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Precise Control of Molecular Arrangements via Multiple Electrostatic Interactions Towards Manipulation of Their Photochemical Properties

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Multivalent interaction is the key in many biological systems. One of the most important (photo-)chemical reactions, photosynthesis, is constructed by regularly aligned molecules by multivalent interactions between proteins and dyes. A grand challenge of modern chemistry therefore includes the construction of supramolecular assemblies and control of their functions for mimicking nature and beyond. While most of synthetic systems depend on covalent, coordination and hydrogen bonds, my approach focuses on multiple electrostatic interactions. Clay mineral nanosheets have atomically flat surfaces with anionic charges, and multi-cationic molecules can form stable complexes by multiple electrostatic interactions. I here show three main achievements from my recent works on manipulation of precise molecular arrangements and photochemical properties.

[Manipulation of photochemical properties of molecules and new emission enhancement phenomenon][1)]

When some molecules strongly adsorb on nanosheets, molecular structures change compared to that in a solution owing to the atomically flat surface. The strong multiple electrostatic interaction between molecules and nanosheets enables the suppression of non-radiative deactivation pathways by a restriction of molecular motions and vibrations, resulting in strong emission enhancement. This new mechanism was universally applicable for wide variety of molecular structures, and named a “Surface-Fixation Induced Emission”.

[Efficient photochemical reactions and artificial photosynthesis model][2)]

Since host–guest electrostatic interaction is the key of structural formation, photochemical reactions between two or more kinds of molecules are easily designable. By controlling the distances, densities, and distributions of molecules, 100% quantum efficiency of excited energy transfer reaction was realized on inorganic surfaces for the first time while it has been hard in most of systems reported so far. Multiple electrostatic interactions enable to suppress unfavorable phenomena such as aggregation, segregation, and fluorescence quenching of molecules, that strongly decrease efficiencies of photochemical processes. These findings allowed to design multi-step systems such as artificial light harvesting system utilizing all visible-light, combined with subsequent electron transfer reaction for mimicking photosynthetic complexes. This strategy was further expanded for cationic organic cavitands capsulating neutral aromatic molecules, and noble metal nanoparticles/clusters.

[Molecular-scale understanding of multiple electrostatic interaction][3)]

To aim the molecular-scale understanding of multiple electrostatic interaction, I recently conducted a scanning transmission electron microscopy (STEM). 3D-tomogram of cationized fluorescent nanoparticles on anionic nanosheet surfaces allowed a first direct localization of stable 3D coordinates of individual nanoparticles on both surface-sides of nanosheet. Also, I have recently succeeded in the first atomic-scale imaging of free-standing monolayer clay nanosheets and its molecular complexes by aberration-corrected STEM technique. I am now further promoting this technique for the direct imaging of molecular and supramolecular structures for understanding their unique functions under multiple electrostatic interactions.

Key references

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