

Research
Report

Red Phosphorescent Organic Light-emitting Diodes

Masamichi Ikai, Hisato Takeuchi, Hisayoshi Fujikawa, Yasunori Taga

赤色りん光有機EL素子

猪飼正道, 竹内久人, 藤川久喜, 多賀康訓

Abstract

Phosphorescent organic light-emitting diodes (OLEDs) have the great advantage of highly-efficient emission compared with conventional fluorescent OLEDs. Pt(II) porphyrins are among the most promising saturated red phosphorescent dyes, yet tuning of their properties by making structural modifications has only been attempted on a modest scale, despite the large structural-diversity of synthetic porphyrins. Here we demonstrate enhancement of the external quantum efficiency of red phosphorescent OLEDs by using a novel facially-encumbered and sterically-bulky meso-aryl-substituted Pt(II) porphyrin. This molecule has a spherical shape ("doubly decamethylene-strapped" Pt(II) porphyrin) although conventional Pt(II) porphyrin

is flat in shape. We assume that the red phosphorescent emission increases in line with the decrease in the number of non-radiative decay pathways by restricting the rotational freedom of the meso-aryl substituents in the Pt(II) porphyrins. There is a trend whereby the triplet excited-state lifetimes become longer with increasing external quantum efficiencies (QEs) in OLEDs that include Pt(II) porphyrins. This finding suggests that one can obtain higher external QE values in red phosphorescent OLEDs by restricting the rotational freedom of the meso-aryl substituents of the Pt(II) porphyrins, and this concept may serve as a guide to the molecular design of highly-emissive materials.

Keywords

Phosphorescent, Pt(II) porphyrin, OLED, Triplet, External quantum efficiency, Steric bulkiness, Doubly-strapped, Rotational freedom

要 旨

りん光有機EL素子は、従来の蛍光有機EL素子と比較し高効率発光となる利点がある。白金ポルフィリンは、赤色りん光発光材料として有望な材料の候補の一つであるが、分子修飾による赤色りん光有機EL素子の発光効率最適化がまだ十分には行われていない。我々は、従来平面形状を有する白金ポルフィリンの分子形状を、球状で立体的に嵩高い分子にした新規白金ポルフィリン("doubly-strapped" 白金ポルフィリン)を設計し、赤色発光材料として用いることで赤色りん光有機EL素子の発光効率を向上させた。白金ポルフィリンのmeso位に結合したフェニル基の

回転自由度を抑制することで非発光成分が減り、結果的に発光成分が増加したと推測される。白金ポルフィリンを用いた有機EL素子のりん光寿命(三重項励起寿命)を測定し比較したところ、発光効率が高い材料の励起寿命が長くなる傾向があった。この結果は、白金ポルフィリンのmeso位に結合するフェニル基の回転自由度を抑制した分子設計をすることで、りん光有機EL素子の発光効率が向上することを示唆しており、この概念は高効率発光材料の分子設計の指針になる可能性がある。

キーワード

りん光, 白金ポルフィリン, 有機EL素子, 三重項, 外部量子効率, 立体的嵩高さ, doubly-strapped, 回転自由度

1. Introduction

Since the first demonstration of thin-film organic light-emitting diodes (OLEDs) by Tang et al.,¹⁾ intensive research efforts have been made to improve their luminous efficiency. Compared with liquid crystal displays, the OLED is one of the most promising lightweight, full-color, high-contrast flat panel displays, and has great advantages for flexible displays.

In recent years, phosphorescent OLEDs have received considerable attention due to their ability to produce highly-efficient emission compared with conventional fluorescent OLEDs. This is possible because, in principle, phosphorescent OLEDs have the potential to provide 4 times greater efficiency (the maximum internal quantum efficiency that can be attained is 100 %) than conventional fluorescent OLEDs, which have a 5 % limit for maximum external quantum efficiency (assuming the light out-coupling efficiency is about 20 % and the maximum internal quantum efficiency is 25 %).²⁻²⁴⁾ Very-high external QEs (approaching 100 % internal quantum efficiency) have already been obtained for green phosphorescent emission.⁶⁻⁸⁾ However, there is still room for improvement in terms of saturated red emission. Pt(II) porphyrin is one of the most promising emissive dyes for obtaining a saturated red color, yet tuning of dyes for red phosphorescent OLEDs' by making structural modifications has only been attempted at a very basic level, in spite of the large structural diversity of synthetic porphyrins.^{19, 20)} We now report on enhancements to the external quantum efficiency of red phosphorescent OLEDs by employing novel facially-encumbered and sterically-bulky meso-aryl substituted Pt(II) porphyrins (**Figs. 1(a), (b)**).

