Transient Absorption Spectroscopic Analysis of Energy Transfer Process in the Solid-state Upconversion System

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Photon upconversion (UC) is a molecular technology that converts a low-energy light to a higher-energy light by employing triplet energy transfer from an energy donor (D) and triplet–triplet annihilation (TTA) of energy acceptors (A). To realize UC in the solid state, efficient triplet energy harvesting and suppression of fluorescence resonance energy-transfer quenching are required. For this purpose, we employed solution-processed polyurethane (PU) composites containing D, an energy mediator (M), and a dyad DPA–Ad–DPA[1,2] as A (Fig. 1). In this work, we analyzed the energy transfer behavior in the PU composites (Fig. 1 and 2) by using transient absorption analysis.

First, we prepared the PU composites containing platinum octaethylporphyrin (PtOEP) and various concentrations of anthracene (Ant) and 9,10-diphenylanthracene (DPA). The Stern–Volmer analysis obtained by phosphorescence quenching of ^{3}PtOEP* by DPA provided quenching rate constant (k_Q) is 1.2×10^8 $M^{-1}s^{-1}$. This k_Q value is almost 1/10 of that in a CH_2Cl_2 solution, suggesting that slow molecular diffusion occurs in the PU composite.

Transient absorption analysis (Fig. 3) was conducted for the PU composite containing PtOEP (0.1 mM), Ant (10 mM), and DPA (1 mM). Photoexcitation of the PU composite provided T–T absorption bands of ^{3}Ant* at 425 nm ($\varepsilon = 4.6 \times 10^4$ $M^{-1}cm^{-1}$) formed by energy transfer from ^{3}PtOEP*. After 10 μs of excitation, broad absorption of ^{3}DPA* was observed at 448 nm (1.5×10^4 $M^{-1}cm^{-1}$) but ^{3}Ant* remained. These results suggest that partial energy harvesting occurred from ^{3}DPA* to DPA to promote TTA.

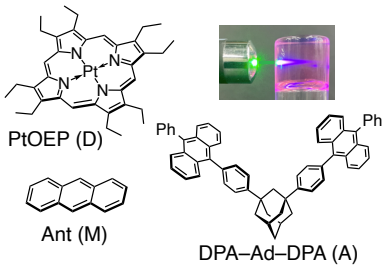

Fig. 1. Structures of PtOEP, Ant, and DPA–Ad–DPA, and a photograph of the PU composite.

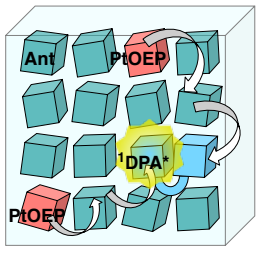

Fig. 2. A schematic representation of polymer composites containing PtOEP, Ant, and DPA–Ad–DPA.

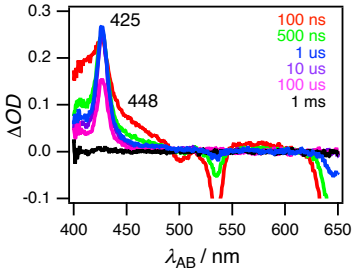

Fig. 3. Transient absorption spectra of the PU composite of PtOEP (0.1 mM), Ant (10 mM), and DPA (1 mM) (λ_{EX} = 532 nm).

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