What are new traits of Si-rhodamine self-assembly in the excited state?

‘In unity there is strength!’ This is also true in the molecular world. Nowadays, “self-assembly”, composed of a large number of one or multiple kinds of small molecules, has attracted considerable attention. That is because special traits which were not available in an individual molecule can be brought out only if molecules are assembled each other. For example, chlorophylls, a green dye molecule in leaves, exist as a ring-shaped assembly in nature. Through multiple self-assemblies of chlorophylls, solar energy can be efficiently absorbed, rapidly transferred, and eventually converted as energy for plant. This kind of molecular assembly is so-called “light-harvesting system” in photosynthesis. Learning from nature, one can use the main principle of light-harvesting system using artificial components instead of chlorophylls. In order to take advantage of full spectrum of solar energy, modifying the individual constituents can lead to widen the absorption range up to near-infrared region.

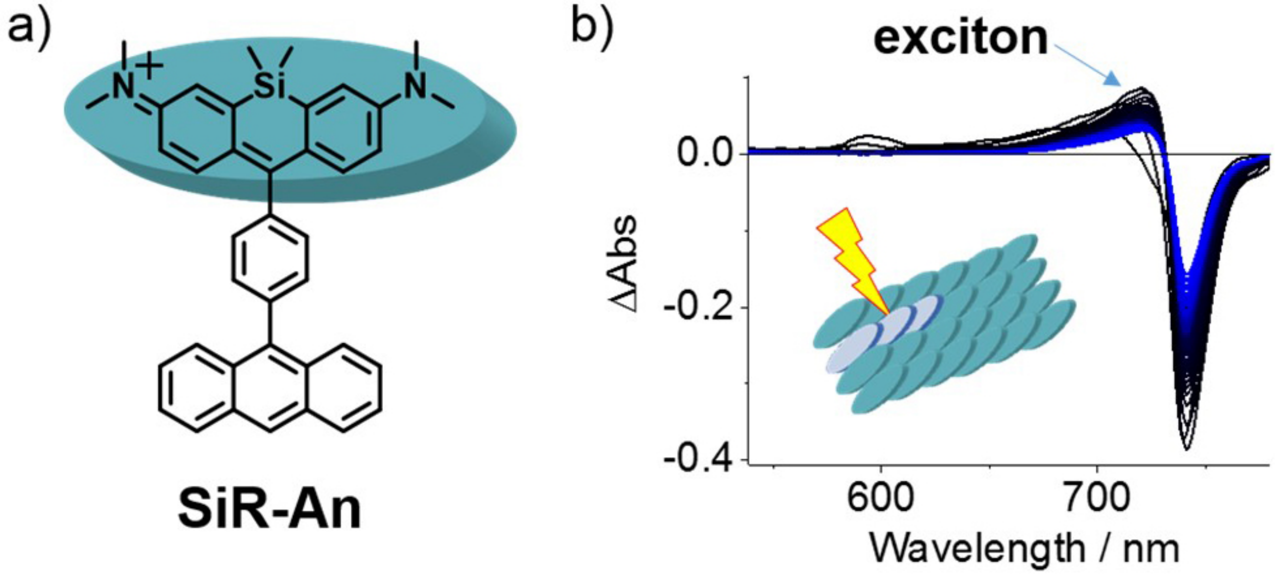

Fig. 1. (a) Chemical structure of SiR-An. (b) Transient absorption spectra of SiR-An J-aggregate in the aqueous solution with [NaCl] = 20 mM. Spectra were taken at 0.2 to 80 ps after a laser pulse (black to blue).

Previously, we have reported pink-to-blue color change of tetramethylrhodamine aggregates by the addition of halide ion. When the constituent is replaced to silicon-containing rhodamine (Si-rhodamine), which is a far-red fluorescent rhodamine dye, similar aggregation behavior was observed. In the presence of 20 mM chloride anion, (9-anthryl)phenylene-substituted Si-rhodamine (SiR-An) forms a slipped-stacked assembly in water induced by cooperative intermolecular interactions between Si-rhodamine and anthracene parts (Fig. 1a). As a result, further red-shift in absorption is triggered by aggregation from far-red to near-infrared region. Thus, we consider that Si-rhodamine can be used for a building block of ultrafast energy transfer materials, such as light-harvesting system.

Provided that more than two molecules make an assembly which is largely slipped each other, this type of aggregates is named J-aggregate and characterized by red-shifted absorption with enhanced fluorescence emission. Although experimental results of optical measurements and X-ray crystallographic analysis support that the slipped-stacking of SiR-An satisfies the criteria of J-aggregate, SiR-An J-aggregate is found to be non-emissive. To clarify this discrepancy and evaluate SiR-An J-aggregate as new energy transfer materials, we have investigated the properties of SiR-An aggregates in the excited state using various time-resolved spectroscopic techniques.

As shown in Fig. 1b, excitons in SiR-An J-aggregates are successfully monitored upon the selective photoexcitation of aggregation. Different from a monomer in the excited state, ‘exciton’ indicates a high energy state generated in the molecular assembly which can diffuse and collide each other (= exciton-exciton annihilation, EEA). The EEA process was indeed observed in SiR-An J-aggregates. We assume that substantial EEA occurring in a short coherent J-aggregate (3~4 monomers) that composes a large J-aggregate (a few hundred nm) is the reason for reduced fluorescence of SiR-An J-aggregate (the inserted illustration of Fig. 1b).

Moreover, excitons in SiR-An exhibit a strong dependency on the intensity power, implying the presence of two-exciton state (cf. the secondary-formed exciton with higher energy as compared to the initially formed exciton after photoexcitation). It is interesting that the spectral shape of the exciton and the presence of two-exciton state in SiR-An J-aggregate resemble the characteristics of porphyrin and cyanine self-assemblies, widely-used building blocks in the energy transport system. In addition, a larger population of exciton remained as the excitation power increases. It means that SiR-An J-aggregate is beneficial especially under the strong excitation condition. Concerning the results of transient absorption measurements and high molecular ? of SiR-An J-aggregate in the near-infrared region (> 10^5 M^{-1} cm^{-1} at around 740 nm), a self-assembly of Si-rhodamine holds the potential in the developments of versatile near-infrared-absorbing materials and a component of artificial photosynthesis system in future.

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