From the point of view of "dye-encapsulation" and "steric protection" of phosphorescent dopants in phosphorescent OLEDs, (which may lead to the maintenance of high QEs through the isolation of triplet excited-states),^{21, 22)} we investigated the external QEs of meso-aryl substituted Pt(II) porphyrins **1-4** as potential dopants for the emissive layer of OLEDs (Figs. 1(a), (b)).^{23, 24)} To date, meso-aryl substituted Pt(II) porphyrins have been reported as being rather ineffective in the red-light

emitting dyes used in OLEDs, and this been ascribed to some conjugative effects of the meso-aryl substituents that are derived from the rotational freedom of the meso-aryl substituents (**Fig. 1(c)**).¹⁹⁾ It is believed that such a conjugative interaction of the meso-aryl substituents accelerates the non-

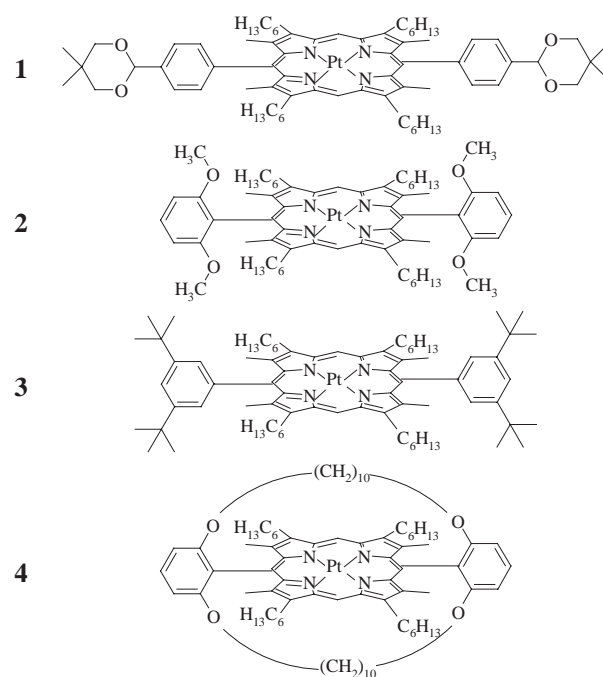


Fig. 1(a) Chemical structures of Pt(II) porphyrin derivatives (**1-4**).

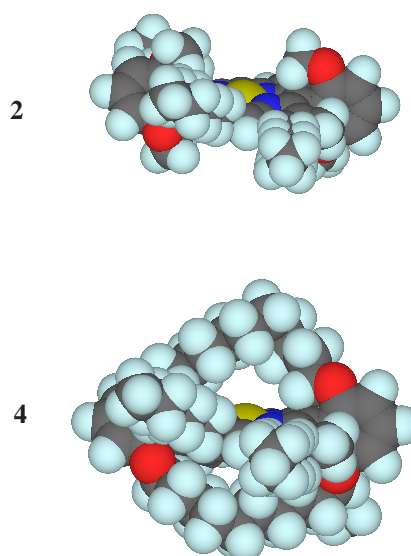


Fig. 1(b) Side view of the three dimensional molecular structures of Pt(II) porphyrins **2** and **4**.

