Quasi-reversible photoinduced displacement of functional organic ligands from colloidal semiconductor nanocrystals

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Organic-inorganic hybrid semiconductor nanocrystals (NCs) coordinated with functional organic ligands have been attractive and widely studied in various fields for optoelectronic materials, such as solar cells, photocatalysis, and photon upconversion. In these materials, coordination bonds of ligand molecules are usually assumed to be stable during or even after optical processes. However, this assumption is not always valid. Surprisingly, even though it is very important to consider the coordination state of surface organic ligand molecules to control photoreactions, there have been very few studies of the coordination environment dynamics of ligands molecules on photoexcitation state.

In this study, we synthesized perylenebisimide-Zinc sulfide nanocrystals (PBI-ZnS, PBI is on Figure 1b inset) and demonstrate that the coordination bonds between ligand molecules and NCs by carboxyl groups are displaced quasi-reversibly by light irradiation (Figure 1a).

The optical properties of PBI-ZnS were analyzed by wide time range spectroscopy (femtosecond to several seconds) and density functional theory (DFT) calculations. Time-resolved transient absorption, and Raman spectroscopy and (DFT) calculations show that the photoinduced ligand displacement is driven by ultrafast hole transfer from PBI to ZnS NCs. Interestingly, the PBI is displaced from NCs surface as a radical anion after light irradiation, and the PBI radical anion survives over the second timescale (Figure 1b). Moreover, DFT calculation suggests that PBI radical anion displace involved the neighbor Zn atom. The long-lived charge-separated state can be generated repeatedly without any degradations.

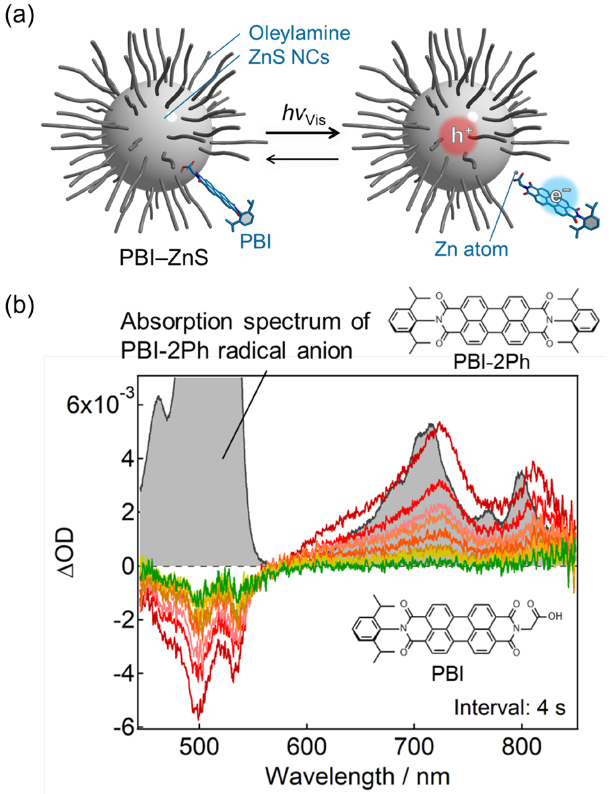

Figure 1. (a) Molecular structure of PBI and (b) schematic of the quasi-reversible photoinduced displacement of PBI coordinated to the surface of ZnS NCs.