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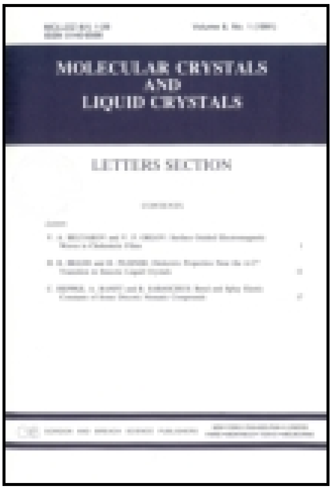

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Synthesis and Luminescence Studies of the Platinum Complexes Chelated with Coumarin Ligands

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The organic light-emitting diodes (OLEDs) using the iridium complexes of coumarin derivatives as emissive dopants were known to be highly efficient and stable. These coumarin-based Ir(III) complexes were reported to trap and transport electrons effectively in the emissive layer. In this paper, the synthesis and photophysical, electroluminescent properties of platinum (II) complexes cyclometallated with coumarin derivatives are reported. We have prepared a new series of phosphorescent platinum (II) complexes containing 3-(2-pyridinyl)coumarin (pc) as an ancillary ligand. The new heteroleptic platinum complexes, Pt(C^N)(pc) (C^N = 2-(2,4-difluorophenyl)pyridine (F_2-ppy), 2-phenylpyridine (ppy) and 2-phenylquinoline (pq)) were characterized by ^{1}H NMR and mass spectrometer. As main ligands, F_2-ppy, ppy and pq were employed, which should provide the drastically different ligand molecular orbital energy levels. The platinum complexes synthesized herein showed various luminescence maxima from 551 to 596 nm with rather wide emission ranges, depending upon the relative energy levels of their main and ancillary ligands. The photoabsorption, photoluminescence and electroluminescence of the complexes were studied.

Keywords Coumarin; platinum complexes; organic light-emitting diodes (OLED); dopant materials

1. Introduction

The organic electroluminescent materials have been intensely applied in the past two decades [1–3]. In an organic light emitting diode (OLED) device, both singlet and triplet excitons are generated in about 1 to 3 ratio by charge recombination [2]. Therefore, only the singlet excitons, that is, about 25% of total excitons generated in the OLED, can be harvested with the use of a fluorescent emitter. However, this issue can be addressed by the use of a phosphorescent emitter, which can harness both singlet and triplet excitons and maximize the internal quantum efficiency [3]. In particular, the platinum complexes that emit phosphorescent light at an ambient temperature have shown attractive applications in OLED devices and have attracted much attention owing to their manifold advantages [4]. Their excellent phosphorescent quantum yields and easy tuning of emission color by ligand molecular structures have led to great development of phosphorescent OLEDs.

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Furthermore, there is a potential ability of these materials for the use of the flat-panel displays and solid state lighting [5–7]. Thus, the synthesis of Pt complexes have been carried out for developing phosphorescent materials with improved their phosphorescent quantum yields, and efficient phosphorescence color tuning.

To obtain the various color emitting materials of good color purity and high performance, we prepared coumarin-based heteroleptic platinum complexes and compared their luminescence characteristics with those of the iridium complexes in this study. According to the previous report, charge transporting groups such as coumarins have been incorporated onto key ligands of the complexes to improve charge injection and transporting ability of phosphorescent materials [8]. The studies of coumarin derivatives demonstrated that they have excellent thermal stability and outstanding optical properties including an extended spectral response, high quantum yields, and superior photostability [9–10]. We expect that chelation of a coumarin ligand to the platinum complexes might also allow emitting color tuning and luminous efficiency increase.

Herein, we described the results of our investigation on the preparation, characterization, electrochemical behavior, and luminescent properties of the heteroleptic platinum complexes containing 3-(2-pyridinyl)coumarin (pc) as an ancillary ligand. F2-ppy, ppy and pc were introduced as main ligands to provide quite drastic energy gaps to the complexes. We analyzed the emission properties of these new platinum complexes to find how the different main ligands may have influence on the luminescence properties of the complexes.

2. Experimental

All of the chemical reagents were purchased from Aldrich and Strem Co., and used without further purification. The reactions were carried out under an argon atmosphere. The solvents were dried by standard procedures. The column chromatography was performed with the use of silica gel (230-mesh, Merck).

