Remarkably Stabilized Charge Separations in Inorganic Nanospace

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A remarkably stable and continuous photoinduced charge separation with a half lifetime longer than 2.5 h in ambient atmosphere was observed at the interface of mesoporous silica and titania nanosheets involving porphyrins and viologen in their nanospaces, respectively.

Electron and/or hole transfers in chemical systems have been widely investigated as an important driving force in the initiation of various chemical reactions. In order to facilitate electron/hole transfers in photochemical reactions such as artificial photosynthesis[1] and photocatalytic reactions,[2] various studies have been carried out on the enhancement of photoinduced electron transfers (ET) and the suppression of back electron transfers (BET) for the stabilization of a charge-separated (CS) state. Interestingly, CS states in the photosynthetic reaction centers of natural leaves are known to be stable for ca. 1 s.[3] Generally, the lifetimes of the photogenerated CS states in homogeneous solutions are very short, surviving only from nano to micro seconds and leading to inefficient photochemical processes. However, it has recently been reported that CS states can survive for several minutes to even hours in artificial homogeneous solution systems.[4] Independently, comparative studies of nonpersistent chemical species such as radicals or radical cations in solid states, e.g., polymer matrices[5] or inorganic nanomaterials, have been carried out with those in solution.[6–9] For example, stable CS state between the inorganic layered niobate semiconductors and the viologens in colloidal dispersions have been reported by Nakato et al.[6c,6d]

In our previous work,[6b] we have synthesized consecutively stacked transparent thin films of titania nanosheets (TNS)[8,10] and mesoporous silica (MPS)[11] hybrid films separately accommodated with 1,1′-dimethyl-4,4′-bipyridinium (methyl viologen; MV^{2+}) and tetrakis(1-methylpyridinium-4-yl)porphyrinatometal(4+) ion (MTMPyP; $M = H_2$, Zn, and Co), respectively.[9,12–14] The hybrid films used in this work were also denoted as (MTMPyP–MPS)/(MV^{2+}–TNS).[12,13] It was confirmed that the MV^{2+} molecules confined within the TNS nanolayers[6b] are efficiently one-electron reduced in (MV^{2+}–TNS) while the H_2TMPyP molecules are consumed in the MPS nanocavities of (MTMPyP–MPS).[12] The characteristic changes observed in the absorption spectra for the (H_2TMPyP–MPS)/(MV^{2+}–TNS) hybrid films upon UV light irradiation are shown in Figure S1 of the Supporting Information (SI) section. Upon UV light irradiation, an increase in the intensities of the bands at 375 and ca. 600 nm, attributed to the formation of one-electron-reduced MV^{2+} ($MV^{+\bullet}$), was observed simultaneously with a decrease in the intensity at the 433 nm band due to the consumption of H_2TMPyP.[12a,12b] These results strongly imply that ET took place through the interface of the integrated MPS/TNS films. On the basis of further observation of the generation of photocurrents in this system[14] and the CS suppression of polystyrene-intervened MPS/TNS film (Figure S2),[12b] the following reaction pathways for this photoinduced ET in the (H_2TMPyP–MPS)/(MV^{2+}–TNS) film were proposed:[12–14]

$$\text{TNS} + h\nu\ (\text{UV-light}) \rightarrow e^-{}_{\text{cb}} + h^+ \qquad (1)$$

$$e^-{}_{\text{cb}} + MV^{2+} \rightarrow MV^{+\bullet} \qquad (2)$$

$$h^+ + H_2\text{TMPyP} \rightarrow (H_2\text{TMPyP})_{\text{ox}}\ (\text{bleaching}) \qquad (3)$$

where $e^-{}_{cb}$, h^+, and $(H_2TMPyP)_{ox}$ indicate the electrons in the conduction band, holes in the valence band of TNS, and the oxidation products of H_2TMPyP, in this order, respectively. The consumption of H_2TMPyP in the MPS nanocavities may be an oxidative reaction induced by the photogenerated h^+ of TNS (eq 3),[12,13] however, direct evidence had yet to be reported until now.

In the present work, we report on: (1) A direct evidence of the oxidative consumption of MTMPyP and the formation of CS state; (2) No reversible electron migration into the original MTMPyP and MV^{2+}; and (3) Estimation of the lifetimes of CS state under various conditions. This is the first observation of the long-survived CS state between two different organic molecules, i.e., the MTMPyP and MV^{2+} in an inorganic–inorganic hybrid film with a unique bottom-up structure.

