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Photophysical properties of cyclometalated Pt(II) complexes attached with pyrene by C–C single bond

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Abstract

Luminescent complexes, $[(\hat{C}\hat{N}\hat{N})Pt(C\equiv CR)](HC\hat{N}\hat{N} = \text{4-(1-phenyl)-6-phenyl-2,2'-bipyridine}, R = Ph$ (**1**, PPPt); $HC\hat{N}\hat{N}$ = 4-(1-pyrene)-6-phenyl-2, 2′-bipyridine; R = Ph (**2**, PyPPt), *p*-Et-Ph (**3**, PyEPPt)), were synthesized and their photophysical properties were investigated in acetonitrile liquid solution and butyronitrile glasses at 77 K. These complexes display steady state dual emissions at room temperature and 77 K. The emission lifetime and transient absorption of these complexes illustrated that the ^{3}IL triplet state of the molecules could be acquired through the intersystem crossing directly from ^{1}MLCT state and the triplet–triplet internal conversion from the ^{3}MLCT state to the ^{3}IL state was negligible in the molecules.

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Keywords: Photophysical properties; Cyclometalated Pt(II) complexes

1. Introduction

Transition metal complexes with metal-to-ligand charge transfer (MLCT) excited state have shown attractive properties in these years [1–3]. In these compounds, the combination of visible light absorption, photoluminescence with long lifetime and inertness for photo-decomposition extends their application in the research fields of solar energy conversion [4], luminescence sensing [5], biotechnology [6] and electro-luminescent display [7].

Most of the studies on the MLCT state focused on d^6 metal polypyridine complexes, e.g. Ru(II) [8], Os(II) [9], and Re(I) [10] complexes. Square-planar d^8 platinum(II) [11–13] complexes containing a chelating diimine ligand represent increasing interest. However, square-planar d [8] complex were proposed to be unstable with respect to a D_{2d} distortion, which could result in radiationless decay process. Therefore, the complexes with tridentate ligand (tpy) [14], which prefers planar geometry, and discourage a D_{2d} distortion, have been studied. Some platinum(II) bearing cyclometalated 6-phenyl-2,2′-bipyridine have been prepared and exhibited different photophysical properties, compared to the diimine platinum complexes [15,16]. In a large number of d^6 and d^8 transition metal complexes, the excited state d with lowest energy was metal-to-ligand charge transfer state. Meanwhile, some ligand localized excited states, intra-ligand (IL) or intra-ligand charge transfer (ILCT), existed in the molecules. The states had the same spin multiplicity as MLCT state and were accessible in energy from ^{1}MLCT state. Although multiple excited states coexisted, luminescence in solution was always observed only from one excited state [17], and in most of the cases the observed steady state emission was exclusively from the triplet state with lowest energy. In some cases [17d], thermal equilibrium in the triplet states could be attained via reversible internal conversion. In general, the equilibrium extended greatly the lifetime of the MLCT state. In a few number of complexes [18], thermal equilibrium could

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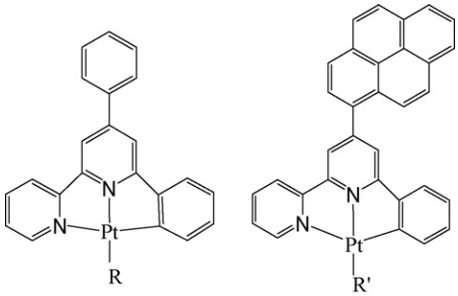

Fig. 1. Structures of complexes: (**1**) R: $\mathrm{PhC{\equiv}C{-}}$; (**2**) R′: $\mathrm{PhC{\equiv}C{-}}$; (**3**) R′: *p*-Et-$\mathrm{PhC{\equiv}C{-}}$; (**4**) R′: Cl–.

not be established rapidly due to weak interactions accompanying with poor internal conversion process in the excited states. Simultaneous emission from different excited states could be observed, particularly in the single crystals or in an organic matrices at low temperature, such the studies on Rh(III), Ir(III), Re(I) and Cu(I) complexes [17e,19]. Although multiple luminescence were observed for these complexes at low temperature in rigid glasses and there were several complexes containing multiple excited states based on MLCT, dual emission were generally not observed in solution at room temperature. More recently, an example of mononuclear Ru(II) complex that exhibited two non-equilibrated excited states at room temperature has been reported and dual emission were observed by using time-resolved technology [19].

In this work, we synthesized two Pt(II) complexes attached with pyrene group by single C–C bond (shown in Fig. 1, complexes **2** and **3**, with two model compounds, **1** and **4**). For both compounds, triplet thermal equilibrium between ^{3}MLCT and ^{3}IL has not been established and dual emission was observed at room temperature and 77 K. It represents a new dual emission case based on MLCT complexes at room temperature without using time-resolved technology. In addition, this work also gives evidence that both ^{3}IL and ^{3}MLCT states can be populated from the excited ^{1}MLCT state.

2. Experimental/materials and methods

2.1. Materials

All reagents for synthesis were obtained from Aldrich Chemical Co. and used without further purification. Spectroscopy grade acetonitrile was purchased from Acros Chemical Co. and butyronitrile solvent was purified according to standard procedures [20].

2.2. General techniques

^{1}H NMR spectra were recorded on a Bruker AV400 spectrometer with the residual proton signal of TMS reference to δ.0. Mass spectra were obtained on Biflex III Maldi-TOF mass spectrometer.

Steady-state electronic absorption spectra and emission spectra were carried out on a Hitachi U3010 and a Hitachi F2500 spectrophotometer, respectively. Low temperature (77 K) emission spectra for glassy samples were measured by means of a 5 mm diameter quartz tube, which were placed in a liquid nitrogen Dewar flask equipped with quartz windows.