2.1 Synthesis of Ligands and Iridium Complexes

Synthesis of F_2-ppy. 2,4-difluoro-2-phenylpyridine was obtained from the reaction of 2-chloropyridine and 2,4-difluorophenylboronic acid by Suzuki coupling [11]. Yield: 65%

Synthesis of pc. 3-(2-pyridinyl)coumarin was obtained from the reaction of salicylaldehyde (0.1 mol), 2-pyridyl acetonitrile (0.1 mol) and piperidine (0.1 mol) [12]. Yield: 71%

Synthesis of Pt(C^N)(pc).[C^N = ppy, F_2-ppy, pq] First, the cyclometallated Pt(II) μ-chloro-bridged dimer, (C^N)Pt(μ–Cl)Ir(C^N) (0.5 mmol), was prepared according to the Nonoyama method [13]. Second, the resulting dimer and 3-(2-pyridinyl)coumarin (1.75 mmol) and Na_2CO_3 were refluxed in 2-ethoxyethanol for 3 hr. After cooling to room temperature, 10-20 ml water was added and the resulting precipitate was filtered off. The crude product was redissolved in dichloromethane (CH_2Cl_2) and purified by silica gel chromatography by using CH_2Cl_2. Pt(C^N)(pc) was obtained as a solid after recrystallization in CH_2Cl_2/methanol [14].

[Pt(F_2-ppy)(pc)]: A red powder (Yield: 67%). FAB-MS: calculated 607; found 385 (M - pc). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.35 (d, 1H) 7.94 (t, 1H) 7.76 (m, 2H) 8.13 (s, 1H) 7.59 (d, 1H) 7.47 (t, 2H) 7.35 (m, 3H) 7.15 (m, 4H) 6.99 (d, 1H) 6.75 (m, 1H). Anal. Calc. for $C_{25}H_{14}N_2O_2F_2Pt$: C, 49.43; H, 2.32; N, 4.61. Found: C, 49.18; H, 2.43; N, 4.56%.

[Pt(ppy)(pc)]: A light orange powder (Yield: 41%). FAB-MS: calculated 571; found 572. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.94 (d, 2H) 8.19 (m, 6H) 7.61 (d, 2H) 7.35 (d, 2H) 7.01 (t, 2H). Anal. Calc. for $C_{25}H_{16}N_2O_2Pt$: C, 52.54; H, 2.82; N, 4.90. Found: C, 52.36; H, 2.88; N, 4.72%.

[Pt(pq)(pc)]: A dark brown powder (Yield: 52%). FAB-MS: calculated 621; found 398 (M - pc).

2.2 Optical and Electrochemical Measurement

UV-Vis absorption spectra were measured on a Hewlett Packard 8425A spectrometer. PL spectra were measured on a Perkin Elmer LS 50B spectrometer. UV-Vis and PL spectra of iridium complexes were measured in 10^{-5} M dilute CH_2Cl_2 solution. Cyclic voltammograms were obtained with Electrochemical Analyser (CHI600C) at scan rate of 100 mV/s, and tetrabutylammonium hexafluorophosphate was added as an electrolyte in CH_2Cl_2 solution.

2.3 Device Fabrication

The OLEDs containing the heteroleptic iridium complexes as a dopant in emitting layers were fabricated. Glass substrate coated with a 180-nm-thick indium tin oxide (ITO) layer had a sheet resistance of 12 Ω/sq. All organic layers were sequentially deposited onto the substrate without breaking vacuum at a pressure of about 5×10^{-7} torr, using the thermal evaporation equipment. The organic materials were deposited as the following structure: 4,4’-bis[N-(naphthyl)-N-phenylamino]biphenyl (NPB, 50 nm) as hole transporting layer (HTL) / 4,4’,4”-tris(N-carbazolyl)triphenylamine (TCTA, 10 nm) as buffer layer / platinum complex phosphors (10%) doped in 4,4’-bis(9-carbazolyl)-1,1’-biphenyl (CBP, 30 nm) as emitting layer / 4,7-diphenyl-1,10-phenanthroline (Bphen, 30 nm) as electron transporting layer (ETL) / lithium quinolate (Liq, 2 nm) as electron injection layer (EIL). The deposition rates were 1.0-1.1 and 0.1 Å/sec for organic materials and lithium quinolate (Liq), respectively. Finally, the aluminum cathode was deposited at a rate of 10 Å/sec. The devices were encapsulated in a glove box with O_2 and H_2O at concentrations below 1 ppm. The devices had emission areas of 3×3 mm^2. The electrical characteristics of devices and the EL spectra were measured and immediately recorded with a Chromameter CS-1000A (Minolta). The current and voltage were controlled with a measurement unit (model 236, Keithely).

