Research paper

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Combined Ultrafast Spectroscopic and TDDFT Theoretical Studies on Dual Fluorescence Emissions Promoted by Ligand-to-Metal Charge Transfer (LMCT) Excited States of Tungsten-Containing Organometallic Complexes

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ABSTRACT: In this work, we first designed and synthesized two tungsten-containing organometallic complexes MeNOON and MeNOOO with novel dual fluorescence emissions. Moreover, the combined femtosecond ultrafast spectroscopy and time-dependent density functional theory (TDDFT) method has been performed to investigate the excited-state dynamics of MeNOON and MeNOOO complexes. It is distinctly demonstrated that dual fluorescence emissions of tungsten-containing organometallic complexes are originated from the localized-on-ligand (LL) and ligand-to-metal charge transfer (LMCT) excited states, respectively. Furthermore, the ultrafast LMCT process has been measured by the femtosecond spectroscopy.

KEYWORDS: Dual Fluorescence; Localized-on-Ligand; Ligand-to-Metal Charge Transfer; Tungsten-Containing Organometallic; Excited State.

Introduction

OLED is a high-brightness [1], wide-visual [2], fully-cured light-emitting device and exhibits unparalleled advantages: high luminous efficiency and high brightness [3-10]. Light-emitting materials in OLEDs can be divided into three categories: organic small molecular [11], organometallic complexes [12-16] and polymer [17-19]. Organometallic complexes have the advantages of organic matter and well inorganic stability [20]. Organometallic chromophores, which have potential utilities in optical and electronic applications, have been widely investigated in recent years [21]. Photophysical investigations of these molecular chromophores are very helpful for understanding of optical properties and further application in OLEDs of organometallic materials [22-25].

There have been many reports about luminescent organometallic complexes with palladium, platinum and iridium as the central metal atom. Tungsten is a transition metal like palladium, platinum, and iridium, and its electron distribution outside the core is similar to iridium. Tungsten oxides and sulfides have been widely used in light-emitting devices such as OLEDs due to their excellent optical properties [26, 27]. It should be noted that tungsten has been used in incandescent bulbs for decades. However, the tungsten-containing organometallic complexes with novel luminescence properties have been rarely reported [28-30].

Recently, density functional theory (DFT) and time-dependent density functional theory (TD-DFT) based calculations have been important tools to understand or predict photophysical properties of organometallic complexes [31-34]. Combining the theoretical methods with experimental investigations could help to understand the correlation between the ligand and metal as well as fluorescence properties for a rationalized application design of tungsten-containing organometallic complexes [35-41]. According to the above principles, we have designed a series of tungsten-containing organometallic complexes and synthesized two typical complexes designated as ligand MeNOON and ligand MeNOOO using a symmetric phenol structural compound containing an imine group as a ligand.

Experimental and Theoretical Methods

Synthesis of Ligand MeNOON. 2,4-dimethylphenol (2.95 g, 24.2 mmol), N,N-dimethylethylenediamine (1.35 mL, 12.3 mmol) and aqueous solution with a formaldehyde concentration of 36% (2.5 mL, 33.6mmol) were dissolved in methanol (10 mL) and stirred at room temperature for 72 h. Put the mixture in the refrigerator overnight. Filtered the mixture and washed thoroughly with ice cold methanol to give white solid. The solid was further purified by recrystallization from methanol to afford ligand MeNOON as a white solid (2.73 g, yield 63%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.85 (d, J = 20.2 Hz, 2H), 6.69 (s, 2H), 3.59 (s, 4H), 2.57 (s, 4H), 2.33 (s, 6H), 2.23 (d, J = 12.6 Hz, 12H).