Emission lifetime and nanosecond transient absorption spectra were performed on a LP-920 pump-probe spectroscopic setup (Edinburgh). The excited source was the unfocused third harmonic (355 nm, 7 ns fwhm) output of a Nd:YAG laser (continuum sureliteII), the probe light was a pulse-xenon lamp. The signals were detected by Edinburgh analytical instruments (LP900) and recoded on a Tektronix TDS 3012B oscilloscope and computer. The picosecond experiments were performed using a classical pump-probe spectroscopic setup with a passively actively mode locked Nd:YAG laser (BM industries). Briefly, the fundamental and third harmonic emissions are used to generate a white light continuum (probe pulse), and to excite the sample (pump pulse), respectively. The details of the experimental setup were described elsewhere [22]. Samples were continuously purged with a stream of argon gas throughout experiments.

2.3. Synthesis

4-(1-Pyrene)-6-phenyl-2,2′-bipyridine (Ppbpy) and 4-phenyl-6-phenyl-2,2′-bipyridine (ph$_2$bpy) were prepared according to the published method [21].

A modification of literature method [12c] was used for syntheses of two target compounds, all synthetic manipulations were performed under an inert and dry argon gas using standard techniques.

2.3.1. PPPt(*1*)

The complex was prepared by literature procedure, and ^{1}H NMR is identical with literature [23]. ^{1}H NMR (d^6-DMSO, 400 MHz): δ 7.07–7.18 (m. 3H), 7.27 (t, 2H, $J = 7.61$ Hz), 7.37 (d, 2H, $J = 7.49$ Hz), 7.58 (m, 3H), 7.74 (d, 1H, $J = 6.98$), 7.87 (m, 2H), 8.10 (d, 2H, $J = 6.72$ Hz), 8.33 (s, 1H), 8.37 (t, 1H, $J = 7.60$), 8.58 (s, 1H), 8.75 (d, 1H, $J = 7.22$ Hz), 9.06 (d, 1H, $J = 5.60$). Maldi-TOF/Ms $(m/z)^+$: 603.0.

2.3.2. PyPPt(*2*)

A stirred solution of K_2PtCl_4 (200 mg, 0.48 mmol) and ppbpy (206 mg, 0.48 mmol) in CH_3CN/H_2O reacted at reflux for 48 h to give a reddish-yellow solution. The reacted mixture was evaporated to dryness by rotary evaporation, the residue was dissolved in dichloromethane and filtered, then the filtrate was reduced to ~3 ml, methanol (10 ml) was dropped slowly, and a yellow solid (complex **4**) was obtained (150 mg, yield 47%). The product (30 mg, 0.045 mmol) and phenylacetylene (0.2 ml, 1.8 mmol) in DMF (4 ml)/Et_3N (3 ml) added 2 mg CuI as catalyst were sonicated 8 h at room temperature under dry high purity nitrogen gas. The reaction solution was filtered, washed sufficiently with water and diethyl ether. The solid residue was extracted with dichloromethane. Then the extract was reduced to ~5 ml under reduced pressure, dropped slowly 15 ml methanol exceeding 1 h. The solution was placed at 4 °C overnight to yield a deep-red compound **2** by filtration. Yield: 23 mg (69%).

Anal. for $C_{32}H_{19}N_2PtCl$ (complex **4**): C, 58.05%; H, 2.89%; N, 4.23%, Found: C, 57.83%; H, 2.78%; N, 4.14%; ^{1}H NMR (d^6-DMSO, 400 MHz): δ 6.98 (t, 1H, $J = 7.328$ Hz), 7.10 (t, 1H, $J = 7.296$ Hz), 7.48 (d, 1H, $J = 7.788$ Hz), 7.66 (d, 1H, $J = 7.288$ Hz), 7.87 (t, 1H, $J = 7.184$ Hz), 8.07 (t, 1H, $J = 7.508$ Hz), 8.18–8.26 (m, 7H), 8.31 (t, 2H, $J = 8.52$ Hz), 8.40 (d, 1H, $J = 8.07$ Hz), 8.45 (s, 1H), 8.57 (d, 1H, $J = 7.89$ Hz), 8.90 (d, 1H, $J = 4.956$ Hz). Maldi-TOF/Ms $(M - Cl)^+$: 626.9.

Anal. for $C_{40}H_{24}N_2Pt \cdot H_2O$: C, 64.43%; H, 3.49%; N, 3.76%; Found: C, 64.83%; H, 3.42%; N, 3.70%. ^{1}H NMR (d^6-DMSO, 400 MHz): δ 7.04 (t, 1H, $J = 7.2$ Hz), 7.16 (m, 1H), 7.29 (t, 2H, $J = 7.60$ Hz), 7.40 (d, 2H, $J = 7.60$ Hz), 7.76 (d, 1H, $J = 8.12$ Hz), 7.80 (d, 1H, $J = 7.33$ Hz), 7.90 (t, 1H, $J = 6.38$ Hz), 8.15 (t, 1H, $J = 7.69$ Hz), 8.25–8.40 (m, 9H), 8.48 (d, 1H, $J = 7.85$ Hz), 8.56 (s, 1H), 8.65 (d, 1H, $J = 8.16$ Hz), 9.11 (d, 1H, $J = 5.30$ Hz). Maldi-TOF/Ms $(m/z)^+$: 727.8.

2.3.3. PyEPPt(**3**)

The procedure for **2** was used except that 0.2 ml *p*-ethylphenyl-acetylene instead of phenylacetylene was used. Yield: 25 mg (72%). Anal. For $C_{42}H_{28}N_2Pt \cdot H_2O$: C, 65.20%; H, 3.90%; N, 3.62%, Found: C, 64.72%; H, 3.78%; N, 3.57%, ^{1}H NMR (d^6-DMSO, 400 MHz): δ 1.03 (t, 3H), 1.18 (q, 2H). 7.04 (t, 1H, $J = 7.41$ Hz), 7.14 (m, 3H), 7.76 (d, 1H, $J = 7.18$ Hz), 7.81 (d, 1H, $J = 7.85$ Hz), 7.90 (t, 1H, $J = 6.55$ Hz), 8.15 (t, 1H, $J = 7.40$ Hz), 8.25–8.40 (m, 9H), 8.48 (d, 1H, $J = 7.68$ Hz), 8.56 (s, 1H), 8.65 (d, 1H, $J = 8.12$ Hz), 9.12 (d, 1H, $J = 5.28$ Hz). Maldi-TOF/Ms $(m/z)^+$: 754.40.