3. Results and Discussion

The synthesis of the heteroleptic platinum complexes, Pt(CˆN)(pc), (CˆN = F_2-ppy, ppy, qc) were straightforward, and Pt(F_2-ppy)(pc), Pt(ppy)(pc) and Pt(pq)(qc) were prepared according to the reported synthetic procedures of the iridium complexes with some modification [11–14]. The yields of the platinum complexes were in the range of 41–67%. The complexes were characterized with ^{1}H NMR and FAB-MS. The overall synthetic schemes are illustrated in Figure 1.

The UV-Vis absorption spectra of the platinum complexes were obtained and compared, as shown in Figure 2. The spectra of Pt(F_2-ppy)(pc), Pt(ppy)(pc) and Pt(pq)(pc) have the strong absorption bands, appearing in the ultraviolet region between 210 and 300 nm. These bands are assigned to the spin-allowed $^1\pi$-π^* transitions of the ligands. Pt(pq)(pc) exhibited absorption at longest wavelengths due to the smallest energy gap of pq ligand among the

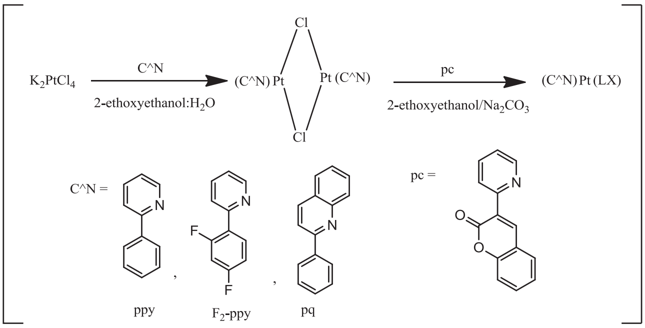

Figure 1. The synthesis of Pt(C^N)(pc), and their platinum complexes.

complexes investigated in this study. The $^1\pi$-π^* bands of the complexes are accompanied by weaker and lower energy features extending into the region of longer wavelengths. These extended absorption bands of platinum complexes are observed in the region from 310 to 360 nm. These absorption bands are assigned to the spin-allowed metal charge transfer (^{1}MLCT) bands. The absorption of Pt(F_2-ppy)(pc) is also observed around 360 - 420 nm while those of Pt(ppy)(pc) and Pt(pq)(pc) are observed at the longer wavelength around 380 – 460 nm. The weaker absorption bands can be attributed to the spin-forbidden ^{3}MLCT and spin-orbit coupling enhanced $^3\pi$-π^* transition. The high intensity of the MLCT bands has been attributed to effective mixing of these charge-transfer transitions with high lying spin-allowed transitions on the cyclometalating ligand [15]. The absorption maxima of Pt(F_2-ppy)(pc) occur at the shortest wavelength, presumably due to the biggest energy gap of F_2-ppy ligand in the complex.

The PL spectra of the platinum complexes in CH_2Cl_2 solution are shown in Fig. 3. The emission wavelength of Pt(F_2-ppy)(pc), Pt(ppy)(pc) and Pt(pq)(pc) appear at 551, 562 and 596 nm, respectively. The PL maxima of Pt(F_2-ppy)(pc) are observed at the shortest wavelength, as expected from the biggest energy gap of F_2-ppy ligand in the complexes.

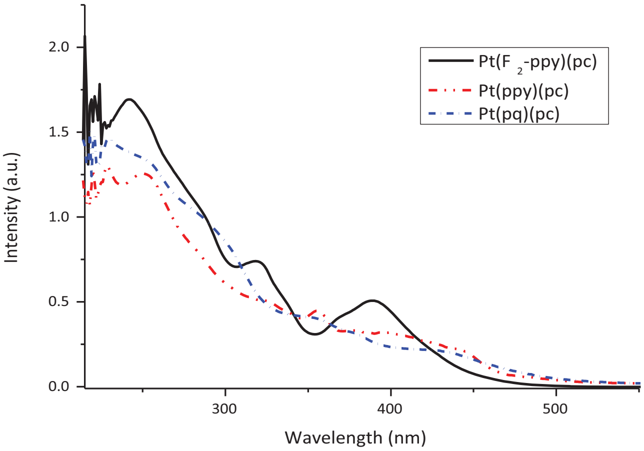

Figure 2. The UV-Vis absorption spectra of the heteroleptic platinum complexes of Pt(C^N)(pc) in a 10^{-4}M CH_2Cl_2 solution.

