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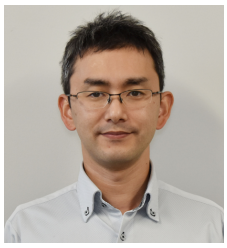
The 92nd KPSI Seminar, QST
A119, KPSI-QST and Web

Exploring Novel Photofunctions of Organic-Inorganic Nanohybrids



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Inorganic nanomaterials, such as semiconductor nanocrystals, have high absorption coefficients and high dielectric constants that facilitates charge separation, and thus, have been applied to various optoelectronic materials. The interfaces of nanomaterials are generally covered with organic ligands such as fatty acids. However, by replacing these ligands with functional organic molecules, it is possible to develop further advanced photofunctional materials such as solar cells, photocatalysis, and hydrogen generation. We have been developing organic-inorganic nanohybrids by combining semiconductor nanocrystals and functional organic molecules and investigating their optical properties by time-resolved spectroscopy. In this presentation, we will introduce two topics that we have recently discovered.

1. Efficient use of higher excited states of organic-inorganic nanohybrids

Stepwise two-photon absorption (2PA) processes are becoming an important technique because it can achieve high reductive photochemical reactions with visible and near infrared light and intensity-gated high spatiotemporal selectivity with much lower power thresholds [1]. However, excited states generated by stepwise 2PA are so short-lived that the efficiency for the stepwise 2PA induced photochemical reactions is usually quite low, which limits the versatility for this technique. Here, we demonstrated that the electron of the higher excited state can be efficiently extracted in a nanohybrid of organic molecules and wide bandgap semiconductor nanocrystals (NCs) using perylene bisimide (PBI)-coordinated CdS NCs as a model compound [2].

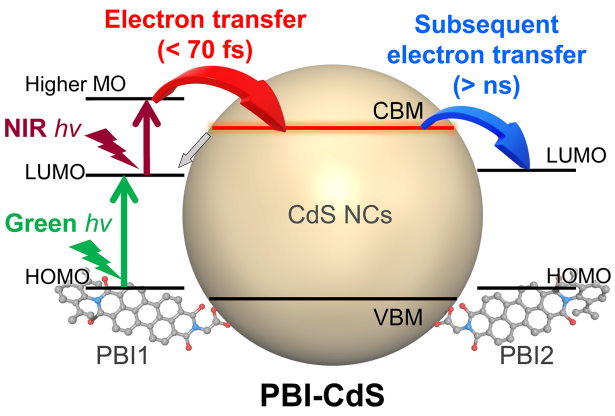

Figure 1. Schematic energy diagram of stepwise two-photon-induced electron injection of PBI-CdS.

2. Quasi-reversible photoelimination of organic ligands on semiconductor nanocrystals

Conventionally, it has been assumed that the organic molecules are tightly bound to the surface of NCs. However, recent studies revealed that the bound organic ligands can be dissociated to free ligands and the bound and free states exist as the thermal equilibrium in the ground state. Surprisingly, although a number of functional organic-inorganic nanohybrids have been reported so far, there are few reports on dynamical behaviors of organic ligands induced by light irradiation. In this study, we carefully investigated the excited-state dynamics of perylene bisimide (PBI)-coordinated colloidal ZnS NCs (PBI-ZnS) and revealed that the coordinated PBIs are released after photoinduced electron transfer and the free radical anion of PBI exists stably over second timescales.

References

[1] Y. Kobayashi, J. Abe, *Chem. Soc. Rev.*, *51*, 2397-2415, (2022).

[2] D. Yoshioka, D. Fukuda, Y. Kobayashi, *Nanoscale*, *13*, 1823-1831, (2021).