In photophysics investigation, such complexes showed good photostablity, which steady-state absorption/emission spectroscopy was reproducible after measurements of transient absorption/emission spectra where several kinds of laser mentioned above were used as light source.

3. Results and discussion

3.1. UV–vis absorption spectra

Absorption spectra of the complexes **1**–**4** were shown in Fig. 2. These absorption spectra obey Beer's Law in the concentration range from 10^{-6} to 10^{-4} mol/L. All the spectra in acetonitrile have intense vibronic-structured absorption bands at $\lambda_{abs} < 370$ nm with extinction coefficients on the order of 10^4 dm^3 mol^{-1} cm^{-1}, and less intense band at 400–500 nm with extinction coefficients on the order of 10^3 dm^3 mol^{-1} cm^{-1}. With reference to previous work [16b] on cyclometalated platinum(II) complexes, the absorption bands of <370 nm are assigned to a serials of intra-ligand (IL) $\pi \rightarrow \pi^*$ transition, while the absorption bands at 400–500 nm are assigned to the metal (Pt(II)) $d \rightarrow \pi^*$ ^{1}MLCT transition. The ^{1}MLCT absorption maximum is red-shifted from 435 nm to 455 nm and becomes broader when the acetylide ligand is instead of chloride ligand, similar to that in the previous work [16a,b]. This phenomenon is explained with the notion that the HOMO of the complex is predominantly metal-based [11c]. An electron-rich acetylide ligand can render the metal center more-electron and raise the metal d orbital energy, more than chloride ligand does, leading to lower energy absorption.

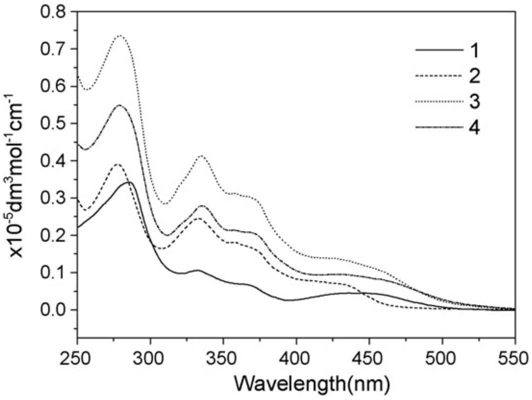

Fig. 2. UV–vis absorption spectra of complexes **1**–**4** in acetonitrile at room temperature.

3.2. Luminescence properties

Emission spectra of all complexes except **4** which emission was very weak were carried out in acetonitrile liquid solution at room temperature and in glassy butyronitrile at 77 K. The observed emission maxima are listed in Table 1 and shown in Fig. 3. The complexes give similar emission spectrum when excited with different excitation wavelengths (300–500 nm), shown in Fig. 4. At room temperature both the complexes **2**

Table 1
Photophysical parameters of the complexes[a]

Complex	λ_{abs} (nm) (logε)	λ_{em} (nm) (298 K)	Φ_{em}[b]	τ_{em} (μs) (298 K)[c]	λ_{em} (nm) (77 K)	τ_{em} (μs) (77 K)[c]	τ_{TA} (μs)[d]
1	446 (3.65) 571	0.174	0.58	548	12.7	0.45	
2	452 (4.03)	632	0.0044	6.02 (∼65%) 0.62 (∼35%)	619	550	7.4
		572(*sh*)		0.61 (>90%)	547	12.9	
3	453 (3.97)	633.	0.0039	12.6 (∼70%) 0.56 (∼30%)	619	552	11.8
		573(*sh*)		0.55 (>90%)	551	11.2	

[a] Argon degassed acetonitrile solution.

[b] Emission quantum yield according to Ru(bpy)$_3$ $\Phi_{em}(H_2O) = 0.042$ as standard [8].

[c] Decay lifetime of emission and component ratio.

[d] Decay lifetime of transient absorption.

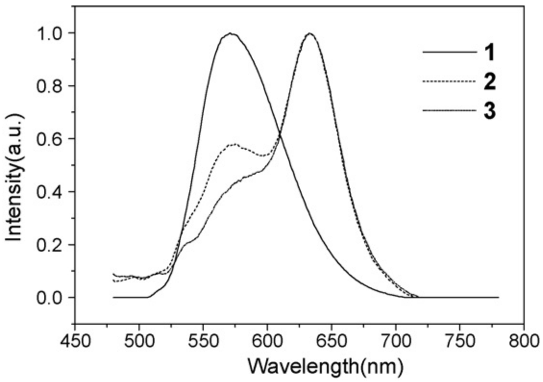

Fig. 3. Normalized emission spectra of complexes **1**–**3** in degassed acetonitrile at room temperature (λ_{ex} 460 nm).

