Artificial Light-Harvesting System by
Supramolecular Host-Guest Assemblies

Yohei Ishida
Department of Applied Chemistry
Tokyo Metropolitan University

It is well-recognized that human beings will face a serious energy crisis due to a shortage of fossil fuels within several decades. Today, much research is focused on developing alternative and renewable energy sources. Among various candidates for solving this problem, artificial photosynthesis utilizing the sunlight is one of the most probable. Artificial photosynthesis can be defined as a light-driven system that transports electron from a water molecule to an appropriate electron-accepting system and consist of a photo-induced substrate conversion reaction system and a light-harvesting system.[1] One of the bottlenecks for a realization of artificial photosynthesis including multi-electron conversion reaction, such as \( \text{O}_2 \) evolution from water splitting via four-electron conversion[2], is to overcome a limitation of low photon-flux density of sunlight. Because the lifetimes of oxidized or reduced species of catalyst are typically short such as microsecond to millisecond time scales and they will decompose or be deactivated before accepting or donating the next electron, the objective multi-electron conversion reaction should be impossible under the normal sunlight condition and thus a light-harvesting system is essential.

In recent years, excellent works have revealed that the light-harvesting system is composed of the amazingly beautiful alignment of chlorophyll molecules, and the regulated alignment realizes the efficient and selective light-harvesting energy transfer processes in purple bacteria (Figure 1).[3] According to this finding, the researches for artificial light-harvesting system have been focused on constructing a regularly arranged assembly of functional dyes.

Figure 1. The structure of LH2 in \( \text{Rps. acidophyla} \) bacteria.
While most approaches for manipulating the structure of dye assembly depend on an interaction between molecules such as in supramolecular molecular architectures\cite{4,5} or covalently linked dendrimer\cite{6,7}, my approach is using clay nanosheets as a host material to build the dye assembly by using a host (nanosheet) – guest (molecule) interaction.

One of clay nanosheets\cite{8}, saponite is an attractive material that is characterized by (1) nanostructured flat sheets, (2) negatively charged surfaces, (3) exfoliation or stack ability of individual nanosheets in water, and (4) optical transparency in the visible region in the exfoliated state when the particle size is small (ca. <200 nm). On these anionic charged surfaces, cationic dyes can be aligned at high-density without aggregation\cite{9}, while typically organic molecules tend to be aggregated on solid surfaces due to the relatively strong guest–guest interaction\cite{8}. Such non-aggregated alignment is resulting from the distance matching due to guest–host Coulombic interaction between positively charged dye molecules and negatively charged clay surface. We termed this effect a “size-matching effect”.

![Figure 2. Schematic representation of clay/dye supramolecular complex.](image)

In my thesis work, I proposed a novel artificial light-harvesting model using this clay/dye supramolecular complex. Since the complexation of clay/dye complex depends on the host–guest interaction, two (or more) kinds of dye can co-exist on the surface easily. Almost 100% efficiency of light-harvesting energy transfer reaction was achieved between two kinds of porphyrin dyes on clay nanosheets. Steady-state fluorescence measurements revealed that the fluorescence of donor was completely suppressed and that of acceptor increased by the energy transfer reaction.
Additionally, the time-resolved measurements and the lifetime profiles also showed the almost 100% energy transfer (Figure 3b and 3c).

Moreover, I revealed the mechanisms to realize 100% energy transfer reaction on solid surfaces.\[^{11,14-16}\] There are three factors lowering the efficiency of photochemical reaction on solid surfaces, i.e. (i) aggregation (interaction of the transition dipole moments between two molecules that drastically decreases the excited lifetimes), (ii) segregation (separated adsorption structure of two kinds of molecules that decreases adjacent probability on 2D surface) and (iii) self-fluorescence quenching (electron transfers and/or thermal deactivation process induced by the collision of molecules on the surface that quenches the excited lifetimes). By systematic experiments, it was found that these three “unfavorable” phenomena are induced by strong guest–guest interactions and thus can be suppressed by relatively strong host–guest interactions. Resulted from the effective suppression of (i) ~ (iii), efficient energy transfer in several dye’s combinations were achieved including porphyrin, pyrene, xanthene and porphyrazine derivatives.\[^{10,13,18,20,21}\]

Figure 3. Steady state fluorescence spectra (a), time-resolved fluorescence spectra (b) and fluorescence decay profiles (c) for porphyrin/clay complex.
An efficient utilization of wide wavelength region of the sunlight has been one of the topics for a realization of efficient energy conversion systems of sunlight. Owing to the great advantage of clay/dye system, we can easily add or exchange the dyes that have appropriate cation charges in their molecular structures. The combination of several kinds of dyes such as shown in Figure 4, which have different absorption regions, will enable to harvest the all visible region of sunlight. As described above each energy transfer steps have been analyzed and are highly efficient, the stepwise and efficient visible-light-harvesting is thus promising. This is that we are now investigating.

![Figure 4](image)

Figure 4. Artificial light-harvesting system by clay/dye supramolecular complex that can absorb the all visible-region of the sunlight.

In conclusion, I proposed a novel methodology to manipulate the assemble structure of functional dyes by using clay nanosheets as a host material toward a realization of an efficient artificial light-harvesting system. In this host-guest assembly almost 100% efficiency of light-harvesting energy transfer reaction could take place. Moreover, the mechanisms for an efficient energy transfer reaction on solid surfaces were revealed. I believe that these demonstrations will contribute in constructing efficient photochemical reaction systems in supramolecular host-guest assemblies, toward a realization of artificial photosynthesis.

References: