

Long-Persistent Luminescence from Organic Molecules

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Keywords: Organic Long-Persistent Luminescence, Photoluminescence, Organic semiconductor

ABSTRACT

We demonstrate long persistent luminescence from simple mixtures of two appropriate organic materials. Moreover, emission color of organic LPL can be tuned by the extra emitter dopants. We also demonstrated a polymer-based organic LPL system that is flexible, transparent, and solution-processable.

1 INTRODUCTION

Glow-in-the-dark materials also known as Long-persistent luminescence (LPL) work by slowly releasing energy absorbed from ambient light. Used in watches and emergency signs, most commercial glow-in-the-dark materials are based on inorganic compounds and include rare metals. However, these materials are expensive and require high temperatures to manufacture. Carbon-based organic materials can overcome many of these disadvantages.

The long-lived emission from organic molecules is known as phosphorescence, which is a transition between different spin states (usually from a triplet excited state to the singlet ground state). However, the phosphorescence does not achieve long-lasting emission over one hour like inorganic system because of the emission mechanism. The LPL is an emission mechanism in which the energy passes through an intermediate states like a trapped state. There is no restriction regarding spin state. While LPL is long lived because of charge separation and subsequent slow recombination (second-order kinetics) of initially generated excitons, phosphorescence is long lived because of the low probability of the transition (first-order kinetics) occurring in the initially generated excitons.

In this study, we realized first organic LPL systems by using intermediate charge separated (CS) states. By mixing an electron donating molecule and an electron accepting molecule, emission lasting for over an hour was demonstrated. Moreover, greenish-blue to red and even warm white emission are achieved by energy transfer from exciplex in the organic LPL (OLPL) matrix to the emitter dopants. The dopants also improve brightness and

emission duration through efficient radiative decay and the trapping of electrons, respectively. We also demonstrated a polymer-based organic LPL system that is flexible, transparent, and solution-processable.

2 EXPERIMENT

Materials used in this study were purchased from TCI Chemicals (Tokyo, Japan), Luminescence Technology Corp (Taipei, Taiwan), ZEON Japan (Tokyo, Japan). Other materials were used as received. All compounds were purified by sublimation and stored in a nitrogen-filled glovebox.

Film fabrication: Thick films (0.4 mm) for the optical measurement were fabricated by a melt-casting method.

Optical measurements: The absorption spectra were recorded on a UV-vis-NIR spectrophotometer (LAMBDA 950, Perkin Elmer). The photoluminescence spectra in air were recorded on a spectrofluorometer (FP-8600, JASCO). The phosphorescence spectra at 77 K were recorded on a multi-channel spectrometer (PMA-12, Hamamatsu Photonics) excited using a 340-nm LED (M340L4, Thorlabs) with a band pass filter (340 ± 5 nm). The absolute photoluminescence quantum yields (Φ_{PL}) were measured using a quantum yield spectrometer (C9920-02, Hamamatsu Photonics). LPL performance was obtained using a homemade measurement setup with an excitation power of 230 μW and excitation duration of 60 s.⁸

3 RESULTS AND DISCUSSION

3.1 Emission mechanism of OLPL system

A blend of the strong electron-donating molecule N,N,N',N'-tetramethylbenzidine (TMB) and the strong electron-accepting molecule 2,8-bis(diphenylphosphoryl)dibenzo[b,d]thiophene (PPT), which has a high triplet energy and provides a rigid amorphous environment to help suppress nonradiative deactivation, was selected to obtain long-lived CS states (Fig. 1a).

After turning off the photo-excitation, LPL with a spectrum identical to that of photoluminescence was

observed from the blend film, indicating that the LPL emission is also derived from exciplexes between TMB and PPT. The emission decay profile of a 1 mol% TMB:PPT film is shown in Fig. 1b. This LPL continues for over 1 h at 300 K. The emission decay profile indicates the emission is not the exponential decay but a power-law decay due to the presence of the intermediate charge separated states.

The duration of the LPL is dependent on the excitation power and time, the sample temperature, and the TMB doping concentration. This excitation time dependence is clear evidence for the generation and accumulation of charge carriers by weak photo-irradiation.