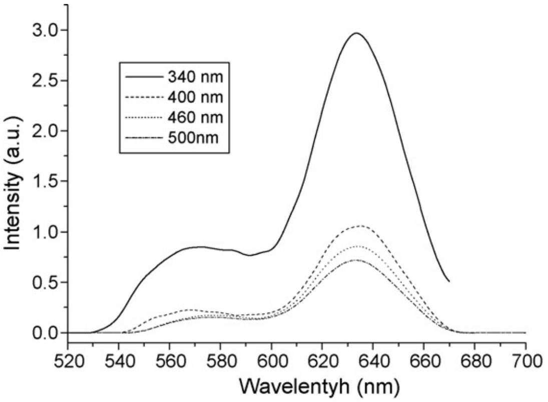

Fig. 4. The emission spectra of complex **2** in degassed acetonitrile at room temperature with different excitation wavelengths.

and **3** show emission maximum at ∼630 nm with a shoulder at ∼575 nm. At 77 K, there appear two absolutely separated emission peaks at ∼550 nm and ∼620 nm, respectively, which are blue-shifted relative to the emissions at room temperature (seen in Fig. 5). Compared with the emission of model compound **1** which exhibited typical ^{3}MLCT emission at different temperatures [12c,16a], the emission band at shorter wavelength is assigned to ^{3}MLCT of the complexes. Additionally the blue-shifted of the band is more evident than that of lower energy emission. This is consistent with that the charge separated state (^{3}MLCT) is more sensitive to temperature variation [24b,25]. The emission at lower energy, however, possibly originated from both ^{3}ILCT and ^{3}IL [19]. Recently, Schmehl et al. observed a mixture of ^{3}MLCT and ^{3}IL ($\pi \rightarrow \pi^*$) states [24a] and dual luminescence [17e] from ^{3}MLCT and ^{3}IL were reported simultaneously by Castellano et al. In our results, the phosphorescence of free ligand (Ppbpy) at 77 K was observed at 609 nm and the shape is quite similar to that of the emission at lower energy bands for complexes **2** and **3** (see the inset in Fig. 5). It indicates that the lower energy emission of complexes **2** and **3** is from their ^{3}IL state and the dual luminescence for the complexes **2** and **3** is originated from ^{3}MLCT and ^{3}IL, respectively.

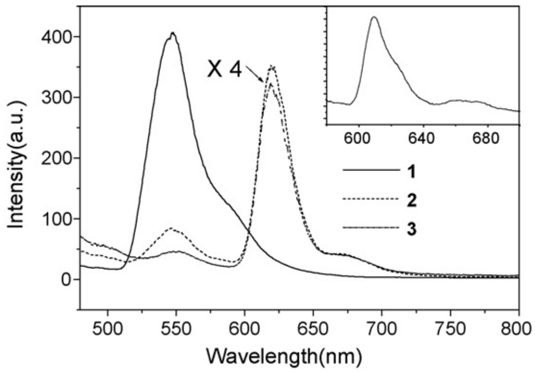

Fig. 5. Emission spectra of the complexes **1**–**3** in glassy butyronitrile at 77 K (λ_{ex} 460 nm); inset: phosphorescence of the ligand (Ppbpy) at 77 K.

The emission quantum yield of complexes **2** and **3** was much lower than the model complex **1** or other known platinum(II) light emission materials [23,26]. Previous paper has investigated substituent effect of electro-withdrawing/donating groups on luminescent properties of square-planar platinum(II) complexes [27] and found that the emission increases with the increase of the ability to withdraw electron and the amount of the substituent groups. In some cases, the electron withdrawing substituents increase ^{3}MLCT luminescence quantum efficiencies because of the depression of the non-radiative decay rate resulting from changes in the MLCT state energy in ways that can be modeled by the energy gap law or by thermal activation of energetically close metal-centered d–d state [27]. In comparison with model complex **1**, complexes **2** and **3** emit weak luminescence was probably because of the relatively stronger electron donating of the pyrenyl group than phenyl in complex **1**.

Time-resolved emission decay processes of the complexes with laser excitation at 355 nm were carried out in degassed acetonitrile at room temperature and in butyronitrile glass at 77 K. Fig. 6 shows the decay processes of complexes **1**–**3** at room temperature and 77 K. The lifetime of the model compound **1** was fitted to mono-exponential decay at all detected wavelength with 0.58 μs at room temperature and 12.7 μs at 77 K (except the setup response from the decay curve in Fig. 6). However, the emission decay of the complexes **2** and **3** give different lifetime at different wavelengths. The lifetimes detected at two emission bands at room temperature and 77 K are also listed in Table 1. It can be seen that two lifetimes were fitted to the decay at different detected wavelengths because of the overlap of the two emission bands. For the complex **2**, the lifetime of the higher energy band is predominantly shorter lifetime component (0.61 μs) at ambient temperature. Meanwhile the lower energy band gives two lifetimes of 0.62 μs and 6.02 μs at room temperature, which originated from concomitant excited state species. Similar results were obtained for complex **3** (seen in Table 1). For the complexes **2** and **3** either at room temperature or 77 K, the emission lifetime obtained at higher energy is similar to that of the model compound **1** and the formation process of the lower energy band is not correlated with the decay of the higher energy band. It implies that the triplet–triplet internal conversion from ^{3}MLCT to ^{3}IL is inefficacious, although the ^{3}IL is lower than ^{3}MLCT in energy. These two separated excited states are involved and formed almost at the same time after the excitation.