radiative decay of the triplet excited state of Pt(II) porphyrins.¹⁹⁾

2. Experimental

2.1 Fabrication of phosphorescent organic light-emitting diodes

The OLEDs that we tested were fabricated by thermal evaporation onto a cleaned glass substrate that had been pre-coated with patterned transparent indium tin oxide (ITO) under high vacuum conditions (the background pressure of the vacuum chamber was 5×10^{-7} Torr for organic materials and 1×10^{-7} Torr for LiF and Al cathode). A glass substrate pre-coated with ITO (Sanyo Vacuum, thickness: 150 nm, sheet resistance: 10 Ω /square) was cleaned ultrasonically in methanol and isopropyl alcohol, and then rinsed in deionized water. Prior to the deposition of the organic films, the substrate was treated with UV-ozone and an O₂/Ar plasma, and was then transferred immediately into an evaporation chamber without breaking the vacuum. The structure of the OLEDs consists of a 25 nm-thick layer of a hole-transport material, which is 4,4'-bis[N-(naphthyl-N-phenylamino)-biphenyl] (α -NPD) in this case, a 35 nm-thick layer of a bipolar-transport material 4,4'-N,N'-dicarbazole-biphenyl (CBP) doped with Pt(II) porphyrins (**1-4**) as an emissive layer, a 20 nm-thick layer of an electron-transport material (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) as a hole-block layer, a 30 nm-thick layer of an electron-transport material tris(8-hydroxyquinoline)-aluminum (Alq₃), a 0.5 nm-thick layer of an electron-injection material LiF, and a 150 nm-thick layer to form the Al cathode (Fig. 2). The film thicknesses were monitored in-

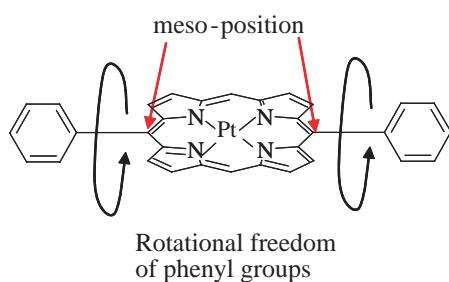


Fig. 1(c) Rotational freedom of phenyl groups at the meso-position of Pt(II) porphyrin.

situ using a calibrated quartz crystal microbalance. The OLEDs were encapsulated with a glass lid sealed with a UV-curable resin under a nitrogen atmosphere. Detailed synthetic procedures for the Pt(II) porphyrins **1-4** are reported elsewhere.²⁴⁾

The EL spectra were measured in the forward direction using a photonic multichannel analyzer (Hamamatsu Photonics, PMA-11). The luminance-voltage-current characteristics were measured using a programmable voltage/current source (Keithley, 2400 SourceMeter) and a photometer (Minolta, LS-110).

2.2 Experimental setup for triplet excited-state lifetime measurements

The transient electrophosphorescence was measured by applying rectangular voltage pulses (1.0 sec) to the device (pulse frequency: 0.5 Hz). The electrophosphorescence was detected by placing a silicon photodiode directly onto the surface of the OLEDs, which were encapsulated using glass (Fig. 3).^{23, 24)} A pulse generator (NF ELECTRONIC

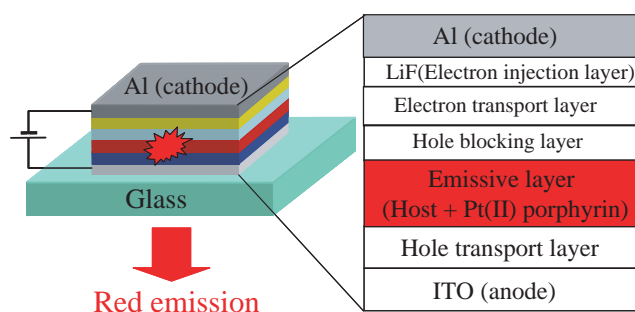


Fig. 2 Device structure of the red phosphorescent organic light-emitting diodes (OLEDs).

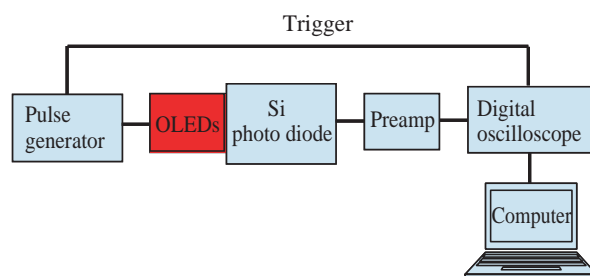


Fig. 3 Schematic diagram of transient electrophosphorescence measurements for triplet radiative decay lifetimes of Pt(II) porphyrins **1-4** in the OLEDs.

