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LETTER

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Photoinduced Electron Transfer between the Anionic Porphyrins and Viologens in Titania Nanosheets and Monodisperse Mesoporous Silica Hybrid Films

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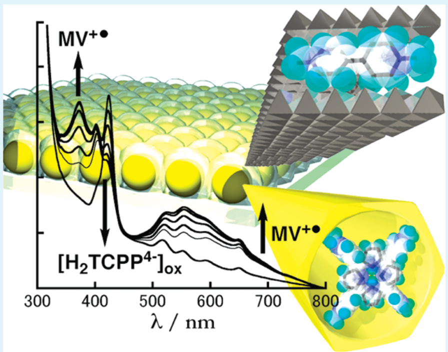
Supporting Information

ABSTRACT: Photoinduced electron transfer between an anionic porphyrin derivative (*tetrakis*(*p*-carboxyphenyl)porphyrin; H_2TCPP^{4-}) and an electron accepting methyl viologen (MV^{2+}) was investigated in two different nanoscale configurations, i.e., layered titania nanosheet (TNS) photocatalysts and ammonium-functionalized monodisperse mesoporous silica (AMMSS) particles. Cationic MV^{2+} intercalated within the TNS interlayers while anionic H_2TCPP^{4-} was accommodated within AMMSS nanocavities to form (MV^{2+}-TNS)/(H_2TCPP^{4-}-AMMSS) hybrid films. Upon irradiation with UV light and excitation of the TNS in the (MV^{2+}-TNS)/(H_2TCPP^{4-}-AMMSS) hybrid films, the consumption of H_2TCPP^{4-} and the formation of a one-electron reduced MV^{2+} ($MV^{+\cdot}$) were simultaneously observed. No consumption of H_2TCPP^{4-} was observed when an electrically insulating poly(styrene) (PS) was also introduced at the interface. These results suggest that photoinduced electron transfer occurred at the interface between the TNS and the AMMSS.



KEYWORDS: mesoporous silica, titania nanosheet, electron transfer, charge separation, inorganic nanospace

The hybridization of nanostructured inorganic hosts with organic photofunctional molecules has been widely and extensively studied.[1−14] The photofunctional organic functional molecules hybridized with nanosized inorganic hosts have been observed to have unique redox properties in photochemical and photophysical processes.[1,15−26] In our previous studies,[27−31] consecutively stacked hybrid thin films of mesoporous silica films (*cubic*-MPS)[32−34] or monodisperse mesoporous silica spheres (MMSS)[35−39] and layered titania nanosheets (TNS)[2,9,40−46] were shown to exhibit unique photoinduced electron transfer between the cationic porphyrins ($MTMPyP^{4+}$; M = H_2, Zn, and Co) and methyl viologen (MV^{2+}), which were separated and were present in different inorganic hosts.[27,28] Upon UV-light illumination of the photocatalytic TNS,[43,47] the (MV^{2+}-TNS)/(H_2TMPyP^{4+}-MMSS), MV^{2+} radical ions ($MV^{+\bullet}$) were formed at the expense of the oxidative consumption of H_2TMPyP^{4+}, resulting in electron transfer through the interface between the TNS and mesoporous silica, thus leading to charge separation at the interface between the two nanostructured inorganic hosts.[27,28,48] The charge separated states obtained in these materials were highly stabilized and lasted for several hours even in the ambient atmosphere.[49]

However, this photoinduced electron transfer through the interface of the TNS and the *cubic*-MPS films or the MMSS microsized particles was only observed for the cationic $MTMPyP^{4+}$ adsorbed in the mesoporous silica nanocavities.[28,30] The cationic $MTMPyP^{4+}$ molecules might adsorb on nondecorated mesoporous silica nanocavities through relatively weak interactions such as van der Waals or hydrophobic interactions. Thus, the adsorbed $MTMPyP^{4+}$ molecules dwell in the MMSS nanocavities over a wide range of aggregation degrees as observed by the broadened Soret bands at ∼437 nm (fwhm ∼50 nm).[30] The dye molecules incorporated into the structure should be isolated from one another to avoid the loss in excitation energy resulting from the concentration quenching of the aggregated dye molecules.

