Visible-Light Induced Charge-Separation between Consecutively Cast Porphyrin and Methyl Viologen Multilayered Titanoniobate Hybrid Films

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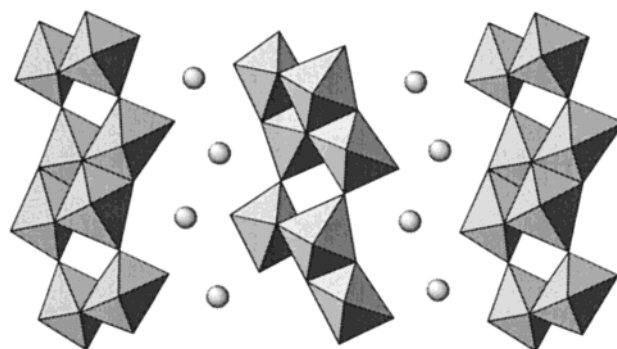
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The photoinduced charge separation between a photosensitizer, 5,10,15,20-tetrakis-(*N*-methyl- pyridinium-4-yl)21H,23Hporphyrin cation (TMPyP^{4+}), and an electron acceptor, methyl viologen (MV^{2+}), intercalated in the different layer sheets of titanoniobate (TiNbO$_5{}^-$) and successively cast on a SiO$_2$ glass slide has been investigated. Illumination of TMPyP^{4+} with light of >420 nm initiated the donation of an electron through the conduction bands of the TiNbO$_5{}^-$ layers, yielding a one-electron reduced acceptor (MV$^{+\cdot}$) isolated from the one-electron oxidized TMPyP^{4+} by the titanoniobate layers. The stacked lamella structure of the thin films consisting of TiNbO$_5{}^-$ hybrids with TMPyP^{4+} and MV^{2+} was also examined.

Introduction

Nanoorder laminate materials obtained by the intercalation of porphyrins and metalloporphyrins into two-dimensional inorganic layered matrixes have been investigated for the purpose of elucidating the photochemical and photocatalytic processes in spatially restricted reaction media.[1,2] Various kinds of two-dimensional layered host materials intercalated by porphyrin derivatives utilizing layered double hydroxides,[3,4] clays,[5,6] zirconium hydrogen phosphate,[7] titanate,[8] niobate,[9−11] and hydrated vanadium pentoxide as host materials have thus far been reported.[12] Domen and co-workers have studied the photocatalytic activities of several layered metal oxide semiconductors (LMOS) for water cleavage by band gap excitation.[13] Additionally, Nakato et al. have studied intercalation compounds of layered niobates which undergo a photoinduced electron-transfer process between the host and intercalated guest species.[14]

Porphyrins have attracted much attention as light-harvesting and electron-donating or -accepting molecules. A number of investigations have been carried out by the use of porphyrins for artificial photosynthesis or photochemical hole burning.[15] Porphyrins are well-known to be excellent candidates as photosensitizers, because they are very efficient light absorbers, particularly in the range 400−700 nm.[16] In the present study, we undertook a study of the porphyrin-sensitized charge separation between porphyrin and methyl viologen (MV^{2+}) intercalated in different layers of titanoniobate to form a hybrid material through their intercalation.

The chemical structures of TiNbO$_5{}^-$, and TMPyP^{4+}, and MV^{2+} are shown in Figures 1 and 2, respectively. Upon illumination of the hybrids with a light longer than 420 nm, a photoinduced electron transfer occurs from the porphyrin to MV^{2+} through the layered titanoniobate. Such heterogeneous laminate films can be seen to control the spatial organization of the donors and acceptors, enhancing the efficiency of the charge separation.

