Investigation of the photoelectric conversion of a novel molecule (*E*)-*N*-methyl-4-{2-[4-(dihexadecylamino)phenyl]ethenyl}pyridazinium iodide, in LB films fabricated on an SnO_2 electrode

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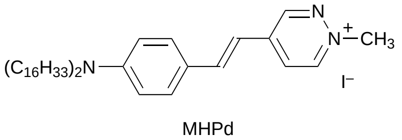
An investigation of cathodic photocurrent response from a novel molecule with strong non-linear optical properties (second harmonic generation), (*E*)-*N*-methyl-4-{2-[4-(dihexadecylamino)phenyl]ethenyl}pyridazinium iodide (MHPd) in LB films on transparent SnO_2 glass has been carried out. A quantum yield of 0.3% was obtained under irradiation with 450 nm light in 0.5 mol dm^{-3} KCl electrolyte solution and ambient conditions. The studies of the relationship between the light intensity and the cathodic photocurrent indicate that MHPd assemblies perform a unimolecular process in charge recombination. The effects of bias voltage, oxygen and nitrogen, electron donors and acceptors such as methyl viologen diiodide, ascorbic acid and hydroquinone were examined and have provided supporting evidence for the proposed electron-transfer mechanism.

Photoconductivity of Langmuir–Blodgett (LB) films has attracted considerable attention in the field of photoelectronics for their variety of applications, such as molecular switches,[1] LB film rectifiers,[2] information storage and processing.[3] Several reports have been made on transient photoelectric responses in LB films.[4–16] A photocurrent response in dye molecules fabricated as LB films has also been reported.[17,18] Key events occurring after photoexcitation of the aggregate are postulated to be: (1) photogeneration of electron–hole pairs within a dye aggregate; (2) electron and hole migration within a dye aggregate; and (3) electron transfer between the excited dye aggregate and an electron donor or acceptor.[19]

Basic studies of the molecular details of the photoinduced electron-transfer process are of particular value not only in terms of their photoconductivity but also for many other man-made molecular effects in devices. The results obtained can be helpful in the design of novel molecular structures with optimal photoelectrical properties in the future.

Recently, researchers have found that dye molecules like squarine,[19,20] stilbenes,[21] azastilbenes[22] and azopyridinium[23,24] have both non-linear optical and photoelectric conversion properties. They act as sensitisers of semiconductor and electron donors and acceptors, at the same time as photocurrent generators. The novel molecule (*E*)-*N*-methyl-4-{2-[4-(dihexadecylamino)phenyl]ethenyl}pyridazinium iodide (MHPd) is a dye molecule. It acts as a good non-linear optical material (second harmonic generation[25]). In the present work, the dye MHPd was transferred as highly ordered molecules onto a transparent SnO_2 electrode from a water/air interface and its photoelectrochemical properties were investigated so that a fundamental understanding of the photoelectrochemical process could be obtained.



MHPd

Experimental

Materials

MHPd was synthesized by condensing 1,4-dimethylpyridazine with one equivalent of *N*,*N*-dihexadecylaminobenzaldehyde in ethanol solution using piperidine as the catalyst.[25] The product was purified by column chromatography at 1 atm pressure (eluent: chloroform–methanol, 10:1). Elemental analysis and NMR spectroscopic results were satisfactory. The water was deionized in-house and purified by passing through a EASY pure RF compact ultrapure water system (Barnstead Co., USA). Chloroform, used as the spreading solvent, KCl, used as the electrolyte for the electrochemical experiment, and ascorbic acid (AA) were of analytical grade and were used without further purification. Hydroquinone (HQ) was recrystallized from water before use. Methyl viologen diiodide (MV^{2+}) was synthesized by the reaction of 4,4′-dipyridyl with excess methyl iodide in refluxing ethanol for 6 h. The product was filtered and washed with ethanol at least four times and gave satisfactory NMR results.