Moreover, careful and tedious experimental procedures were performed to separately adsorb the two guest molecules MV^{2+} and $MTMPyP^{4+}$ into the TNS and mesoporous silica host materials, respectively. To achieve separate adsorption and fixation of porphyrins in mesoporous silica nanocavities, the monodisperse mesoporous silica spherical particles possessing the ammonium-functionalized silanol groups (AMMSS)[50,51] were used to fix the anionic organic dye. In this respect, AMMSS

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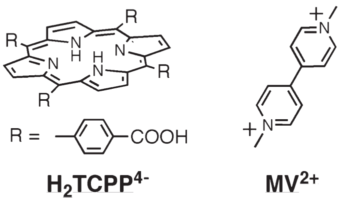
Chart 1



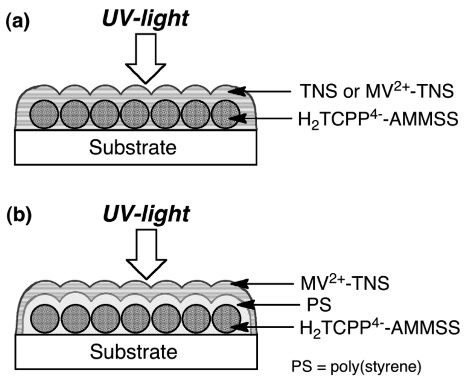


Figure 1. Schematic structures of the (a) (MV^{2+}-TNS)/(H_2TCPP^{4-}-AMMSS) and (b) (MV^{2+}-TNS)/poly(styrene) (PS)/(H_2TCPP^{4-}-AMMSS) hybrid films on a glass substrate.

electrostatically favors the anionic porphyrins (*tetrakis*(*p*-carboxyphenyl)porphyrin; H_2TCPP^{4-}),[11] while anionically charged TNS adsorbs MV^{2+}. The present paper reports on the preparation of the hybrid films adsorbed separately by MV^{2+} and H_2TCPP^{4-} in TNS and cationic AMMSS, respectively, and presents a study of the photoinduced electron transfer in this hybrid film.

The Supporting Information section summarizes the experimental details of the preparation of the hybrid films. The amounts of ammonium groups in AMMSS frameworks were estimated to be 0.49 × 10^{-3} mol/g (nitrogen/AMMSS) on the basis of elemental combustion analysis.[50] The amounts of H_2TCPP^{4-} adsorbed into the AMMSS nanocavities were estimated to be 0.19 × 10^{-3} mol/g (H_2TCPP^{4-}/AMMSS) based on the H_2TCPP^{4-} absorption intensities of the filtrate solutions, which correspond to the electrostatic binding of ca. 40% equivalents of the available ammonium groups of AMMSS. The H_2TCPP^{4-} molecules electrostatically bind with the ammonium groups at the carboxylate anions, ca. 60% of which remained as free anions. On the basis of the number of adsorbed H_2TCPP^{4-} molecules and the surface area of the AMMSS, the average occupied area,[28,52−55] and average distance between H_2TCPP^{4-} molecules in AMMSS nanocavities were estimated to be 10.5 nm^2 and 3.4 nm, respectively. The absorption spectra of the H_2TCPP^{4-}-AMMSS hybrid (without TNS film) on the quartz substrate showed strong light scattering in the visible regions due to colloidal crystal formation,[39] as shown in Figure S1 in the Supporting Information. Moreover, the H_2TCPP^{4-}-AMMSS hybrid showed Soret absorption maxima at 426 nm, red-shifted compared to those in aqueous solutions (414 nm). The Soret band maxima of the porphyrins are known to be sensitive to the polarity of the solvent used, i.e., in a less polar solvent environment, the absorption maximum shifts toward the red.[16,52] The red-shift observed here suggests a decrease in the polarity of the environment surrounding H_2TCPP^{4-} molecules within the AMMSS nanocavities, showing that H_2TCPP^{4-} molecules were adsorbed in the AMMSS nanocavities without any aggregation.[16,52,54,55]

