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## Unusual photoluminescence characteristics of tetraphenylpyrene (TPPy) in various aggregated morphologies

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## Abstract

We found that 1,3,6,8-tetraphenylpyrene (TPPy) demonstrates unusual photoluminescence (PL) characteristics in the solid-state morphologies. We investigated the PL characteristics of TPPy in various morphologies including powder, deposited film, and solutions. The TPPy powder (A), which was prepared through column chromatography, recrystallization, and train sublimation, showed blue fluorescence with a peak of maximum wavelength of  $\lambda_{max} = 451$  nm. The TPPy powder (B), which was obtained by thermal annealing of TPPy powder (A) in a quartz tube in nitrogen, showed green fluorescence with  $\lambda_{max} = 510$  nm. Furthermore, the TPPy powder (B) was reversibly converted into TPPy powder (A) by recrystallization. We conclude that TPPy dimers form locally in the TPPy monomer aggregates during thermal annealing and redissociate into the monomer states during recrystallization.

Recent research has actively investigated various organic electronic devices, such as organic light-emitting diodes (OLEDs) [1–3], organic thin-film transistors (TFTs) [4–9], organic switching and memory devices [10–12], and organic solar cells (OSCs) [13–15]. Various molecular structures have been used widely in these devices. Condensed aromatic hydrocarbons, such as pentacene and rubrene, have been revealed to be particularly useful for use in the active layer in organic field-effect transistors (OFETs). In particular, very high hole mobilities ( $\mu_{hole}$ ) exceeding 1 cm<sup>2</sup>/V s [16,17] using a pentacene deposited film as an active layer have been achieved. Furthermore, an OFET using a rubrene single crystal showed extremely high hole mobility ( $\mu_{hole}$ ) of 10 cm<sup>2</sup>/V s [18], indicating that the highly packed molecular aggregates having tight intermo-

lecular  $\pi$ -stacking demonstrate notably high carrier mobilities in organic light-emitting FETs (OLEFETs). In addition to the high carrier mobility, some of the polyacene derivatives have been found to show high PL quantum efficiency ( $\Phi_{PL}$ ) even in the solid state films, making it possible to have a novel organic light-emitting device, i.e., an OLE-FET, which requires both light-emitting and field-effect transistor characteristics [9]. In this device, aromatic compounds including tetracene [7], oligothiophene [8], and 1,3,6,8-tetraphenylpyrene (TPPy) [9] were revealed to have excellent OLEFET characteristics. Using TPPy in OLE-FETs, we attained bright electroluminescence (EL) with an external EL efficiency of  $\eta_{ext} =$  of 0.5%.

During the OLEFET study using TPPy, we encountered unusual photoluminescence (PL) characteristics of TPPy. The TPPy deposited film showed different PL spectra depending on the purification procedures, such as thermal annealing and recrystallization. In this study, we investi-

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gated detailed PL characteristics of TPPy in various morphologies such as powder, deposited film, and solution, and examined the unique PL characteristics with special focus on dimer formation.

We synthesized TPPy by the Suzuki coupling of 1,3,6,8tetrabromopyrene and 4-phenylbronic acid with Pd(PPh<sub>3</sub>)<sub>4</sub> in a toluene solution by refluxing for 9 h under nitrogen gas, yielding 68% in the crude product. The synthesized TPPy powder was purified by column chromatography (silica gel, toluene) to remove the palladium catalyst, recrystallized from toluene, and finally purified twice using the train sublimation method [19] ( $<3 \times 10^{-3}$  Pa). Here, we abbreviate this purified TPPy powder as TPPy (A). We thermally annealed the TPPy (A) powder at T = 300 °C for 2 h in nitrogen and obtained TPPy powder (B). The purities of these powders were confirmed to be higher than 99 +% by high performance liquid chromatography (HPLC); the exact purity of the powders was (A): 99.5% and (B): 99.4%.

In the formation of the TPPy deposited films, the organic sources were heated in a high-vacuum  $(<3 \times 10^{-3} \text{ Pa})$  thermal evaporation system. The deposition speed was monitored with a quartz sensor and maintained at 0.3 nm s<sup>-1</sup>. To fabricate single layer organic light-emitting diodes (OLEDs), we used a clean glass substrate precoated with a 110 nm thick indium–tin-oxide (ITO) layer with a sheet resistance of approximately  $20 \Omega/\Box$ . Prior to use, the substrate was degreased with solvents and cleaned in a UV–ozone chamber (Nippon Laser & Electronics Lab., NL-UV253) before it was loaded into an evaporation system. A 100 nm-thick TPPy layer was deposited and a shadow mask with 1 mm-diameter openings was used to define the cathode consisting of 100 nm-thick MgAg and 10 nm-thick Ag layers as a cover layer.

