Near-infrared emission in Ag_{29} nanoclusters induced by the modification with metal complexes

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Metal nanoclusters (NCs) composed of defined numbers of metal atom and ligand show structure-dependent optical properties. The property of NCs can be modulated by metal atom doping and ligand engineering. The ionic nature of NCs also affects their optical properties especially in photoluminescence (PL) property through controlling the ionic interaction with counter ions. We previously reported the accumulation of Na^+ counter ions in a local surface site of $[Ag_{29}(BDT)_{12}(TPP)_4]^{3-}$ NC (BDT: 1,3-benzenedithiol; TPP: triphenylphosphine) resulted in the induction of intense NIR PL at 770 nm.[1] Although the use of Au-doped Au_xAg_{29-x} NCs further increased the PLQY over 45% at 800 nm in the solution state, the conjugation of NCs with Na^+ counter ions required the condition of photoirradiation which could lead to a simultaneous degradation of chemically less stable silver-based NCs.

In the present study, we found that transition metal complexes such as silver(I) complex could bound to the peripheral region of Ag_{29} NCs, leading to the strong NIR PL without light irradiation. The binding of silver(I) complexes to Ag_{29} NCs is confirmed by the single-crystal X-ray diffraction measurement, which is further supported by the ESI-MS and NMR measurements. The change of excited-state dynamics triggered by the binding of silver(I) complexes is discussed based on the results of transient absorption study as well as temperature-dependent PL study. The modification of Ag_{29} NCs with silver(I) complexes is considered to give rise to a triplet excited-state responsible for the intense NIR PL (Fig. 1).

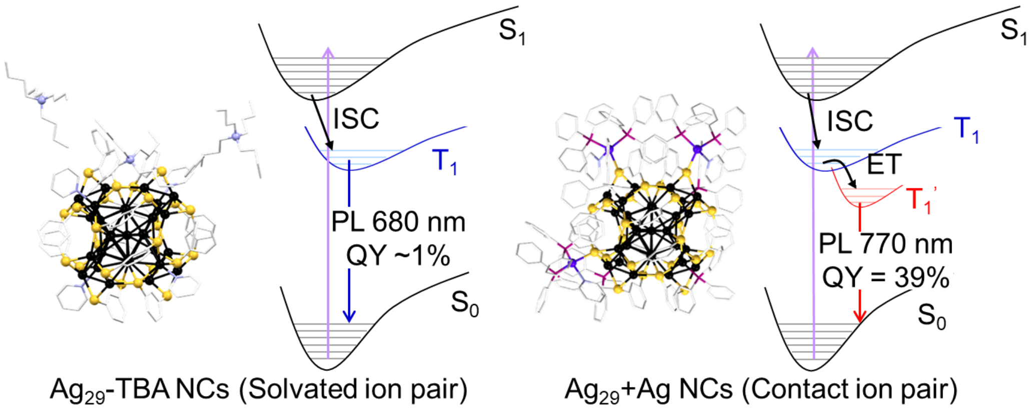

Fig. 1 Schematic diagrams of excited state relaxation for Ag_{29} NCs in the absence and presence of Ag(I) complexes.

1) W. Ishii et al., *Chem*. *Commun*. **2021**, *57*, 6483.