Preparation, Characterization, and Electroluminescence Characteristics of α-Diimine-type Platinum(II) Complexes with Perfluorinated Phenyl Groups as Ligands

Jun-ichi Nishida, Akihiro Maruyama, Takeshi Iwata,[†] and Yoshiro Yamashita*
Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering,
Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8502
[†]*Central Reserch Labolatory, Takasago International Corporation, Nishiyawata, Hiratsuka 254-0073*

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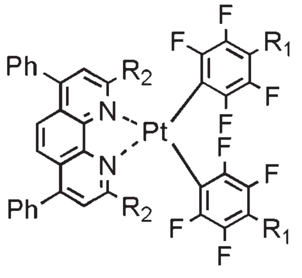
The α-diimine-type platinum(II) complexes having bulky perfluorinated phenyl groups were prepared and the molecular and crystal structures were revealed by X-ray analysis. They showed phosphorescence and electron-accepting properties. The organic light-emitting diode (OLED) devices showing green luminescence were fabricated.

Electrophosphorescent materials incorporating heavy transition metals have attracted considerable attention because of their application to highly efficient electroluminescent (EL) emitters.[1] Platinum complexes such as porphyrin-type and phenylpyridine-type platinum(II) complexes have been used for OLED devices.[2,3] However, the numbers of platinum complexes are less than those of iridium ones.[4] This is due to their square planar d^8 structures, which lead to close intermolecular Pt–Pt contacts or π stacking resulting in quenching the phosphorescence. α-Diimine-type platinum(II) complexes based on bidentate ligands such as bipyridine and 1,10-phenanthroline have been prepared and the properties and structures have been studied.[5] However, OLED devices using these complexes as EL emitter are rare probably because of the less phosphorescence efficiency.[6] If bulky phenyl groups are introduced in these complexes, they would weaken intermolecular interactions and increase the phosphorescence efficiency. Moreover, the substituents on the phenyl groups can perturb the metal d orbitals and tune the emitting color. In this context, we have prepared a series of α-diimine-type platinum(II) complexes **1** having bulky and electron-withdrawing perfluorinated phenyl groups[7] and investigated their structures and physical properties. We have also fabricated OLED devices based on them for the first time.



1a: $R_1 = F, R_2 = H$
1b: $R_1 = CF_3, R_2 = H$
1c: $R_1 = F, R_2 = Me$
1d: $R_1 = CF_3, R_2 = Me$

Pentafluorophenyl (pfp) derivatives **1a**, **1c** were prepared in 96 and 47% yields, respectively, by the reaction of the corresponding 4,7-diphenylphenanthrolines with bis(pfp)(cod)platinum(II).[8] 4-Trifluoromethyl-2,3,5,6-tetrafluorophenyl (tfp) derivatives **1b**, **1d** were obtained in 72 and 40% yields, respectively, by the reaction of the corresponding diphenylphenanthrolines with bis(tfp)(cod)platinum(II) which was prepared by the reaction of dichloro(cod)platinum(II) with (tfp)lithium in 54% yield. These compounds were purified by recrystallization and sublimation.

Molecular structures of **1a**–**1d** were elucidated by X-ray analyses.[9] Complexes **1a**, **1b** have a similar square planar geometry around the metal center and the two bulky pfp or tfp rings are twisted with the angle of ca. 70° from these square planes (Figure 1). These molecular geometries are similar to a series of platinum(II) complexes having electron-donating bulky mesityl (2,4,6-trimethylphenyl) groups.[5] The Pt–C distances of **1a**, **1b** are in a range of 1.994(6)–2.016(6) Å, which are similar to those of other α-diimine-type platinum(II) complexes (1.99–2.04 Å)[5] and slightly shorter than those of other platinum complexes containing pentafluorophenyl groups (2.03–2.12 Å).[7] These shorter bond lenghs seem favorable for protecting the platinum center. The phenyl substituents at the 4-, 7-positions of the phenanthroline are also considered to disturb intermolecular interactions. Although the complex **1a** forms a dimer structure between the planar phenanthroline units, the interplanar distance is ca. 3.62 Å, which is longer than that of a 3,4,7,8-tetramethylphenanthroline derivative.[5b] On the other hand, **1c**, **1d** having methyl groups at the 2-, 9-positions of phenanthroline adopt unique bending structures as depicted in Figure 1b, where the dihedral angles between the N–Pt–N plane and the phenanthroline are ca. 24°. The Pt–N distances are slightly longer than those of **1a**, **1b** [**1a**; 2.082(5)–2.083(5) Å, **1b**; 2.082(6)–2.083(5) Å, **1c**, 2.102(5)–2.124(5) Å, **1d**; 2.101(3)–2.131(3) Å], which can be attributed to the steric hindrance of the methyl groups.