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Figure 1. Structure of KTiNbO$_5$. Squares repersent the TiO$_6$(and NbO$_6$) octahedra, and circles indicate the exchangeable cation K$^+$ in the interlayer.
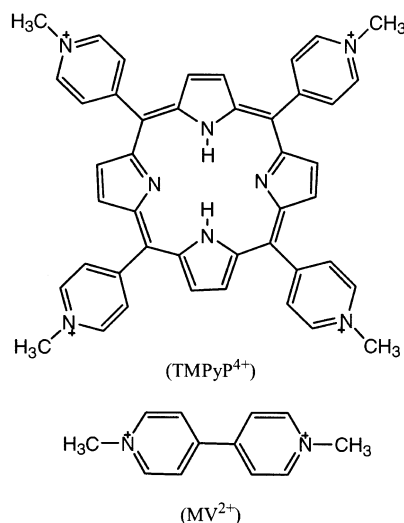
Figure 2. Structural formula of the TMPyP^{4+} and MV^{2+} ions.

Experimental Section

Materials. Potassium titanoniobate was prepared by heating homogeneously mixed powders of K$_2$CO$_3$, TiO$_2$ (anatase, High Purity Chemicals) and Nb$_2$O$_5$ in molar ratios of 1:2:1 at 1150

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°C for 24 h in accordance with previous literature.[17] Commercially available tetrakis(*N*-methylpyridinium −4-yl)porphyrin cation (TMPyP^{4+}), methyl viologen (i.e., *N*,*N*′-dimethyl-4,4′-bipyridinium iodide) (MV^{2+}), and *n*-propylamine (Tokyo Kasei Co.) of extra pure grade were used as received.

Intercalation into Layered Titanoniobates. One gram of a powdered potassium titanoniobate was treated three times with 100 mL (each) of 1 mol/dm^3 HCl for 24 h at room temperature. The resulting titanoniobic acid powder was washed with deionized water (180 mL x 5 times) until free of Cl$^-$ and then air-dried. Porphyrin and methyl viologen could not be intercalated directly when K$^+$ or H$^+$ titanoniobate (TiNbO$_5^-$) was used. In contrast to usual ion-exchange procedures, bulkier guest molecules such as porphyrins and methyl viologens could subsequently be ion-exchanged after preintercalation of the propylamine in the titanoniobic acid through acid−base neutralization. A powder of the titanoniobic acid (500 mg) was sealed in a 200 mL glass ampule with 15 mL of an aqueous 50% *n*-propylamine solution and allowed to stand for two weeks at 70 °C. The precipitate powder was washed with alcohol (180 mL × 5 times) and dried at 25 °C in air. The obtained white powder (200 mg) was again put in a 200 mL glass ampule sealed with either 90 mL of an aqueous 5 mmol/dm^3 TMPyP^{4+} or 5 mmol/dm^3 MV^{2+} solution and allowed to stand for two weeks at 60 °C, respectively. The amounts of TMPyP^{4+} and MV^{2+} were adjusted to 2.5 times those calculated from the ion-exchange capacity (CEC) of the titanoniobic acid. The resultant products were washed with deionized water until the TMPyP^{4+} and MV^{2+} absorption could no longer be detected at 425 and 257 nm, respectively, in the filtrate solution after washing with water.

Characterizations of the TMPyP^{4+}− and MV^{2+}−TiNbO$_5^-$ hybrid powders were carried out by means of X-ray powder diffraction, IR, UV, and polarized UV spectroscopies as well as combustion analysis. X-ray diffraction analysis was carried out by a RINT 2000 diffractometer (Rigaku), using Cu Kα radiation (0.15418 nm) with 2θ from 2.5° to 50° in every 0.20° step. The infrared spectra were recorded on a JASCO FT-IR 610 spectrometer using KBr pellets, whereas the UV absorption spectra were recorded on a JASCO V-550 spectrophotometer. The compositions of the hybrid products were measured by a PERKIN ELMER CHN 2400 II elemental analysis instrument. Ultraviolet absorption spectroscopic measurements with polarized light were performed by this same spectrophotometer combined with a polarized unit attachment (JASCO RSH-452).

