

Thermally activated delayed fluorescence (TADF) from Sn⁴⁺-porphyrin complexes and their application to organic light emitting diodes – novel pathway for high efficiency electroluminescence

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OLED, Thermally assisted delayed fluorescence, Porphyrin

Abstract

We developed Sn⁴⁺-porphyrin complexes that show thermally activated delayed fluorescence (TADF). TADF intensities increased with an increase of temperature because of an acceleration of the reverse intersystem crossing from triplet to singlet excited states by heat activation. TADF component provides a novel pathway for high efficiency OLEDs.

1. Introduction

In recent years, organic light emitting diodes (OLEDs) have been greatly anticipated to be used in flat-panel display and general lighting applications because of characteristic features of organic materials such as low-cost fabrication and flexibility over a large area, in addition to their high performance optoelectronic characteristics. In order to enhance the emission efficiency, various fluorescence and phosphorescence materials have been widely developed¹⁻⁵. Although OLEDs using fluorescence materials achieved high reliability, the electroluminescence (EL) efficiencies (η_{EL}) are intrinsically low compared with those of phosphorescence materials because of their limitation of the singlet exciton production efficiency ($\eta_{exciton} \sim 25\%$) under electrical excitation⁴. In contrast,

while OLEDs using phosphorescence materials achieved almost $\eta_{exciton} \sim 100\%$, a significant roll-off of η_{EL} has been observed with an increase of current density because of the acceleration of the triplet exciton annihilation processes⁶. Therefore, in order to avoid these shortcomings, the use of a novel light emitting mechanism has been anticipated.

One of the potential mechanisms to achieve compatibility of harvesting both singlet and triplet excitons and to avoid of triplet annihilation is the use of the thermally activated delayed fluorescence (TADF)^{7,8}. In TADF materials, heat accelerates the reverse intersystem-crossing (ISC) from a triplet excited state (T_1) to a singlet excited one (S_1) and thus lead to an increase of the fluorescence intensity. Therefore, when the TADF materials are used in OLEDs, heating the device would accelerate the reverse ISC and thus make it possible to fabricate OLEDs with a high EL efficiency but without any roll-off characteristics. However, the efficiencies of reverse ISC in the previous TADF materials were significantly low and we have been difficulties to verify the effectiveness of TADF for novel electroluminescence mechanism.

Recently, Furukawa and Igarashi reported that the complex of the tin (IV) chloride and coproporphyrin III (SnCl₂-Copro III) showed a strong TADF, and they applied it to the optical oxygen sensor, which is based on the dependence of the TADF lifetime on the

oxygen concentration⁹. On the basis of this previous report, we searched for more efficient TADF materials and found more efficient ones in the six types of the tin (IV) fluoride-porphyrin complexes, SnF₂-porphyrin: octaethylporphine (OEP), etioporphyrin I (Etio I), hematoporphyrin IX (Hemato IX), protoporphyrin IX (Proto IX), mesoporphyrin IX (Meso IX), and Copro III. The chemical structures of these complexes are shown in Fig. 1. These SnF₂-porphyrin complexes showed a rather strong TADF over room temperature, and they also clearly showed a visible increase of the fluorescent intensity with rising temperature.

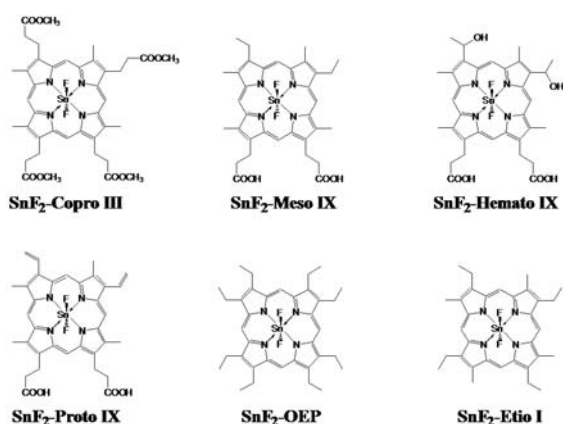


Fig. 1. Molecular structures of Sn(IV) porphyrin complexes showing thermally activated delayed fluorescence (TADF).

All SnF₂-porphyrin complexes were synthesized by using a modified Furukawa's method: tin (II) fluoride and porphyrin were dissolved into DMSO and then heated at 150°C for 5 h. Tin (II) was oxidized to tin (IV) through this complexation reaction. The mixture was then cooled, poured into 1 % aqueous HF solution, and the sedimented complex was then collected by filtration. This crude complex was dried under reduced pressure and recrystallized from MeOH/CH₂Cl₂ to produce a pure SnF₂-porphyrin complex.