Synthesis of Ligand MeNOOO. 2,4-dimethylphenol (1.95 g, 16.0 mmol), 2-methoxyethylamine (0.52 mL, 6.00 mmol) and aqueous solution with a formaldehyde concentration of 36% (1.2 mL, 16.0 mmol) were dissolved in methanol (6 mL) and refluxed at 75°C for 24 h. After completion of the reaction, the mixture was cooled at room temperature and filtered. The solid was dissolved in methanol and refluxed at 75°C for 2 h. The mixture was cooled at room temperature and filtered to give white solid. The solid was further purified by recrystallization from methanol to afford ligand MeNOOO as a white solid (2.42 g, yield 58%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 2H), 6.78 (s, 2H), 6.60 (s, 2H), 3.65 (s, 4H), 3.52 (dd, *J* = 11.2, 6.1 Hz, 2H), 3.40 (s, 3H), 2.63 (t, *J* = 5.1 Hz, 2H), 2.13 (d, *J* = 4.6 Hz, 12H).

Synthesis of Complex MeNOON. To a degassed solution of the intermediate ligand MeNOON (0.97 g, 2.72 mmol) in dry toluene were added WO_2Cl_2 (0.80 g, 2.72 mmol) and pyridine (0.45 mL, 5.92 mmol). The reaction mixture was refluxed for 24 h under N_2 atmosphere. The reaction mixture was evaporated and dissolved in dichloromethane. The reaction mixture was filtered through sand and the filtrate was collected. The solvent was then removed under reduced pressure and the yellow residue was dissolved in dichloromethane. The addition of methanol to the dichloromethane solution led to the precipitation of a yellow solid. The solid was filtered and dried under vacuum to afford complex MeNOON as a yellow solid (1.01 g, yield 65%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.96 (d, *J* = 20.0 Hz, 2H), 6.66 (s, 2H), 4.75 (d, *J* = 13.8 Hz, 2H), 3.57 (d, *J* = 13.8 Hz, 2H), 2.76 – 2.66 (m, 2H), 2.55 (s, 6H), 2.29 (dd, *J* = 13.5, 7.5 Hz, 2H), 2.19 (d, *J* = 3.8 Hz, 12H). MS (+ve, m/z): 571.18 [M^+].

Synthesis of Complex MeNOOO. The procedure was similar to that described for the preparation of complex MeNOON except intermediate ligand MeNOOO (0.93 g, 2.72 mmol) was used instead of ligand MeNOON. Got complex MeNOOO through the above experiment as a yellow solid (0.86 g, yield 59%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.69 (d, *J* = 16.6 Hz, 2H), 6.67 (s, 2H), 4.70 (d, *J* = 13.6 Hz, 2H), 3.77 (s, 3H), 3.66 (t, *J* = 16.8 Hz, 2H), 3.18 (t, *J* = 6.0 Hz, 2H), 2.81 (t, *J* = 6.0 Hz, 2H), 2.18 (t, *J* = 18.0 Hz, 12H). MS (+ve, m/z): 559.15 [M^+].

Scheme 1.

UV-vis absorption spectra were obtained using an Ocean Optics PH-2000-BAL spectrophotometer at 25°C. The test solvents were *n*-hexane and methanol. The steady-state fluorescence was recorded using F-380 fluorescence spectrofluorometer at 25°C. The *n*-hexane and methanol were used as the measurement solvents. Femtosecond transient absorption was recorded using femtosecond transient absorption (Femtoframe Ⅱ) at 25°C.

All quantum chemical calculations were performed using Gaussian 09 program[42]. Ground-state geometry and the excited states optimization was carried out by DFT method with the Cam-b3lyp functional. The 6-31G basis set was chosen for nonmetallic elements and LANL2DZ basis sets was selected for tungsten atoms. Geometry optimizations of both the ground state and excited state were carried out using the DFT/TDDFT method without symmetry constraints [43-45].

Results and Discussion

As shown in Figure 1, the UV-Vis spectra of complexes exhibit absorptions in the UV region (213–221 and 251–270 nm) with strong absorption intensity ($\varepsilon \sim 10^6$ L mol^{-1} cm^{-1}). One can note that the position and intensity of the absorption peaks cannot be significantly affected by the different solvents. In addition, both MeNOON and MeNOOO complexes have dual fluorescence emissions in the ultraviolet and visible regions, respectively. Moreover, both the two emission peak positions cannot shift at different excitation wavelength of 218 nm, 260 nm, 266 nm, respectively. The relevant data are summarized in Table 1.