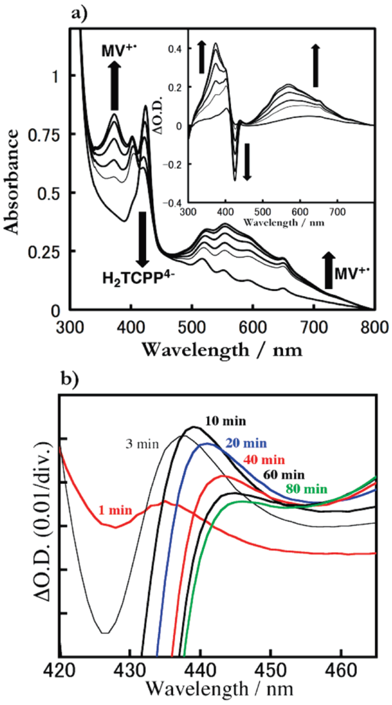


Figure 2. Changes in the absorption spectrum and its differential (inset) upon UV irradiation (0−60 min) of the (MV^{2+}-TNS)/(H_2TCPP^{4-}-AMMSS) hybrid films (a), with the differential spectra in the 420−465 nm region expanded in (b).

Two hybrid film types, AMMSS with H_2TCPP^{4-} (i.e., H_2TCPP^{4-}/AMMSS) and TNS with MV^{2+} (i.e., MV^{2+}/TNS), were successively integrated in this order on a 2 × 2 cm quartz substrate to form transparent integrated hybrid thin films as shown in Figure 1. Intercalation of MV^{2+} into the TNS layer was confirmed by XRD analysis.[28,47]

Figure 2a shows the absorption spectral changes of the (MV^{2+}-TNS)/(H_2TCPP^{4-}-AMMSS) hybrid following irradiation with 300−380 nm UV-light, with the results showing that MV^{2+} molecules were intercalated in TNS interlayers.[28,47] Before UV-light irradiation, the H_2TCPP^{4-} molecules accommodated in the AMMSS cavities of the (MV^{2+}-TNS)/(H_2TCPP^{4-}-AMMSS) hybrid showed a sharp Soret absorption band at 424 nm (fwhm = 15 nm) that was red-shifted compared to those in aqueous solutions (414 nm). This otherwise bathochromic shift implies that the environment for the adsorbed H_2TCPP^{4-} in the AMMSS nanocavities is less polar, thus leading the H_2TCPP^{4-} molecules to be selectively adsorbed on the surface of AMMSS nanocavities without any aggregate formation. Upon UV light irradiation for 60 min, the intensities of typical absorption bands of $MV^{+\cdot}$ (one-electron reduced species of MV^{2+}) steadily increased at around 370 and 500 − 700 nm,[10,11,47,56−60] simultaneously with a decrease in the intensity of the H_2TCPP^{4-} Soret band at 424 nm. In addition, a weak but characteristic absorption band appeared in the 430−450 nm region, similar to the absorption spectra of the one-electron oxidized zinc-tetraphenylporphyrin (ZnTPP)[61] or other porphyrin derivatives.[62−70] These results suggest that the H_2TCPP^{4-} in AMMSS oxidized

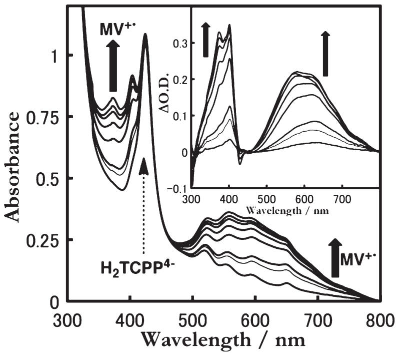


Figure 3. Changes in the absorption spectrum and its differential (inset) upon UV irradiation (0−60 min) of the $(MV^{2+}$-TNS)/PS/(H_2TCPP^{4-}-AMMSS) hybrid films.

upon UV irradiation. This new absorption band gradually decreased with further UV irradiation for 80 min, however, this intermediate is stable even under the aerated condition. Although the detailed mechanisms have yet to be clarified, stabilization of nonpersistent chemical species within the inorganic nanospace have been reported in various systems.[26,47,49,60,71−79] The stability in the present system may be explained by the rapid diffusion of the photogenerated electrons or holes within the TNS layers,[75] the difficult and negligible diffusion of atmospheric oxygen gas or water molecules in the nanospaces,[47,78,79] and/or the charge neutralization of these species within the nanospaces.[26,72] More detailed investigations are now underway on this issue such as the identification of the unknown intermediates and the determination of their stability.