Preparation and characterization of LB films

Monolayers of MHPd were obtained by spreading a chloroform solution of MHPd (*ca.* 0.5 mg ml^{-1}) onto a pure water subphase (25 ± 1 °C, pH 5.6) in a British NIMA Technology Langmuir–Blodgett Model 622 trough. The substrate was transparent SnO_2 glass and was hydrophilically pretreated.† Its lateral resistance was *ca.* 50 Ω. The LB films were made by dipping the precleaned substrate into the aqueous subphase and raised at a rate of 5 mm min^{-1} with a surface pressure of 35 mN m^{-1}. Transfer ratios were *ca.* 1.0. The MHPd–SnO_2 assemblies used in the photoelectrochemical experiments consisted of a single layer of MHPd on an SnO_2 electrode.

The characterization of the aggregation of MHPd in LB films was carried out by UV–VIS absorption spectroscopy.

Photoelectrochemical experiments

In all the photoelectrochemical experiments, the measurements were carried out in a conventional three-electrode cell which consisted of a polished platinum wire as the counter electrode, an Ag/AgCl reference electrode and the MHPd LB film-modified SnO_2 glass as the working electrode the effective area of which was 0.8 cm^2. The supporting electrolyte used was 0.5 mol dm^{-3} KCl aqueous solution. In preparing samples with

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† In cleaning the substrate, the SnO_2 glass was immersed in 50% sulfuric acid below 70 °C for less than 10 min, then rinsed with ultrapure water at least three times.

different concentrations of donor and acceptor, solid samples were added directly to the 0.5 mol dm^{-3} KCl electrolyte solution. All measurements were made at 25 ± 1 °C on a Model 600 voltammetric analyser (CH Instruments, USA). In the photochemical experiment, a 500 W xenon lamp (Ushio Electric, Japan) was used as the excitation source. The incident white light was perpendicular to the contact area of the working electrode. The intensity of the incident beam was checked using a model LM-91 Photopower meter (National Institute of Metrology, Beijing, China). Different wavelengths were obtained by using filters (Toshiba, Japan) with certain bandpasses. For instance, 450 nm light was obtained by using a filter the transmission of which was centred at 450 nm with a bandpass of 15 nm. IR light was filtered with a Toshiba IRA-25S (Japan) filter in all the experiments.

Spectroscopic measurements

All the UV–VIS spectra were obtained from a Shimadzu UV-3100 spectrometer (Japan).

Results and Discussion

Characterization of the MHPd LB film modified SnO_2 electrode

The quality of the MHPd monolayer on the hydrophilically pretreated SnO_2 electrode was controlled by the surface pressure (35 mN m^{-1}) and the transfer ratio (1.0 ± 0.1). At a surface pressure of 35 mN m^{-1}, the film was in the solid phase and the π–A isotherm in this range is steep and smooth. The high collapse pressure (60 mN m^{-1}) ensures that the film at 35 mN m^{-1} is stable. The unity transfer ratio ensures that the obtained film on the substrate was 100% transferred and retained the packing pattern as on water/air interface. The area per molecule was *ca.* 60 Å^2. In the UV–VIS absorption measurements (Fig. 1), a large blue shift from 578 nm in chloroform solution as the monomer to 524 nm for the LB films on the SnO_2 substrate was found. This shift indicates that H-aggregates formed in films. It is possible that the aggregation of the molecules resulted from the interactions between the chromophores.

Photocurrent generation of the MHPd–SnO_2 electrode

A cathodic photocurrent was observed from the MHPd–SnO_2 electrode. From ten parallel MHPd–SnO_2 electrodes, a factor of *ca.* 2.6 variation in the photocurrent data was found. Samples in 0.5 mol dm^{-3} KCl generated 150–400 nA photocurrent when they were irradiated with 240 mW cm^{-2} of white light. Photocurrents generated from samples which were stored in a refrigerator (4 °C) for two weeks and in 0.5 mol dm^{-3} KCl solution for two days were within this range. Fig. 2 shows the action spectra of the cathodic photocurrent with no bias voltage. Its spectral response coincided well with the absorption spectra of LB films (Fig. 1), suggesting that the aggregation of MHPd in LB films is responsible for photocurrent generation. Under the same working conditions as those used to obtain the action spectrum, the photocurrent obtained at 450 nm (light intensity 1.8×10^{16} photons cm^{-2} s^{-1}) ranged from 57 to 63 nA. This photocurrent means that the quantum yield, which is cited per absorbed photon, is *ca.* 0.3% (the absorbency of the LB film at 450 nm is *ca.* 0.92%).