Figure 1.

Table 1.

By observing the UV-Vis absorption and fluorescence emission spectra of the two complexes, it is found that the absorption and emission of the complexes MeNOON and MeNOOO are not significantly different. The difference between the two complexes is that the amine branch of the middle part of the ligand is respectively connected to an imino group and a methoxy group, so the absorption spectra and emission spectra of two complexes are similar.

DFT/TDDFT theoretical calculations are performed to study the dual fluorescence emissions mechanism [46]. The ground state configurations of the complexes MeNOON and MeNOOO are optimized. The data of the two complexes are basically the same, indicating that the differences caused by the imino group and methoxy group in the ligand have little effect on the configuration of the complexes.

Figure 2.

The calculated electronic transition energies and corresponding oscillator strengths (*f*) of the singlet excited states for complexes MeNOON and MeNOOO are listed in Table 2. It is shown that the calculated wavelength absorptions for complexes MeNOON and MeNOOO are at 271, 263, 217 and 270, 266, 197 nm respectively, which are almost consistent with the experimental results. As shown in Table 2, excited state S_1, S_3 and S_{14} of complex MeNOON correspond to the contribution of the HOMO to the LUMO, the HOMO-4 to the LUMO+1 and the HOMO-5 to the LUMO+1. Excited state S_1, S_2 and S_{19} of complex MeNOOO correspond to the contribution of the HOMO to the LUMO, the HOMO-1 to the LUMO and the HOMO-2 to the LUMO. It can be clearly noted from the Figure 2 that the charge population of HOMO and LUMO orbitals are dominantly localized on the ligand and some other orbitals are relevant to both the ligand and metal for complexes. So some excited states could be only localized on ligand (LL) while some excited states will involve ligand to metal charge transfer (LMCT) character. The LL and LMCT characters for some involved excited states are also listed in Table 2.

Table 2.

The high-energy fluorescence emission peak at about 292 nm is very close to the S_1 state absorption peak at 266 nm. Consequently, the Stokes shift for the high-energy emission is as small as 26 nm for both MeNOON and MeNOOO complexes. The small Stokes shift confirms that the high-energy emission and the S_1 state absorption peak are originated from the same excited state with the LL character. As a result, both the S_1 state absorption and high-energy fluorescence emission are mainly originated from the absorption and fluorescence emission of their ligand for both MeNOON and MeNOOO complexes.

Figure 3.

It is worth noting that the low-energy fluorescence emission peak has a remarkable redshift to about 570 nm and the Stokes shift is as large as 304 nm. Both the very large fluorescence spectral redshift and Stokes shift propose that the low-energy fluorescence emission might be originated from a new excited state with prominent charge transfer character between ligand and metal. We have successfully optimized the excited state geometric conformation with TDDFT method for both MeNOON and MeNOOO complexes in methanol solvent and presented the calculated fluorescence emission value and relevant molecular orbitals in Figure 3a. One can see that the calculated fluorescence emission value from this excited state is 535 nm and 575 nm, which is in good agreement with the experimental low-energy fluorescence emission peak in methanol solvent for MeNOON and MeNOOO, respectively. At the same time, it is distinct that the excited state is obvious LMCT state from the analysis of relevant molecular orbitals. Therefore, it has been demonstrated that the tungsten-containing organometallic complexes are directly photoexcited to the S_1 excited state of the LL character and hence could emit the LL fluorescence as shown in Figure 3b. Subsequently, the ligand to metal charge transfer process will take place and finally emit the LMCT fluorescence from the stable LMCT excited state.

Figure 4.