Visible Light Illumination. An aqueous colloidal dispersion of the MV^{2+}−TiNbO$_5^-$ hybrid powder was obtained by suspending 0.2 g of the powder methyl viologen−titanoniobate hybrid, which had been milled in advance, in 20 mL of H$_2$O; the suspension was stirred overnight and then centrifuged at 1000 rpm for 20 min. The resulting colloidal suspension was cast onto a conventional quartz glass plate (20 mm × 40 mm) and was allowed to dry at room temperature for 2 days. An aqueous colloidal suspension of the TMPyP^{4+}−TiNbO$_5^-$ hybrid was similarly prepared and then successively cast onto the previously prepared MV^{2+}−TiNbO$_5^-$ hybrid film. The obtained film was allowed to dry at room temperature for 2 days. It was established that TMPyP^{4+} or MV^{2+} settled in the different layers of TiNbO$_5^-$ by the fact that their desorption could not be observed in the hybrid powder even when kept in water for a day. The visible spectra of the product were also recorded on the above UV spectrometer before and after irradiation with a 250 W Hg lamp (UI-502Q). Irradiation was carried out at a distance of ca. 15 cm from the light source and passed through
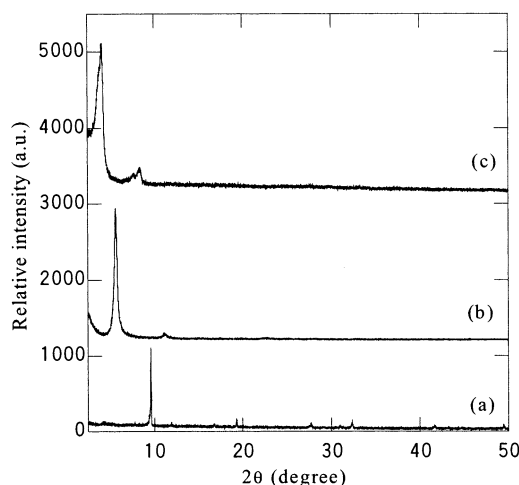
Figure 3. Powder X-ray diffraction patterns of (a) KTiNbO$_5$, (b) PrNH$_3^+$−TiNbO$_5$, and (c) TMPyP^{4+}−TiNbO$_5$ hybrids.

TABLE 1: X-ray Powder Diffraction Data

compound	d_{002}/nm	Δd^a/nm
KTiNbO$_5$	0.92	0.07
NTiNbO$_5$	0.85	0
PrNH$_3^+$−TiNbO$_5^-$	1.57	0.72
TMPyP^{4+}−TiNbO$_5^-$	2.10	1.25
MV^{2+}−TiNbO$_5^-$	1.42	0.57

^{a} The increase in d$_{002}$ from that of HTiNbO$_5$.

a filter (SCF-50S-42L) to isolate light longer than 420 nm. Measurements of the action spectra for the formation of MV$^{+\bullet}$ against the incident monochromatic light at wavelengths between 360 and 590 nm were carried out using a 450 W xenon lamp with a monochromator to isolate monochromatic light of ±5 nm.

Results and Discussion

Synthesis of the Porphyrin−Titanoniobate Hybrids. Because KTiNbO$_5$ is known to have difficulty reacting with aliphatic amines,[18] the protonation of KTiNbO$_5$ to give titanoniobic acid (HTiNbO$_5$) was carried out by the addition of HClaq (1 mol/dm^3)[19] into the interlayers of which *n*-propylamine could easily intercalate by neutralization of the amine. The interlayer spacings of the propylamine intercalated titanoniobate became shortened from 0.92 to 0.85 nm, as can be seen in the XRD powder diffraction patterns in Figure 3. The propylammonium ion intercalated hybrid with 1.57 nm of the d$_{002}$ was subsequently treated with TMPyP^{4+} to produce a TMPyP^{4+}−TiNbO$_5$ hybrid, resulting in an increase of the d$_{002}$ value to 2.10 nm. The basal spacings and the Δ*d* values of these products are shown in Table 1.

