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Synthesis and polarized photoluminescence of novel phosphorescent cyclometalated platinum dimer

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Abstract

A novel phosphorescent cyclometalated platinum dimer with bis-[2-(*p*-dodecyloxyphenyl) pyridyl]-hexane-1,6-diol as ligand and 1,3-(1-*n*-hexyl,3-*n*-heptadecyl) diketone as ancillary ligand was synthesized. The chemical structure and liquid crystal property of the dimer were characterized by ^{1}H NMR, ESI-MS, polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The aligned film of title compound on the rubbed polyimide film is intensely emissive at room temperature with emission maximum at 516 nm. The luminescence dichroic ratio ($I_{\parallel}/I_{\perp}$) at 516 nm is 3.1.

Keywords: Phosphorescent cyclometalated platinum dimer; Liquid crystal; Polarized photoluminescence; Synthesis

Recently, polarized organic luminescent materials and polarized organic light-emitting diodes (OLEDs) have attracted much interest because of their possible application in industry of information, for example, they can be used as back-lights for conventional liquid crystal displays [1–3]. In techniques of oriented thin films for polarized photoluminescence (PL) and electroluminescence (EL), liquid crystalline luminescent materials are appropriate candidates for their unique self-organizing nature and fluidity, which can be aligned on suitable alignment layers. Generally, polarized light emission have been accomplished by annealing liquid crystalline polymeric luminescent films, such as substituted poly(*p*-phenylenevinylene) (PPV), polyfluorene (PF) and their oligomers, on alignment layers [4–12] or by aligning low molecular weight liquid crystal compounds with either benzothiazole or oxadiazole units as chromophores [3,12–14]. Up to now, most liquid crystalline luminescent materials are fluorescent. In this paper, a novel liquid crystalline phosphorescent cyclometalated platinum dimer, with bis-[2-(*p*-dodecyloxyphenyl)-pyridyl]-hexane-1,6-diol as ligand and 1,3-(1-*n*-hexyl, 3-*n*-pentadecyl) diketone as ancillary ligand, was synthesized and its polarized photoluminescence properties were investigated.

The synthetic route of title compound is shown in Scheme 1. The title compound was characterized by ^{1}H NMR and ESI-MS. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.656 (d, 2H, J = 5.2 Hz), 8.161 (d, 2H, J = 8.4 Hz), 7.220 (d, 2H, J = 4 Hz),

