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Journal of Photochemistry and Photobiology A: Chemistry 93 (1996) 21–25

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A:CHEMISTRY

Transition identification of tailed porphyrin–Mn(III) complex in the near-UV and near-IR regions using surface photovoltage spectrum

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Received 15 March 1995; accepted 22 June 1995

Abstract

The photovoltaic properties and charge transfer process of the tailed porphyrin–Mn(III) complex, meso-mono-[*o*-(4-diethylamino)-butyramidophenyl]triphenyl porphyrin–Mn(III) (MDBPTPPMn(III)Cl), were investigated by surface photovoltage spectroscopy (SPS) and electric-field-induced surface photovoltage spectroscopy (EFISPS) techniques. The absorption spectra in the near-UV and near-IR regions were also assigned.

Keywords: Electron transition; Mn(III) porphyrin; Photovoltage; Field induction

1. Introduction

There is increasing interest among chemists and physicists in metalloporphyrins, because of the unique nature of the coordination chemistry of these materials, their optical characteristics, electron transfer processes and structures which can be used as biological models [1,2]. Manganese(III) porphyrins and iron(IV) porphyrins are isoelectronic; the latter is an important intermediate of haemoglobins during catalytic processes. A thorough understanding of Mn porphyrins would be useful in evaluating the closely related and biologically important Fe system and to obtain a general understanding of metalloporphyrin spectra and structures. Although investigations of porphyrin complexes have been performed [3,4], due to their unusual electronic structure, Mn(III) porphyrins show abnormal absorption bands in the near-IR and near-UV regions in addition to Soret and Q bands, and these bands have yet to be fully identified. It is very important to interpret these bands in order to understand the photocatalysis mechanism and charge transfer processes of porphyrins. Boucher [5] has emphasized their importance in his authoritative review. In this paper, we report our research on the photovoltaic properties and photoconductive behaviour of meso-mono-[*o*-(4-diethylamino)butyramidophenyl]triphenyl porphyrin–Mn(III) (MDBPTPPMn(III)Cl) using surface photovoltage spectroscopy (SPS) and electric-field-induced surface photovoltage spectroscopy (EFISPS) and give a new assignment for the near-UV and near-IR bands.

2. Experimental details

2.1. Preparation and characterization of samples

The synthetic method and characterization of MDBPTPPMn(III)Cl (Fig. 1) have been reported in Ref. [6]. The UV–visible absorption spectra of the samples were recorded on a Shimadzu-3100 spectrometer.

2.2. SPS and EFISPS

The surface photovoltage (SPV) was measured with a home-built apparatus described in Ref. [7]. The electrode was made of optical glass coated with indium and tin oxides (ITO). The photovoltage cells consisted of an ITO/sample(solid)/ITO sandwich structure. Sample thicknesses were about 10 μm. All experiments were carried out at room temperature (approximately 20 °C). The effects of the light

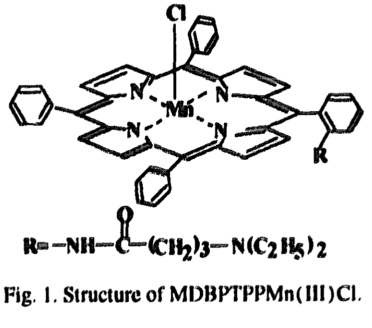

Fig. 1. Structure of MDBPTPPMn(III)Cl.

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SSDI 1010-6030(95)04142-7

source and ITO film were corrected by computer programming.

EFISPS is a technique which combines the field effect principle with SPS. With a d.c. electric field applied to the two sides of the sample, the mobile direction and diffusive distance of photogenerated charge carriers can be varied, and the built-in field of the sample surface also changes. Therefore the electric field affects the SPV response of the sample in two ways: (1) in the dark, the directional motion of the free charge carriers and partially tied charges alters the charge density in the space-charge region and the electronic state of the atoms or molecules on the surface, and affects the absorption of the sample; (2) on illumination, the direction (positive or negative electric field) and intensity of the external electric field control the mobile direction of the photogenerated electrons and holes and the diffusion length of the charge carriers, producing a partial imbalance of charge. These two factors directly affect the response intensity of SPS and the photovoltaic characteristics. An external electric field affects free and localized photogenerated charge carriers in different ways. Thus, with the aid of EFISPS, the photoinduced charge transfer process can be detected clearly, and the spectral characteristics can be interpreted.