Absorption and PL spectra of the organic layers were measured using a fluorospectrometer (FP-6300, Jasco) and a UV–Vis spectrometer (UV-3100, Shimadzu). In the PL measurement of the TPPy powders, the powders were carefully sandwiched between two quartz plates. The absolute PL quantum efficiency was measured using an integrating sphere [20]. The highest occupied molecular orbital (HOMO) levels of the metal and the organic layers were measured using an ultraviolet photoelectron spectroscope, AC-1 (Riken Keiki Co.). Current density–voltage–luminance (J-V-L) characteristics were measured using a semiconductor parameter analyzer (HP4145, Agilent), with the external EL quantum efficiency directly obtained by placing and centering the OLEDs on the surface of a largediameter calibrated Si photodiode.

X-ray analysis of the deposited film and the single crystal were measured, respectively, using X-ray diffraction systems [21] (out of plane measurement: RINT-TTRIII and refraction measurement: RINT-UlatimaIII, Rigaku) and an X-ray crystal structure analysis system [18] (RAXIS RAPID, Rigaku). The TPPy single crystals were grown using the train sublimation method [22] at T = 300 °C with a flow of argon gas (60 ml/min.). Fig. 1(I) shows the PL characteristics of the TPPy (A) and TPPy (B) powders. The TPPy (A) powder showed fluorescence with a maximum wavelength ( $\lambda_{max}$ ) of 451 nm, while the TPPy (B) powder showed fluorescence with  $\lambda_{max} = 510$  nm. Further, the TPPy (B) powder can be reversibly converted to the TPPy powder (A) by recrystallization with toluene. Thus, blue to green by thermal annealing and green to blue by recrystallization processes are mutually reversible.

Fig. 1(II) shows the PL characteristics of 100 nm-thick TPPy deposited films using these powders as the deposition sources. The TPPy (A) deposited film showed fluorescence



Fig. 1. Photoluminance (PL) and absorption spectra of TPPy powders and deposited films. (I) TPPy powders: (A) recrystallized form and (B) after thermal annealing of TPPy (A) powders at T = 300 °C. (II) TPPy deposited films evaporated from the TPPy (A) and TPPy (B) powders. The deposited films have similar PL spectra to those of the powders. Inset shows TPPy molecular structure.

with  $\lambda_{\text{max}} = 455$  nm, transient PL lifetime of  $\tau_{\text{PL}} \sim 2$  ns and absolute PL efficiency of  $\Phi_{\text{PL}} = 68 \pm 2\%$ ; the TPPy (B) deposited film showed fluorescence with  $\lambda_{\text{max}} = 503$  nm,  $\tau_{\text{PL}} \sim 6$  ns and  $\Phi_{\text{PL}} = 45 \pm 2\%$ . Thus, the PL spectra of the TPPy deposited films are very similar to those of the powders, indicating that the locally aggregated structures in the TPPy powder's deposition sources are preserved in their deposited films. Thus, the sublimation occurs as a TPPy cluster and does not necessarily occurs as an individual isolated molecule. Here, the absorption spectra of the deposited films showed no appreciable differences despite the significant differences of their PL characteristics.

To investigate the correlation between PL characteristics and morphologies of the TPPy films and powders, we conducted X-ray analysis for both the deposited films and the single crystals. In the X-ray diffraction patterns, no sharp diffraction peaks were observed in either of the TPPy films, indicating that the TPPy deposited films have amorphous morphologies. We also calculated the densities of the TPPy deposited films from the X-ray reflection curves, suggesting that the densities of both TPPy deposited films are the same at  $1.25 \pm 0.03$  g/cm<sup>3</sup>: no significant difference between A and B was observed. We next conducted X-ray analysis for the single crystals of TPPy (A) and (B). Fig. 2 shows the PL characteristics and photographs of TPPy (A) and (B) single crystals prepared by the gas flow-train sublimation method [22]. The TPPy (A) single crystals had flakelike shapes with blue fluorescence with  $\lambda_{max} = 450 \text{ nm}$ , while the TPPy (B) single crystal had needle-like shapes with green fluorescence with  $\lambda_{max} = 540$  nm. Although the PL characteristics are completely different, the structure analysis clearly confirmed that the single crystals have exactly the same crystal form, an orthorhombic structure the lattice parameters of a = 11.324(2) Å, with b = 12.400(2) Å, and c = 19.105(3) Å (Fig. 2b).

Next, we investigated the PL and absorption spectra of TPPy (A) and (B) in a dichloromethane (DCM) solution. We dissolved the TPPy powders (A) and (B) in separate



Fig. 2. (a) Photoluminescence (PL) spectra of TPPy single crystals (A and B). Inset shows photographs of the crystals. (i) TPPy single crystals having flake-like shapes have blue PL and (ii) those having needle-like shapes have green PL. (b) Both TPPy (A) and (B) structures have the same crystal form, an orthorhombic structure with lattice parameters of a = 11.324(2) Å, b = 12.400(2) Å and c = 19.105(3) Å.