The propylammonium ions were completely ion-exchanged with TMPyP^{4+}, as could be confirmed by their infrared spectroscopies (Figure 4). The IR spectra exhibited no absorption bands, indicating a N−H bond at 1507 cm^{-1} and C−H bond at 1468 cm^{-1} for the propylammonium ions in the hybrids. A number of characteristic absorption bands of TMPyP^{4+} could be observed at 1640, 1536, 1457, and 1355 cm^{-1} for the C=N of the pyridinium and C=C and C=N of the pyrrol rings, respectively.[20]

The UV and visible absorption spectra of TMPyP^{4+} intercalated in the titanoniobate exhibited diffuse reflectance spectra different from those of the unintercalated TMPyP^{4+} in the Soret and Q-bands at 425, 522, 555, 586, and 641 nm (Figure 5). That is, the TMPyP^{4+} intercalated in TiNbO$_5^-$ possesses Soret
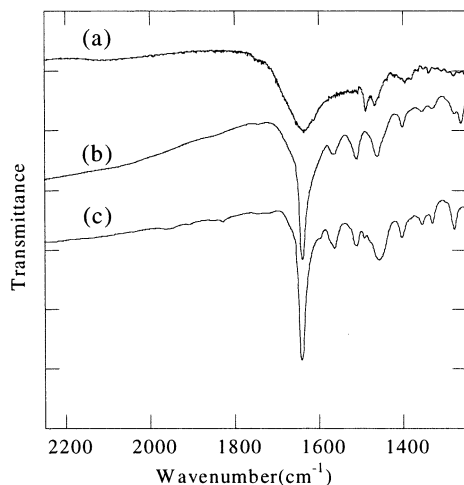
Figure 4. Infrared spectra of (a) $PrNH_3^+$–$TiNbO_5$ hybrids, (b) $TMPyP^{4+}$–$TiNbO_5$ hybrids, and (c) $TMPyP^{4+}$ powder in the KBr disk.
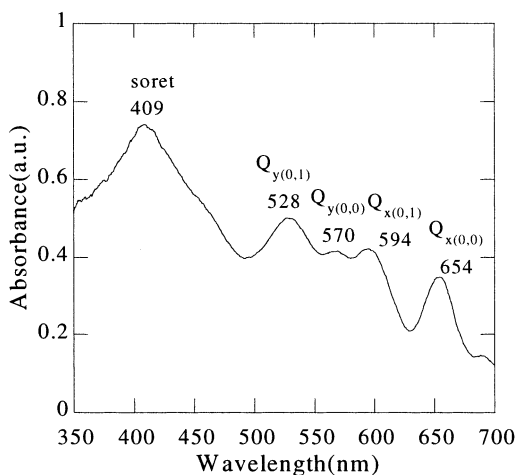

Figure 5. Diffuse reflectance spectrum of $TMPyP^{4+}$–$TiNbO_5$ hybrids.

and Q-bands which are blue-shifted by 16 nm and red-shifted by 8−15 nm, respectively. These results imply that the $TMPyP^{4+}$ molecules are stacked in parallel orientation and interacts with each other in a face-to-face manner within the interlayer spaces.[21] The results of the XRD, IR, and UV diffuse reflectance spectra investigations have confirmed that $TMPyP^{4+}$ is anisotropically organized in the form of a porphyrin−titanoniobate hybrid.

On the basis of the observed C, H, and N distribution of 15.08%, 2.50%, and 3.26% of the hybrid powder, respectively, the composition formula for the $TMPyP^{4+}$–$TiNbO_5^-$ hybrid could be assigned as $(TMPyP)_{0.09}H_{0.64}TiNbO_5 \cdot 1.8H_2O$, in which the calculated C/N molar ratio, 5.4, is in good agreement with the observed value, 5.5. These results indicate that *n*-propylammonium ions are completely removed from the hybrid.

