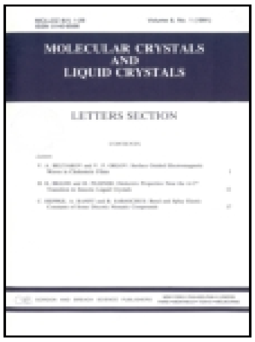

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Photo- and Electroluminescence from Organoplatinum(II) Complexes Bearing Oligofluorene-Based Cyclometalated Ligands

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To develop phosphorescent materials for organic light-emitting diodes (OLEDs), novel organoplatinum(II) complexes bearing oligofluorene-based cyclometalated ligands were synthesized. These materials exhibited intense reddish orange photoluminescence (PL) and thus were applied as emitting dopants to OLEDs. The fabricated OLEDs showed electroluminescence identical to PL of the corresponding dopants. A non-doped device was also successfully fabricated using the developed complex as an emitting layer.

Keywords Platinum complex; Phosphorescent material; Organic light-emitting diode; Electroluminescence; Fluorene; Cyclometalated ligand

Introduction

Organic light-emitting diodes (OLEDs) have attracted much attention because their characteristics of full-color emission with quick on-off response as well as thin device structures are applicable to flat panel displays and lighting apparatuses [1]. To obtain high efficiency OLEDs, it is the most reliable way to utilize phosphorescent materials because they generate both of singlet and triplet excitons [2]. Although a number of phosphorescent heteroleptic cyclometalated platinum(II) complexes have so far been reported [3,4,5], there are few reports of those bearing oligo-arene cyclometalated ligands. Here we report the synthesis and photo- and electroluminescence properties of novel organoplatinum(II) complexes bearing oligofluorene-based cyclometalated ligands.

Experimental

Materials

The starting materials **1**, **3** and 2-iodo-9,9-dihexyl-9H-fluorene were prepared according to reported procedures [6]. Other commercially available reagents for the syntheses were

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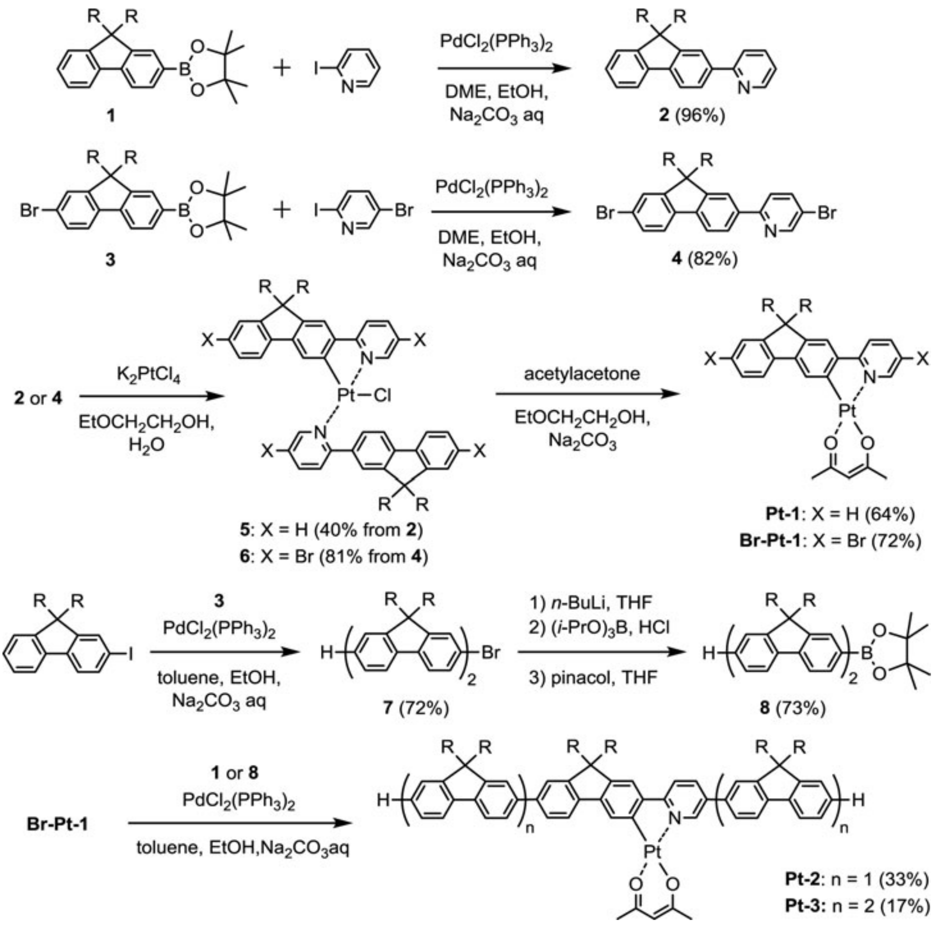

Scheme 1. Synthesis of **Pt-1**–**Pt-3**. Each of substituent R is a hexyl group.

used without further purification. Complexes **Pt-1** and **Br-Pt-1** were prepared from **2** and **4**, respectively, by a reported procedure [4]. The complexes **Pt-2** and **Pt-3** were prepared according to Scheme 1. Their characterization data are listed below.