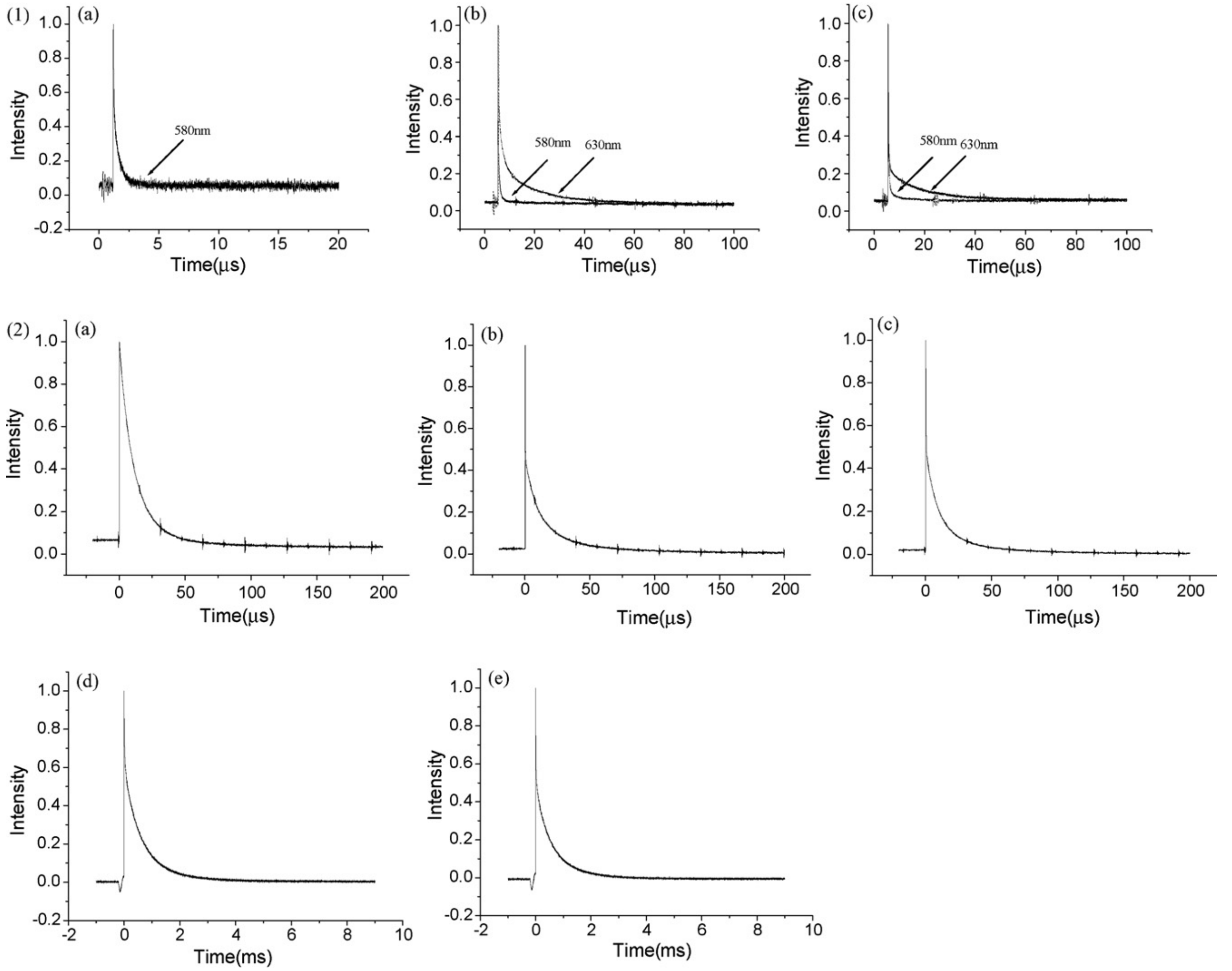

Fig. 6. (1) Decay profile of complex **1**(a), **2**(b) and complex **3**(c). Complexes were dissolved in degassed acetonitrile solution (excited by 355 nm laser pulse). (2) Decay profile of complexes **1**(a), **2**(b, d) and complex **3** (c, e) in butyronitrile glass at 77 K (a–c: detected wavelength: 550 nm; d, e: detected at 620 nm).

According to the absorption spectrum, the excitation at 355 nm is to the ^{1}IL state and at 460 nm is to the ^{1}MLCT state. However, similar emissions were observed with different excitation wavelengths. Thus the internal conversion from the ^{1}IL to the ^{1}MLCT is efficacious. Meanwhile the results above illustrate that the ^{3}IL states of the complex can be acquired through direct intersystem crossing from ^{1}MLCT excited states even at room temperature, not from ^{3}MLCT triplet–triplet internal conversion. It affords an evidence to explain that the singlet ^{1}MLCT can be partitioned to ^{3}MLCT and ^{3}IL states with intersystem crossing process, which was suggested in other work [17e,24a].

As a supporting evidence for population of a ^{3}IL (or other triplet state) directly from ^{1}MLCT state, a common approach is to evaluate the ratio of the luminescence quantum yield Φ and the lifetime of the emitting state τ_{em}. The ratio yields the product of the intersystem crossing η_{isc} and the radiative decay rate constant of the emissive state κ_{r} [18,24a]:

$$\eta_{\mathrm{isc}} k_{\mathrm{r}} = \frac{\Phi}{\tau_{\mathrm{em}}} \qquad (1)$$

The $\eta_{\mathrm{isc}}\kappa_{\mathrm{r}}$-value of complex **1** calculated using Eq. (1) is $3.0 \times 10^5\ \mathrm{s}^{-1}$ and is typical for only ^{3}MLCT excited state from ^{1}MLCT. Whereas $\eta_{\mathrm{isc}}\kappa_{\mathrm{r}}$-values using the shorter decay components for complexes **2** and **3** are $7096\ \mathrm{s}^{-1}$ and $6964\ \mathrm{s}^{-1}$, respectively. When longer decay component was used, values are $730\ \mathrm{s}^{-1}$ and $309\ \mathrm{s}^{-1}$ for **2** and **3**. In fact, the $\eta_{\mathrm{isc}}\kappa_{\mathrm{r}}$ for ^{3}MLCT should be lower than above values because Φ is total quantum yield including ^{3}MLCT and ^{3}IL emitting states in our work. These lower $\eta_{\mathrm{isc}}\kappa_{\mathrm{r}}$ values suggest a competitive intersystem crossing coexists from the ^{1}MLCT state to form another triplet states besides the ^{3}MLCT in these complexes [18].