3. Results and discussion

3.1. Characteristics of UV–visible absorption

Mn(III) porphyrins show a striking exception to normal metalloporphyrin spectra, such as Fe(III) porphyrins, which is probably related to the strong interaction of the metal d orbital with the porphyrin π orbital. For the Mn(III) ion of D_{4h} symmetry, the $e_g(d_{xz},d_{yz})$ orbital is of appropriate symmetry to interact with the $e_g^*(\pi)$ orbital of the porphyrin. The most favourable geometry for metal–ligand π overlap occurs when the metal is in the plane of the porphyrin. Since Mn(III) has a high-spin d^4 configuration, the four lowest energy d orbitals are singly occupied and the strongly antibonding $b_{1g}(d_{x^2-y^2})$ orbital remains empty. The energy of the $a_{1g}(d_{z^2})$ metal level will depend on the axial anion, whereas the $b_{2g}(d_{xy})$ level is non-bonding. Not only is the $\pi\rightarrow\pi^*$ spectrum altered, but a number of charge transfer bands are observed in the spectrum because of the metal–porphyrin π mixing [5].

The UV–visible absorption spectrum (full line) and SPV response (broken line) of MDBPTPPMn(III)Cl are given in Fig. 2. The absorption is typical of Mn(III) porphyrins, i.e. consistent with the absorption spectrum of the five-coordinate MnTPPCl complex [3], indicating that the Mn(III) ion enters into the porphyrin ring and the tailed nitrile base does not coordinate with the central Mn(III) ion. Boucher [5] has assigned some of the Mn(III) porphyrin absorption bands: band I, between 550 and 620 nm, is the Q band corresponding to the $a_{2u}(\pi)\rightarrow e_g^*(\pi)$ transition, while band II at 460 nm is the Soret band which is an $a_{1u}(\pi)\rightarrow e_g^*(\pi)$ transition.

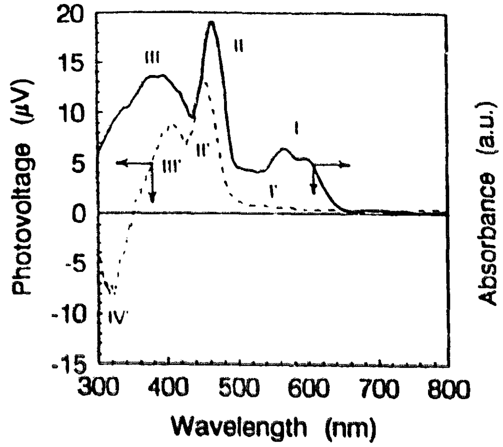

Fig. 2. UV–visible absorption spectrum (full line) and SPV response (broken line) of MDBPTPPMn(III)Cl.

The broad absorption band in the 300–450 nm region was not given a definite assignment.

3.2. Measurement of SPS

Mn(III) porphyrins, as conjugated π systems, have obvious organic semiconducting characteristics. The bonding π orbital is analogous to the valence band and the antibonding π orbital to the conduction band. Photogenerated charge carriers in the π system are non-localized; their motion is free within the energy band of the π system. Photogenerated holes move in the valence band, and photogenerated electrons in the conduction band. For this kind of system, the band to band transition is characterized as a $\pi\rightarrow\pi^*$ transition exhibiting chiefly Soret and Q bands. The broken line in Fig. 2 shows the photovoltage response of MDBPTPPMn(III)Cl in the 300–520 nm region; the Soret band manifests a strong positive photovoltage response, while the Q band does not show an SPV response.