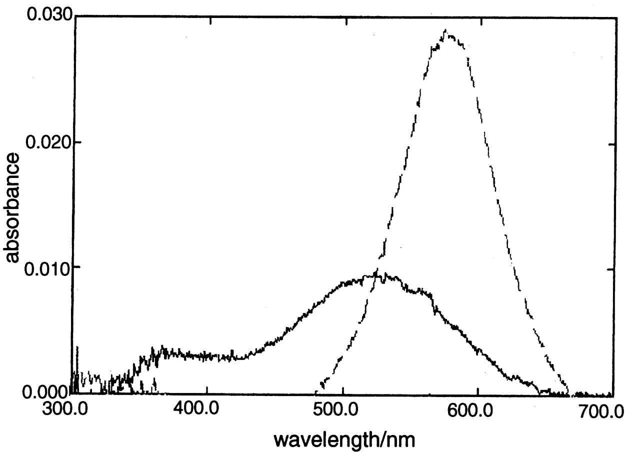


Fig. 1 UV spectra of MHPd in chloroform solution (dashed line) and in LB films on SnO_2 substrate (solid line)

Effect of bias voltage and light intensity

The effect of bias voltage was investigated to explore the electron transfer process between the MHPd LB film and the SnO_2 electrode. A linear relationship was found between the cathodic photocurrent generation and the bias voltage applied to the working cell under ambient conditions. The equation for this line is $i_{ph} = -1.96\ V + 406$ (deviating coefficient $R = 0.9957$, Fig. 3), where i_{ph} is the photocurrent and V is the bias voltage applied. The negative slope (-1.96 nA mV^{-1}) of the line implies that the polarity of the electrical field caused by the applied negative voltage is the same as the polarity of the inner electrical field from which the cathodic photocurrent is produced. This provides circumstantial evidence for the explanation that the cathodic photocurrent is produced by a flow of electrons from the working electrode through the LB film to the electrolyte solution.

To probe the recombination pathway MHPd may take, the

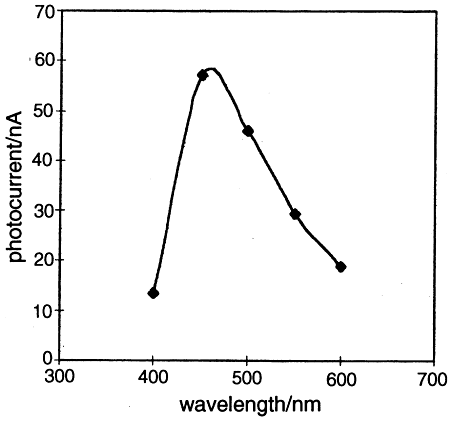


Fig. 2 Action spectrum (electrolyte solution 0.5 mol dm^{-3} KCl, light intensity 1.8×10^{16} photons cm^{-2} s^{-1}, 450 min)

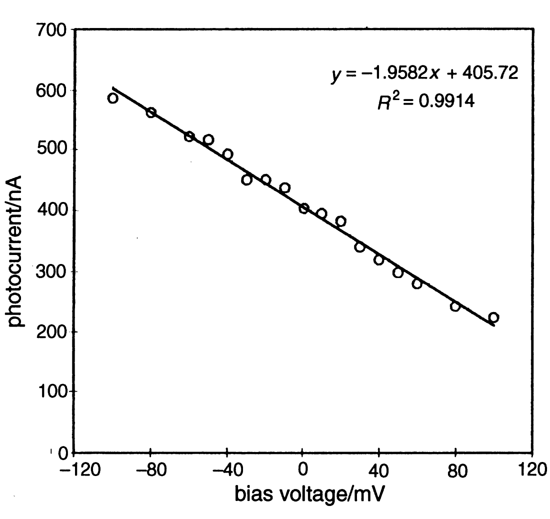


Fig. 3 Effect of bias voltage on photocurrent generation (0.5 mol dm^{-3} KCl, light intensity 240 mW cm^{-2}, ambient conditions)