INSTRUMENTS, Wave Factory 1941) was used to apply the voltage pulses. The resulting electrophosphorescence was analyzed using a Digital oscilloscope (IWATSU, Digital Storagescope DS-9242-AM (400 MHz)) by taking the average of 64 measurements to reduce the noise. The background signal was also measured without applying voltage pulses to the OLEDs, and was subtracted from the transient electrophosphorescence data. All of the transient measurements were performed at room temperature. The voltage pulse values applied to each sample were determined just before the measurements of the triplet excited-state lifetimes by injecting current densities of 0.55, 1.1, 2.2, and 5.5 mA/cm².

3. Results and discussion

3.1 EL spectra and chromaticity coordinates

All of the devices that contained Pt(II) porphyrins **1-4** showed a main electroluminescence (EL) peak at 657 nm and an additional shoulder in the curve at around 730 nm (**Fig. 4(a)**). No additional light emission at 450 nm was observed when the current densities applied to the OLEDs were increased, indicating that light emission only occurred from the Pt(II) porphyrin dopants (**1-4**). There was no spectral shift for Pt(II) porphyrin **4** compared with the "non-strapped" Pt(II) porphyrins (**1-3**). Therefore, it is concluded that "double decamethylene-straps" have little influence on the profiles of the EL spectra. The CIE (Commission Internationale de

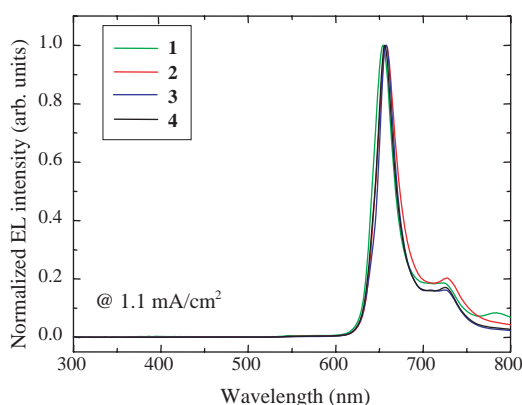


Fig. 4(a) Electroluminescent spectra of the red phosphorescent OLEDs at an injection current density of 1.1 mA/cm² for Pt(II) porphyrins **1-4**.

L'Eclairge) chromaticity coordinates (x, y) for the OLEDs at an injection current density of 1.1 mA/cm² with Pt(II) porphyrins (**1-4**) are (0.693, 0.290), (0.699, 0.286), (0.704, 0.286), (0.698, 0.287), respectively, indicating that the red color is sufficiently saturated (**Fig. 4(b)**). A red phosphorescent OLED panel constructed using Pt(II) porphyrin **4** is shown as a demonstration in **Fig. 4(c)**.

3.2 Device characteristics of phosphorescent organic light-emitting diodes

The external QEs of the phosphorescent emissions were determined as a function of injection current

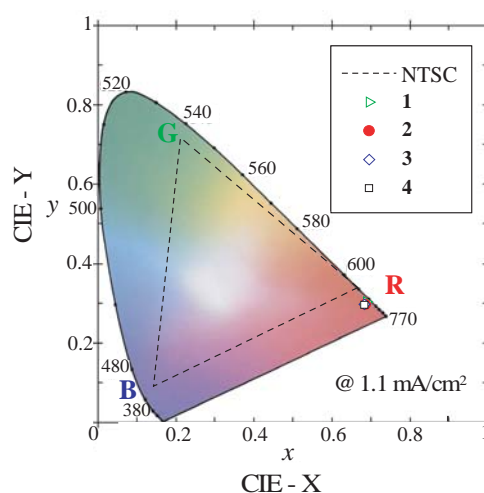


Fig. 4(b) The CIE (Commission Internationale de L'Eclairge) chromaticity coordinates (x, y) of the red phosphorescent OLEDs at an injection current density of 1.1 mA/cm² with Pt(II) porphyrins **1-4**. (NTSC is an acronym for National Television Systems Committee. NTSC is the analog television system in use in Japan, the United States, and certain other places.)