The excited H_2TCPP^{4-} (E_{red}* = −1.14 V vs SCE)[80,81] is sufficiently negative to be reduced by an electron of the conduction band of TNS (− 1.02 V vs SCE).[82] The changes in the absorption spectra were quite similar to the cases of the (MV^{2+}-TNS)/(H_2TMPyP^{4+}-*cubic*-MPS) or (MV^{2+}-TNS)/(H_2TMPyP^{4+}-MMSS) hybrid films, where cationic H_2TMPyP^{4+} is incorporated in *cubic*-MPS or MMSS hybrids.[28,30,49]

The quantum efficiency of H_2TCPP^{4-} consumption (ϕ; see the Supporting Information) within the hybrid films in the presence and absence of the electron acceptor MV^{2+} are 7.0 × 10^{-3} and 4.4 × 10^{-3}, respectively. The (MV^{2+}-TNS)/(H_2TCPP^{4-}-AMMSS) hybrid films showed a ϕ 1.6 times higher than the (TNS)/(H_2TCPP^{4-}-AMMSS) hybrid. That is, intercalated MV^{2+} might enhance the oxidative consumption yields of the H_2TCPP^{4-} molecules in AMMSS nanocavities.[31] These results suggest that the porphyrin molecules in the AMMSS are capable of transferring their electrons through the interface to the MV^{2+} in the TNS nanosheets.

These results strongly suggest that the MV^{2+} ions were reduced to $MV^{+\cdot}$ within the TNS by the electrons in the conduction band (e^{-}_{cb}), and at the same time, the H_2TCPP^{4-} molecules within the AMMSS nanocavities were oxidized by the holes (h^{+}) of the excited TNS. It can reasonably be assumed that the oxidation of H_2TCPP^{4-} molecules in AMMSS can be coupled with the reduction of MV^{2+} molecules in the TNS layers. During this process, e^{-}_{cb} and/or h^{+} can migrate through the TNS/AMMSS interface.[29,34]

To obtain evidence for the simultaneous occurrence of the oxidation of H_2TCPP^{4-} molecules within the AMMSS cavities and the reduction of MV^{2+} within the TNS interlayers, i.e., to determine whether the electron (and/or hole) migration through the TNS/AMMSS interface takes place, poly(styrene) (PS) film was placed between the (MV^{2+}-TNS) and the (H_2TCPP^{4-}-AMMSS) component films as an electrically insulating third layer.[28,30] Figure 1b shows films containing the inserted PS layer, i.e., (MV^{2+}-TNS)/PS/(H_2TCPP^{4-}-AMMSS) films, and Figure 3 shows their absorption spectra following UV irradiation. Note that the H_2TCPP^{4-} molecules exist in a nonaggregated form based on the sharp Soret band (424 nm, fwhm = 15 nm) of the H_2TCPP^{4-} molecules. The intensities of the bands at around 350−400 and 450−700 nm, both of which are assigned to $MV^{+\cdot}$, increased under UV irradiation, but no change was observed in the intensity of the Soret band of H_2TCPP^{4-}, even after 60 min UV irradiation. This is in stark contrast to the case of the (MV^{2+}-TNS)/(H_2TCPP^{4-}-AMMSS) hybrid films, where reduction of MV^{2+} and oxidation of H_2TCPP^{4-} occur simultaneously. These results indicate that the electrically insulating PS film suppresses the electron (and/or hole) migration through the TNS/AMMSS interface.

In summary, consecutively stacked hybridization of ammonium-functionalized monodisperse mesoporous silica spheres (AMMSS) with anionic porphyrins (H_2TCPP^{4-}) on a glass substrate resulted in the formation of transparent thin films, in which nonaggregated H_2TCPP^{4-} adsorbed within the AMMSS nanocavities. UV irradiation of the (TNS)/(H_2TCPP^{4-}-AMMSS) films induced the oxidative consumption of the H_2TCPP^{4-} molecules. These behaviors were quite similar to those of the other TNS/MPS hybrid systems containing a cationic $MTMPyP^{4+}$.[27−30,49] The photochemical behavior in the present organic and inorganic hybrid films can be applied in unique photofunctional devices such as capacitors, triggers for chemical reactions, artificial Z-schemes, or applications for solar energy storage.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Synthesis of the hybrid film, experimental detail, and absorption spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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