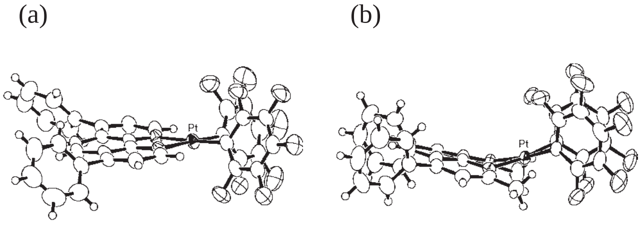


Figure 1. Molecular structures of (a) **1a** and (b) **1c**.

Complexes **1a**, **1b** show weak emission in solution at room temperature. The emission maxima in dichloromethane appeared at 515 nm in **1a** and 509 nm in **1b**, which are much blue-shifted than that of a platinum complex with dimesityl groups and 4,7-diphenylphenanthroline (660 nm in toluene and 620 nm in solid).[5c] This result indicates that the introduction of electron-withdrawing fluorine and trifluoromethyl substituents at the phenyl ring induces blue-shifts of emission. On the other hand, the emission of **1c**, **1d** in solution could not be observed at room temperature. However, all of the complexes **1** showed

Table 1. Emission maxima and redox potentials[a] of **1**

	λ_{em} (nm)		$E_{1/2}$ (V)
	Solution[b]	Solid[c]	
1a	515	534	-1.31
1b	509	508	-1.29
1c	—[d]	484sh, 507	-1.45
1d	—[d]	501	-1.41

[a] In CH_2Cl_2 containing 0.1 mol dm^{-3} n-Bu_4NPF_6, vs SCE, Pt electrode. [b] In CH_2Cl_2. [c] In crystal. [d] Not observed.

strong photoluminescence in the solid state. The emission maxima are summalized in Table 1. The differences of the emission maxima between in solid and in solution are small, indicating that the intermolecular interactions are weak in the solid state as expected.

Complexes **1** having the electron-withdrawing perfluorinated phenyl groups are expected to show electron-accepting properties. To prove this point, their redox potentials were measured by cyclic voltammetry. All of the voltammograms exhibited a reversible one-electron reduction wave at -1.29 to -1.45 V vs SCE (Table 1), which are lower than those of similar α-diimine complexes having nonsubstituted phenyl groups.[5] The electron-withdrawing ligand is considered to lower the levels of d orbitals of platinum, which leads to blue-shifts of emission. On the other hand, the reduction waves of **1c**, **1d** having dimethyl groups were observed at lower potentials than those of **1a**, **1b**. This is attributed to the electron-donating effects of methyl groups.