Fig. 3. Absorption spectra of TPPy (A and B) depending on the TPPy concentrations in dichloromethane (DCM) solutions of  $10^{-3}$  M ( $\circ$ ),  $10^{-4}$  M ( $\Delta$ ) and  $10^{-5}$  M ( $\nabla$ ). Inset: photoluminescence (PL) spectra of TPPy (A and B) depending on the concentration.

solutions of DCM. Fig. 3 shows the PL and absorption spectra of TPPy (A) and TPPy (B) in a DCM solution depending on the TPPy concentrations. We changed the TPPy concentrations from  $10^{-5}$  to  $10^{-3}$  M and with this increase, the PL spectra of TPPv (A) showed a slight red shift of 13 nm from  $\lambda = 420$  nm to  $\lambda = 433$  nm. The PL spectra of TPPy (B) under the low concentration of  $10^{-5}$  M showed blue fluorescence with  $\lambda_{max} = 421$  nm, which coincides well with that of TPPy (A). With a higher concentration of  $>10^{-3}$  M, however, the PL showed additional peaks (shoulders) at  $\lambda_{max} = 500 \text{ nm}$ and  $\lambda_{\rm max} = 525$  nm in addition to the similar red shift. Furthermore, although the absorption spectra of TPPy (A) showed no significant difference when the TPPy concentration was changed, TPPy (B) showed new absorption peaks at  $\lambda_{\text{max}} = 450 \text{ nm}$  and  $\lambda_{\text{max}} = 478 \text{ nm}$  with the higher concentration of  $10^{-3}$  M, indicating the formation of dimer aggregates only in the TPPy (B) solution.

Based on the PL characteristics we found in the various morphologies of the single crystal, deposited film, and solution, we can discuss the unique PL characteristics of TPPv. In the TPPy (B) solid-state aggregates, it is probable that a very small amount of dimer formation occurs in the TPPv monomer host matrix and the excitons created in the TPPy monomer diffuse into the dimer sites through exciton migration, resulting in exciton decay at the dimer states (green emission). The longer  $\tau_{\rm PL}$  in the green emission compared with that in the blue emission also support the idea of the dimer formation. In the TPPv (B) solutions, we clearly observed dimer formation at the high concentration, while no dimer formation occurred at the low concentration. In the case of TPPy (A), however, no dimer formation was detected in either the solid states or the solution, leading to monomer emission (blue emission). Therefore, a very small number of the TPPy molecules must have formed dimer aggregates during the thermal annealing of the TPPv (A) powder. We infer that the large  $\pi - \pi$  stacking interaction between the pyrene cores induced such dimerization during thermal annealing, as is well known for un-substituted pyrene [23]. Activation on the rotation of the attached phenyl rings by thermal annealing probably enhanced this aggregation. However, the number of such dimer formations was so small that we could not detect them by X-ray analysis. We have to conclude that once the dimer was formed, it would not be dissociated easily in the DCM solution and it dissociated through recrystallization. In a dilute solution, the energy transfer between the isolated TPPy molecules is inefficient, resulting in TPPy monomer emission. At the high concentration, however, the energy transfer became more active and TPPy dimer emission occurred through efficient energy transfer. No possibility exists that the TPPy molecules will decompose during thermal annealing; we carefully checked the purities by HPLC and column chromatography and detected no appreciable decomposition.

Finally, to confirm a related aspect of the unusual PL characteristics, we examined the electrical characteristics of the TPPy (A) and TPPy (B) deposited films. Fig. 4a shows the current density-voltage (J-V) and external EL quantum efficiency–current density ( $\eta_{ext}$ –J) characteristics of single layer OLEDs with TPPy (A) and TPPy (B) as an active layer in the configuration of ITO/TPPy (100 nm)/MgAg(100 nm)/Ag(10 nm). Even the EL spectra showed differences between TPPy (A) and (B). The OLED with TPPy (A) showed blue EL with an EL spectra at  $\lambda_{\text{max}} = 450 \text{ nm}$ , while the OLED with TPPy (B) showed green EL with an EL spectra at  $\lambda_{max} = 503$  nm. Also, the J-V characteristics with TPPy (B) showed a shift of the driving voltage to high voltage compared with that of TPPy (A), and  $\eta_{ext}$  with TPPy (B) showed 20 times higher efficiency than that of TPPy (A), suggesting that charge carriers were well trapped by the dimer sites. Although the HOMO level and the lowest unoccupied molecular orbital (LUMO) level showed the same values of 5.7 eV and 2.7 eV in both TPPy (A) and (B) deposited films, the



Fig. 4. (a) Current density (*J*) depending on voltage (*V*) and external quantum efficiency ( $\eta_{ext}$ ) and current density (*J*) characteristics in OLEDs using the TPPy powders (A and B) as the deposition sources. (b) EL spectra in the OLEDs with the TPPy powders (A and B).

dimer sites should form localized states within the HOMO and LUMO levels and contribute to increasing direct carrier injection from the cathode, improving exciton generation efficiency. These electrical measurements are consistent with the PL characteristics, supporting our conclusions.

In summary, we demonstrated unique PL characteristics in TPPy powders and deposited films. The thermal annealing and recrystallization reversibly converted the PL spectra. We concluded that the fluorescence around 500– 550 nm originates from the formation of TPPy dimer states. We examined other TPPy derivatives having various substituents and observed that the shift of the PL spectrum depends heavily on the substituent. Comparing the substituent effects would provide a more comprehensive discussion.

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