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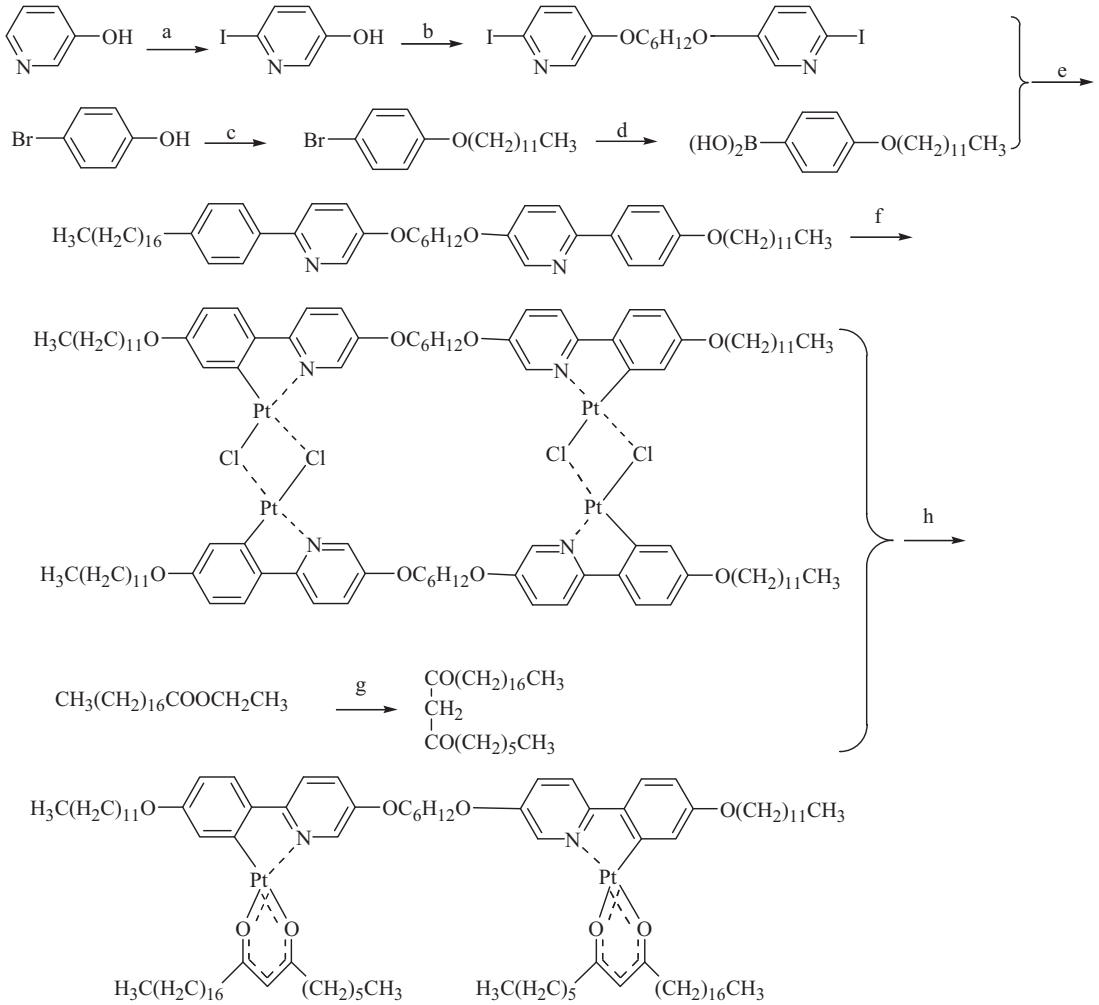

Scheme 1. Synthetic route to the title compound. reagents and conditions: (a) water solution of potassium hydroxide (20%), iodine, potassium iodide, room temperature, 8 h; (b) K_2CO_3, DMF, 1,6-dibromohexane, 110 °C, 4 h; (c) K_2CO_3, DMF, dodecyl bromide, 110 °C, 4 h; (d) argon, tributy-borate, magnesium, THF, iodine, 40 °C, 4 h; (e) $Pd(PPh_3)_4$, tetrabutylammonium bromide, K_2CO_3, toluene, ethanol, water, 80 °C, 10 h; (f) K_2PtCl_4, 3:1 mixture of 2-ethoxyethanol and water, 80 °C [15], 17 h; (g) sodium hydride, dimethylsulfoxide, 2-octanone, ethyl stearate, reflux, 6 h; (h) 2-ethoxyethanol, cesium carbonate, 100 °C, 3 h.

7.190 (d, 2H, J = 1.2 Hz), 6.929 (dd, 2H, J_1 = 5.6 Hz, J_2 = 8.4 Hz), 6.627 (dd, 2H, J_1 = 2.8 Hz, J_2 = 8 Hz), 5.436 (s, 2H), 4.114 (t, 4H, J = 6.4 Hz), 4.059 (t, 4H, J = 6.8 Hz), 2.243 (dd, 8H, J_1 = 7.2 Hz, J_2 = 13.2 Hz), 1.996–2.014 (m, 4H), 1.680–1.839 (m, 16H), 1.425–1.561 (m, 8H), 1.282–1.325 (m, 96H), 0.887 (t, 18H, J = 2.4 Hz). MS (ESI): 2047.35[M+23]$^+$.

The mesogenic behaviour of title compound was investigated by differential scanning calorimetry (DSC) and hot stage polarizing optical microscopy (POM). The enantiotropic liquid crystal (LC) phase is assigned based on DCS (Fig. 1) and polarized optical picture (Fig. 2). The title compound shows phase transition at 42 °C for crystalline-to-LC and at 76 °C for LC-to-isotropic at the heating scan and at 65 °C for isotropic-to-LC and at 29 °C for LC-to-crystalline at the cooling scan. The fanlike texture of title compound under polarized light indicates that title compound shows smectic phase.

