Optical Properties of Thianthrene-containing Imide Compound and Polyimides Exhibiting Long-wavelength Fluorescence and Phosphorescence

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I. INTRODUCTION

Polyimides (PIs) exhibiting large Stokes-shifted (*SS*) luminescence are promising candidates for solar spectrum down-convertor owing to their excellent properties such as thermal stability, chemical resistance and mechanical strength [1]. Efficient down-convertors require high optical transparency in the visible region as well as large *SS* emission. In general, phosphorescence exhibits larger *SS* than fluorescence owing to the intersystem crossing (ISC) process [2]. We have recently reported that the PIs containing thioether (–S–) linkage in the main chain exhibit efficient ISC than those containing ether (–O–) linkage [3]. Moreover, it is reported that thianthrene moiety promotes the formation of excited triplet state owing to its n–π^* transition [4]. In this study, we investigated the photoluminescent properties of thianthrene-containing PIs and a corresponding model compound (**Fig. 1**).

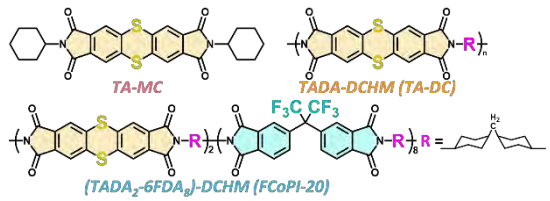

Fig. 1. Chemical structures of TA-MC, TA-DC and FCoPI-20.

II. RESULTS AND DISCUSSION

Fig. 2(a) shows the excitation and emission spectra of TA-MC in the polycrystalline state, dissolved in $CHCl_3$, and dispersed in PMMA matrix. TA-MC shows yellowish coloration due to the aggregation in the polycrystalline state and exhibits dual emissions of fluorescence and phosphorescence. Moreover, the strong intermolecular π–π interactions suppress the molecular motion, resulting in a higher quantum yields (Φ = 0.27) than in other conditions. On the other hand, two fluorescence peaks were observed at 395 nm and 600 nm in $CHCl_3$ solution.

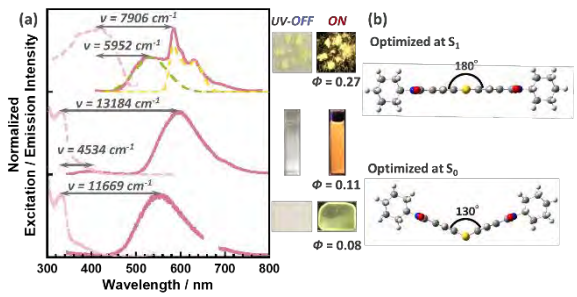

Fig. 2. (a) Excitation / emission spectra of TA-MC in polycrystalline state, dissorved in $CHCl_3$ (5×10^{-5} M), dispersed in PMMA matrix (1.0 wt%).(b) optimized structures optimized at ground state (S_0) and excited singlet state (S_1) by TD–DFT method.

The former fluorescence with a small *SS* at 395 nm is emitted from a metastable structure close to the Frank-Condon state, while the latter fluorescence with an extremely large *SS* at 600 nm (ν =13,184 cm^{-1}) is originated from the large structural relaxation from the V-shape to the planar structure (**Fig. 2**(b)) in the excited state. The PMMA-dispersed film is transparent and exhibits a fluorescence with a large *SS* (ν =11,669 cm^{-1}) at 550 nm due to the conformational change in the excited state. Moreover, it exhibits bright phosphorescence at low temperatures (< 240 K) due to the suppression of molecular motion, and the Φ value reached to 0.36 at 77 K.

In contrast, the PI of TA-DC shows yellowish coloration due to the aggregation and exhibits bright orange fluorescence (**Fig. 3**(a)). It also exhibits phosphorescence at lower temperatures, but its Φ value was only 0.15 at 77 K. To clarify the difference, the phosphorescence rate constants (k_P), non-radiative deactivation process rate constants from the triplet state to the ground state (k_{TS}) were estimated for TA-DC and PMMA-dispersed film of TA-MC (**Fig. 3**(b)). The k_p of TA-DC was almost the same as that of TA-MC, while the k_{TS} was much larger than that of TA-MC, which indicates that the deactivation process of exciton energy transfer is more significant in TA-DC due to the aggregation, resulting in the small Φ. To suppress aggregation, copopyimides (Co-PI) was synthesized using 6FDA having bulky $-CF_3$ substituents. The UV-vis absorption and emission spectra were blue-shifted compared to those of TA-DC, indicating that aggregation was suppressed. The Φ value at 77 K was increased to 0.41, and the k_{TS} was decreased than TA-DC. This indicates that the introduction of 6FDA suppressed the aggregation of TADA as well as the exciton energy transfer, resulting in the improved phosphorescence properties.

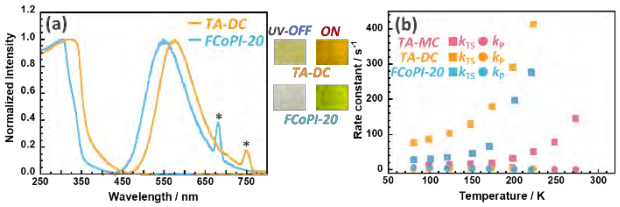

Fig. 3. (a) UV-vis absorption / emission spectra of TA-DC and FCoPI-20, and (b) phosphorescence rate constants (k_P) and non-radiative deactivation rate constants from triplet state to ground state (k_{TS}) of TA-MC, TA-DC, and FCOPI-20. ($k_P = \Phi_P / \Phi_{ISC}\tau_P$, $k_{TS} = \Phi_{TS} / \Phi_{ISC}\tau_P$)

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