The signal detected by SPS is equivalent to the change in the surface potential barrier on illumination: $\delta V = V'_s - V_s^0$. V'_s and V_s^0 are the surface potential heights before and after illumination respectively. As far as band to band transitions are concerned, a positive response of SPV ($\delta V > 0$) means that the sample is characterized as a p-type semiconductor, whereas a negative response means that the sample is an n-type semiconductor. The photoinduced charge transfer, electron–hole separation and change of V_s in p-type MDBPTPPMn(III)Cl are shown in Fig. 3. E_c, E_v and E_f are the minimum energy of the conduction band, the maximum energy of the valence band and the Fermi energy level respectively. E_m is the occupied orbital (a) or empty orbital (b), and E_g is the forbidden bandwidth. Fig. 3(a) illustrates the charge transfer process with positive SPV response. Band to band transitions occur when $h\nu \geqslant E_g$; electrons are excited to the conduction band, while holes are left in the valence band. Under the action of the built-in field, holes in the valence band move towards the bulk, while electrons in the conduction band diffuse to the surface, resulting in a net positive

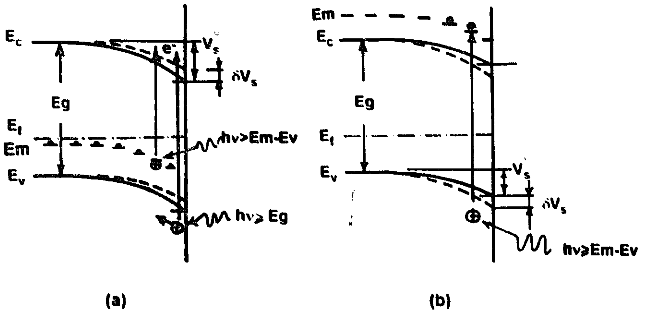

Fig. 3. Photoexcitation and photogenerated charge transfer processes in MDBPTPPMn(III)Cl: (a) response of SPV is positive; (b) response of SPV is negative.

charge in the space-charge region; band bending decreases and δV_s is positive. Comparing the two curves in Fig. 2, it can be seen that the broad absorption in the 300–450 nm region is divided into positive ($P_{III'}$) and negative ($P_{IV'}$) photovoltage response bands. Boucher [5] deduced that band III could be attributed to mixing transitions of $a_{1u}(\pi),a_{2u}(\pi) \rightarrow e_g^*(\pi)$ and $a_{2u}(\pi),b_{2u}(\pi) \rightarrow e_g(d\pi)$; however, he did not identify this mixing transition and did not explain the positions corresponding to the two kinds of transition. The SPV result indicates that absorption band III is not due to mixing transitions; it should be assigned to two kinds of transition with independent and different mechanisms. The photovoltage response of $P_{III'}$ is similar to that of $P_{II'}$ which can be attributed to a $\pi \rightarrow \pi^*$ transition. In view of its higher excitation energy, $P_{III'}$ should be an $a_{1u}(\pi)$ or $b_{2u}(\pi) \rightarrow e_g^*(\pi)$ transition, while $P_{IV'}$ is negative and involves a more complex process. According to the principles of SPS, a negative SPV response of p-type materials indicates that photoinduced transitions result in a net negative charge increase in the space-charge region or positive charge accumulation at the surface. The result can be attributed to the processes shown in Fig. 3(b). Since the E_m energy levels are localized, π electrons photoexcited to the empty orbitals of the metal (E_m) in porphyrins are tightly bound, while holes in the valence band are non-localized. Different diffusion velocities and directions of electrons and holes result in an increase in negative charge in the space-charge region. This is the so-called Dember effect [8]. From the point of view of energetics, this transition can be assigned to $a_{2u}(\pi)$ or $a_{1u}(\pi) \rightarrow b_{1g}(d_{x^2-y^2})$ which is called a ligand to metal charge transfer (LMCT) transition.

