between Re(I) and 2, 2'-bipyridine ligand or CO ligands will lead to different electron transition characters.

### Table 1. The selected bond lengths and bond angles of 1 - 5 complexes in S₀ state and T₁ state calculated at the B3LYP/6-311++G(d, p)/LANL2DZ level. Distances are in angstrom and angles are in degree.

|     | 1(-H) | 2(-NO₂) | 3(-PhNO₂) |
|-----|-------|---------|-----------|
|     | S₀    | T₁      | S₀        | S₁        | T₁      | S₀        | S₁        | T₁      |
| Bond Length (Å) |       |         |           |           |         |           |           |         |
| Re-C₁     | 2.574 | 2.548   | 2.480     | 2.543     | 2.469   | 2.547     | 2.483     |
| Re-C₂     | 1.915 | 1.910   | 1.952     | 1.914     | 1.955   | 1.911     | 1.949     |
| Re-C₃     | 1.907 | 1.925   | 1.947     | 1.927     | 1.942   | 1.926     | 1.939     |
| Re-C₄     | 2.058 | 1.925   | 1.981     | 1.931     | 1.984   | 1.927     | 1.985     |
| Re-N₂₆   | 2.163 | 2.171   | 2.137     | 2.153     | 2.094   | 2.170     | 2.083     |
| Re-N₂₇   | 2.171 | 2.171   | 2.095     | 2.169     | 2.159   | 2.164     | 2.157     |
| Bond Angles (°) |       |         |           |           |         |           |           |         |
| N₂₆-Re-N₂₇ | 74.7  | 75.48   | 77.78     | 75.76     | 77.27   | 75.41     | 77.24     |
| C₂-Re-C₄  | 95.9  | 91.82   | 89.45     | 91.69     | 88.67   | 91.79     | 88.77     |
| C₂-Re-C₃  | 90.3  | 91.82   | 93.92     | 91.68     | 92.96   | 91.79     | 92.49     |
| C₂-Re-N₂₆ | 90.7  | 93.83   | 90.72     | 94.26     | 92.61   | 94.00     | 93.22     |
| C₂-Re-N₂₇ | 86.0  | 93.83   | 90.13     | 94.08     | 89.74   | 93.72     | 90.45     |
| C₃-Re-N₂₇ | 97.5  | 97.01   | 96.66     | 96.79     | 96.71   | 97.02     | 96.44     |
| C₄-Re-N₂₆ | 97.8  | 97.01   | 98.03     | 96.85     | 97.55   | 97.06     | 96.99     |
| C₄-Re-C₁₈ | 91.24 | 86.77   | 91.12     | 90.47     | 91.08   | 90.16     |           |

|     | 4(-NH₁) | 5(-TPA) |
|-----|---------|---------|
|     | S₀      | T₁      | S₀      | T₁      |
| Bond Length (Å) |       |         |         |         |
| Re-C₁     | 2.551  | 2.499   | 2.551  | 2.513  |
| Re-C₂     | 1.907  | 1.942   | 1.909  | 1.933  |
| Re-C₃     | 1.923  | 1.982   | 1.924  | 1.934  |
| Re-C₄     | 1.923  | 1.939   | 1.925  | 1.970  |
| Re-N₂₆   | 2.171  | 2.079   | 2.172  | 2.156  |
| Re-N₂₇   | 2.173  | 2.143   | 2.167  | 2.086  |
| Bond Angles (°) |       |         |         |         |
| N₂₆-Re-N₂₇ | 75.23 | 77.73   | 75.32  | 77.27  |
| C₂-Re-C₄  | 91.83  | 92.15   | 91.79  | 89.91  |
| C₂-Re-C₃  | 91.83  | 89.02   | 91.79  | 92.21  |
| C₂-Re-N₂₆ | 93.52  | 90.58   | 93.88  | 93.27  |
| C₂-Re-N₂₇ | 93.80  | 93.59   | 93.60  | 91.45  |
| C₃-Re-N₂₇ | 97.13  | 96.02   | 97.03  | 96.23  |
| C₄-Re-N₂₆ | 97.17  | 96.14   | 97.15  | 96.61  |
| C₄-Re-C₁₈ | 91.34  | 89.52   | 90.99  | 89.91  |

Experimental values from [34]. Calculated optimized parameters shows octahedral coordination structure and interaction between Re (I) and 2, 2'-bipyridine ligand of all complexes.

