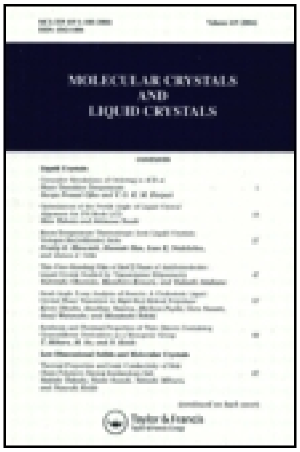

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Photoelectric Conversion by Monolayer Assemblies

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PHOTOELECTRIC CONVERSION BY MONOLAYER ASSEMBLIES

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Abstract Simulation of photoelectric conversion in the photosynthetic reaction center by monomolecular layer assemblies of a folded or a linear type A-S-D triad carried out in this laboratory is reviewed. The oriented triad molecule acts as a charge separation unit and is named a molecular photodiode. The combined system with the linear triad and an antenna pigment is also discussed in terms of the charge separation and the light harvesting.

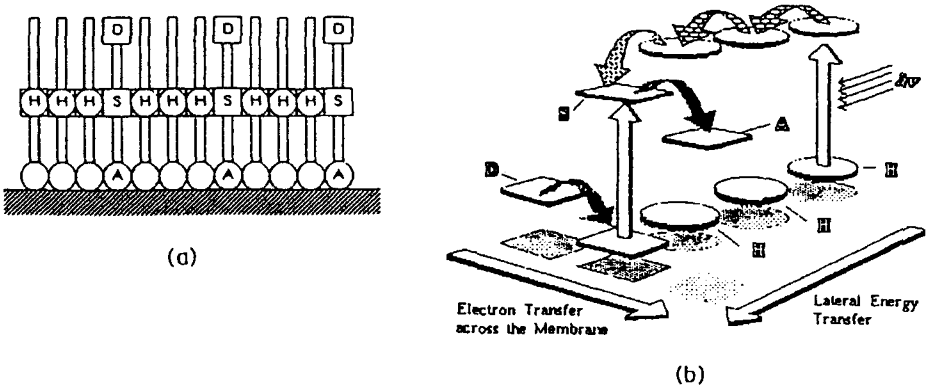
INTRODUCTION

In biosystems the molecules organize themselves into complex functional entities with coorperating components of molecular dimensions. In the photosynthetic reaction center, solar energies harvested by antenna pigments are funneled to the special pair, where multi-step electron transfer reactions proceed to separate an electron-hole pair far apart across the lipid bilayer thylakoid membrane. The well-organized and asymmetric molecular arrangement across the membrane paly an important role in charge separation in photosynthesis.[1-4] For the design of artificial photosynthetic molecular devices,[5-10] it is of great interest to mimic the elaborate molecular machinery.

Recently, intramolecular electron transfer reactions have also been studied intensively by several groups[11-15] in connection with photosynthesis. Some groups have investigated the two-step photodriven charge separation and back electron transfer reactions of triad molecules[16-18] of the $S\text{-}A_1\text{-}A_2$ or A-S-D types, where A, S, and D denote an electron acceptor, a sensitizer and an electron donor moiety, respectively, and reported that the lifetimes of the final charge-separated states $S^{+}\text{-}A_1\text{-}A_2^{-}$ and $A^{-}\text{-}S\text{-}D^{+}$ were much longer than those of the two-component intramolecular systems.[11-15] For the effcient charge separation, the present theory of electron transfer[19] predicts that the distances, the orientations, and the energy gaps are the most important factors determining the electron transfer rates.

