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Active species transfer-type artificial light harvesting system in the nanosheet – Dye complexes: Utilization of longer wavelength region of sunlight

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ABSTRACT

A novel light harvesting system that captures long-wavelength light of sunlight by the use of hole transfer was newly investigated. Ga phthalocyanine(Ga^{III}TMAPc^{4+}(D)) and Ru porphyrin(Ru^{II}DMPyMP^{2+}(A)) co-adsorbed reaction system on the synthetic nanosheet was examined as an artificial light harvesting system. By irradiating 660 nm light, where Ga^{III}TMAPc^{4+}(D) absorbs, to the system under a presence of $PtCl_6^{2-}$ as an electron acceptor, cation radical of Ru^{II}DMPyMP^{2+}(A) was produced despite that Ru porphyrin adsorbs only 413 and 533 nm light. The efficient hole transfer reaction from Ga^{III}TMAPc^{4+}(D)$^{+\cdot}$, that is generated from its excited state, to Ru^{II}DMPyMP^{2+}(A) takes place on the nanosheet.

Introduction

In recent years, artificial photosynthesis[1–7] has attracted much attention as a source of sustainable new energy. For all systems aiming at solar energy conversion, the initial step is light absorption and thus the sunlight absorption efficiency affects the total energy conversion efficiency. Therefore, artificial light harvesting systems (LHSs)[8,9] that collect sunlight effectively, are essential to construct efficient solar energy conversion system. So far, LHSs using Förster or Dexter type energy transfer has been reported. Organic-inorganic hybrids have been received attention because of their unique photochemical properties.[10,11] We have succeeded in constructing efficient LHSs by using anionic nanosheet – cationic dyes complexes where dye assembly structure is well regulated on the nanosheet surface.[12–17] The precise matching of the intramolecular cationic points distance and the inter anionic points one on the clay surface (Size-matching effect) is a key principle to realize such unique assembly structure.[18,19] However, in such systems using energy transfer, only shorter wavelength light of sensitizer is available in principle.

In order to utilize long wavelength region of sun-light, up-conversion[20] and plasmonics[21] have been studied. Although they are attractive technique, they still have difficulties to use because of the low efficiency. In this paper, a light harvesting system that can collect longer wavelength light was investigated by using active species (hole in this case) transfer mechanism in nanosheet – dye complexes. Hydroxo [tetrakis (*N*,*N*,*N*-trimethylanilium) phthalocyaninato]gallium (III) tetra *p*-tosylate (Ga^{III}TMAPc^{4+}(D), Fig. 1(a)) and 5,10-di [2,6-dimethyl-4-(*N*-methylpyridinium-3-yl) phenyl]-15,20-di (2,4,6-trimethylphenyl)porphyrinato ruthenium (II) carbonyl dichloride (Ru^{II}DMPyMP^{2+}(A), Fig. 1(b)) were used as light harvesting hole donor and active species acceptor, respectively. As a result, cation radical of Ru^{II}DMPyMP^{2+}(A) that acts as a photo-catalyst in the photochemical material conversion reactions, was produced by the longer wavelength light irradiation in this active species transfer type LHS. The previously reported reaction mechanism[22,23] for the photochemical material conversion reactions where Ru^{II}DMPyMP^{2+}(A) works as a photo-catalyst[24], is shown in Fig. S1. Although the intrinsic role of Ga^{III}TMAPc^{4+}(D) in this system is photosensitizer, Ga^{III}TMAPc^{4+}(D) works as light harvesting dye in terms of results. This active species transfer is a kind of intermolecular charge shift reaction. Charge shift has been well

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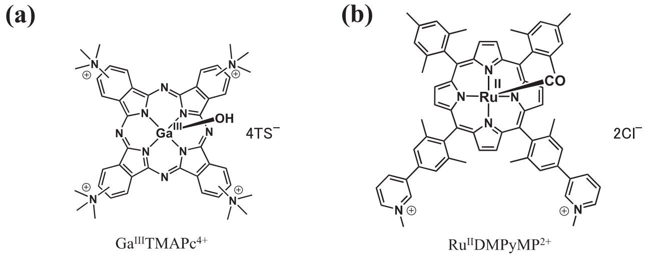
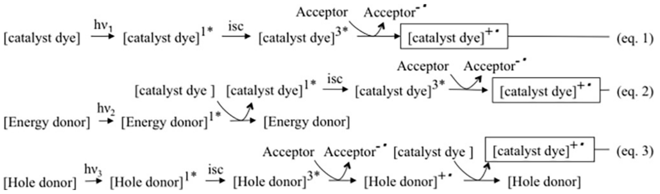