The femtosecond transient absorption (fs-TAS) spectroscopy has been performed to investigate the ultrafast LMCT process upon excitation at 266 nm for MeNOON and MeNOOO complexes [47]. Time-resolved spectra are recorded in the spectral range 360-660 nm. The transient absorption spectra of complexes MeNOON and MeNOOO at different times after excitation are shown in Figure 4. It can be seen from the Figure 4a) and c) that the complex MeNOON has an S_1 excited state absorption at about 365 nm. Combined with the calculated data, it is known that this process is attributed to LMCT. Comparing the fluorescence emission spectra, it is known that the complex MeNOON has stimulated emission at about 630 nm. For complex MeNOOO, we can also see the excited state absorption at about 405 nm that process is attributed to LMCT and the stimulated emission at about 630 nm from Figure 4b) and 4d). These femtosecond transient absorption results are consistent with the DFT/TDDFT results. According to Figure 4e) and f), the time constants of the LMCT process are experimentally measured as 453 ps and 959 ps for complexes MeNOON and MeNOOO, respectively.

Conclusion

In summary, the dual fluorescence emission mechanism of tungsten-containing organometallic complexes MeNOON and MeNOOO was studied through steady-state and time-resolved spectroscopy experiments and quantum chemical calculations. High-energy emission peaks can be attributed to the LL state of the ligand. Low-energy emission peaks can be attributed to the excited states formed by the LMCT process. At the same time, the femtosecond transient absorption spectrum also confirmed the existence of LMCT process in the excited state. It is conceivable that as we adjust and improve its ligand structure, the tungsten complex will be as competitive as other luminescent complexes and have broad application prospects in the field of OLEDs. At the same time, its emission in the deep ultraviolet region indicates its application potential in the fields of water sterilization, disinfection and confidential communication.

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Note. The authors declare no competing financial interests.

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Figure captions:

Table 1. Spectral data of complexes MeNOON and MeNOOO in *n*-hexane and methanol.

Table 2. Selected calculated electronic transition energies and correspond oscillator strengths of the singlet excited state of complexes MeNOON and MeNOOO^{a}.

Figure 1. UV-Vis absorption spectra in methanol, fluorescence emission spectra in *n*-hexane and methanol and the structure of complexes MeNOON and MeNOOO.

Figure 2. Calculated frontier molecular orbitals for the singlet states of complexes MeNOON and MeNOOO.

Figure 3. a) Frontal molecular orbitals of the excited state molecules and calculated and experimental values of fluorescence emission wavelength of complexes MeNOON and complex MeNOOO; a) Fluorescence emission mechanism, Abs = Absorbance, LL = Localized-on-Ligand, LMCT = Ligand-to-Metal Charge Transfer.

Figure 4. Femtosecond transient absorption spectra of a) complex MeNOON and b) complex MeNOOO; c) temporal evolution for complex MeNOON; d) temporal evolution for complex MeNOOO; e) experimental (○) and fitted (lines) intensity decay profiles of fs-TAS for complex MeNOON and f) experimental (○) and fitted (lines) intensity decay profiles of fs-TAS for complex MeNOOO upon photoexcitation at λ = 266 nm. Solvent contribution was subtracted.

Scheme 1. Synthesis of ligand MeNOON, MeNOOO and complex MeNOON, MeNOOO, reagents and conditions, ligand MeNOON: 2,4-dimethylphenol, N,N-dimethylethylenediamine, formaldehyde and methanol, rt, yield: 63%; complex MeNOON: ligand MeNOON, toluene, 120°C; yield: 65%; ligand MeNOOO: 2,4-dimethylphenol, 2-methoxyethylamine, formaldehyde and methanol, 75°C, yield: 58%; complex MeNOOO: ligand MeNOOO, toluene, 120°C; yield: 59%.

Table 1.

Complex	Solution	$\boldsymbol{\lambda_{abs.1}}$ (nm)	$\boldsymbol{\lambda_{abs.2}}$ (nm)	$\boldsymbol{\lambda_{abs.3}}$ (nm)	$\boldsymbol{\lambda_{em.1}}$ (nm)	$\boldsymbol{\lambda_{em.2}}$ (nm)
MeNOON	*n*-hexane	266	260	217	292	570
	MeOH	266	260	217	294	574
MeNOOO	*n*-hexane	266	261	217	292	570
	MeOH	266	260	218	294	573

Table 2.