Fig. 4(c) Demonstration of a red phosphorescent OLED panel with Pt(II) porphyrin **4**.

densities for an OLED where 2.4 mol% Pt(II) porphyrins were doped into CBP (**Fig. 5**). Pt(II) porphyrin **1** confirmed the reported poor performances of meso-aryl Pt(II) porphyrins, exhibiting at most 1 % maximum external efficiency at injection current densities of 1-10 mA/cm². For Pt(II) porphyrin **2**, the peak external QE was improved to 4.2 % at 0.1-0.3 mA/cm², thus indicating the importance of facial-encumbrance and/or some restriction of rotational freedom imposed by the 2,6-dimethoxyphenyl meso-substituents. The external QE value was much higher for Pt(II) porphyrin **3**, which carries bulkier 3,5-di-tert-butylphenyl substituents. The maximum external QE achieved with Pt(II) porphyrin **3** was 7.3 % at 0.33 mA/cm², although the QE value suddenly dropped below 0.2 mA/cm², as shown in Fig. 5. The trend whereby the performance of red phosphorescent dyes in OLEDs increased in the order of **1** < **2** < **3** may therefore be correlated with facial encumbrance and steric bulkiness.

Here, we expected that the "double-strap-fabrication" of a Pt(II) porphyrin would lead to the prevention of π - π stacking interactions, as well as introducing severe restrictions to the rotational freedom of the meso-aryl substituents, and hence enabling even better performance for the OLEDs. Thus, we prepared doubly-strapped Pt(II) porphyrin **4** (Figs. 1(a), (b)) and investigated its performance. The highest external QE value in our experiments

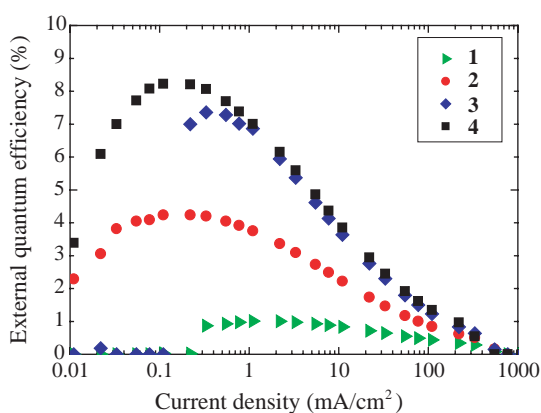


Fig. 5 External quantum efficiency (%) of Pt(II) porphyrin-based red phosphorescent OLEDs as a function of injection current densities (mA/cm²).

was achieved with **4**, attaining 8.2 % at injection current densities of 0.1-0.2 mA/cm², as illustrated in Fig. 5.

3.3 Triplet excited-state lifetimes

The triplet excited-state lifetimes of these Pt(II) porphyrins **1-4** in OLEDs were measured by transient electrophosphorescence measurements at injection current densities of 0.55, 1.1, 2.2, and 5.5 mA/cm² (**Fig. 6(a)**). The triplet excited-state lifetimes were determined by fitting with a single exponential decay. For example, the triplet excited-state decay curves of the OLEDs at an injection current density of 1.1 mA/cm² are shown in Fig. 6(b).

The triplet excited-state lifetimes for Pt(II)

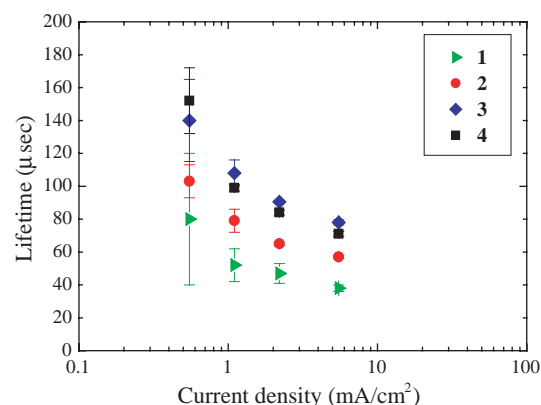


Fig. 6(a) Triplet excited-state lifetimes of Pt(II) porphyrins **1-4** in the phosphorescent OLEDs at injection current densities of 0.55, 1.1, 2.2, and 5.5 (mA/cm²).