Fig. 1. Molecular structures of (a) Hydroxo[*tetrakis*(*N,N,N-trimethylanilium*) *phthalocyaninato*]gallium(III) tetra *p*-tosylate (Ga^{III}TMAPc^{4+}(D)) and (b) 5,10-di [2,6-dimethyl-4-(*N*-methylpyridinium-3-yl)phenyl]- 15,20-di(2,4,6-trimethylphenyl) porphyrinato ruthenium(II) carbonyl dichloride (Ru^{II}DMPyMP^{2+}(A)).

studied in covalently linked molecular system from a viewpoint of controlling charge separation.[25,26] In this research, such charge shift is realized in supramolecular system including many dye molecules on the nanosheet and is applied to the artificial LHS.

The schemes for cation radical formation 1) without LHS, 2) with Förster type LHS and 3) with active species transfer type LHS are shown in eq. 1, 2 and 3, respectively. By the use of active species transfer process, both photons absorbed by catalyst dye (Ru^{II}DMPyMP^{2+}(A)) and hole donor dye (Ga^{III}TMAPc^{4+}(D)) can be used in the reaction system. While case 2 can utilize only shorter wavelength light compared to the absorption of catalyst dye, case 3 can utilize longer wavelength light in principle. The energy diagram for case 3 (Hole transfer) that indicates how a longer wavelength light can be used, is shown in Fig. S2.



Experimental section

Materials

Ga^{III}TMAPc^{4+}(D) and Ru^{II}DMPyMP^{2+}(A) were synthesized according to the previous reports.[24,27] The absorption spectra of Ga^{III}TMAPc^{4+}(D), Ru^{II}DMPyMP^{2+}(A) and solar spectrum are shown in Fig. 2. Because photon number of sunlight[28] at longer wavelength region is large, the generation frequency of Ru^{II}DMPyMP^{2+}(A)$^{+\cdot}$ could be effectively enhanced by the active species transfer from Ga^{III}TMAPc^{4+}(D). It should be noted that even ε of Ru^{II}DMPyMP^{2+}'s Q-band is larger than $10^4\ \mathrm{M^{-1}\ cm^{-1}}$. Synthetic clay minerals, Sumecton SA (SSA)[29], is chosen as a platform to construct supramolecular assembly of Ga^{III}TMAPc^{4+}(D) and Ru^{II}DMPyMP^{2+}(A). SSA was received from Kunimine Industries Co. Ltd. From the stoichiometric formula of SSA (Fig. S3), the average negative charge distance on the SSA surface is known to be 1.2 nm.[18]

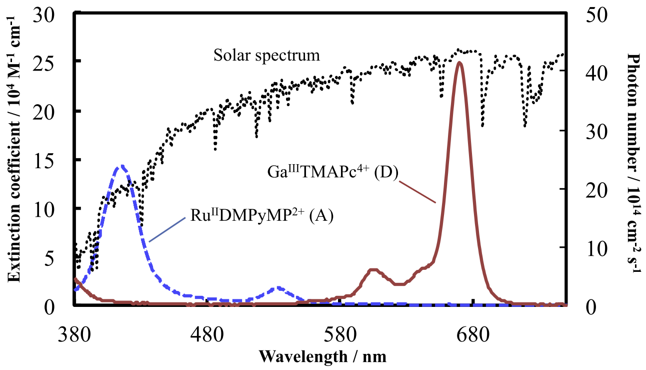


Fig. 2. UV–visible absorption spectra of Ga^{III}TMAPc^{4+}(D) and Ru^{II}DMPyMP^{2+}(A) in water and photon number of sunlight.