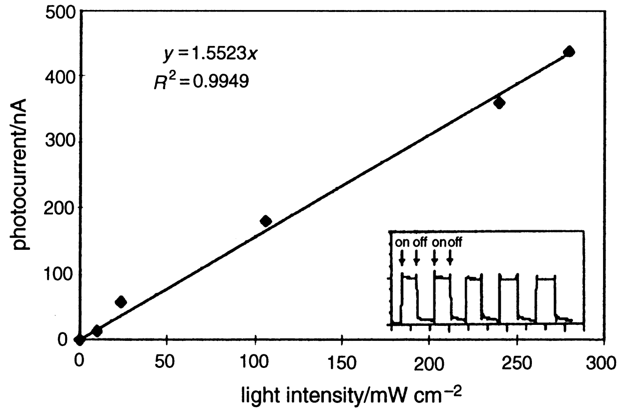


Fig. 4 Effect of light intensity on photocurrent generation (0.5 mol dm^{-3} KCl, ambient conditions)

effect of the irradiation light intensity was investigated. A good linear relationship between the light intensity ($\leqslant$240 mW cm^{-2}) and the photocurrent was observed. The equation for this line is $i_{ph} = 1.55I$ (deviation coefficient 0.997, Fig. 4), where I is the light intensity. Comparing this equation with the generally used form, $i_{ph} = kI^m$, one can see that, in our case, $k = 1.55$ and $m = 1$. According to Donovan *et al.*[9] $m = 1$ is the characteristic of unimolecular recombination. Thus, MHPd underwent unimolecular recombination in the charge loss process.

Effect of donor and acceptor

Oxygen and nitrogen. Unless deliberately degassed, oxygen exists in aqueous solutions. Since oxygen itself is a good electron acceptor,[19] the photocurrents generated under ambient, nitrogen-degassed and oxygen-saturated conditions were studied. At the beginning, the photocurrent under ambient conditions (0.5 mol dm^{-3} KCl, 25 °C, pure water) was 250 nA. Then, as shown in Fig. 5, upon degassing with nitrogen the cathodic photocurrent decreased gradually to *ca.* 100 nA and was unchanged thereafter. Regarding the nitrogen-degassed solution as an oxygen-free system, oxygen was bubbled into it. As expected, cathodic photocurrent enhancement was observed. The photocurrent increased from *ca.* 100 nA to *ca.* 250 nA and remained constant thereafter. These results indicate that oxygen acts as potential electron acceptor and the ambient oxygen concentration (*ca.* 2.7×10^{-4} mol dm^{-3})[26] is the most effective one. Oxygen effectively accepted electrons from the MHPd film and thus promoted electron transfer between the SnO_2 electrode, the MHPd film and the electrolyte. Although oxygen is a major factor, it is not the only one which affects the photocurrent in the electrolyte solution, because only 60% of the photocurrent was attributed to it.

Other donors and acceptors. The effects of other donors and acceptors were studied for further elucidation of the conclusion obtained above, and also to gain a better view of the probable mechanism of photocurrent generation in the MHPd–SnO_2 system. In this approach, the cathodic photocurrent was generated by irradiation with 240 mW cm^{-2} white light in 0.5 mol dm^{-3} KCl solution under nitrogen-degassed conditions. Hydroquinone (HQ), methyl viologen diiodide (MV^{2+}) and ascorbic acid (AA) were used as donors and acceptors. Hydroquinone, whose redox potential is +0.13 *vs.* Ag/AgCl (red.) quenched the cathodic photocurrent markedly (Fig. 6) when added to the MHPd–SnO_2 system. If the quantity of HQ added is greater than 0.042 mmol dm^{-3} (calculated according to the data obtained), it will reverse the photocurrent from cathodic to anodic. This greater attenuation and reversal of the cathodic photocurrent suggested that by donating electrons to MHPd LB assemblies, HQ can not only inhibit electron transfer from the SnO_2 electrode to MHPd films, but also redirect the flow of electrons.