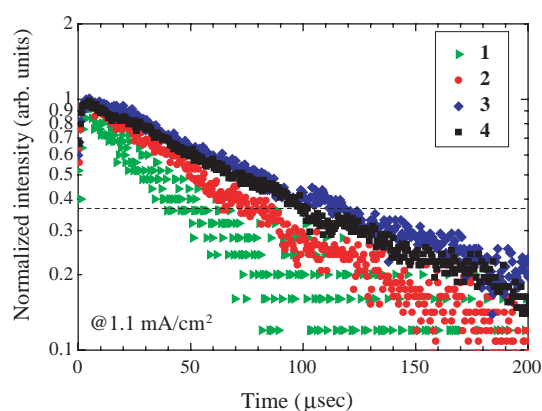


Fig. 6(b) Triplet decay curves of the phosphorescent OLEDs containing Pt(II) porphyrins **1-4** at an injection current density of 1.1 mA/cm².

porphyrins **1-4** in OLEDs at an injection current density of 0.55 mA/cm^2 were 80 ± 40 , 103 ± 10 , 140 ± 25 , and $152 \pm 20 \text{ } \mu\text{s}$, respectively (Fig. 6(a)). Upon increasing the injection current densities, the triplet lifetimes of Pt(II) porphyrins **1-4** all gradually decreased, possibly due to triplet-triplet annihilation and/or triplet-charge carrier recombination (Fig. 6(a)). At an injection current density of 1.1 mA/cm^2 , the triplet lifetimes for Pt(II) porphyrins **1-4** in OLEDs were 52 ± 10 , 79 ± 7 , 108 ± 8 , and $99 \pm 2 \text{ } \mu\text{s}$, respectively (Fig. 6(a)). Although the trend in the order of the lifetime measurements changed from $1 < 2 < 3 < 4$ to $1 < 2 < 4 < 3$ above an injection current density of 1.1 mA/cm^2 , the triplet excited-state lifetime data obtained in this way are similar to the external QE value profiles. This finding suggests that facial-encumbrance and steric bulkiness help to suppress non-radiative decay. In addition, it is believed that the "double decamethylene-straps" may severely restrict rotational freedom of the meso-aryl groups in the case of Pt(II) porphyrin **4**.

4. Conclusions

We obtained highly-efficient external QEs using facially-encumbered and sterically-bulky meso-aryl Pt(II) porphyrins as dopants in the emissive layer of red phosphorescent OLEDs. "Double decamethylene-straps" between the meso-substituted aryl groups of Pt(II) porphyrin impose severe restrictions on the rotational freedom of the meso-aryl groups, and provide more effective facial encumbrance. Thus, it is considered that they are effective in confining triplet excitons in the Pt(II) porphyrins and this concept may be applicable to the future design of highly-emissive materials.

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and Taga, Y. : Adv. Funct. Mater., **16**(2006), 515
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Masamichi Ikai

Research fields : Phosphorescent organic
light-emitting diodes
Academic degree : Dr. Sci.
Academic society : Chem. Soc. Jpn.,
Jpn. Soc. Appl. Phys.



Hisato Takeuchi

Research fields : Organic material
synthesis
Academic degree : Dr. Eng.
Academic society : Chem. Soc. Jpn.,
Synthetic Org. Chem.,
Am. Chem. Soc.



Hisayoshi Fujikawa

Research fields : Organic light-emitting
devices
Academic degree : Dr. Eng.
Academic society : Jpn. Soc. Appl. Phys.



Yasunori Taga

Research fields : Thin film materials
Academic degree : Dr. Eng.
Academic society : Am. Vacuum Soc.,
Soc. Inf. Displays, Eur. Mater. Res.
Soc., Jpn. Inst. Metals
Awards : R&D 100 Award, 1998
Jpn. Inst. Metals, 2002
ASM Award, 2002
Technical Award of Jpn. Fine
Ceram. Assoc., 2003, etc.
Present affiliation : Chubu Univ.