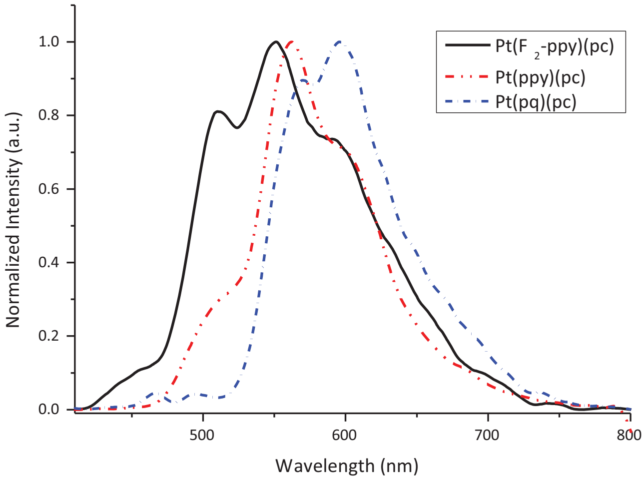

Figure 3. The PL spectra of the heteroleptic platinum complexes of Pt(C^N)(pc) in a 10^{-4}M CH_2Cl_2 solution.

As designed, the platinum complex containing F_2-ppy as main ligand showed the most hypsochromic phosphorescence shift. According to these trends, we expected that the emission of Pt(pq)(pc) should be shown at the longest wavelength since the extended π conjugation length of pq main ligand could lead to the smallest energy gap of the platinum complex, among the main ligands we employed in this study. In fact, Pt(pq)(pc) exhibited the maxima at the longest wavelengths in both absorption and emission spectra. The luminescence wavelength ranges of these Pt complexes are noteworthy. Particularly, the photoemission by Pt(F_2-ppy)(pc) occurs from 470 to 680 nm, covering most of the visible range which may lead to white emission. The other complexes also exhibit rather wide full-width-at-half-maximum (FWHM) and may shed light on application to white phosphorescent OLEDs [16]. Further studies regarding development of white OLEDs involving these Pt complexes are undergoing in our laboratory.

The electroluminescence (EL) properties of the complexes were investigated for their OLED application. The configuration of the EL devices with the platinum complexes used as a dopant was ITO / NPB / TCTA / CBP:DOPANT (10%) / Bphen / Liq / Al. However, the Pt complexes prepared in this study seemed to undergo decomposition upon the thermal sublimation. For instance, the EL peaks of the device with Pt(F_2-ppy)(pc) were observed at 494(sh) and 625 nm, which are different from its PL maxima at 551 nm. In addition, the performance of the device was rather poor with the maximum luminous efficiencies of 0.35 cd/A at 4.00 V. We also tried to investigate the devices involving Pt(ppy)(pc) and Pt(pq)(pc) as a phosphor for luminescence comparison, but the device fabrication was failed. This failure is attributed to the π- π stacked aggregation of the Pt dopants in CBP host due to their planar structures [17].

4. Conclusions

We reported the synthesis of the new heteroleptic platinum(II) complexes coordinated with 3-(2-pyridinyl)coumarin, pc, as an ancillary ligand. The platinum complexes, Pt(F_2-ppy)(pc), Pt(ppy)(pc) and Pt(pq)(pc), prepared in this study exhibited from the green emission to orange at 551, 562 and 596 nm, respectively. F_2-ppy was chosen as one of the C^N ligands on the basis of its high triplet energy and large energy gap compared to ppy, while pq ligand had a small energy gap between HOMO and LUMO compared to ppy. As expected, Pt(F_2-ppy)(pc) and Pt(pq)(pc) which were designed to have the biggest and the smallest energy gaps, respectively, underwent the most hypsochromic and bathochromic PL shifts among the platinum complexes synthesized in this study. Pt(F_2-ppy)(pc) showed a wide luminescence range from 470 to 680 nm, which may be applied as a promising candidate for white phosphorescent material. The EL device fabrication of these platinum complexes, however, was unsuccessful due to their thermal instabilities and poor performances.

Acknowledgments

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