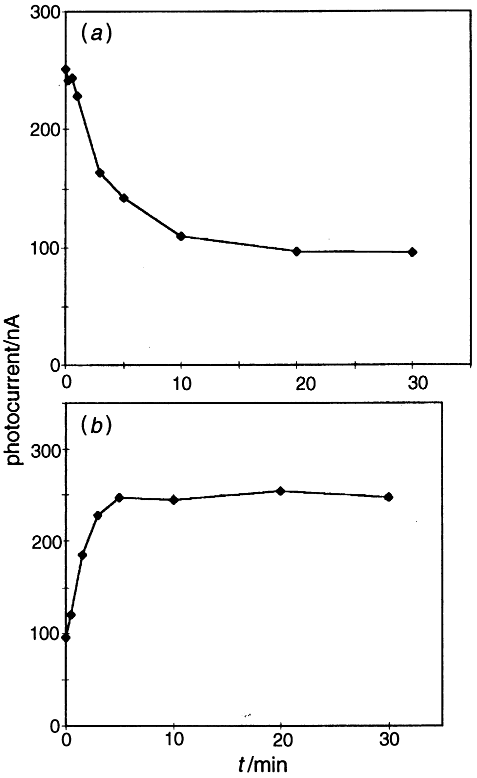


Fig. 5 Effect of oxygen and nitrogen on photocurrent generation [0.5 mol dm^{-3} KCl, degassed conditions for (*a*), ambient conditions for (*b*); light intensity 240 mW cm^{-2}]

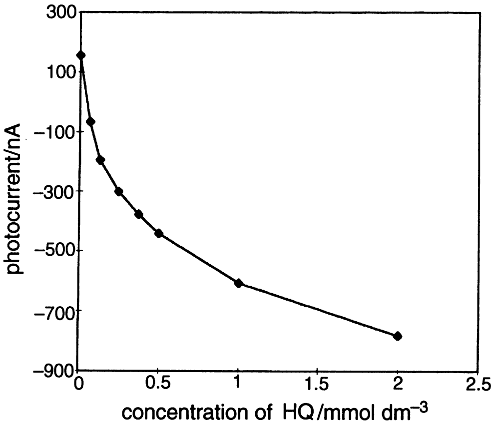


Fig. 6 Effect of hydroquinone on photocurrent generation. (0.5 mol dm^{-3} KCl, nitrogen degassed conditions, light intensity 240 mW cm^{-2})

For the electron acceptor methyl viologen diiodide, the opposite effect was found (Fig. 7). Methyl viologen diiodide ($E^{A/A^-} = -0.23$ *vs.* Ag/AgCl) increased the cathodic photocurrent markedly and stabilized the photocurrent at the enhanced value. The photocurrent increased gradually with increasing concentration of MV^{2+}. This means that MV^{2+} acted as a supersensitizer in accepting electrons from the MHPd assemblies and therefore increased the concentration of electrons involved in the electron transfer process. The levelling off of the increasing effect began at 10 mmol dm^{-3} where the photocurrent was *ca.* 1300 nA. The effects of both hydroquinone and methyl viologen diiodide have provided further support for our conclusions.