In addition, under the same conditions, complexes **2** and **3** exhibit greater emission compare with the model compound (Ppbpy)PtCl (**4**), in which phenylacetylene replaced by chlorine atom. No emission was detected for complex **4**, neither at room temperature nor at 77 K. This is attributed to the electron-rich donor of the acetylide ligand, which decreases the energy level of the ^{3}MLCT excited state and enlarges d–d split due to the stronger ligand field, then increases the energy gap between the ^{3}MLCT and ^{3}d–d state of the Pt(II) metal center. In general, the ^{3}d–d state is facile to relax to ground state by the radiationless

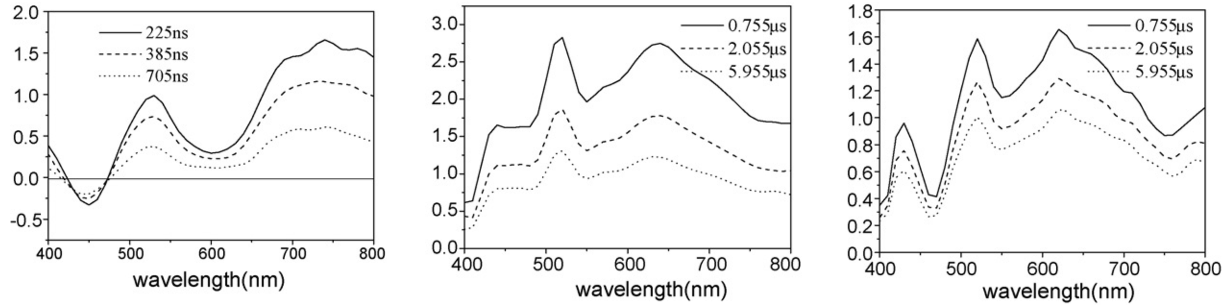

Fig. 7. Nanosecond transient absorption of complexes **1**–**3** in degassed acetonitrile solution: (a) PPPt (**1**), (b) PyPPt (**2**), (c) PyEPPt (**3**) (excited by 355 nm laser pulse).

transition [3c,14b,14d,16a]. Thus the radiationless transition of the complexes **2** and **3** via the ^{3}d–d state is blocked somewhat and it results in the emission enhancement.

The relative energy level of the ^{3}MLCT and ^{3}IL states of the complexes at different temperatures can be estimated directly from the emission position. For **2** and **3**, at 77 K, the emission from ^{3}IL states is found to be ~16,155 cm^{-1}, which is red-shifted ~265 cm^{-1} relative to the phosphorescence of the free ligand (16420 cm^{-1}). The ^{3}MLCT emission energy of the complexes at 77 K is ~18,214 cm^{-1}, which matches well with the model compound **1**. At room temperature the energy levels of ^{3}MLCT and ^{3}IL are 17,301 cm^{-1} and 15,823 cm^{-1}, respectively. So the energy gap between ^{3}MLCT and ^{3}IL is approximately 1478 cm^{-1} and 2059 cm^{-1} from room temperature to 77 K. This relatively large energy gap blocked internal conversion between two excited states [17e, 24b].

3.3. Transient absorption spectra

Nanosecond transient absorption spectra of the complexes in degassed acetonitrile are shown in Fig. 7. All decays of the transient absorption were fitted well with single-exponential process in all detected wavelength and the lifetimes (τ_{TA}) are also listed in Table 1. The transient absorption of complex **1** (Fig. 7(a)) displays bleaching of the ground state absorption to ^{1}MLCT at 400–500 nm, and dipping at 550–650 nm due to emission of ^{3}MLCT. Because the decay lifetime is quite similar with that of the emission of ^{3}MLCT, this moderate intense absorption throughout whole visible region is original from the absorption of lowest state of ^{3}MLCT to higher ^{3}MLCT states. However, the transient absorption of the complexes **2** and **3** (Fig. 7(b) and (c)) shows significant difference to that of the complex **1**. The complex **2** gives a broad spectrum with three maxima at ~430 nm, ~520 nm and ~630 nm, respectively. All the absorption maxima followed the same decay process and it can be fitted to single-exponential with a lifetime of 7.4 μs. It is consistent with the emission lifetime of the ^{3}IL state for the complex **2** (6.02 μs). The complex **3** has a similar transient absorption to that of complex **2** except a dipping observed at 460 nm. The results indicate that the transient absorption for the complexes **2** and **3** is the transition from the lowest state of ^{3}IL to higher excited state(s).

Picosecond transient absorption of compound **2** was carried out for the origin of the transient species. Because of the relatively longer decay process (in μs), only the growing process of the triplet state was observed in detected time-scale. As shown in Fig. 8, the absorption spectrum is the same with that obtained with the nanosecond setup. It means that the formation process of the ^{3}IL state was monitored. At all the absorption peak wavelengths, the rise-time of the triplet formation is less than 10 ps, which illustrates that the formation rate constant of triplet state of ^{3}IL is higher than 10^{11} s^{-1}. This suggests that intersystem crossing to populate accessible triplet state is a rapid process [18]. As shown in the results above, the ^{3}MLCT of the complex emits at ~575 nm and the decay process is with lifetime of ~0.6 μs, correlatively the decay rate constant of ^{3}MLCT is about 10^6 s^{-1}. It is much slower than that of the formation of the ^{3}IL. This also implies that the ^{3}IL is not formed from the ^{3}MLCT.

Fig. 9 describes an energy level diagram for complexes **2** and **3**. From the view of energy level, the ^{3}IL state is lower than that

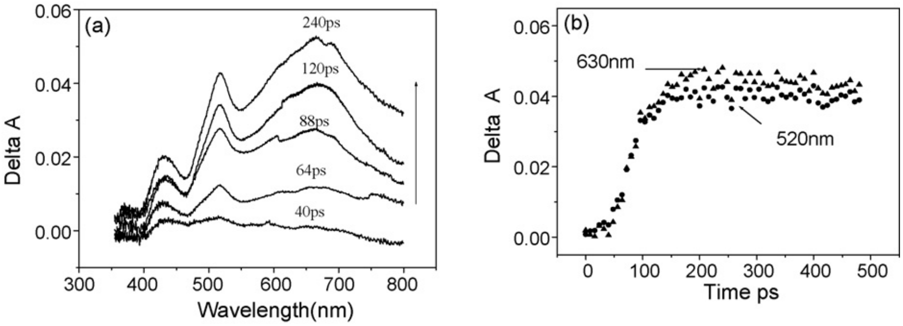

Fig. 8. (a) Time-resolved picosecond transition absorption of complex **2** in degassed dichloromethane solution. (b) Triplet excited state forming kinetics of complex **2** (●) 520 nm, (▲) 630 nm (excited by 355 nm laser pulse).