Pt-2: ^{1}H NMR δ 0.66–0.78 (m, 30H), 1.02–1.13 (m, 36H), 2.01–2.12 (m, 18H), 5.54 (s, 1H), 7.29–7.38 (m, 6H), 7.45 (s, 1H), 7.58–7.66 (m, 6H), 7.72–7.78, (m, 4H), 7.81 (d, $J =$ 8.2 Hz, 1H), 7.88 (d, $J = 7.8$ Hz, 1H), 8.01 (s, 1H), 8.07 (dd, $J = 2.0$ and 8.4 Hz, 1H), 9.34 (d, $J = 2.3$ Hz, 1H); MALDI-TOF MS *m*/*z* 1369 ([M]$^+$). Anal. Calcd for $C_{85}H_{107}NO_2Pt$: C, 74.53; H, 7.87; N, 1.02. Found: C, 74.27; H, 7.79; N, 1.01.

Pt-3: ^{1}H NMR δ 0.56–0.84 (m, 50H), 0.98–1.19 (m, 60H), 1.96–2.19 (m, 26H), 5.57 (s, 1H), 7.28–7.39 (m, 6H), 7.50 (s, 1H), 7.62–7.95 (m, 25H), 8.16 (dd, $J = 2.0$ and 8.4 Hz, 1H), 9.37 (d, $J = 1.8$ Hz, 1H); MALDI-TOF MS *m*/*z* 2033 ([M]$^+$). Anal. Calcd for $C_{135}H_{171}NO_2Pt$: C, 79.68; H, 8.47; N, 0.69. Found: C, 79.83; H, 8.64; N, 0.81.

For OLED fabrication, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) solutions (Clevios P VP CH8000 and P VP AI4083) were purchased from Heraeus Clevios GmbH. 2-(4-Biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) was purchased from Tokyo Chemical Industry Co., Ltd.. Poly(9-vinylcarbazole) (PVCz,

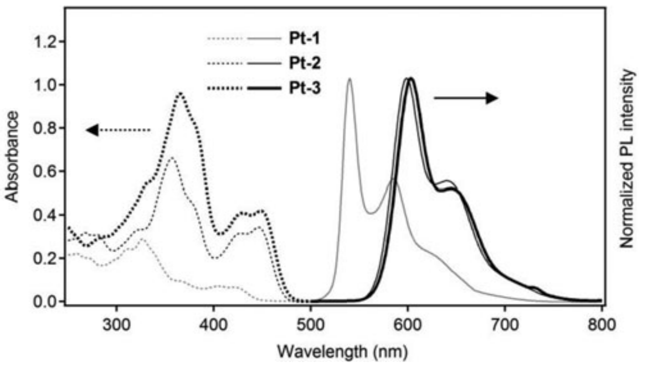

Figure 1. UV-vis absorption and PL spectra of **Pt-1**–**Pt-3** (10 μM) in deaerated CH_2Cl_2 at rt.

$M_w = 25{,}000$–$50{,}000$) were purchased from Sigma-Aldrich Co., and purified before use by reprecipitation from THF to methanol.

Results and Discussion

We have designed three types of organoplatinum(II) complexes: one is a heteroleptic complex with a 2-(fuluoren-2-yl)pyridine cyclometalated ligand (**Pt-1**), and the other two are those possessing additional fluorenyl and bifluorenyl side-arms on both sides of **Pt-1** (namely, **Pt-2** and **Pt-3**, respectively). In Scheme 1 is shown the synthesis of **Pt-1**–**Pt-3**. First, **2** was prepared by the Suzuki coupling of **1** and 2-iodopyridine. Similarly, **3** was reacted with 5-bromo-2-iodopyridine to afford **4**. The compounds **2** and **4** were reacted with K_2PtCl_4 to obtain the mononuclear intermediates **5** and **6**, respectively, followed by ligand exchange with acetylacetonate to yield **Pt-1** and **Br-Pt-1**, respectively. Under the Suzuki coupling conditions, **Br-Pt-1** was reacted with **1** to afford **Pt-2**. Similarly, **Pt-3** was obtained by the reaction of **Br-Pt-1** with **8** that was prepared from 2-iodofluorene *via* **7**.