### 3.2. Molecular Orbital Properties

The properties of the frontal molecular orbital (FMOs) have a significant effect on the excited states and electronic transitions of OLED materials. It is well known that the optical properties of the complexes are associated with FMOs especially, HOMO and LUMO [27].

The contour plots of HOMO (H) and LUMO (L) of 1 - 5 complexes are shown in Figure 3 and the main FMO energy levels are plotted in Figure 4.
It can be seen that HOMOs of 1 - 5 complexes mainly consist of orbitals of Rhenium atom \([d(Re)]\), p orbitals of chlorine atom \([p(Cl)]\) and \(\pi\) orbitals of three CO ligands \([\pi(CO)]\) while LUMOs predominantly contributed from \(\pi^*\) anti-bonding orbitals of 2, 2'-bipyridine ligand with its substituents. The introductions of different substituent groups on 2, 2'-bipyridine ligand have little effect on FMO compositions. According to Figure 4, when EWG and EDG groups were introduced on the R position, the energy levels of HOMOs changes little. But energy levels of LUMOs shows significant variation due to different substituent groups attached on the 2, 2'-bipyridine ligand. The introductions of EWGs \((R = -NO_2, 2 \text{ and } -PhNO_2, 3)\) decreases the energy level of LUMO \((E_{LUMO})\) while the introductions of EDGs \((R = -NH_2, 4 \text{ and } -TPA, 5)\) increases \(E_{LUMO}\). The order is \(E_{LUMO}(-2.816 \text{ eV}) (4) > E_{LUMO}(-2.904 \text{ eV}) (5) > E_{LUMO}(-3.122 \text{ eV}) (1) > E_{LUMO}(-3.8974 \text{ eV}) (3) > E_{LUMO}(-4.447 \text{ eV}) (2)\). Therefore, the energy gap of 1 - 5 complexes decreases with the electron withdrawing substituent group and increases with electron donating substituent groups.

![Figure 3. Contour plot of HOMO and LUMO of 1 - 5 complexes.](image)

### 3.3. Absorption Spectra

Based on the optimized ground state geometry, the absorption properties of 1 - 5 complexes have been determined. TDDFT/B3LYP/LANL2DZ (for Re atom) and 6-311++G(d, p) (for C, H, N, O and Cl atoms) theoretical method with PCM in CH$_2$Cl$_2$ media was used to calculate absorption spectra of all complexes. The transition behavior, the relevant energies/wavelengths, oscillator strength, dominant orbital excitations with configuration interaction (CI) coefficients and their assignments as well as experimental values from the literature [34] of complex 1 are collected in Table 2. By using GAMESS software, the corresponding simulated UV-Visible absorption spectra of 1 - 5 complexes are sketched in Figure 5. For complex 1, the calculated lowest lying energy absorption is at 423 nm, which is assigned to electronic transition from H-1 to L. HOMO is contributed by \([d(Re) + p(Cl) + \pi(CO)]\), while
LUMO predominantly located on π*(2, 2’-bipyridine). H-1 and L+1 have a similar charge transfer character with H and L. The MLCT type is commonly observed in the lowest energy transitions for transition metal complex [28-29]. So this electronic transition can be described as [d(Re) + p(Cl) + π(CO)] → π*(2, 2’-bipyridine) with MLCT/XLCT/LLCT in good agreement with the experimental value 420 nm. The moderately intense band is at 448 nm. Similarly, the transition of this band is from H to L with characteristic MLCT/XLCT/LLCT character. Therefore, it indicates that the calculated value is precise and reliable to explain absorption spectra. As observed in table 2, the lowest energy and moderately intense absorption bands of complexes 2 - 5 have a similar transition character as compared to the absorption bands of complex 1. But the strong absorption bands of complexes 2 and 3 are different from that of complex 1. Specifically, for complex 2, the strongest absorption band at 420 nm is from H to L with LLCT/XLCT character. For complex 3, the strong absorption band at 419 nm is also from H to L+1 with MLCT/XLCT/LLCT character. Moreover, for complexes 4 and 5, the strong absorption bands are different from bands of complex 1.