To confirm the oxidative consumption of H_2TMPyP in the MPS nanocavities, electron spin and paramagnetic resonance (ER) experiments were carried out using the one-electron oxidation of cobalt(II) to cobalt(III) in Co^{II}TMPyP. Co^{II}–porphyrin was generally reported to exhibit signals with hyperfine structures at 2700–3300 G, while no ER signals were observed within this magnetic field for the one-electron-oxidized species, i.e., Co^{III}–porphyrin.[15] The ER spectra of the (Co^{II}TMPyP–MPS)/(MV^{2+}–TNS) films before and after UV light irradiation are shown in Figure S3. Before UV light irradiation, characteristic octet hyperfine signals attributed to Co^{II}TMPyP were observed at 2750–3250 G accompanied by small amounts of $MV^{+\bullet}$ at 3250–3350 G (Figure S3a). The as-prepared hybrid film exhibited the existence of the one-electron-reduced methyl viologen ($MV^{+\bullet}$) even at the stage of the preparation of the hybrid thin film. This is presumably due

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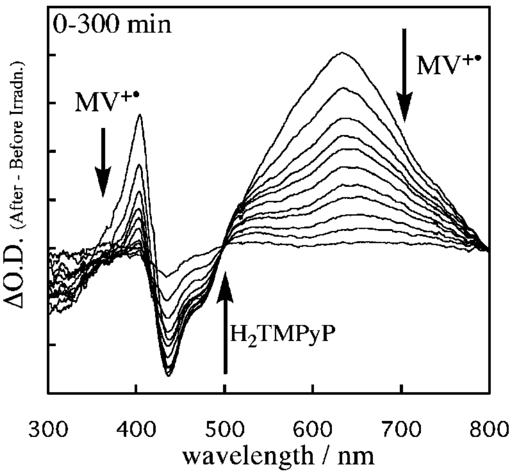

Figure 1. Changes in the differential absorption spectra of the (H_2TMPyP–MPS)/(MV^{2+}–TNS) films. These spectra were obtained by subtracting the nonirradiated spectrum from those obtained after 10 min UV-light irradiation and standing for 0–300 min under dark and ambient atmosphere.

to a scattered room light, though the origin is not known. Upon UV light irradiation for 15 min (Figure S3b), the ER signals of the octet hyperfine couplings disappeared, suggesting the one-electron oxidation of Co^{II}TMPyP into Co^{III}TMPyP, accompanied by the appearance of very strong signals at 3290 G due to the formation of $MV^{+\bullet}$ (Figure S3c).[16] These results clearly indicate the concurrent occurrence of the reduction of MV^{2+} in the TNS interlayer and the oxidation of MTMPyP in the MPS nanocavities, as proposed in eqs 1–3. The photoinduced ET on the interface of the MPS and TNS films, thus, resulted in the formation of a CS state between the one-electron-oxidized porphyrin $(MTMPyP)_{ox}$ in the MPS film and one-electron-reduced viologen ($MV^{+\bullet}$) in the TNS film. In an independent study, we have observed photocurrent generation through the interface of the MPS and TNS films consecutively stacked on a FTO electrode, accompanied by the oxidative consumption of H_2TMPyP in the MPS nanocavities.[14]

The resulting redox pair, $(MTMPyP)_{ox}$ and $MV^{+\bullet}$, gradually reverted back into each original species when kept standing under dark conditions (Figure S4). The differential absorption spectra of the UV-illuminated (H_2TMPyP–MPS)/(MV^{2+}–TNS) films after standing for 0–300 min under dark and ambient atmospheric conditions are shown in Figure 1. Here, the spectra were normalized by subtracting the nonirradiated spectrum from the spectra obtained after 10 min UV-irradiation and standing for 0–300 min under dark and ambient atmosphere.

Just after UV light illumination, characteristic absorptions of $MV^{+\bullet}$ at around 395 and 630 nm appeared, accompanied by the disappearance of the Soret band of H_2TMPyP at 433 nm, as shown in Figure S1. However, after standing under dark and ambient atmosphere, the H_2TMPyP Soret band was slowly recovered, albeit at the expense of the disappearance of the $MV^{+\bullet}$ absorption, as shown in Figure 1. The absorption spectrum then gradually turned to its original, nonilluminated state, indicating the formation of the starting H_2TMPyP and MV^{2+} coupled state. These results, thus, indicated the realization of a stable CS state even under dark and ambient atmosphere.

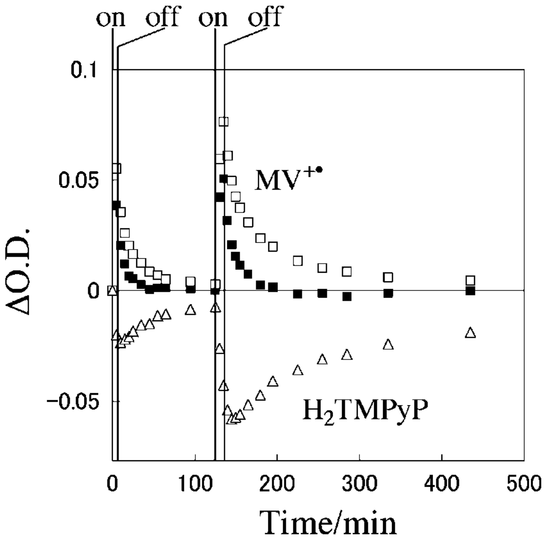

Figure 2. Changes in the absorption intensity of (H_2TMPyP–MPS)/(MV^{2+}–TNS) under ambient conditions as measured by the absorption maxima of $MV^{+\bullet}$ at 395 nm (solid squares) and 610 nm (open squares), and those of H_2TMPyP (open triangles) at 433 nm. Reversible changes were observed after the alternating UV light irradiation and dark condition cycle was repeated twice.