Generally, the Soret bands and Q bands of porphyrins and phthalocyanines show strong photovoltage or photovoltaic current, but the Q bands of Mn(III) porphyrins do not exhibit a photovoltage response and show abnormal characteristics. A very rapid decay of the absorption in the 500–600 nm region following photoexcitation has been observed [9–11], with lifetimes of 17 ps for Mn(III)TPPCl and 55 ps for Mn(III)mesoP(Cl). The SPV spectrum is a type of action spectrum, its signal intensity being directly proportional to the optical absorption and lifetime of an excited state. Usually, when the lifetime of an excited state τ is more than 10^{-9} s, obvious photovoltage can be observed. This confirms the results given in Refs. [9–11].

3.3. Measurement of EFISPS

The SPV response with different external electric fields is given in Fig. 4. The response of $P_{II'}$ increases linearly with positive electric fields (see Fig. 4(a)), which demonstrates that the external electric field is of the same sign as the built-in field, further indicating the p-type characteristics of the material. Comparing Figs. 4(a) and 4(b), we find that $P_{III'}$ and $P_{II'}$ exhibit a "simultaneous response" with a change in the positive or negative electric field intensity. The SPV response is positive in a positive electric field, but negative in a negative electric field. A simultaneous response to the electric field indicates that $P_{III'}$ and $P_{II'}$ can both be assigned to $\pi \rightarrow \pi^*$ transitions. However, the rate of variation of $P_{III'}$ and $P_{II'}$ with an increase in the positive or negative electric field intensity is noticeably different. A large positive increase in the SPV response with positive electric field is observed for $P_{III'}$, while $P_{II'}$ exhibits a fast negative increase along the negative direction. Because the common upper energy level transition in the π system is $e_g^*(\pi)$, the difference stems from the lower energy levels. This phenomenon shows that the lower energy levels of these transitions are at different depths from the valence band, indicating different photogenerated hole diffusion lengths. It can also be seen in Fig. 4(a) that the response of the Q band is induced in a positive electric field. Consistent with the Soret band, this is due to the fact that the external electric field reduces the recombination rate of photogenerated charges and prolongs the lifetime of the excited state. Moreover, it can also be seen in Fig. 4 that $P_{IV'}$ almost disappears with increasing positive electric field and increases by an order of magnitude in a negative field. With a positive electric field, the holes in the valence band diffuse towards the bulk, which increases the probability of recombination with localized electrons, resulting in a decrease in the SPV response. With a negative field, holes in the valence band are drawn to the surface, which reduces the recombination rate of photogenerated electron–hole pairs, leading to negative charge in the space-charge region. This result con-

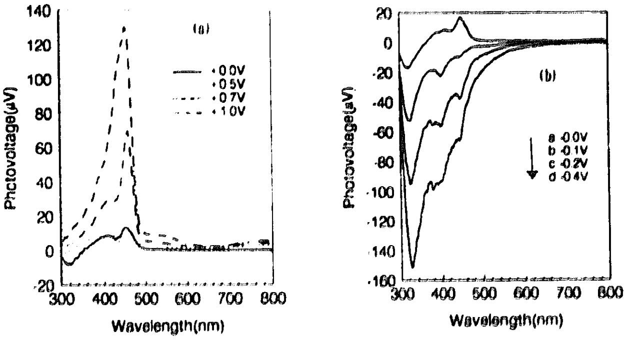

Fig. 4. SPV response of MDBPTPPMn(III)Cl for different external electric fields: (a) different positive electric fields; (b) different negative electric fields.

firms that $P_{IV'}$ corresponds to an LMCT transition. In addition, a new photovoltage response band appears in the 800–1000 nm region, which may belong to another type of transition (see below).