However, ascorbic acid which we supposed to be an electron donor [$E^{D^+/D} = +0.10$ *vs.* Ag/AgCl (red.)], resulted in an unexpected increase of the cathodic photocurrent from

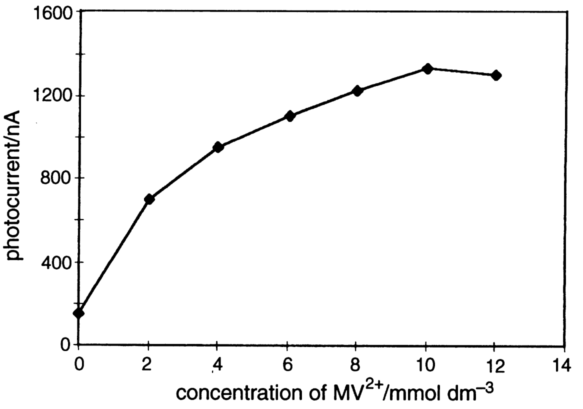


Fig. 7 Effect of methyl viologen diiodide on photocurrent generation. (0.5 mol dm^{-3} KCl, degassed conditions, light intensity 240 mW cm^{-2})

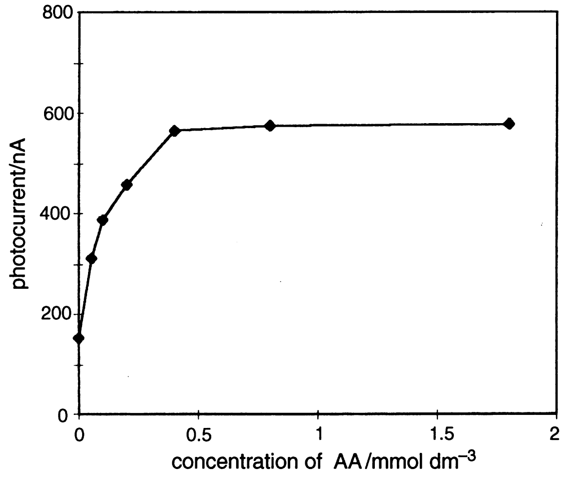
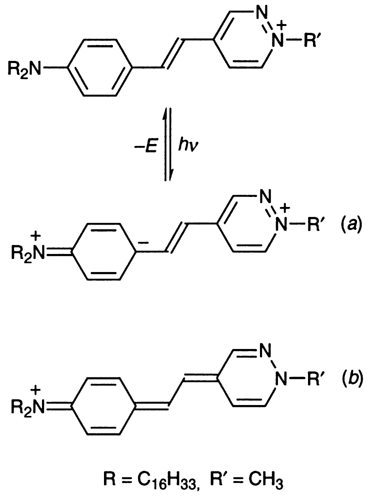


Fig. 8 Effect of ascorbic acid on photocurrent generation. (0.5 mol dm^{-3} KCl, degassed conditions, light intensity 240 mW cm^{-2})

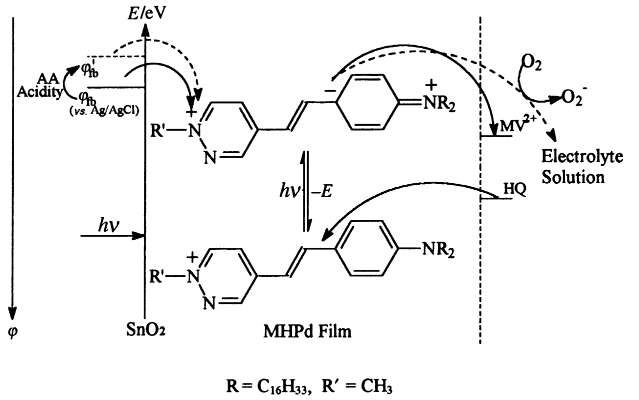
ca. 150 nA to *ca.* 580 nA (Fig. 8). We attribute this unusual observation to the acidity of ascorbic acid whose pK_a is *ca.* 4.3.[27] Evidence supporting this is as follows: (1) calculations show that 0.4 mmol dm^{-3} of AA brings the pH of the solution to 3.93; (2) pH variations caused by $>$0.4 mmol dm^{-3} AA are much smaller than those caused by $<$0.4 mmol dm^{-3} AA; (3) in a Britton–Robinson electrolyte solution, the peak photocurrent increased from *ca.* 300 nA at pH 6.5 to 1278 nA at pH 4.0; (4) our previous work had proven that pH can affect the ϕ_{fb} (flat band potential) of SnO$_2$ and the acidic environment is thus beneficial to cathodic photocurrent generation. The levelling off of photocurrent, which begins at 0.4 mmol dm^{-3} AA, may result from the combination of positive AA effect and the negative acidic effect, which was slowed by the smaller pH difference.