For complex 4, the transition character of a strong absorption band is H-3 to L which is having a mixed character of XLCT/ILCT while the absorption band of complex 5 is assigned to H-3 to L and H to L+2 excitations with mixing MLCT/XLCT/LLCT. From Figure 5, it can intuitively be seen that the calculated absorption bands for 1 - 5 complexes have almost identical profiles but the positions of absorption bands are different. It is noteworthy that the contribution of MLCT is more remarkable in the lowest energy absorption bands with the large compositions of Re atom in HOMOs and HOMO-1s. The lower energy absorption bands of 1 - 5 complexes follow the order: 2 (634nm) > 3 (505nm) > 1 (423nm) > 4 (404nm) > 5 (400nm). It reveals that the introduction of EWG on 2, 2’-bipyridine ligand (mainly for complex 2 and 3) absorption bands red shifted (longer wavelength). On the hand when EDG substituents introduced on 2, 2’-bipyridine ligand (complex 4 and 5) the absorption band become the blue shifted (shorter wavelength).

![Figure 4. The main FMO energy level of 1 - 5 complexes.](image)

| E(eV/nm) | Oscillator strength | Transition | |Assign| λ_exp(nm) |
|---|---|---|---|---|---|
| 1 | 2.765/448 | 0.0027 | H→L | MLCT/XLCT/LLCT | 420nm |
| | 2.929/423 | 0.0680 | H-1→L | MLCT/XLCT/LLCT |
| | 3.275/378 | 0.0002 | H-2→L | MLCT/XLCT/LLCT |
| | 3.804/325 | 0.0005 | H→L+1 | MLCT/XLCT/LLCT |
| | 3.906/317 | 0.0004 | H-1→L+1 | MLCT/XLCT/LLCT |
| | 3.919/316 | 0.0047 | H→L+2 | LLCT/XLCT |
| | 1.761/703 | 0.0039 | H→L | MLCT/XLCT/LLCT |
| | 1.953/634 | 0.0852 | H-1→L | MLCT/XLCT/LLCT |
| | 2.314/535 | 0.0002 | H-2→L | MLCT/XLCT/LLCT |
| | 2.829/438 | 0.0039 | H→L+1 | MLCT/XLCT/LLCT |
| | 2.944/421 | 0.0076 | H-1→L+1 | MLCT/XLCT/LLCT |
| | 2.950/420 | 0.0058 | H→L+2 | LLCT/XLCT |
| $E$(eV/nm) | Oscillator strength | Transition | $|C_I|$ | Assign | $\lambda_{exp}$(nm) |
|-----------|---------------------|------------|--------|--------|-----------------|
| 2.345/529 | 0.0179              | H → L      | 0.673  | MLCT/XLCT/LLCT |
| 2.454/505 | 0.0843              | H−1 → L   | 0.687  | MLCT/XLCT/LLCT |
| 2.822/439 | 0.0015              | H−2 → L   | 0.667  | MLCT/XLCT/LLCT |
| 2.888/429 | 0.0001              | H−1 → L+1 | 0.687  | MLCT/XLCT/LLCT |
| 2.958/419 | 0.0455              | H−9 → L   | 0.677  | LLCT/XLCT     |
| 3.261/380 | 0.0025              | H−1 → L   | 0.6775 | MLCT/XLCT/LLCT |
| 2.896/428 | 0.0111              | H−2 → L   | 0.6966 | MLCT/XLCT/LLCT |
| 3.063/404 | 0.0781              | H−1 → L   | 0.6931 | MLCT/XLCT/LLCT |
| 3.439/360 | 0.0002              | H−2 → L   | 0.6952 | MLCT/XLCT/LLCT |
| 3.689/336 | 0.0382              | H−3 → L   | 0.6857 | MLCT/XLCT/LLCT |
| 3.769/328 | 0.0027              | H−L+1     | 0.703  | MLCT/XLCT/LLCT |
| 3.901/317 | 0.0111              | H−1 → L+1 | 0.703  | MLCT/XLCT/LLCT |
| 2.348/528 | 0.3559              | H−L       | 0.703  | XLCT/LLCT     |
| 2.793/443 | 0.0017              | H−1 → L   | 0.699  | MLCT/XLCT/LLCT |
| 2.948/420 | 0.0804              | H−2 → L   | 0.695  | MLCT/XLCT/LLCT |
| 3.096/400 | 0.5118              | H−L+1     | 0.699  | MLCT/XLCT/LLCT |
| 3.297/376 | 0.0000              | H−3 → L   | 0.701  | XLCT/LLCT     |
| 3.381/366 | 0.0401              | H−L+2     | 0.701  | XLCT/LLCT     |

Experimental values from [34]

![Graph 1](image1)

![Graph 2](image2)

![Graph 3](image3)
The contribution of MLCT/XLCT/LLCT is remarkable in lowest energy absorption band with the order of 2 > 3 > 1 > 4 > 5. All spectra have identical profiles but they have different absorption bands.