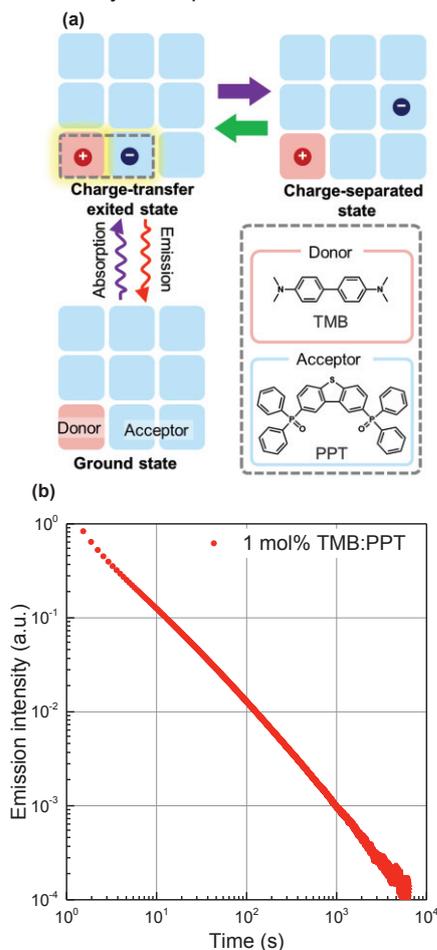


Fig.1. (a) Emission mechanism and materials of OLPL system. (b) Emission decay profile of 1 mol% TMB/PPT system.

3.2 Color-tuning of OLPL system

The OLPL emission originates from the charge-transfer transition of the excited state complex formed between a donor and an acceptor. Since the excited state complex (exciplex) usually exhibits low color purity and low emission efficiency, the emission duration of OLPL system is still shorter than that of inorganic LPL systems. To improve the color purity and emission intensity, we

introduced extra dopants (Fig. 2).

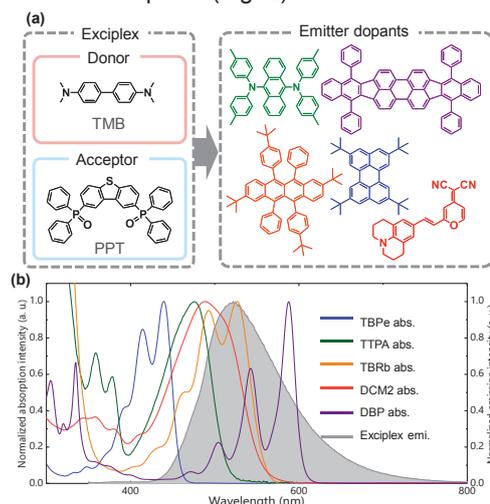


Fig. 2. (a) Chemical structures of the exciplex and emitter dopants. (b) The emission spectrum of the exciplex and the absorption spectra of the emitter dopants in toluene solution.

The exciplexes exhibit a broad emission from 400 to 800 nm attributed to a charge-transfer transition from the lowest unoccupied molecular orbital (LUMO) of PPT to the highest occupied molecular orbital (HOMO) of TMB. This broad emission spectrum of the exciplexes overlaps with the absorption spectra of a wide variety of fluorescent emitter dopants (Fig. 2). As a result, the generated exciplexes can transfer their energy to the emitter dopants as long as the emission spectrum of the exciplex sufficiently overlaps with the absorption spectrum of the emitter dopant.

As the result, greenish-blue to red and even warm white emission are achieved by energy transfer from exciplex in the OLPL matrix to the emitter dopants (Fig. 3). The dopants also improve brightness and emission duration through efficient radiative decay and the trapping of electrons, respectively.



Fig. 3. Photograph of OLPL.

3.3 Flexible and transparent OLPL system

The presented OLPL system has poor flexibility because it consists of only small molecules, which are flexible in very thin films but are brittle and can crack in the bulk state. Therefore, a flexible OLPL system is required for the development of future applications such as fibers, films, and curved products. We demonstrate the polymer-based OLPL system made by a blend of TMB and a polymer having electron accepting units. (Fig. 4).

This polymer-based OLPL material can provide the mechanical flexibility needed for the fabrication of various plastic products, fibers, and films. Because the acceptor polymer PBPO is an engineering plastic, this OLPL system has high performance in terms of mechanical properties and thermal stability.

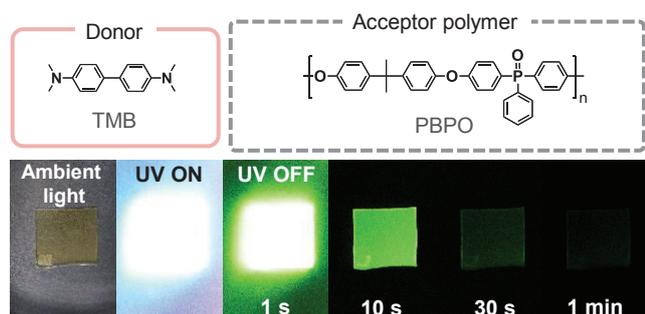


Fig. 4. Chemical structure of the polymer-based OLPL and photograph of the LPL emission.

4 CONCLUSIONS

We demonstrated a novel emission mechanism of the OLPL system. By optimizing the materials and emission pathway, the LPL performance was improved. Future investigation of the donor, acceptor, and emitter will enable full-color and even UV and NIR organic glow-in-the-dark paints.

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