Complex	Electronic transition	Absorption wavelength/nm (energy/eV)	*f*	Contrib	CI	Character
MeNOON	S_0-S_1	271(4.57)	0.0971	H→L	0.381	LL
	S_0-S_3	263(4.72)	0.1459	H-4→L+1	0.331	LMCT
	S_0-S_{14}	217(5.71)	0.0516	H-5→L+1	0.402	LMCT
MeNOOO	S_0-S_1	270(4.59)	0.1008	H→L	0.567	LL
	S_0-S_2	266(4.66)	0.1057	H-1→L	0.558	LMCT
	S_0-S_{19}	197(6.30)	0.0964	H-2→L	0.577	LMCT

[a]H means the highest occupied molecular orbital (HOMO), and L means the lowest unoccupied molecular orbital (LUMO), LL = Localized-on-Ligand, LMCT = Ligand-to-Metal Charge Transfer.

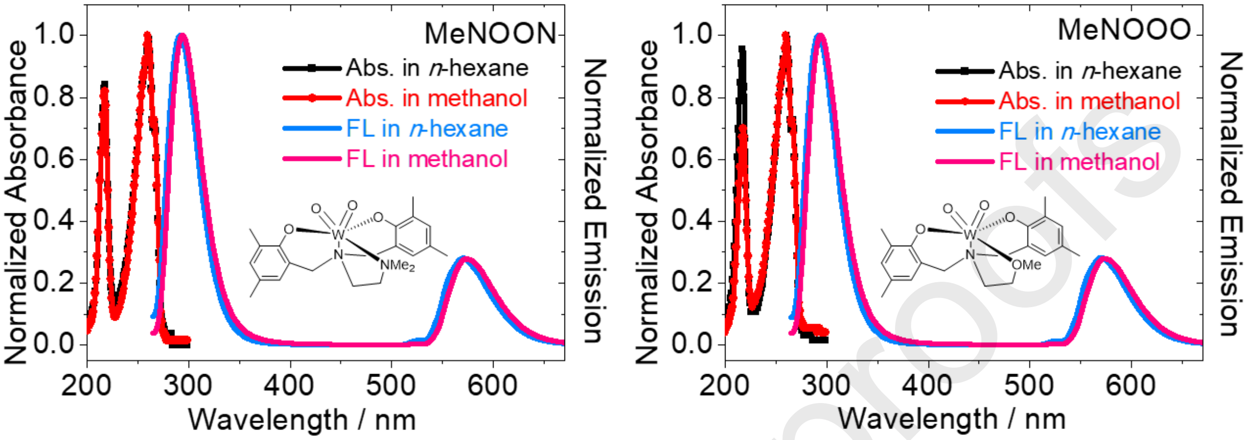

MeNOON
Abs. in n-hexane
Abs. in methanol
FL in n-hexane
FL in methanol
O
O
O
W
O
N
NMe2
Normalized Absorbance
1.0
0.8
0.6
0.4
0.2
0.0
Normalized Emission
200
300
400
500
600
Wavelength / nm
MeNOOO
Abs. in n-hexane
Abs. in methanol
FL in n-hexane
FL in methanol
O
O
O
W
O
N
OMe
Normalized Absorbance
1.0
0.8
0.6
0.4
0.2
0.0
Normalized Emission
200
300
400
500
600
Wavelength / nm

Figure 1.