In Figure 1 are shown the electronic absorption and photoluminescence (PL) spectra of **Pt-1**–**Pt-3** in deaerated dichloromethane at rt. The spectral data are also summarized in Table 1. For the absorption spectrum of **Pt-1**, intense absorption bands were found in the near-UV region, assignable to the ligand-centered (LC) transitions. Broad absorption bands with relatively low absorptivity were also found at > 400 nm, assignable to the singlet metal-to-ligand charge transfer (^{1}MLCT) transitions. In **Pt-2** and **Pt-3**, the π-extension in their cyclometalated ligands led to bathochromic shifts as well as absorption enhancement for

Table 1. Electronic absorption and PL spectral data of **Pt-1**–**Pt-3**[a]

Compd	λ_{abs} /nm	λ_{PL} /nm	τ_{PL} /μs	Φ_{PL}	k_r /10^6 s^{-1}	k_{nr} /10^6 s^{-1}
Pt-1	258, 327, 404, 421	540, 585	7.11	0.26	0.037	0.10
Pt-2	267, 357, 427, 446	599, 639	6.31	0.10	0.016	0.14
Pt-3	366, 430, 449	603, 645	6.36	0.11	0.017	0.14

[a] Obtained in deaerated CH_2Cl_2 at rt. [Pt(II) complex] $= 10\ \mu$M.

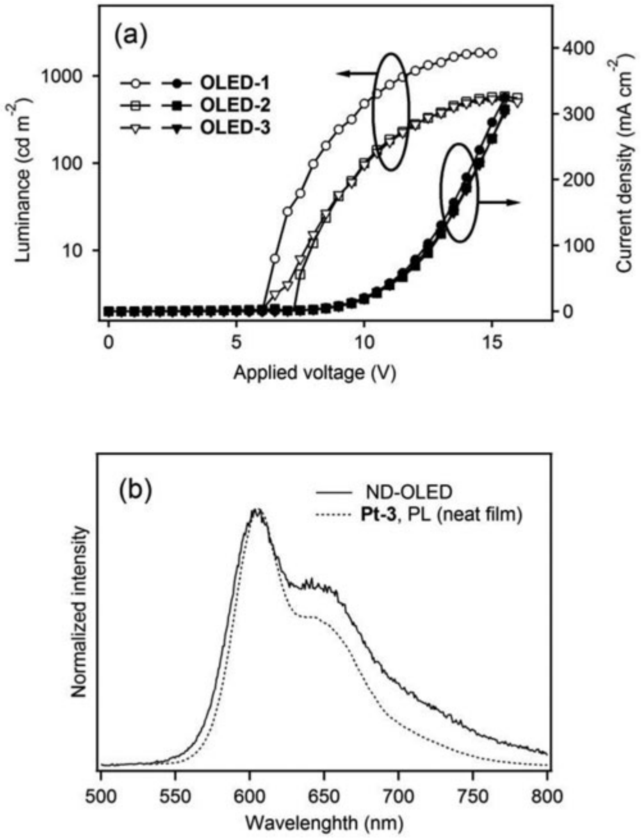

Figure 2. (a) *J-V-L* curves for OLED-1–OLED-3. (b) PL spectrum of **Pt-3** (neat film) and EL spectrum of ND-OLED.

LC and ^{1}MLCT transitions. In the present case, the singlet-triplet mixed MLCT transition bands were hardly observed. For the PL spectrum of **Pt-1**, yellow emission was observed at 540 and 585 nm with a PL quantum yield (Φ_{PL}) of 0.26. Introducing additional fluorenyl components at the both ends, **Pt-2** exhibited red-shifted PL at 599 and 639 nm, emitting reddish orange. The Φ_{PL} is deteriorated down to 0.10, according to so-called *energy gap law* [7]. Further extension of the π-conjugation in the cyclometalated ligand gave rise to just a modest red shift of PL: **Pt-3** emitted reddish orange at 603 and 645 nm with the Φ_{PL} of 0.11. Each of **Pt-1**–**Pt-3** showed PL decays in the order of microseconds (6.31–7.11 μs), assignable to phosphorescence. The relatively short emission lifetimes for the phosphorescent materials indicate effective intersystem crossing between the singlet and triplet states, caused by the strong spin-orbit interaction. The radiative and non-radiative decay rate constants k_{r} and k_{nr} were also obtained, respectively, according to the following equations (1) and (2) (Table 1);

$$k_r = \Phi_{\mathrm{PL}}/\tau_{\mathrm{PL}} \tag{1}$$

$$k_{\mathrm{nr}} = k_{\mathrm{r}}(1-\Phi_{\mathrm{PL}})/\Phi_{\mathrm{PL}} \tag{2}$$