XRD studies also showed the $TMPyP^{4+}$ molecules to be anisotropically oriented in the interlayers of the porphyrin−titanoniobate hybrid thin films prepared by casting the aqueous suspension on the glass plate. Upon intercalation of $TMPyP^{4+}$ into the interlayers, the basal spacings increased to 1.25 nm. It was then possible to estimate the tilt angle of ca. 46° by assuming ca. 3 nm^2 as the molecular area of $TMPyP^{4+}$.[8,22] On the assumption that the $TMPyP^{4+}$ molecules are regularly aligned in the thin films of the layered titanoniobate, angles γ between the normal line of the glass plate and the molecular axis could be evaluated by employing spectroscopic studies using polarized light.[23−25] Here, angles γ can be expressed as
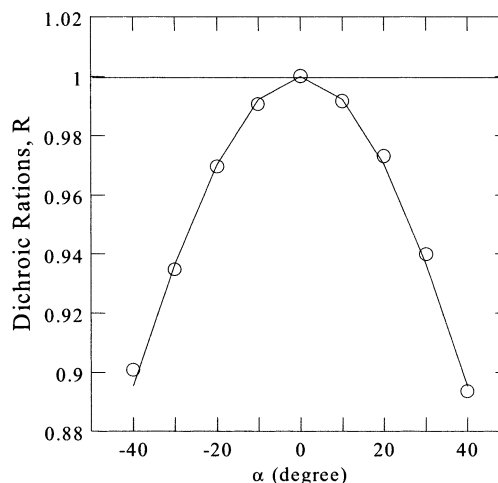

Figure 6. Dependence of the incident angle, α, on the dichroic ratios R of the porphyrin-titanoniobate hybrid thin film.

depicted in eq 1, where R is the dichroic ratio of A_y to A_x, denoting the absorption intensities for the horizontal and vertical polarized incident lights, respectively. θ and α represent the angles between the molecular axis and the optical transition moment and the incident light and the substrate plane, respectively. The film exhibits an optical anisotropy because of the organized alignment of the molecules, because the R values varied according to angle α. Thus, angle γ was obtained by eq 1. Here, angle θ between the molecular axis and the optical transition moment was determined to be 90° by using the transition moments deduced from MO calculations using PM3 and ZINDO/S. Figure 6 shows the dependence of the R values of the hybrid sample on the α values, with a maximum at $\alpha = 0°$. Angle γ was estimated by using eq 1 and indicates that the intercalated $TMPyP^{4+}$ molecular plane has an inclination angle of 47°, which corresponds to the results of the above estimated angle of 46° using XRD measurements.

$$R = A_y/A_x = \frac{2[\sin^2\theta + \sin^2\sigma (3\cos^2\theta - 1)] - (3\sin^2\alpha - 1)(3\cos^2\theta - 1)\sin^2\gamma}{2\sin^2\theta + (2 - 3\sin^2\theta)\sin^2\gamma} \quad (1)$$

Alignment of Methyl Viologen in the MV^{2+}−Titanoniobate Hybrids. The intercalation of MV^{2+} into the hybrid was analyzed by the X-ray powder diffraction patterns of the product. Treatment of the *n*-propylammonium−titanoniobate with methyl viologen (MV^{2+}) resulted in a decrease in the d_{002} value to 1.42 nm from 1.57 nm of the original untreated *n*-propylammonium-titanoniobate hybrid, as shown in Figure 7. The layer expansion (0.57 nm) from the unintercalated $HTiNbO_5$ is comparable to cases of MV^{2+} intercalated in other LMOS semiconductors such as HNb_3O_8 (0.54 nm) and $K_4Nb_6O_{17}$ (0.41 nm).[14] The arrangement of the intercalated MV^{2+} ion could be assumed on the basis of the increase in the layer distance (Δd). The flat aligned MV^{2+} monolayers in the layered materials show Δd values of between 0.28 and 0.33 nm.[26−28] From these results, the MV^{+2} ions were shown to be tilted at around 45° from the layer surface in the present case. Combustion analysis showed that these MV^{2+}−titanoniobate hybrids consist of 14.38%, 2.28%, and 2.88% C, H, and N, respectively, indicating that the hybrid is covered by ca. 30% MV^{2+}, whereas the composition formula is assigned as $(MV)_{0.3}H_{0.4}TiNbO_5 \cdot 1.2H_2O$.