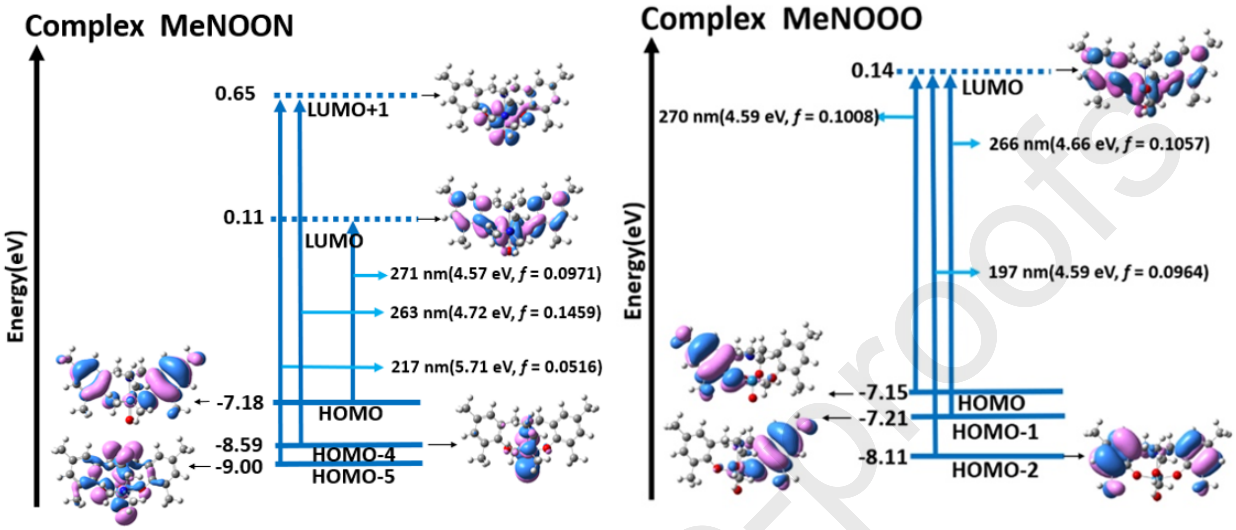

Complex MeNOON
Energy(eV)
0.65
LUMO+1
0.11
LUMO
271 nm(4.57 eV, f = 0.0971)
263 nm(4.72 eV, f = 0.1459)
217 nm(5.71 eV, f = 0.0516)
-7.18
HOMO
-8.59
-9.00
HOMO-4
HOMO-5
Complex MeNOOO
Energy(eV)
0.14
LUMO
270 nm(4.59 eV, f = 0.1008)
266 nm(4.66 eV, f = 0.1057)
197 nm(4.59 eV, f = 0.0964)
-7.15
HOMO
-7.21
HOMO-1
-8.11
HOMO-2

Figure 2.

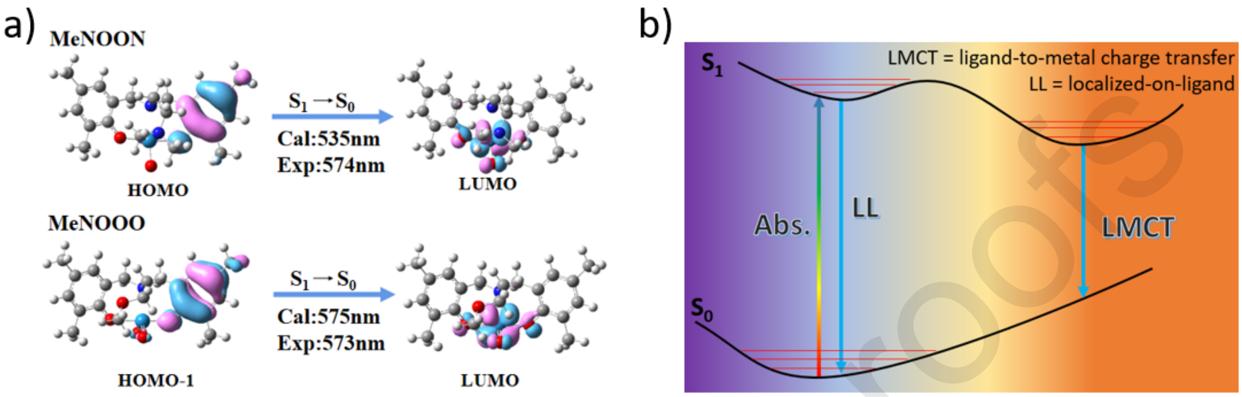

a)
MeNOON
HOMO
S1 → S0
Cal:535nm
Exp:574nm
LUMO
MeNOOO
HOMO-1
S1 → S0
Cal:575nm
Exp:573nm
LUMO
b)
S1
LMCT = ligand-to-metal charge transfer
LL = localized-on-ligand
Abs.
LL
LMCT
S0

Figure 3.