The dependence of the rates on the distance has been studied with chemically modified electrodes,[20-22] Langmuir-Blodgett (LB) films,[6,8] and intramolecular A-D systems with rigid hydrocarbon spacers.[23,24] The rates for all cases decreased exponentially with an increase in their distances. The inverted parabolic energy gap law was predicted theoretically by Marcus[19] and recently confirmed experimentally with intramolecular systems with a constant distance and an identical mutual orientation.[25]

In a series of works,[26-30] we have tried to simulate the light harvesting and the succeeding charge separation processes by a monomolecular layer assembly consisting of synthetic antenna pigments and triad molecules as illustrated in Figure 1. These synthetic amphiphilic triad mole-



(a)

(b)

FIGURE 1 Schematic representaion of artificial photosynthetic reaction center by monolayer assembly of antenna and A-S-D triad molecules for light harvesting (H), energy migration and transfer, and charge separation via multi-step electron transfer. a, side view of monolayer assembly; b, energy diagram for photoelectric conversion in a monolayer assembly.

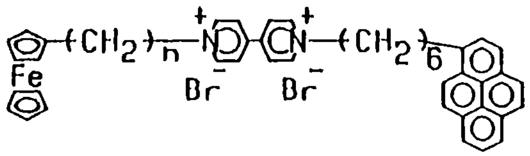
cules have three functional moieties within a molecule, i.e. a hydrophilic electron-acceptor viologen (A), a hydrophobic sensitizer pyrene or perylene (S) and a hydrophobic electron-donor ferrocene (D) moiety. The amphiphilic antenna molecule has a light harvesting pyrene (H) moiety in the middle of the alkyl chain of fatty acid. Because of overlap of the emission spectrum of the antenna pyrene and the absorption spectrum of the sensitizer perylene moiety of the triad, light energies harvested by the antenna molecules were efficiently transferred to the sensitizer moiety of the triad and finally converted to electrical energies via multi-step electron transfer across the monolayer through the charge separation unit of the triad molecule in the highly oriented monolayer assembly.

MOLECULAR PHOTODIODES CONSISTING OF UNIDIRECTIONALLLY ORIENTED AMPHIPHILIC FOLDED TYPE TRIADS S-A-D

In this section, the photodiode function played by highly oriented triad molecules of the folded type[26,27] is described. The molecular structure of the folded type triad is shown in Figure 2 together with the linear type triad. The photodiode consists of a monolayer of unidirectionally oriented triad 1 or 2 deposited on a gold semitransparent electrode. Subunits A and S were linked together with a C_6 alkyl chain, while subunit D was linked to subunit A with another longer C_{11} or C_{16} alkyl chain.

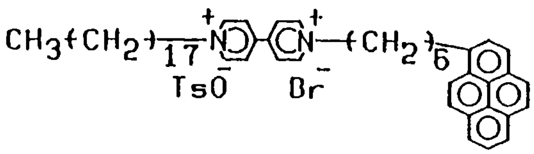
The energy conversion from light into vectorial electricity could be successfully attained at molecular levels by utilizing a tendency of the amphiphilic triads to be oriented unidirectionally at any phase boundary. It seems quite reasonable from the surface pressure dependence of the efficiency of the photoinduced charge separation in this type of molecular device to assume that, when the triad monolayer was deposited at high surface pressure, the A, S, and D units were located in this order perpendicularly from the electrode surface as depicted in Figure 3.

A higher efficiency of triad 2 than that of triad 1 was



n = 11 : 1

n = 16 : 2



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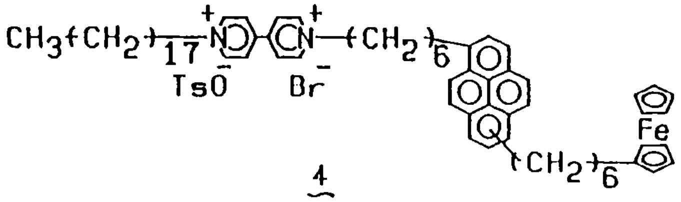

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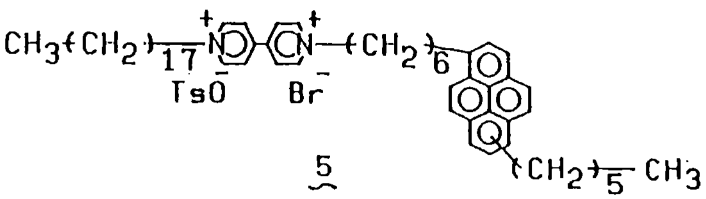