Preliminary OLED devices of **1a**–**1c** were fabricated by a thermal deposition method onto a clean glass substrate with indium-tin-oxide (ITO). A 40-nm-thick layer of 4,4′-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl (NPD) for hole transport, a 35-nm-thick layer of 4,4′-*N*,*N*′-dicarbazolylbiphenyl (CBP) consisting of 6% complexes **1**, a 10-nm-thick layer of 2,9-dimethy-4,7-diphenylphenanthroline (BCP) for hole-block and a 35-nm-thick layer of tris(8-hydroxyquinoline)aluminium (Alq_3) for electron transport, a 0.5-nm-thick LiF and a 100-nm-thick Al layer as cathode electrode were successively deposited. The EL spectrum of **1a** is similar to the emission spectrum in solution with a little red-shift (4 nm) of the maximum (519 nm). The Commission Internationale de l'Eclairage (CIE) coordinate of the device of **1a** ($x = 0.329$, $y = 0.551$) corresponds to the green region. The external quantum efficiency (η_{ext}) and the power efficiency at 100 cd m^{-2} were 2.1% and 2.4 lm W^{-1}, respectively. The maximum luminance of 4795 cd m^{-2} was obtained at 15 V. Devices using **1b**, **1c** showed the EL peak maxima at 516 nm ($x = 0.297$, $y = 0.513$) and 523 nm ($x = 0.329$, $y = 0.514$), respectively. The devices showed lower η_{ext} values of 0.82% for **1b** and 0.91% for **1c** at 100 cd m^{-2}.

In conclusion, we have prepared novel α-diimine-type platinum(II) complexes having perfluorinated phenyl groups and succeeded in fabricating their OELDs exhibiting green luminescence. α-Diimine-type complexes having bulky phenyl groups are attractive candidates for EL emitters and the structures would be easily modified to improve the EL performance.

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9 Crystal data for **1a**: $C_{36}H_{16}N_2F_{10}Pt$, $M_r = 861.61$, monoclinic $P2_1/c$, $a = 13.919(5)$, $b = 16.383(6)$, $c = 14.994(7)$ Å, $\beta = 105.39(3)^\circ$, $V = 3296(2)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.736$ g/cm^3, $R_1 = 0.042$, $wR_2 = 0.131$, $S = 1.72$. **1b**: $C_{38}H_{16}N_2F_{14}Pt \cdot CHCl_3$, $M_r = 1081.00$, triclinic $P\bar{1}$, $a = 11.237(4)$, $b = 11.509(5)$, $c = 16.302(5)$ Å, $\alpha = 106.23(3)^\circ$, $\beta = 107.87(3)^\circ$, $\gamma = 91.41(3)^\circ$, $V = 1912(1)$ Å^3, $Z = 2$, $D_{\mathrm{calcd}} = 1.877$ g/cm^3, $R_1 = 0.054$, $wR_2 = 0.159$, $S = 1.27$. **1c**: $C_{38}H_{20}N_2F_{10}Pt$, $M_r = 889.66$, monoclinic $P2_1/c$, $a = 12.606(7)$, $b = 15.025(9)$, $c = 17.131(9)$ Å, $\beta = 101.31(5)^\circ$, $V = 3181(3)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.857$ g/cm^3, $R_1 = 0.047$, $wR_2 = 0.107$, $S = 0.98$. **1d**: $C_{40}H_{20}N_2F_{14}Pt$, $M_r = 989.68$, monoclinic $C2/c$, $a = 30.10(1)$, $b = 15.249(6)$, $c = 16.600(7)$ Å, $\beta = 114.34(4)^\circ$, $V = 6941(5)$ Å^3, $Z = 8$, $D_{\mathrm{calcd}} = 1.894$ g/cm^3, $R_1 = 0.030$, $wR_2 = 0.077$, $S = 0.95$. The details of the crystal data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 264434-264437.

10 ^{1}H NMR Data (300 MHz, $CDCl_3$); **1a**: δ 8.73 (d, 2H, $J = 5.1$ Hz), 8.06 (s, 2H), 7.75 (d, 2H, $J = 5.1$ Hz), 7.60 (m, 10H); **1b**: 8.65 (d, 2H, $J = 5.1$ Hz), 8.09 (s, 2H), 7.79 (d, 2H, $J = 5.1$ Hz), 7.56 (m, 10H); **1c**: 7.90 (s, 2H), 7.55 (m, 12H), 2.43 (s, 6H); **1d**: 7.92 (s, 2H), 7.55 (m, 12H), 2.43 (s, 6H).

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