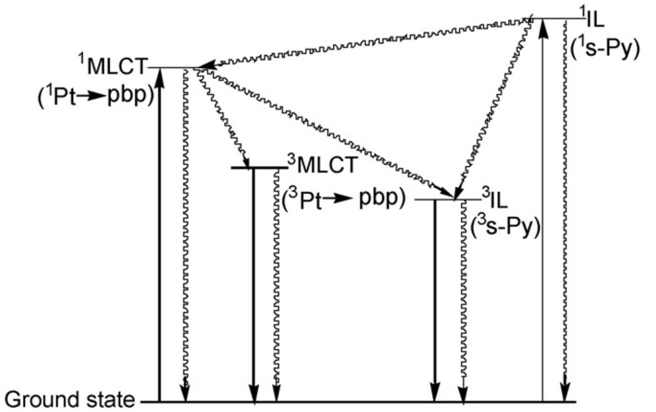

Fig. 9. Energy level description for the photophysical processes of complexes **2** and **3**.

of the ^{3}MLCT. In generally, when ^{1}IL and ^{1}MLCT were excited, the ^{3}IL state could be accessed by intersystem crossing from the excited single-state or by triplet–triplet internal conversion from ^{3}MLCT state. The results of the transient studies indicate that there is not the relationship between the decay of ^{3}MLCT state and the formation of the ^{3}IL state. The triplet–triplet internal conversion from the ^{3}MLCT is not a favorite path to access the ^{3}IL state. So the triplet states are formed directly from the singlet states of the complex.

4. Conclusions

Two cyclometalated Pt(II) complexes (**2** and **3**) attached with pyrene were synthesized and their photophysical properties were investigated. Compared to model complex **1** (with a strong ^{3}MLCT luminescent band) and complex **4** (no emission), compexes **2** and **3** exhibited moderate emission and complicated photophysical properties. Dual emission from ^{3}MLCT and ^{3}IL of the complexes were simultaneously observed at room temperature and 77 K. From the decay of transient absorption, growth of the triplet state and kinetic analysis of the luminescence, it was concluded that triplet–triplet internal conversion from ^{3}MLCT to ^{3}IL was negligible. The absence of the internal conversion from ^{3}MLCT to ^{3}IL also illuminated that the ^{3}IL state could be formed directly from the ^{1}MLCT state via intersystem crossing even when the ^{1}MLCT state was selectively excited.

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References

[1] J.P. Paris, W.W. Brandi, J. Am. Chem. Soc. 81 (1959) 5001–5002.
[2] (a) J. Van Houten, R. Watts, J. Am. Chem. Soc. 98 (1976) 4853–4858;
(b) T.J. Meyer, Prog. Inorg. Chem. 30 (1983) 389–440;
(c) A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, Coordin. Chem. Rev. 84 (1988) 85–277;
(d) A.J. Lee, Chem. Rev. 87 (1987) 711–743;
(e) V. Balzani, A. Juris, M. Venturi, S. Campagna, S. Serroni, Chem. Rev. 96 (1996) 759–834.
[3] (a) J.F. Endicott, Y.J. Chen, Coordin. Chem. Rev. 251 (2007) 328–350;
(b) Y. Yamaguchi, W. Ding, C.T. Sanderson, M.L. Borden, M.J. Morgan, C. Kutal, Coordin. Chem. Rev. 251 (2007) 515–524;
(c) X. Han, L.Z. Wu, G. Si, J. Pan, Q.Z. Yang, L.P. Zhang, C.H. Tung, Chem. A: Eur. J. 13 (2007) 1231–1239;
(d) A. Vogler, H. Kunkely, Coordin. Chem. Rev. 250 (2006) 1622–1626;
(e) S.E. Angell, C.W. Rogers, Y. Zhang, M.O. Wolf, W.E. Jones, Coordin. Chem. Rev. 250 (2006) 1829–1841;
(f) M.H.V. Huynh, D.M. Dattelbaum, T.J. Meyer, Coordin. Chem. Rev. 249 (2005) 457–483.
[4] D. Kuciauskas, J.E. Monat, R. Villahermosa, H.B. Gray, N.S. Lewis, J.K. McCusker, J. Phys. Chem. B 106 (2002) 9347–9358.
[5] M.K. Brennaman, J.H. Alstrum-Acevedo, C.N. Fleming, P. Jang, T.J. Meyer, J.M. Papanikolas, J. Am. Chem. Soc. 124 (2002) 15094–15098.
[6] (a) A.R. Dunn, I.J. Dmochowski, J.R. Winkler, H.B. Gray, J. Am. Chem. Soc. 125 (2003) 12450–12456;
(b) D.-L. Ma, C.-M. Che, Chem. Eur. J. 9 (2003) 6133–6144.
[7] (a) M. Buda, G. Kalyuzhnny, A.J. Bard, J. Am. Chem. Soc. 124 (2002) 6090–6098;
(b) S. Bernhard, J.A. Barron, P.L. Houston, J.L. Ruglovksy, X. Gao, G.G. Malliaras, J. Am. Chem. Soc. 124 (2002) 13624–13628.
[8] J.V. Caspar, T.J. Meyer, J. Am. Chem. Soc. 105 (1983) 5583–5590.
[9] M. Staffilani, P. Belser, F. Hartl, C.J. Kleverlaan, L. De Cola, J. Phys. Chem. A 106 (2002) 9242–9250.
[10] L.A. Wori, R. Duesing, P. Chen, L. Della Ciana, T.J. Meyer, J. Chem. Soc., Dalton Trans. (1991) 849–859.
[11] (a) V.M. Miskowski, V.H. Houlding, Inorg. Chem. 30 (1991) 4446–4452;
(b) C.-W. Chan, T.-F. Lai, C.-M. Che, S.-M. Peng, J. Am. Chem. Soc. 115 (1993) 11245–11253;
(c) V.M. Miskowski, V.H. Houlding, C.-M. Che, Y. Wang, Inorg. Chem. 32 (1993) 2518–2524;
(d) W.B. Connick, V.M. Miskowski, V.H. Houlding, H.B. Gray, Inorg. Chem. 39 (2000) 2585–2592.
[12] (a) J.A. Zuleta, J.M. Bevilacqua, J.M. Rehm, R. Eisenberg, Inorg. Chem. 31 (1992) 1332–1337;
(b) W. Paw, S.D. Cumming, M.A. Mansour, W.B. Connick, D.K. Geiger, R. Eisenberg, Coordin. Chem. Rev. 171 (1998) 125–150;
(c) M. Hisser, W.B. Connick, D.K. Geiger, J.E. McGarrah, R. Eisenberg, Inorg. Chem. 39 (2000) 447–457;
(d) J.E. McGarrah, R. Eisenberg, Inorg. Chem. 42 (2003) 4355–4365.
[13] (a) I.E. Pomestchenko, C.R. Luman, M. Hissier, R. Ziessel, F.N. Castellano, Inorg. Chem. 42 (2003) 1394–1396;
(b) C.E. Whittle, J.A. Weinstein, M.W. George, K.S. Schanze, Inorg. Chem. 40 (2001) 4053–4062.
[14] (a) J.A. Bailey, V.M. Miskowski, H.B. Gray, Inorg. Chem. 32 (1993) 369–370;
(b) T.K. Aldridge, E.M. Stacy, D.R. Mcmillin, Inorg. Chem. 33 (1994) 722–727;
(c) J.F. Michalec, S.A. Bejune, D.R. Mcmillin, Inorg. Chem. 39 (2000) 2708–2709;
(d) J.F. Michalec, S.A. Bejune, D.G. Cuttell, G.C. Summerton, J.A. Gertenbach, J.S. Field, R.J. Haines, D.R. McMillin, Inorg. Chem. 40 (2001) 2193–2200;
(e) D.R. Mcmillin, J.J. Moore, Coordin. Chem. Rev. 229 (2002) 113–121;
(f) V.W.W. Yam, R.P.L. Tang, K.M.-C. Wong, K.K. Cheung, Organometallics 20 (2001) 4476–4482.