Photochemical Electron Transfer. The successively stacked hybrid films incorporating $TMPyP^{4+}$ and MV^{2+} and separately intercalated in the titanoniobate were designed to induce

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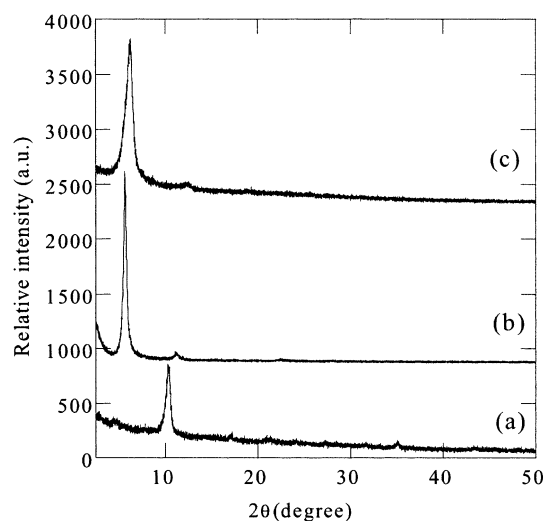
Figure 7. Powder X-ray diffraction patterns of (a) $HTiNbO_5$, (b) $PrNH_3^+-TiNbO_5$, and (c) $MV^{2+}-TiNbO_5$ hybrids.

**SCHEME 1: Schematic Drawing of a Multilayer Film Containing a Light-harvesting Porphyrin ($TMPyP^{4+}$), and a Viologen Electron Acceptor (MV^{2+}) Layers Separated from Each Other by the Semiconducting $TiNbO_5^-$ Sheets**
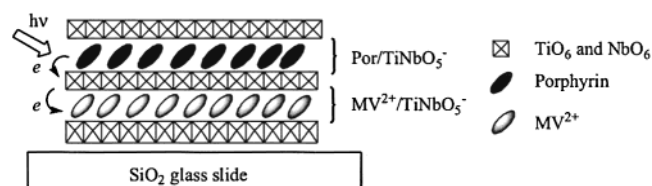

photochemical charge separations, as illustrated in Scheme 1. The stacked film consists of a self-assembly of porphyrin and viologen as the photosensitizer and electron acceptor, respectively, which are present separated from each other by the $TiNbO_5^-$ layers. The thus obtained multilayer film consisting of a $MV^{2+}/TiNbO_5^-/TMPyP^{4+}$ triad was capable of inducing a charge separation, as indicated by the appearance of MV^+ formation (405 and 605 nm) upon illumination with visible light ($\lambda > 420$ nm), as shown in Figure 8.

It is evident from the action spectrum, monitored at ca. 405 nm, for the formation of $MV^{+\bullet}$ against the incident monochromatic light at wavelengths between 360 and 590 nm, that the porphyrin sensitizes the electron transfer to the conduction bands of the titanoniobate layers, as can be seen in Figure 9. The action spectrum corresponds to that of porpyrin with Soret and Q-bands at 425 and 522 nm, respectively. Moreover, it could definitely be seen in the control experiments for an electron transfer from the excited titanoniobate to MV^{2+} that there was no increase in the absorption maxima for $MV^{+\bullet}$ at 405 and 605 nm in the absence of the porphyrin layers. [29]

These observations clearly indicate an electron transfer from porphyrin to methyl viologen through the $TiNbO_5^-$ semiconductor layers. Here, the semiconductor layers, i.e., $TiNbO_5^-$ sheets, play an important role in mediating the electron-transfer reaction from the excited $TMPyP^{4+}$ to MV^{2+}. It should be noted here that the flat-band potential of $TiNbO_5^-$ (−0.66 V vs SCE) [30] intervenes between the formal potential of $TMPyP^{4+}$ (−0.84 V vs SCE) [31] and MV^{2+} (−0.56 V vs SCE). [30] In the electron-transfer processes, the $TiNbO_5^-$ sheets are capable of promoting a charge separation by mediating an electron from the excited $TMPyP^{4+}$ and then transferring an electron to the viologen acceptor isolated from the oxidized porphyrin molecule by the
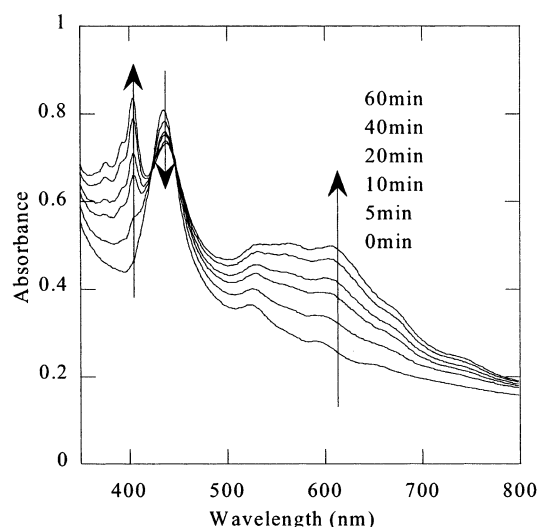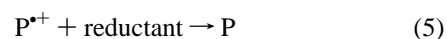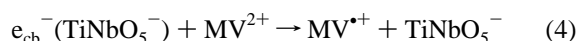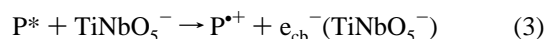