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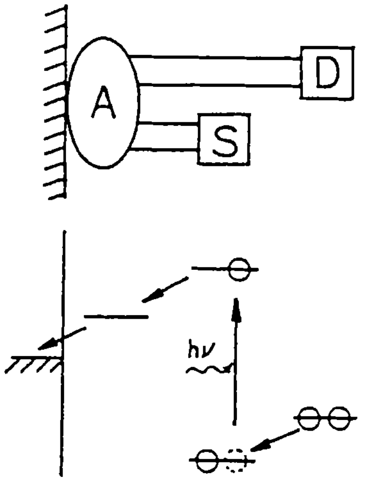
FIGURE 2 Structural formulae of amphiphilic triads and their reference compounds.



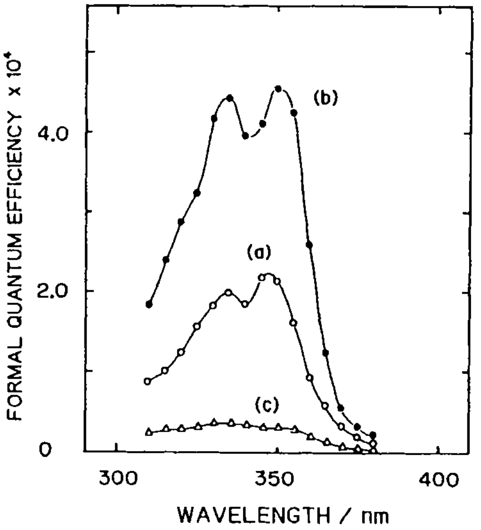


FIGURE 3 Schematic representation of oriented folded type triad at an AuOTE-aqueous electrolyte interface and corresponding energy diagram.

FIGURE 4 Effect of chain length and the presence of the D moiety on the photocurrent: spectrum a, triad 1; spectrum b, triad 2; spectrum c, compound 3.

also observed, which might be attributed to a better matching in concurrent electron transfer reactions between A and S and between S and D owing to an improved balance between the A-S and S-D distances.

Another amphiphilic compound 3 without the D moiety was also synthesized to confirm a positive contibution of the D moiety in triads 1 and 2. In Figure 4, photocurrent spectra normalized to the number of incident photons for the mixed monlayer of 1, 2, or 3 with arachidic acid (1:2) are shown.

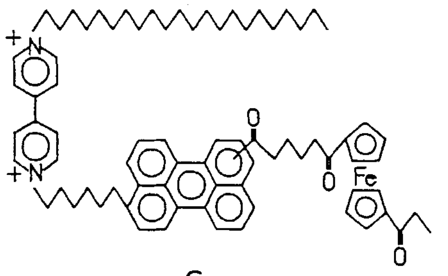
MOLECULAR PHOTODIODES CONSISTING OF UNIDIRECTIONALLLY ORIENTED AMPHIPHILIC LINEAR TYPE TRIADS A-S-D

The more efficient electrochemical photodiode than the folded type S-A-D was successfully fabricated by depositing a mixed monolayer of a liner triad A-S-D 4 with behenic acid.[28] Three functional moieties, i.e. the A, S, and D moiety, were linked covalently one another by normal hydrocarbon chains in the form of A-S-D in this linear triad. The higher efficiency indicates that the more ideal spatial arrangement of the A, S, and D moiety were attained in the linear triad molecules in the mixed monolayer. The favorable orientation for the photoelectric conversion of the linear triad molecule was also accomplished at a relatively low surface pressure of 15 mN m^{-1} in contrast with the inactive orientation of the folded triad molecule deposited at this surface pressure. The importance of the presence of the D moiety was again confirmed by comparison of the photoelectric conversion efficiency of the linear triad and that of a reference compound 5.