Mechanism of photocurrent generation

In terms of the stilbene compounds, there are two possible states they may adopt after illumination with light or absorption of energy: a geometry change, such as *trans–cis* isomerization,[22] and electron redistribution, *e.g.* charge separation or valence tautomerization. In the case of facile *trans–cis* isomerization, a marked decrease of the *trans–cis* quantum yield ($\phi_{t\text{–}c}$) was found when the amino group was dimethyl substituted ($\phi_{t\text{–}c}$ was $<$0.001, and the *cis* component was $<$2%). It can be reasonably assumed that when the amino group is dihexadecyl substituted, like in MHPd, the large hindrance can result in an even smaller $\phi_{t\text{–}c}$ and a smaller *cis* component. Therefore facile *trans–cis* isomerization may not be the pathway taken by MHPd. Calculations[22] show that the dimethyl-substituted aminostilbene has enhanced double-bond character of the central ethenic bond in the first excited singlet state compared with the ground state, whereas the reverse was found for the unsubstituted stilbene. Therefore, for dihexadecyl-substituted amino MHPd, the central ethenic bond may have enhanced double-bond character. Thus the electron redistribution may lead to the charge separated state (*a*) but not to valence tautomerization state (*b*) which results in reduced double-bond character in the central ethenic bond, as shown in Scheme 1.



Scheme 1



Scheme 2

The proposed mechanism for the electron transfer process can be described as shown in Scheme 2. MHPd was transformed to MHPd* (excited state) after irradiation with white light. The higher energy level of the excited state allowed the overlap of the energy of MHPd* and E_{CB} (energy of the conducting band) of SnO$_2$. According to the Frank–Condon principle, the only possibility under these circumstances is electron transfer between the SnO$_2$ substrate and MHPd* in the LB films. As shown in Scheme 2, electrons flow from the SnO$_2$ semiconductor to the excited state of MHPd* in the LB films and the excited state loses electrons to the electrolyte. The MHPd* acts like an electron transporter. Whatever factors cause this to occur, as long as they can improve the electron transporting ability, they may enhance the photocurrent MV^{2+}, for example, can accept electrons from the exited state, and it increases the cathodic photocurrent. HQ, which donates electrons to the ground state of MHPd, prohibits the flow of electrons from SnO$_2$ to MHPd*, thus resulting in a reduced photocurrent and even reversing the electron flow. AA, which increased ϕ_{fb} to a higher energy level, caused electrons to flow from SnO$_2$ more easily. Thus, an enhanced photocurrent was observed with the use of AA.

Conclusions

A cathodic photocurrent was obtained from MHPd LB films fabricated on an SnO_2 electrode. The quantum yield for photocurrent generation upon irradiation of the electrode with 450 nm light in 0.5 mol dm^{-3} KCl solution and under ambient conditions is 0.3%. When the MHPd–SnO_2 electrode was subjected to more favourable conditions, such as in an electron acceptor solution of methyl viologen diiodide (10 mmol dm^{-3}) under ambient conditions and with an applied negative bias voltage (-100 mV), the quantum yield increased to *ca.* 0.8–0.85%, because the cathodic photocurrent under these conditions is stronger. The effects of methyl viologen diiodide, ascorbic acid, hydroquinone and the bias voltage support the conclusion that the cathodic photocurrent was produced by the flow of electrons from the SnO_2 electrode through the MHPd assemblies to the electrolyte solution. An electron-separated excited state was considered to be involved in the proposed mechanism for the cathodic photocurrent generation.

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