Figure 8. Changes in the absorption spectra by irradiation ($\lambda > 420$ nm) of the laminate film consisting of $TMPyP^{4+}$ and MV^{2+} layers separated by $TiNbO_5^-$ sheets.
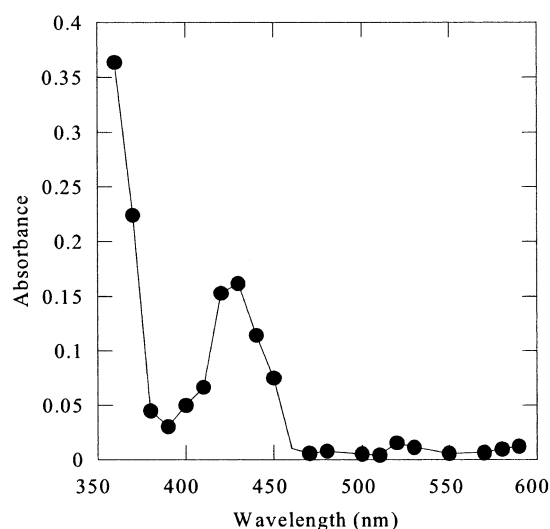
Figure 9. Action spectrum for the formation of $MV^{+\bullet}$ against the incident monochromatic light at wavelengths between 360 and 590 nm in the photolysis of multilayer films consisting of a $MV^{2+}/TiNbO_5^-/TMPyP^{4+}$ triad. The spectrum maxima at ca. 430 and 520 nm correspond to the absorption maxima of $TMPyP^{4+}$. (Monitored at 405 nm).

semiconductor layers. The plausible overall reaction pathways are depicted in eqs 2−5. The sheets may efficiently suppress the back electron transfer in the reverse process of eqs 3 and 4, because the formal potential of viologen is more positive than the flat-band potential of the semiconductor.

$$P \xrightarrow[\lambda > 420\,\text{nm}]{h\nu} P^* \qquad (2)$$

$$P^* + TiNbO_5^- \rightarrow P^{\bullet+} + e_{cb}^-(TiNbO_5^-) \qquad (3)$$

$$e_{cb}^-(TiNbO_5^-) + MV^{2+} \rightarrow MV^{\bullet+} + TiNbO_5^- \qquad (4)$$

$$P^{\bullet+} + \text{reductant} \rightarrow P \qquad (5)$$

Conclusions

$TMPyP^{4+}-TiNbO_5$ hybrids were prepared by a guest ion-exchange technique using $PrNH_3^+-TiNbO_5$ as the precursor. XRD and polarized spectroscopic data have confirmed the

molecular plane of TMPyP^{4+} to be present as a tilted monolayer aggregate at an angle of 47° inside the layered host. Similarly, the synthesized MV^{2+}−TiNbO$_5$, showed an inclined orientation (ca. 45°) of MV^{2+} within the host layer. Upon illumination of the successively stacked thin films of the two independently prepared hybrids by >420 nm light, an electron transfer was found to occur from the porphyrin to MV^{2+} through the layered titanoniobate, forming a blue MV$^{+•}$.

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