SIMULATION OF THE PRIMARY PROCESS IN PHOTOSYNTHETIC REACTION CENTER BY MONOLAYER WITH TRIAD AND ANTENNA MOLECULES

Absorption and Fluorescence Spectra

In Figure 6, the UV and visible absorption and fluorescence spectra of the dialkylpyrene derivative 7 in Figure 5 as the



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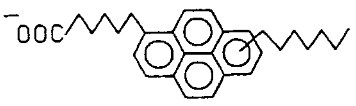

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FIGURE 5 Structural formulae of amphiphilic triad 6 and antenna 7 molecules.

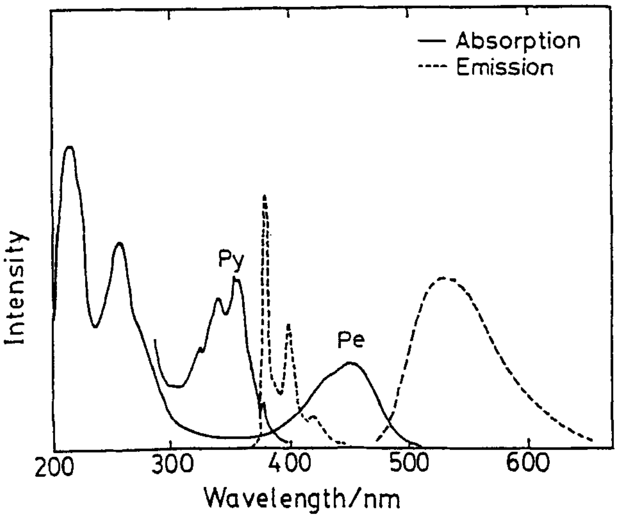

FIGURE 6 UV and visible absorption (soild lines) and fluorescence (dashed lines) spectra of antenna pyrene 7 and monoacylperylene derivative in ethanol.

antenna pigment[29] and the monoacylperylene derivative in ethanol are shown. The perylene derivative was obtained by Friedel-Crafts acylation of perylene with 6-bromohexanoyl chloride as an intermediate product to synthesize triad A-S-D 6 and did not contain the A and D moieties. The partial overlap of these bands indicates that excitation energies for the pyrene antennas ranging from 300 to 380 nm, where very little absorption was observed for the perylene moiety, shall be transferred to the perylene moiety in the charge separation unit of the perylene triad 6.[30] The fluorescence spectra of the pure and mixed cast films of the perylene with the pyrene derivative support concomitance of the energy transfer and the direct excitation mechanism for the 530 nm emission from the perylene moiety as follows.

Energy transfer mechanism:

$$\text{Py} + h\nu \text{ ----> } \text{Py*} \quad (1)$$

$$\text{Py*} + \text{Pe} \text{ ----> } \text{Py} + \text{Pe*} \quad (2)$$

$$\text{Pe*} \text{ ----> } \text{Pe} + h\nu' \quad (3)$$

Direct excitation mechanism:

$$\text{Pe} + h\nu'' \text{ ----> } \text{Pe*} \quad (4)$$

$$\text{Pe*} \text{ ----> } \text{Pe} + h\nu' \quad (3)$$

As described above, the energy transfer from the antenna pyrene to the sensitizer monoacylperylene molecules in the condensed phase was confirmed. Therefore, quenching of the excited antenna molecules by the perylene triad in a mixed monolayer assembly was examined next. The result strongly supports our expectation that the harvested excitation energies were transferred to the perylene moiety of the perylene triad 6 and the succeeding charge separation proceeded very rapidly. The latter rapid charge separation process accounts for disappearance of the emission from the perylene moiety in the mixed monolayer in contrast with the cast film of the perylene derivative described above.