3.4. Photovoltage response in near-IR region

MDBPTPPMn(III)Cl shows two weak absorption bands at 810 and 930 nm in the near-IR region. These bands are characteristic of Mn(III) porphyrins. The origin of these bands has been disputed for some time. Baker and Perumareddi [12] attributed these bands to d–d transitions of Mn^{3+} ions, while Boucher [11] assigned them to transitions from the π orbitals of the porphyrin to the d orbital of the metal: $a_{1u}, a_{2u} \rightarrow e_g(d\pi)$. However, the results of SPS in different electric fields suggest a different mechanism. The SPV response in the near-IR region is shown in Fig. 5. The photovoltage response at 810 nm (P_1) and 930 nm (P_2) is called P_{ir}. Although the intensities of P_1 and P_2 are different, their responses to the external electric field are similar. This indicates that these transitions are identical. P_{ir} is positive without an external electric field, increases with a positive external electric field and decreases with a negative external electric field. Comparing Figs. 5 and 4, it is found that the SPV response in the near-IR region is not only different from $P_{II'}$ and $P_{III'}$, which show symmetrical reversal with positive or negative fields, but also different from $P_{IV'}$ which exhibits a negative value. This indicates that P_{ir} cannot be attributed to $\pi \rightarrow \pi^*$ transitions or LMCT transitions. We can illustrate the photovoltaic process of P_{ir} using Fig. 3(a). E_m may be d_{z^2}, d_{xz} and d_{yz}. After illumination ($h\nu > E_c - E_m$), the electrons in these energy levels are excited to the conduction band (π^*) and localized positive charges are produced on E_m. Due to the Dember effect and the influence of the built-in field, electrons in the conduction band diffuse to the surface, resulting in excess positive charge in the space-charge region and a positive SPV response. With a positive electric field, the built-in field is enhanced, increasing the diffusion length of electrons in the conduction band, more electrons reach the surface and the response of P_{ir} increases. With a negative electric field, electrons in the conduction band move towards the bulk, partly neutralizing the positive charge on E_m, and therefore the SPV response decreases. Results of EFISPS and photovoltaic experiments indicate that P_{ir} can be attributed to a transition from the d orbital of the Mn(III) ion to the π^* orbital of the porphyrin. The transition is therefore a metal to ligand charge transfer (MLCT) transition. Energetically, peak P_1 corresponds to a $d_{z^2} \rightarrow e_g^*(\pi)$ transition, while peak P_2 corresponds to a $d_{xz}, d_{yz} \rightarrow e_g^*(\pi)$ transition. According to the above interpretation, the charge transfer processes and absorption bands of MDBPTPPMn(III)Cl are illustrated in Fig. 6.

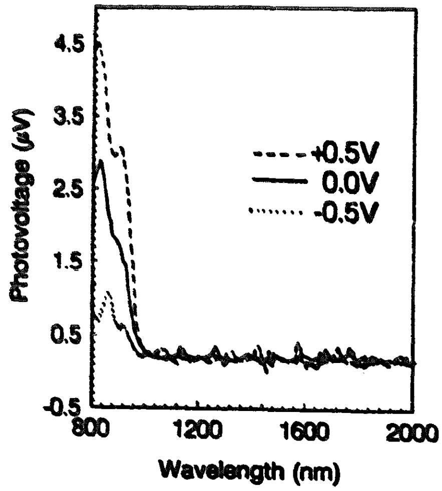

Fig. 5. SPV response of MDBPTPPMn(III)Cl in the near-IR region.

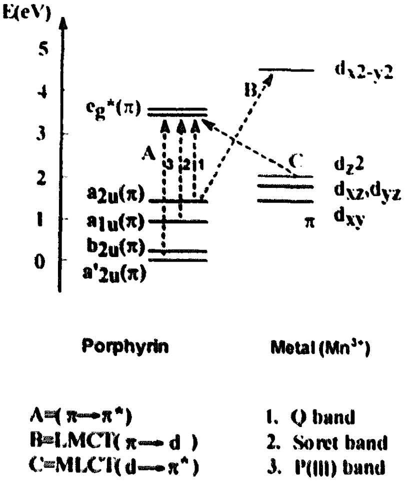

Fig. 6. Molecular level diagram and absorption band assignment for MDBPTPPMn(III)Cl.

4. Conclusions

Studies on the surface photovoltaic properties of the tailed porphyrin–Mn(III) complex MDBPTPPMn(III)Cl have provided new evidence for interpreting the electronic structure of the porphyrin as an organic semiconductor. The charge carriers in the porphyrin and their mobilities were also characterized with the help of EFISPS.

Acknowledgment

This reserch was supported by the National Science Foundation of China.

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