### 3.4. Phosphorescence Spectra

With the optimized $T_1$ structures as the starting point, the emission spectra of complexes 1 - 5 were determined by the TDDFT/B3LYP methods with PCM in CH$_2$Cl$_2$ media. The energy/wavelengths, dominant transitions with larger CI coefficients and their assignments are collected in Table 3. The contour plots of HOMO and LUMO for all complexes are shown in Figure 6 and main FMOs energy levels are plotted in Figure 7. Table 3 shows that the energy emissions of 1 - 5 complexes mainly originate from LUMO to HOMO transition. According to Table 3, it also can be seen that LUMOs are mainly localized on $\pi^*(2',2''$-bipyridine) orbital for all complexes, while HOMOs are primarily on $[\text{d(Re)}]$, $[\text{p(Cl)}]$ and $\pi$(CO) ligands. To intuitively understand the emission transition, the plots of HOMO and LUMO emissions of 1 - 5 complexes are presented in Figure 6.

For 1 - 5 complexes, HOMO energy levels are similar to each other, but LUMO energy levels present an obvious variation. The introduction of -NO$_2$ and PhNO$_2$ on R position of 2, 2'-bipyridine ligand can decrease the $E_{\text{LUMO}}$. The introduction of -NH$_2$ and -TPA increases the $E_{\text{LUMO}}$. So, the introductions of -NO$_2$ and -PhNO$_2$ lead to the lowest energy emission bands red shifted relative to complex 1. The introduction of -NH$_2$ group in complex 4 and -TPA in complex 5 can cause a corresponding blue shift. Moreover, complex 5 emit light in the visible range, but other complexes occur in the near-infrared region. There is no experimental assignment for the emissions of these complexes [30]. Therefore, the introduction of stronger electron donating group on the R positions of 2, 2'-bipyridine ligand blue-shifted the spectra with the lowest energy emission band.

| Complex | $E$ (eV/nm) | Transition | CI | Assignment |
|---------|-------------|------------|----|------------|
| 1       | 1.3603/911  | L→H       | 0.9313 | $^1\text{MLCT}/^\pi\text{LCT}/^\pi\text{LLCT}$ |
| 2       | 1.142/1085  | L→H-1     | 0.9718 | $^1\text{MLCT}/^\pi\text{LCT}/^\pi\text{LLCT}$ |
| 3       | 0.836/1483  | L→H       | 0.8304 | $^1\text{MLCT}/^\pi\text{LCT}/^\pi\text{LLCT}$ |
| 4       | 1.4271/869  | L→H       | 0.8832 | $^1\text{MLCT}/^\pi\text{LCT}/^\pi\text{LLCT}$ |
| 5       | 1.5815/784  | L+3→H     | 0.6790 | $^1\text{MLCT}/^\pi\text{LCT}/^\pi\text{LLCT}$ |
3.5. Effect of Solvent on Absorption and Emission Spectra

Different solvents have different polarity. Different solvents can cause different excitation energies due to their polarity. For the lowest energy absorption and emission wavelengths, solvent effects are assessed using the PCM method as shown in Table 4 for complexes 1 - 5. Both the lowest energy absorption and emission bands have red shifted (longer wavelength) with the decrease in solvent polarity while blue shifted (shorter wavelength) with the increase in solvent polarity for all complexes. Compared with the experimental
method, it is easy for theoretical calculations to change solvents. This is another advantage of theoretical calculations.

### Table 4. The lowest energy absorption and emission wavelength of 1 - 5 complexes in the different polarity solvents in case of dichloromethane, acetone and methanol.

| Solvent | Polarity | Absorption (nm) | Emission (nm) |
|---------|----------|-----------------|---------------|
|         |          | Complex 1 2 3 4 5 | Complex 1 2 3 4 5 |
| CH₂Cl₂  | 3.4      | 423 634 505 404 | 400 935 935 939.5 841 1195 |
| CH₃COCH₃ | 5.4      | 412 617 493 395 | 399 842 914 939 837 1193 |
| CH₃OH   | 6.6      | 409 612 489 391 | 398 840 906 938 835 1189 |