The aligned films of title compound on rubbed polyimide film were obtained by drop-casting CH_2Cl_2 solution of the title compound (10^{-5} mol/L) onto glass substrate whose surface was coated with mechanically rubber polyimide film and the films were dried and annealed at 65 °C for 2 h, and then quenched to room temperature. The luminescence dichroic ratio ($I_{\parallel}/I_{\perp}$) is defined as the luminescence intensity parallel over that perpendicular to rubbed polyimide film.

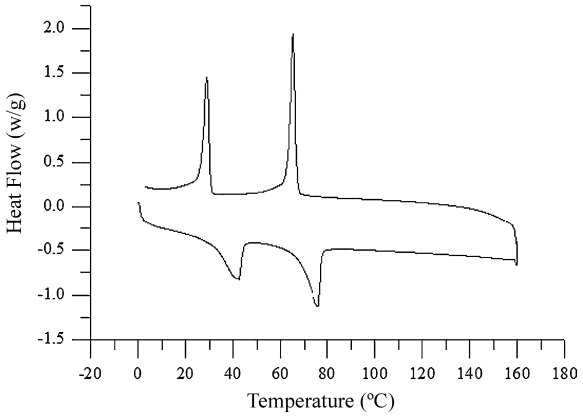

Fig. 1. DSC thermogram of title compound (10 °C/min of heating and cooling rate).

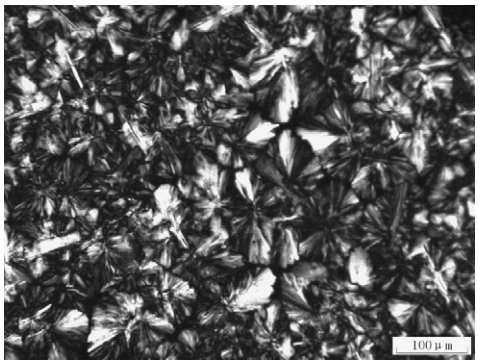

Fig. 2. Polarized optical texture of title compound at 55 °C (obtained on cooling).

The luminescence dichroic ratio at room temperature was recorded on a Perkin Elmer LS55 fluorometer with the aid of a polarizer. Fig. 3 shows polarized photoluminescence spectra of an aligned film of title compound. It is found that the photoluminescence polarized parallel to the rubbed polyimide direction is much higher than that polarized perpendicular to the rubbed polyimide direction. The luminescence dichroic ratio ($I_{\parallel}/I_{\perp}$) is 3.1 at 516 nm when excitation wavelength is 390 nm. It is anticipated that title compound can be used as potential candidate for polarized

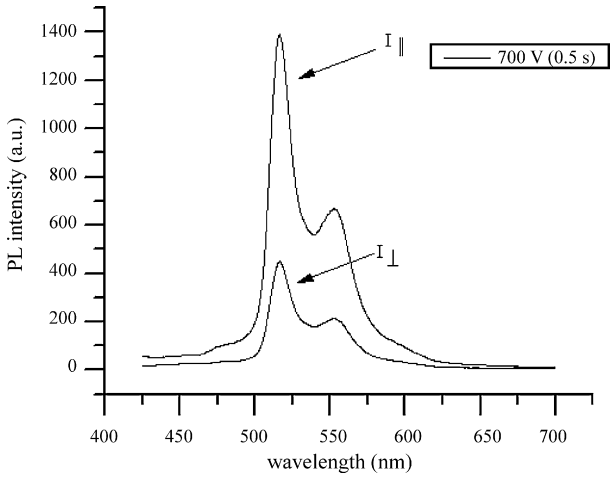

Fig. 3. Polarized photoluminescence spectra of title compound aligned on rubbed polyimide at RT (λ_{ex} = 390 nm).

OLEDs because of its intensive phosphorescence and liquid crystal characteristics. The further research to improve the degree of polarization of aligned film and the polarized OLED fabricated with title compound is in progress.

Acknowledgments

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