Table 2. Device performance of OLED-1–OLED-3

Device	Emitter	L_{max} /cd m^{-2} (@V)	$\eta_{j\ max}$ /cd A^{-1} (@V)	$\eta_{p\ max}$ /lm W^{-1} (@V)	$\eta_{ext\ max}$ /% (@V)	λ_{EL} /nm
OLED-1	**Pt-1**	1850 (14.5)	3.19 (8.0)	1.25 (8.0)	1.00 (8.0)	541, 584
OLED-2	**Pt-2**	579 (15.5)	0.56 (9.0)	0.20 (8.5)	0.34 (8.5)	598, 639
OLED-3	**Pt-3**	543 (15.0)	0.52 (9.0)	0.18 (9.0)	0.34 (9.0)	601, 642
ND-OLED	**Pt-3**	1140 (12.5)	0.31 (6.5)	0.15 (6.0)	0.24 (6.5)	604, 642

The k_rs for **Pt-1–3** were 3.7×10^4, 1.6×10^4, and 1.7×10^4 s^{-1}, respectively, and the k_{nr}s for **Pt-1–3** were 1.0×10^5, 1.4×10^5, and 1.4×10^5 s^{-1}, respectively. Thus, the attachment of the fluorenyl and bifluorenyl components to the core complex leads to deceleration of the radiative decay rather than acceleration of the non-radiative decay, and the deterioration of Φ_{PL} of **Pt-2** and **Pt-3** should be explained by the energy gap law.

Using **Pt-1–Pt-3** as emitting dopants, PVCz-based OLEDs were fabricated (OLED-1–OLED-3, respectively). The device structure is as follows; ITO (anode, 150 nm)/PEDOT:PSS (Clevios P VP CH8000, 40 nm)/emitting layer (EML, 120 nm)/CsF (1.0 nm)/aluminum (cathode, 250 nm). PEDOT:PSS and EML were embedded by a spin-coating technique. The EML consists of PVCz doped with PBD and the platinum(II) complex (PVCz:PBD:platinum(II) complex = 100:16.4:1.41 (mol/mol/mol), where the molar ratio of PVCz is based on the monomer unit). In Figure 2a is shown the current density (J)-voltage (V)-luminance (L) curves for OLED-1–OLED-3, and the device data are summarized in Table 2. The device efficiencies show good correspondence to Φ_{PL}s of the emitting dopants, and the maximum current and power efficiencies ($\eta_{j\ max}$ and $\eta_{p\ max}$, respectively) as well as the maximum external quantum efficiencies ($\eta_{ext\ max}$) of OLED-2 and OLED-3 are inferior to those of OLED-1. In each device, the EL spectrum corresponding to the PL spectrum of the doped organoplatinum(II) complex was observed: OLED-1 emitted yellow EL, whereas OLED-2 and OLED-3 emitted reddish orange EL. The CIE chromaticity coordinates (x, y) were (0.46, 0.51), (0.60, 0.38), and (0.60, 0.37) for OLED-1–OLED-3, respectively. Thus, **Pt-1–Pt-3** are useful as phosphorescent emitters in OLEDs.

We also fabricated a non-doped OLED, where **Pt-3** was used as a single emitting layer (ND-OLED). The device structure of ND-OLED is as follows; ITO (anode, 150 nm)/PEDOT:PSS (Clevios P VP AI4083, 40 nm)/**Pt-3** (55 nm)/CsF (1.0 nm)/aluminum (cathode, 250 nm). In spite of a low-mass molecule, **Pt-3** formed a smooth thin film with surface roughness of less than ±2 nm (estimated by AFM). The EL spectrum of ND-OLED is shown in Figure 2b, together with the PL spectrum of a spin-coated film of **Pt-3** (λ_{PL} = 605 nm, $\Phi_{PL} = 0.08$). These spectra were almost identical to the PL spectrum in solution (Figure 1), and any emission from an excimer or an aggregate were not observed. As shown in Table 2, ND-OLED afforded reddish orange EL (CIE (x, y); (0.62, 0.37)) with the device performance comparable to OLED-1–OLED-3. Therefore, **Pt-3** is a potential emitting material for non-doped phosphorescent OLEDs.

Conclusion

We here demonstrated the development of a new type of phosphorescent organoplatinum(II) complexes employing the oligofluorene-based cyclometalated ligands. Relatively efficient reddish orange PL was obtained, and phosphorescent OLEDs were fabricated using the developed complexes as emitting dopants. Interestingly, the non-doped OLED was also successfully fabricated using bifluorene-appended organoplatinum(II) complex as an emitting layer, yielding reddish orange EL similar to the corresponding doped device.

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