2. Experimental

For solid-state TADF measurement, we dissolved 10 mg of porphyrin complex in 10 ml of 10 % MeOH/CH₂Cl₂ and dropped 100 μl of this solution onto a filter paper and dried it. Furthermore, we prepared molecularly doped polymer films composed of 2 mol % SnF₂-OEP complex as a dopant and poly(vinylcarbazole) (PVCz) as a host matrix. Fluorescence, phosphorescence, and TADF

characteristics were measured under a N₂ atmosphere using a streak camera system (C4334, Hamamatsu ther,Co.). For electrical excitation, we prepared an OLED composed of ITO/PEDOT/2wt%-SnF₂OEP: PVCz/MgAg/Ag with SnF₂OEP as an emitter. The details of device fabrication and measurement procedures are provided in the previous papers. In this experiment, particularly, we employed short pulse electrical excitation and analyzed both a prompt and delayed electroluminescence by the streak camera system.

3. Results and discussion

The photoluminescence spectra of SnF₂-Meso IX complex immersed in the filter paper are shown in Fig. 2. Strong fluorescence and TADF were observed at 570 nm while the weak room temperature phosphorescence was also observed at 703 nm. With an increase of temperature from 30 to 100 C, the emission intensity significantly increased, which showed an acceleration of the reverse intersystem crossing from T₁ to S₁ excited states caused by heat activation. The S₁-T₁ thermal energy gap, which is necessary in order to induce the reverse intersystem crossing, was estimated to be 37 – 40 kJ/mol from the fluorescence and phosphorescence spectra. These intense TADF characteristics are anticipated to the dopant in the OLED architecture, so we fabricated polymer dispersed films which contain SnF₂-OEP complex for use as a dopant in the emitting layer. We prepared a polymer dispersion film of 2 mol%-SnF₂-OEP: PVCz. The emission spectra with their streak images at T = 8.5 K (a), 300 K (b), and 400K (c) and a summary of the temperature dependence of the emission spectra (d) are shown in Fig. 3. The streak

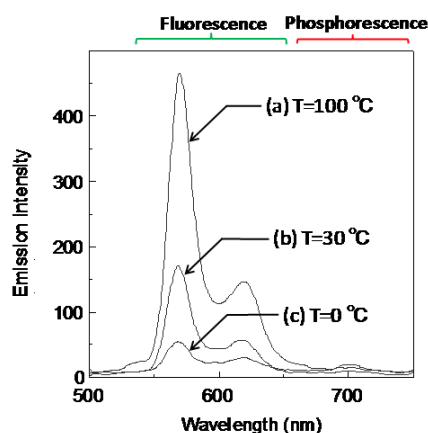


Fig. 2. Spectral change of thermally activated delayed fluorescence of SnF₂ (Meso IX) complex with T = 0°C (a), 30°C (b), and 100°C (c).

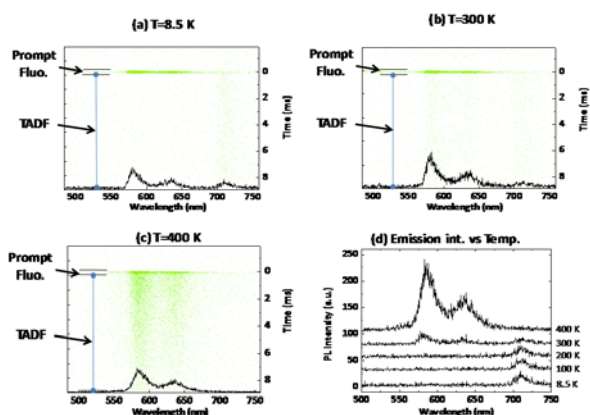


Fig. 3. Emission spectra with their streak images of 2wt%-SnF₂-OEP: PVCz films at T = 8.5 (a), 300 (b), and 400 K (c) and relationship between temperature and integrated emission intensity (d).

images visually provide the ratio of prompt fluorescence (PF) and delayed fluorescence (TADF). The intense emissions around $t=0$ correspond to the PF and the long tailing part corresponds to TADF. At T = 9 K, although we observed the faint TADF component, an intense TADF emission was observed at T = 400 K. The fluorescence intensity significantly increased with an increase of temperature, which indicated that acceleration of the reverse intersystem crossing was caused by heat activation. We roughly estimated the photoluminescence efficiency (Φ_{PL}) of these processes at 400 K, which indicates that the PF efficiency is $\Phi_{PF} \sim 1\%$ and the TADF efficiency (Φ_{TADF}) is a few times higher than Φ_{PL} .

Further, we fabricated an ITO/PEDOT/2wt%-SnF₂OEP:PVCz/MgAg/Ag device with SnF₂OEP as an emitter. The current density (J)-voltage (V) characteristics showed a typical shape having abrupt onset of current injection at around 6V and intense electroluminescence was observed. Under short pulse electrical excitation, we clearly observed both prompt and delayed electroluminescence components based on TADF which provides a novel pathway for high efficiency electroluminescence.

5. References

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