Photocurrents by Monolayer Assemblies consisting of Antennas and Triads

Photocurrents of the mixed monolayer of A-S-D and antenna pigments and the pure monolayer of antenna itself deposited on gold semi-transparent electrodes (AuOTE) at 20 mN m^{-1} were recorded by using the electrochemical cell previously reported.[20,31] Figure 7 shows the photocurrent - time re-

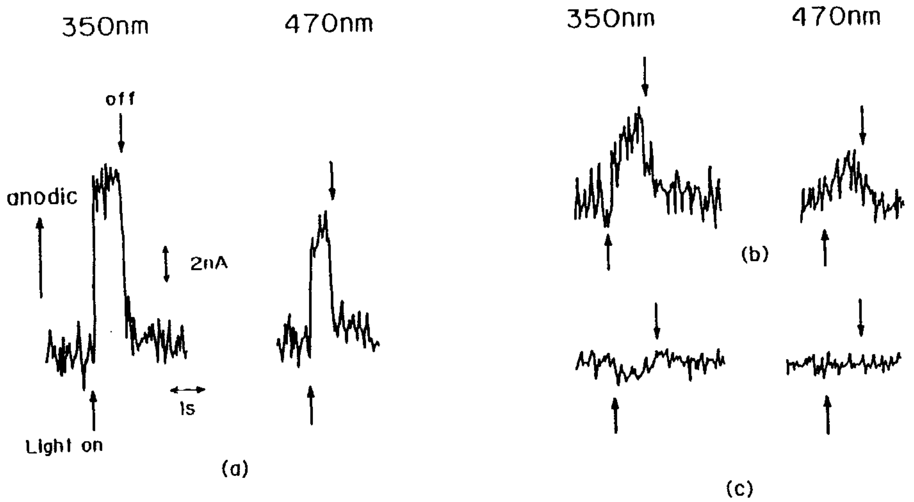

FIGURE 7 Photocurrent - time curves of the mixed monolayers of antenna 7 and triad 6 with molar ratio of (a) 4:1 and (b) 50:1 and (c) the pure antenna 7 monolayer.

sponse caused by stepped illumination with light of wavelengths 350 and 470 nm under a controlled potential at + 0.2 V with respect to a saturated calomel electrode (SCE). Both of the mixed monolayers of the molar ratio of antenna to triad 4:1 and 50:1 exhibited the anodic photocurrents with 350 and 670 nm excitation corresponding to the absorption maxima of the pyrene and the perylene moieties.[30]

The anodic direction of the photocurrent agreed with our expectation from the energy diagram and the orientation of triad shown in Figure 1. This indicates that charge separation in the triad molecules was initiated by light absorption both with the perylene sensitizer itself and with the pyrene antennas followed by the energy transfer. The photocurrent spectrum of the mixed monolayer with the molar ratio of 4:1 shown in Figure 8[30] further substantiates the

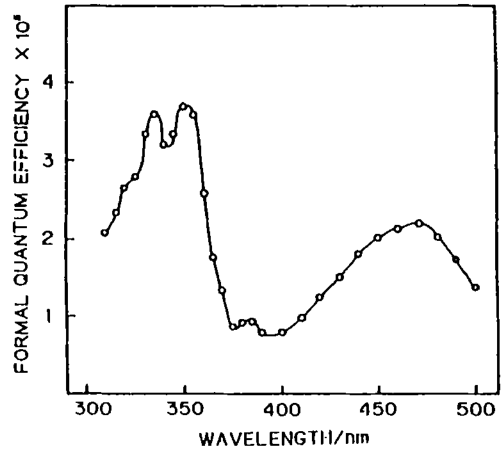

FIGURE 8 Photocurrent spectrum of the mixed monolayer of antenna 7 and triad 6 with molar ratio of 4:1.

present idea. Namely, the fluorescence band of the antenna pyrene was fairly overlapped with the UV absorption band of the perylene (Pe) moiety of A-S-D, hence the efficient energy transfer from photoexcited Py^* to Pe resulted. Accordingly, the charge separation in the A-S-D triad was observed under the illumination of light whose wavelengths were those in the absorption bands of pyrene antennas as well as those in the bands of the perylene moiety in A-S-D. In contrast with negligible photoresponse with the pure antenna monolayer, the anodic responses observed in the presence of 2 mol % of triad confirmed the validity of the present molecular design.

CONCLUSION

The experimental results indicate that light harvesting by antenna pigments followed by energy transfer and succeeding charge separation in the reaction center in the photosynthetic primary process can be simulated artificially by monomolecular layer assemblies of synthetic antenna pigments and triads.

ACKNOWLEDGMENT

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