### 3.6. Electronic Affinity (EA), Ionization Potential (IP) and Reorganization Energy (λ)

The electronic affinity (EA), ionization potential (IP) and reorganization energy (λ) are very significant in performance ability of PHOLED materials. IP and EA are usually used to assess the energy barrier for the injection of holes and electrons from the anode into the emitting materials [31]. The EA can be either for vertical excitations or adiabatic excitations denoted by EA (v) and EA (a). Similarly, IP is denoted by IP (v) and IP (a). The IP describes the energy difference between the cation and its neutral molecule. The EA is defined as the energy difference between the cation and its neutral molecule at the equilibrium geometry of the neutral molecule. Similarly, the EEP is the energy difference between neutral molecules and anionic systems calculated using cationic geometric structures. In this study vertical and adiabatic of EA and IP (EAv, EAv, IPv, and IPa), EEP, HEP, electron transport reorganization energy (λelectrons), hole transport reorganization energy (λholes) and the difference between λholes and λelectrons for all complexes were calculated with DFT method and collected in Table 5. The introduction of EWG on R position facilitates the electron injection ability, while the introduction of EDG facilitates the hole injection ability. As shown in Table 5, it can be found that all of the complexes possess lower λelectrons in comparison to λholes except complex 5, 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. But, as it can be seen complex 5 has a relatively small difference between λelectrons and λholes which can improve the charge transfer balance and further enhance the device performance of PHOLEDs. So complex 5 is more suitable to be used as an emitter in OLEDs in this regard. The above analysis result reveals that the different substituent groups on the R position of 2, 2'-bipyridine ligand 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.

### Table 5. The calculated vertical and adiabatic of EA and IP (EAv, EAv, IPv and IPa all in eV), EEP in eV, HEP in eV, λelectrons in eV, λholes in eV and the difference between λholes and λelectrons of the complexes.

| Complex | EAv | EAa | IPv | IPA | HEP | EEP | λelectrons | λholes | λelectrons - λholes |
|---------|-----|-----|-----|-----|-----|-----|-------------|--------|---------------------|
| 1       | -1.954 | -1.785 | 7.622 | 7.416 | 7.195 | -1.619 | 0.335 | 0.425 | 0.092                |
| 2       | -3.185 | -3   | 7.969 | 7.769 | 7.55 | -2.813 | 0.372 | 0.419 | 0.047                |
| 3       | -2.857 | -7.396 | 2.987 | 2.781 | 7.271 | -7.222 | 4.365 | 4.284 | 0.081                |
| 4       | -1.721 | -1.525 | 7.344 | 7.101 | 4.287 | -3.135 | 0.396 | 0.517 | 0.121                |
| 5       | -2.029 | -1.839 | 6.713 | 6.645 | 6.356 | -1.652 | 0.377 | 0.147 | -0.23           |

### 3.7. The Emission Quantum Yield in CH₂Cl₂ Media

The emission quantum yield (Φ) can be affected by the competition between radiative decay rate constant (Kr) and non-radiative decay rate constant (Ke) [32].

Φ = Krτem = k_r / k_r + k_nr

Where, τem is the emission decay time. From the above formula, the large Kr and small Knr are required to increase the value of emission quantum yield (Φ). The K_r and K_nr can expressed as:

K_r = \left( \frac{\Psi_{S1}^H | H_{S0} \Psi_{T1}^H | ^2 \mu_{sl}^2}{\Delta E_{S1-T1}} \right)

K_n = \frac{16\pi^2 n^4 E_{T1}}{3h\epsilon_0}

Where, α and β are constant, μ_{sl} is transition electric dipole moment from S0 to S1, ΔE_{S1-T1} is the energy gap between S1 and T1 states, E_{T1} is the energy of the lowest triplet excited state for phosphorescence and n, h and ε are refractive index,
bands have red-shift with the decrease of solvent polarity for photophysical properties such as absorption and emission blue-shifted. The solvent effect on absorption and emission spectra indicates that 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 λelectron and λhole of complex 5 is the smallest among these complexes, enhancing the device performance of OLEDs further. The emission quantum yield of complex 5 is possibly higher than other complexes. Therefore, complex 5 is more suitable to be used as an emitter in the PHOLEDs. Lastly, theoretical investigations can provide constructive information in the design and synthesis of novel and high-efficiency OLEDs materials. The Re(I) tricarbonyl complexes with incorporated hole transporting group to the 2, 2'-bipyridine ligand exhibit wonderful luminescent properties.

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Competing Interests

Authors have declared that no competing interests exist.

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