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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, $[(C\hat{N}\hat{N})Pt(C{\equiv}CR)]$($HC\hat{N}\hat{N}$ = 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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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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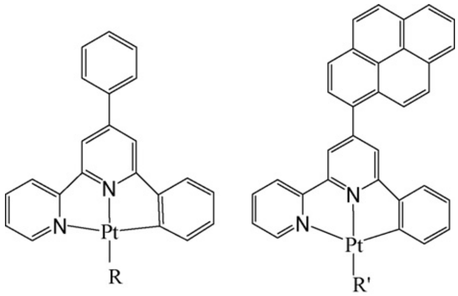

Fig. 1. Structures of complexes: (**1**) R: PhC≡C–; (**2**) R′: PhC≡C–; (**3**) R′: *p*-Et-PhC≡C–; (**4**) R′: Cl–.

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%).

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