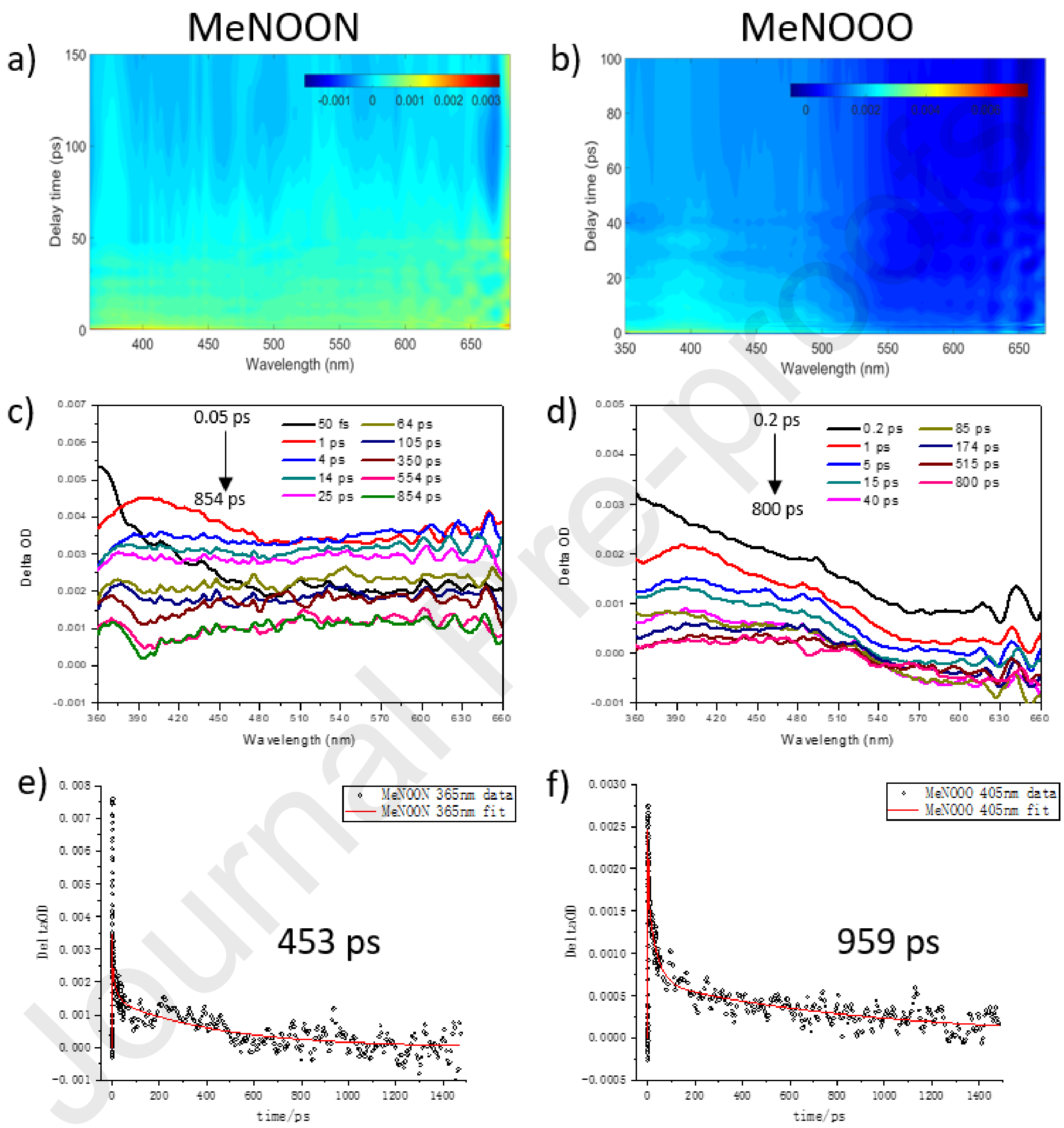
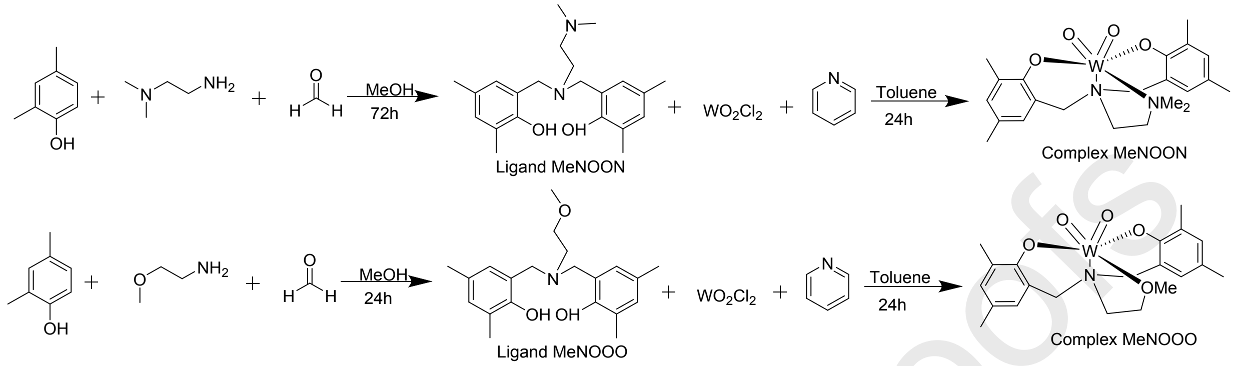