[15] E.C. Constable, M.J. Hannon, Inorg. Chim. Acta 211 (1993) 101–110.

[16] (a) S.-W. Lai, C.-W. Chan, T.-C. Cheung, S.M. Peng, C.-M. Che, Inorg. Chem. 38 (1999) 4046–4055;
(b) S.-W. Lai, H.-W. Lam, W. Lu, K.-K. Cheung, C.-M. Che, Organometallics 21 (2002) 226–234.

[17] (a) W.E. Ford, M.A. Rodgers, J. Phys. Chem. 96 (1992) 2917–2920;
(b) A. Harriman, M. Hissier, A. Khatyr, R. Ziessel, Chem. Commun. (1999) 735–736;
(c) D.S. Tyson, F.N. Castellano, J. Phys. Chem. 103 (1999) 10955–10960;
(d) D.S. Tyson, J. Bialecki, F.N. Castellano, Chem. Commun. (2000) 2355–2356;
(e) D.S. Tyson, C.R. Luman, X. Zhou, F.N. Castellano, Inorg. Chem. 40 (2001) 4063–4071.

[18] A.I. Baba, J.R. Shaw, J.A. Simon, R.P. Thummel, R.H. Schmehl, Coordin. Chem. Rev. 171 (1998) 43–59, and therein references.

[19] L.-Q. Song, J. Feng, X.-S. Wang, J.-H. Yu, Y.-J. Hou, P.-H. Xie, B.-W. Zhang, J.-F. Xiang, X.-C. Ai, J.-P. Zhang, Inorg. Chem. 42 (2003) 3393–3395.

[20] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, 3rd ed., Pergamon Press, 1988.

[21] F. Kröhnke, Synthesis (1976) 1–24.

[22] F. Morlet-Savary, C. Ley, P. Jacque, J.P. Fouassier, J. Photochem. Photobiol. A: Chem. 126 (1999) 7–14.

[23] C.-M. Che, W. Lu, M. C.-W. Chan, US 2002/0179885.

[24] (a) J.A. Simon, S.L. Curry, R.H. Schmehl, T.R. Schatz, P. Piotrwiak, X. Jin, R.P. Thummel, J. Am. Chem. Soc. 119 (1997) 11012–11022;
(b) A.D. Del Guerzo, S. Leroy, F. Fages, R.H. Schmehl, Inorg. Chem. 41 (2002) 359–366.

[25] (a) L. Wallace, C. Woods, D.P. Rillema, Inorg. Chem. 34 (1995) 2875–2882;
(b) L. Wallace, D.C. Jackman, D.P. Rillema, J.W. Merkert, Inorg. Chem. 34 (1995) 5210–5214.

[26] S.C.F. Kui, I.H.T. Sham, C.C.C. Cheung, C.-W. Ma, B. Yan, N. Zhu, C.-M. Che, W.-F. Fu, Chem. Eur. J. 13 (2007) 417–435.

[27] (a) S.E. Hobert, J.T. Carney, S.D. Cummings, Inorg. Chim. Acta 318 (2001) 89–96;
(b) S.-W. Lai, M.C.W. Chan, K.-K. Cheung, C.-M. Che, Inorg. Chem. 38 (1999) 4262–4267.