The reaction mixture of (Ga^{III}TMAPc^{4+}(D) + Ru^{II}DMPyMP^{2+}(A))-clay complex was prepared in a quartz cell (1.0 × 1.0 × 4.0 cm) with branched tubule and septum cap. The solvent composition is water-acetonitrile (30/70(v/v)). Oxygen in solution was removed by argon bubbling for 30 min under the dark condition. Concentrations of Ga^{III}TMAPc^{4+}(D), Ru^{II}DMPyMP^{2+}(A), SSA and $\mathrm{K_2[Pt^{IV}Cl_6]}$ as an electron acceptor were 1.5×10^{-6}, 4.5×10^{-6}, 1.2×10^{-4} equiv. $\mathrm{L^{-1}}$ and 5.0×10^{-4} M, respectively. D/A ratio was set to 1/3 which is the ratio where the acceptor surrounds the donor. The total loading level of dyes was 12.5% (5% for Ga^{III}TMAPc^{4+} (D) and 7.5% for Ru^{II}DMPyMP^{2+}(A)) versus cation exchange capacity (CEC) of the clay. It has been already reported that both Ga^{III}TMAPc^{4+} (D) and Ru^{II}DMPyMP^{2+}(A) adsorb on the clay surface without any aggregation, judging from their absorption spectral behavior.[24,27] Thus, they keep their intrinsic excited lifetimes and photochemical activities on the SSA surface. Expected images of the supramolecular assembly structure are shown in Fig. S4. Monochromatic light (λ_{max} = 660 or 420 nm, LED light source) was irradiated to the stirred sample solutions through 4 cm light path. All photochemical reactions were monitored with UV–visible spectrometer through 1.0 cm light path. UV–visible absorption spectra were obtained on Shimadzu UV-3150 spectrophotometer.

Results and discussions

The photochemical reactions were carried out for the samples where the photo-catalyst system was (a) Ga^{III}TMAPc^{4+}, (b) Ru^{II}DMPyMP^{2+}, (c) Ga^{III}TMAPc^{4+} and Ru^{II}DMPyMP^{2+}, (d) Ga^{III}TMAPc^{4+}-clay complex, (e) Ru^{II}DMPyMP^{2+}-clay complex and (f) (Ga^{III}TMAPc^{4+} + Ru^{II}DMPyMP^{2+})-clay complex, respectively. Samples (a) - (c) are for control experiment without clay, that is, no formation of any supramolecular assembly in the reaction system. The photochemical reactions without clay were monitored by absorption spectral change (Fig. 3, a-c). In the case of reaction system (a), Q-band at 670 nm of Ga^{III}TMAPc^{4+}(D) decreased and disappeared by 25 min irradiation. This spectral change suggests that the photo-induced electron transfer proceeded from exited Ga^{III}TMAPc^{4+}(D) to $\mathrm{K_2[Pt^{IV}Cl_6]}$, and produced Ga^{III}TMAPc^{4+}(D)$^{+\cdot}$ decomposed. In the case of reaction system (b), despite light irradiation at 660 nm for 40 min, there was no change in absorption spectra of Ru^{II}DMPyMP^{2+}(A). On the other hand, by irradiation at 420 nm, Ru^{II}DMPyMP^{2+}(A)$^{+\cdot}$ was generated in 1 min (Fig. S5). These results indicate that Ru^{II}DMPyMP^{2+}(A) cannot absorb 660 nm light and thus is inactive for 660 nm light irradiation. In the case of reaction system (c) where Ga^{III}TMAPc^{4+}(D) and Ru^{II}DMPyMP^{2+}(A) coexist in homogeneous solution, the observed spectral change was similar to that for reaction system (a). This result indicates that produced Ga^{III}TMAPc^{4+}(D)$^{+\cdot}$ does not react with Ru^{II}DMPyMP^{2+}(A) within its lifetime. Like this, the hole transfer reaction from Ga^{III}TMAPc^{4+}(D)$^{+\cdot}$ to Ru^{II}DMPyMP^{2+}(A) did not proceed in the homogeneous system.

In a similar way, the photochemical reactions under the presence of clay were monitored by absorption spectral change (Fig. 3, d-f). In the case of reaction system (d), Q-band at 673 nm of Ga^{III}TMAPc^{4+} (D) decreased and disappeared by 40 min irradiation. In the case