Excited-State Dynamics of 1-Pyrenecarboxylic Acid-Coordinated ZnS Nanocrystals

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Organic-inorganic hybrid nanomaterials have attracted much attention in recent years for their applications in photocatalysis and photon upconversion. While efficient electron transfer and long-lived charge-separated states often play important roles in such hybrid nanomaterials, their fundamental understanding is still insufficient because of the lack of the variety of these hybrid nanomaterials. In this study, we report on the synthesis of 1-pyrenecarboxylic-acid-coordinated zinc sulfide (ZnS) NCs (PCA-ZnS) as a model system and investigated their optical properties (Fig. 1a).

PCA-ZnS was prepared simply by mixing PCA and ZnS NCs in chloroform. The absorption spectra of PCA-ZnS in chloroform at low concentrations of PCA and ZnS NCs (9.1×10^{-7} and 4.2×10^{-8} M for PCA and ZnS NCs, respectively) are almost identical to the superposition of the absorption spectra of PCA and ZnS NCs, suggesting that there is no electronic interaction, i.e., PCA is not coordinated to the surface of ZnS NCs under the condition. On the other hand, the absorption spectrum of PCA-ZnS with the concentration of (2.1×10^{-4} and 9.6×10^{-6} M for PCA and ZnS NCs, respectively) is different from those of the superposition of PCA and ZnS NCs, suggesting that PCA is coordinated to the surface of ZnS NCs. (Fig. 1b) The weak coordination of PCA may be due to the direct substitution of the carboxy group on pyrene for PCA.

To reveal the excited-state dynamics of PCA-ZnS, transient absorption spectra were measured using a 360-nm femtosecond pulse as the excitation light. In PCA-ZnS in chloroform, additional small transient absorption band in addition to the excited-state absorption of the S1 at 510 nm was observed at 450 nm. Considering the potentials of PCA and ZnS NCs, selective excitation of pyrene at 360 nm is expected to induce electron transfer from the lowest unoccupied molecular orbital (LUMO) of pyrene to the conduction band (CB) of ZnS. Since the cation radical of pyrene is reported to be observed around 450 nm, this result suggests that a fast electron transfer has occurred in PCA-ZnS.

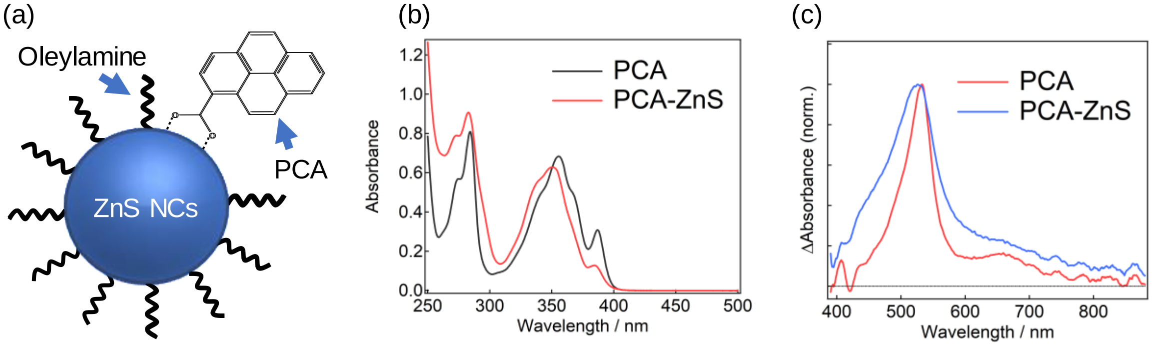

Fig. 1 (a) Schematic of PCA-ZnS and (b) The absorption spectra of PCA and PCA-ZnS (PCA/ZnS = 22) in chloroform; 2.1×10^{-4} M PCA in the 1-mm cuvette. (c) The transient absorption spectra at 30 ps of PCA and PCA-ZnS exited with a 360 nm femtosecond laser pulse (20 nJ/pulse).