The absorption maxima of $MV^{+\bullet}$ at 395 and 610 nm and the Soret band of H_2TMPyP at 433 nm were plotted against the time in the dark after UV-light illumination, as shown in Figure 2. A rapid increase in $MV^{+\bullet}$ accompanied by a decrease in H_2TMPyP were observed upon UV light illumination followed by the slow and gradual disappearance of the CS state with the passage of time under dark conditions. Significantly, the present photoinduced ET, i.e., the rapid appearance of the CS state, was followed by its slow and gradual disappearance and a return to the starting H_2TMPyP and MV^{2+} coupled state. This redox process between the two hybrids was found to be reversible and repetitive. The repetitive cycles of CS state generation and disappearance, however, were not attributed to the electron exchange or back electron transfers between the $(H_2TMPyP)_{ox}$ and $MV^{+\bullet}$ species, since the CS state may have disappeared by the reaction with the surrounding oxygen and water, as described below. Although the exact lifetimes of the CS state could not be estimated due to the overlap in intensities of the decreasing $MV^{+\bullet}$ and the increasing H_2TMPyP, judging from the multiexponential functions of the decay profiles. Though roughly estimated, the half lifetime ($\tau_{1/2}$) of the CS state was approximated at 2.5 h by measuring the increasing Soret band intensity of H_2TMPyP at 433 nm.

However, it was noted that the lifetimes of the present CS state were observed to be quite sensitive to atmospheric conditions and the $\tau_{1/2}$ under various conditions were summarized in Table 1. It was also interesting that the CS state immediately disappeared upon the formation of the original H_2TMPyP and MV^{2+} coupled state when moisture-saturated argon gas was introduced into the system. The $\tau_{1/2}$ under moisture-saturated Ar was estimated to be 20–30 min, indicating the disappearance of the CS state due to reactions with the water molecules. Surprisingly, the CS state survives in vacuo

Table 1. Half Lifetimes of CS State ($\tau_{1/2}$) in (H_2TMPyP–MPS)/(MV^{2+}–TNS) Hybrid Films under Various Conditions

Conditions	$\tau_{1/2}$
Ambient	ca. 2.5 h
Degassed	>10 day
H_2O-saturated Ar gas	20–30 min

for a longer period than in atmospheric conditions, i.e., over 90% of the CS state could be retained even after one week. Nevertheless, even this long-lasting CS state in vacuo rapidly disappeared upon the introduction of moisture-saturated Ar gas on the hybrid films and the starting H_2TMPyP and MV^{2+} coupled state was immediately regenerated. These results showed that, in vacuo, the proposed CS state can survive for several days to over a week without any irreversible decomposition of H_2TMPyP and MV^{2+} in these hybrid films. It was also observed that no back electron transfer proceeds in this system, and thus, $MV^{+\bullet}$ and $(MTMPyP)_{ox}$ react with the oxygen and water molecules in the systems, respectively. In fact, radicals and radical cations of various organic molecules are known to be stabilized by inorganic layered materials.[6] Although the detailed mechanisms have yet to be clarified, the long survival of the resulting redox pair, $MV^{+\bullet}$ and $(MTMPyP)_{ox}$, may be explained by the rapid diffusion of the photogenerated electrons or holes within the TNS layers,[6a] the difficult and negligible diffusion of atmospheric oxygen gas or water molecules in the nanospaces,[6b] and/or the charge neutralization of these species within the nanospaces.[6–8] A similar stabilization of an open-shell cation radical in zeolite cavities has also been observed by Ikeda et al.[7a,7b]

In conclusion, we have observed a remarkably long-lived CS state, without back electron transfers between H_2TMPyP and MV^{2+} separately accommodated within the TNS/MPS hybrid films, which was initiated by the photocatalytic properties of the TNS semiconductors. This is the first report of a long-lived CS between two different organic molecules for over 2.5 h under ambient atmospheric conditions and over a week in vacuo in these inorganic–inorganic hybrid films. It is notable that the absence of back electron transfers due to the separate accommodation of MTMPyP and MV^{2+} may induce the long survival of the resulting CS states. The present stable charge separation can be applied to the development of novel chemical systems such as capacitors, triggers for chemical reactions, or applications in the control of electron migrations and chemical reaction systems such as the *Z*-scheme in artificial photosynthesis.[9] Investigations on the mechanisms behind such unique and interesting, long-lived charge-separated states are now underway.

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Supporting Information

Absorption and ER spectral change with UV-light irradiation of the hybrid films. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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