a)
MeNOON
Delay time (ps)
Wavelength (nm)
-0.001 0 0.001 0.002 0.003
b)
MeNOOO
Delay time (ps)
Wavelength (nm)
0 0.002 0.004 0.006
c)
Delta OD
0.05 ps
854 ps
50 fs
1 ps
4 ps
14 ps
25 ps
64 ps
105 ps
350 ps
554 ps
854 ps
Wavelength (nm)
d)
Delta OD
0.2 ps
800 ps
0.2 ps
1 ps
5 ps
15 ps
40 ps
85 ps
174 ps
515 ps
800 ps
Wavelength (nm)
e)
DeltaOD
MeNOON 365nm data
MeNOON 365nm fit
453 ps
time/ps
f)
DeltaOD
MeNOOO 405nm data
MeNOOO 405nm fit
959 ps
time/ps

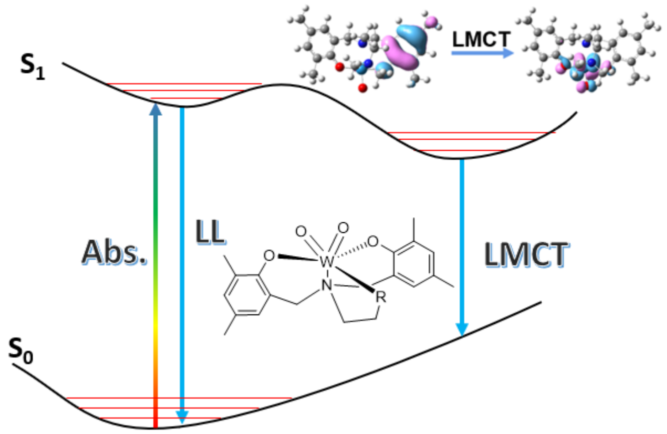
Figure 4.



NH2
MeOH
72h
Ligand MeNOON
WO2Cl2
Toluene
24h
Complex MeNOON
NMe2
MeOH
24h
Ligand MeNOOO
Complex MeNOOO
OMe

Scheme 1.

Graphical abstract



HIGHLIGHT：

Novel tungsten-containing organometallic complexes are synthesized.

Dual fluorescence emissions are originated from localized-on-ligand (LL) and ligand-to-metal charge transfer (LMCT) excited states.

Femtosecond transient absorption is used to explain charge transfer in organometallic complexes.

Credit Author Statement

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Yurong Guo: Methodology, Software, Data Curation, Writing - Original Draft, Visualization

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Yanan Wang: Data Curation, Validation, Resources, Formal analysis, Data Curation

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: