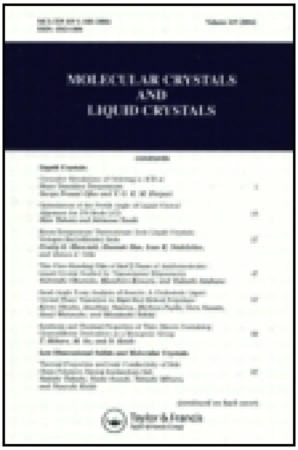

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Conversion of Light into Electrical Power in a Molecular Layer Structure

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CONVERSION OF LIGHT INTO ELECTRICAL POWER IN A MOLECULAR LAYER STRUCTURE*

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Abstract A stepwise change in the standard redox potential with a total drop of about 0.5 eV has been realized in a molecular structure containing 3 different chromophores in successive molecular layers. With red light the molecular structure delivers a current yield of 0.3 holes per absorbed photon. Current yield and power conversion efficiency of the molecular converter are expressed in simple formulas in terms of experimentally accessible quantities.

INTRODUCTION

Separation of photo-generated electron-hole pairs in a downhill potential gradient is an essential feature of semiconductor solar cells achieving conversion of light into electrical power (1). A similar downhill electron-hole pair separation can be realized in a molecular system through a stepwise change in the electrochemical standard redox potential along a molecular chain of acceptors for the mobile electron (or donors for the mobile hole). Such a downhill

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**permanent address: Afdeling Organische Scheikunde, Katholieke Universiteit Leuven, Celestijnenlaan 200 F, 3030 Leuven (Heverlee), Belgien reaction sequence occurs in the electron transfer chain of the reaction center of bacterial photosynthesis (2).

An electron transfer chain is not required for a molecular system where efficient electron-hole pair separation is to be achieved without concern for the energy loss. For example electron-hole pair separation with a yield close to 1 has been found for the case of dye sensitized charge injection in the presence of a high applied electric field at the surface of ultrapure anthracene crystals where the mobile hole moves about between identical molecules or sites in the crystal (3,4). In this case the hole has to climb up a Coulombic hill (endergonic reaction sequence) in order to escape from recombination with its counter charge, i.e. the electron on the reduced dye. Yet recombination losses can be suppressed since the rate constant for recombination is in the range of 10^8 s^{-1} in the singlet spin state of the electron hole pair and the effective rate constant for irreversible escape is enhanced to $>10^9$ s^{-1} at applied electric fields $>10^5$ V cm^{-1}.

However, application of a large external voltage as in the above case is prohibitive when aiming at the conversion of light into electrical power since, for carrying out external work, the electrochemical potential of the charge carriers at the exit of the structure is equally as important as the current yield. Therefore, a downhill potential gradient provided by a change in electrochemical standard redox potential along an electron transfer chain is a necessary feature of a molecular device for the conversion of light into electrical energy. The simplest form of such an electron transfer chain comprises 3 chromophores. Moore et al. (5) were the first to report on such a functioning in-vitro electron transfer chain built in the form of a molecular triad.

A macroscopic molecular structure has to consist of a great number of such electron transfer chains. In this case recombination between electrons and holes at opposite ends of neighbouring chains is to be prevented. This is achieved by aligning all the chains in the same direction perpendicular to the surface of the structure.

To fulfill the above requirement in a simple molecular structure we have assembled three different molecular layers on top of each other. An anthracene monolayer followed by a mixed dye arachidic acid monolayer were deposited on top of a vapor grown perylene crystal. By using the surface layer of a single crystal as the third functional monomolecular layer instead of a corresponding third Langmuir-Blodgett film we have been able to utilize experimental techniques (3,4) for the investigation of light driven charge separation at the surface of an organic insulator crystal. In our 3-layer structure electron-hole pairs are generated by excitation of the dye layer with red light. The anthracene layer functions as primary donor and the uppermost molecular layer of the perylene crystal functions as secondary donor for downhill hole transfer. Our paper addresses the question whether such a molecular 3-layer structure can perform directional light driven electron-hole separation. We have not attempted to prepare a practical photovoltaic device.

EXPERIMENTAL SYSTEM

The molecular structure assembled by the Langmuir-Blodgett technique is shown in Fig. 1. Details of the chemical preparation procedures and of experiments revealing the almost vertical orientation of the anthracene molecules with respect to the macroscopic surface of the layer structure will

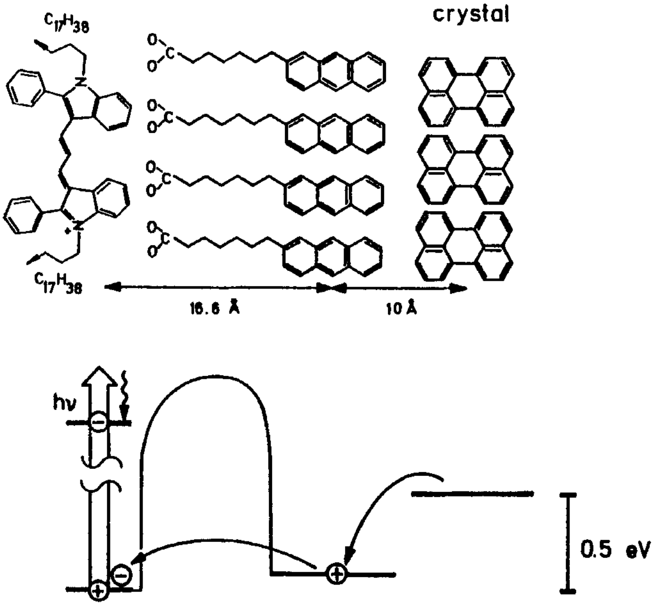

FIGURE 1. The molecular layer structure shown with the differences in the standard redox potentials for the consecutive stages which provide a downhill gradient for hole transfer.

be described elsewhere. The steps in the electrochemical standard redox potential shown below the structure have been estimated as follows.

The change in electrochemical standard redox potential when the hole moves from the excited singlet state of the dye to the surface layer of the perylene crystal is in the range of 0.5 eV downhill. This estimate is based on the following data. The standard reduction potential is about 0 V(NHE) for the dye 2,2-phenylindolocyanine in methanol (6). A relative change in solvation energy by about 30 per cent is expected from the Born approximation (7) when the environment of the dye changes from a dielectric constant 32 to 3 (8) as has been determined for a system similar to our present one. A plausible estimate of the solvation energy of a large aromatic molecule in a solvent with a high dielectric constant appears to be 1.6 eV (7). Thus, in the present environment we expected the reduction potential of the dye shifted to about -0.5 V(NHE). In the excited singlet state this level is shifted by 1.9 eV (6), i.e. to about 1.4 V (NHE). The standard oxidation potential of the surface layer of perylene in contact with water (9, 10) is 0.86 V (NHE) and that of the anthracene crystal 1.33 V (NHE). In a medium with approximately the same dielectric constant, about 3, as the organic crystal these values increase by about 0.25 eV (9). Finally we have to consider the Coulombic attraction between electron and hole in a medium of dielectric constant about 3. At 17 Å distance (hole on the anthracene monolayer) it is about 0.28 eV and at 27 Å distance (hole on the surface layer of perylene) it is about 0.17 eV. Thus, we arrive at a crude estimate of 0.5 eV downhill drop in standard redox energy for the transfer of the hole from the excited singlet state of the dye to the surface layer of the perylene crystal. Since there is an anthracene monolayer in the present system, and not a crystal surface, we expect that the oxidation potential is slightly higher than in the above estimate and the first step is only slightly downhill or even isoenergetic. In Fig. 1 the barrier for hole transfer between anthracene and excited dye serves as an illustration of the actually much more involved reduction in electronic overlap due to the presence of the saturated fatty acid chain (11).

Aqueous contact solutions containing 1M KCl served as electrodes on both sides of the sample. The dye monolayer was separated from aqueous contact by several further layers of Cd arachidate not shown in Fig. 1. The excitation spectrum and current voltage curve of the stationary photocurrent were measured in a conventional set-up previously described (12). The 100 ps time resolved photocurrent transients were measured with the sample mounted on a microstrip using a sampling technique which will be described in detail elsewhere.

REACTION SEQUENCE AND CURRENT YIELD

Fig. 2 gives a comparison of the absorption spectrum (solid curve) of the dye monolayer on a glass slide and of the excitation spectrum of the stationary hole photocurrent (dashed curve) obtained with a similar dye layer (1 dye molecule to 2 arachidic acid molecules) incorporated into the structure as shown in Fig. 1. The solid curve in Fig. 2 was determined from a measurement of the transmission. A

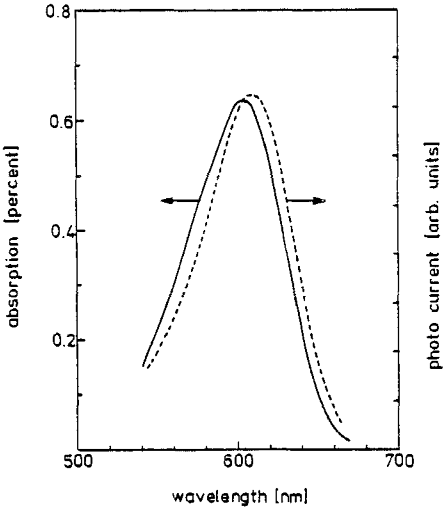

FIGURE 2. Excitation spectrum of the hole photocurrent in the layer structure of Fig. 1 and absorption spectrum of the dye monolayer.

more precise determination of the absorption spectrum would require in addition the measurement of the weak reflected light (13). However, we consider the close similarity of the two spectra in Fig. 2 as sufficient evidence for the generation of electron-hole pairs via the excited singlet state of the dye molecules as is well known in the case of dye sensitized charge carrier injection into organic crystals (3,4,12) and into semiconductors (12). Thus, the reaction sequence of hole transfer occurring in perpendicular direction to the surface of the monolayers is that shown in Fig. 1. As a first approximation we are neglecting here transport processes and reactions that might occur within each of the monomolecular layers.

The stationary photocurrent is plotted in Fig. 3 versus the applied electric field $F = Ud^{-1}$, where U = applied voltage and d = crystal thickness, typically 5 to 10 μm.

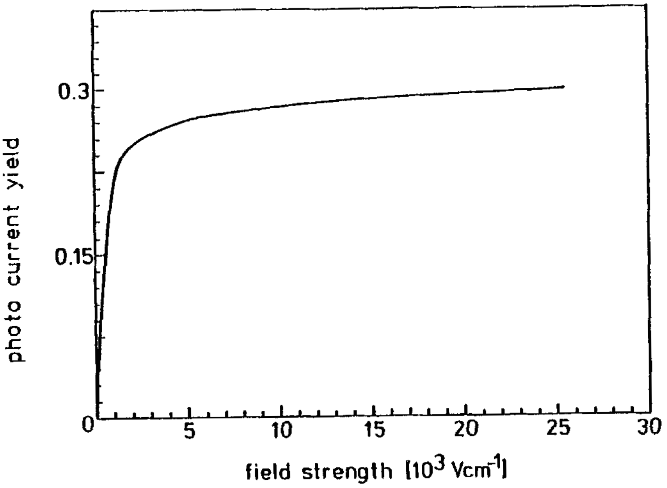

FIGURE 3. Current yield versus applied field strength in the layer structure of Fig. 1.

The shape of the curve in Fig. 3 is typical for charge carrier injection into an organic insulator crystal for the case of negligible non-geminate recombination (10). The steeply rising branch is due to the influence of the injected space charge in the organic crystal. The space charge becomes negligible when the horizontal branch is reached. Only this latter branch is indicative of charge carrier injection at the crystal surface (10) and thus of light-induced electron hole pair separation in the 3 layer structure on top of the crystal. The weak remaining increase at field strengths $>10^4$ Vcm^{-1} is attributed to a slight acceleration of the fairly slow electron transfer from the anthracene monolayer through the saturated fatty acid chain to the excited singlet state of the dye (see below). We have found a current yield of 0.3 holes per absorbed photon from the absorption of the dye layer and from the magnitude of the photocurrent in the flat portion of the curve in Fig. 3.

The rise time of the photocurrent in a similar system to that shown in Fig. 1, but with the perylene crystal exchanged for an anthracene crystal, has been determined as 900 ps from a time-resolved photocurrent measurement at an applied field strength of 7×10^4 $\mathrm{V\ cm}^{-1}$ (Fig. 4). The noisy curve is the experimental current transient that can be fitted by a calculated transient (drawn out curve) with a rate constant of 1.1×10^9 for the rise time (3). In contrast to the previously investigated case of the directly adsorbed dye (3) this rise time is attributed here to the decay time of the excited dye molecules. The corresponding calculated rise and decay of the excited dye population is also shown in Fig. 4 where this response is convoluted to match the time resolution in the actual photocurrent

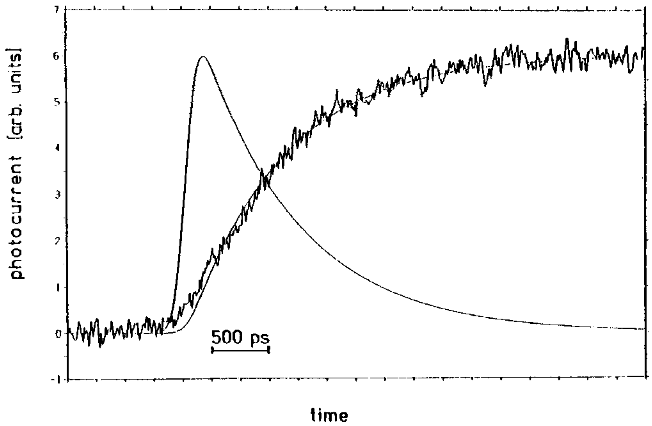

FIGURE 4. Experimental (noisy curve) and calculated (drawn out curve) photocurrent transient indicating the decay of the excited dye layer with a time constant of $1.1\text{x}10^{9}\ \text{s}^{-1}$. Also shown is the corresponding calculated rise and decay of the excited singlet state in the dye layer .

measurement also shown in Fig. 4. An anthracene crystal has been used for this experiment because of its much higher crystal purity compared to our perylene crystals. This allowed for a trap free fit of the transients without introduction of additional parameters for trapping and detrapping events in addition to that for the rise time.

Since the exchange of the crystal should not affect the decay of the excited dye molecules in the layer system we can take this value also for the layer structure shown in Fig. 1. The current yield of 0.3 holes per absorbed photon indicates that the rate constant for electron transfer is one third of the measured decay constant, i.e. in the range of $3.\text{x}10^{8}\ \text{s}^{-1}$ at low electric fields. This rather low value is ascribed to the reduction in electronic overlap due to the 12 Å long saturated fatty acid chain separating the two chromophores.

The stationary photocurrent showed a decrease not larger than 10 per cent when a total number of charge carriers corresponding to several times the total number of dye molecules in the sample had passed as current through the structure. Our present conjecture on the reaction that regenerates the ground state of the dye involves the diffusion of molecular oxygen through the monolayers to the reduced dye and its reoxidation by O_2. Such a regeneration process occurs when the dye molecules are in direct contact with an electrolytic contact containing oxygen (12).

CONVERSION EFFICIENCY

The stationary power output at the exit of a molecular light to electrical power converter is the product $j\mu_f$. In our present system the exit is defined to be between first and second surface layer of the perylene crystal since the 3-layer structure is sufficient for electron-hole pair separation and the perylene crystal is used only to allow for a convenient experimental investigation of the current flow through the 3-layer structure. j = charge carrier flux and μ_f = electrochemical energy difference (potential times elementary charge) between the exit of the electron transfer chain when exposed to the light and of its ground state in the dark, i.e. $\mu_f = \mu_f^o - \mu_g^o + kT \ln \frac{\varsigma_f}{\varsigma_g}$. The ς_s are the occupation probabilities and the index zero indicates the standard state. The charge carrier flux can be written $j = \varsigma_f k_e$ where k_e is an effective rate constant at the exit explained below. For any reasonable converter we can assume that the occupation probability ς_f under light is much greater than that in the dark. It is helpful to express μ_f further in terms of quantities that can be determined in suitable experiments:

$$\mu_f = \mu_i^o - \mu_g^o + (\mu_f^o - \mu_i^o) + kT \ln \frac{k_e \varsigma_f}{I_\sigma \varsigma_g} - kT \ln \frac{k_e}{I_\sigma} =$$

$$= (\mu_i^o - \mu_g^o - kT \ln \frac{\varkappa_i}{I_\sigma}) - (\mu_i^o - \mu_f^o) - kT \ln \frac{k_e}{\varkappa_i} + kT \ln \frac{\dot{j}}{I_\sigma \varsigma_g}$$

Introducing the quantities $Y = \frac{\dot{j}}{I_\sigma \varsigma_g} = \frac{\dot{j}}{g}$ and $\mu^m = \mu_i^o - \mu_g^o + kT \ln \frac{I_\sigma}{\varkappa_i}$ and finally

$\Delta\mu_{i,f}^o = (\mu_i^o - \mu_f^o)$ that will be discussed below one obtains:

$$\mu_f = \mu^m - \Delta\mu_{i,f}^o - kT \ln \frac{k_e}{\varkappa_i} + kT \ln Y \qquad (1)$$

μ^m = maximum free energy change in the dye layer upon illumination in the absence of electron transfer quenching (16). $\Delta\mu_{i,f}^o$ = difference in the electrochemical standard redox potentials of the initial and the final stage, corresponding to the position of the mobile charge carrier at the origin and at the exit of the electron transfer chain, kT = thermal energy, k_e = effective rate constant for the charge carrier at the exit of the electron transfer chain, $\varkappa_i$ = decay rate constant in the dye layer in the absence of electron transfer quenching typically of the order $10^9\ s^{-1}$. Y = number of charge carriers passing through the structure per absorbed photon, i.e. the experimental current yield. For reasonable devices Y > 0.1 and the last term in eqn. (1) can be neglected in comparison to the others. I_σ = effective excitation rate constant (14). This depends on the absorption cross section σ of the dye and the spectral distribution of the incident photon flux. Thus $g = I_\sigma \varsigma_g$ is the excitation rate or the average number of photons absorbed per second by a single dye molecule.

We will use as an estimate $\mu^m = 1.3$ eV for a typical monolayer of dye molecules with a lifetime of 1 ns, an absorption cross section of some 10^{-16} cm^2, an energy of the excited state of about 1.9 eV as for the present dye, and an experimental photon flux of 10^{14} $cm^{-2}s^{-1}$. The value of μ^m can change significantly with the light intensity, its spectral distribution, and with the absorption spectrum of the dye layer. The above estimate corresponds to monochromatic light at the absorption maximum. Guided by the functioning of bacterial photosynthetic reaction centers (2) we will assume $k_e \approx 10^6$ s^{-1} as the feasible effective exit rate constant representing a reaction sequence that utilizes the electrical energy to form suitable chemical products. Except for this assumption we are not concerned here with this extraordinarily difficult part of a conversion cycle. In our present experimental system the hole enters the perylene crystal when leaving the electron transfer chain. The rate constant k_e at the exit, in our case between the first and second molecular layer of the perylene crystal, can in principle be controlled by the applied electric field so as to assume the above value of 10^6 s^{-1}. The third term is then in the range of 0.17 eV. The by far highest energy loss is caused by the necessary drop in standard redox potential along the electron transfer chain. Our estimate for the present structure is in the range $\Delta\mu^o_{i,f}$ = 0.5 eV (see above). Thus, the usable electrochemical potential difference μ_f at the exit of our structure under the above conditions is about 1 V.

With $\bar{E}$, the mean energy of the absorbed photons, we can define the power conversion efficiency PCE as ratio of power output to power input, i.e. PCE = $\frac{J\mu_f}{g\bar{E}} = \frac{1}{\bar{E}}$ $Y\mu_f$. The experimental current yield, i.e. transferred charge carriers per absorbed photon is Y = 0.3 so that our conversion efficiency with respect to absorbed photons is about 15 per cent for monochromatic photons with hν = 1.9 eV near the absorption peak at the above photon flux.

KINETIC STEPS DETERMINING THE CURRENT YIELD

The kinetic steps that control the current yield in our molecular structure can be determined with the simple model illustrated in Fig. 5. First order rate constants connect the different stages of the electron transfer chain corresponding to different positions of the mobile charge carrier in the chain. The rate constant κ_i and k_e have been explained above. k_{1f} describes the electron-hole pair generation and k_{1r} the back reaction. κ_1 represents the recombination reaction of the electron-hole pair. Recombination at

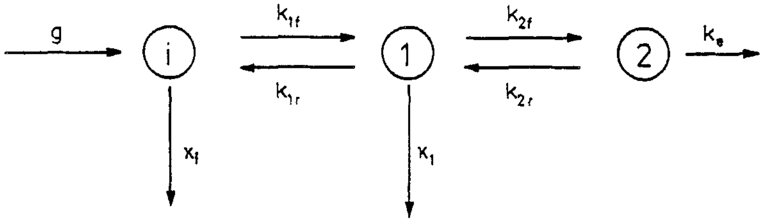

FIGURE 5. Kinetic scheme for the current flow perpendicular to the plane of the 3-layer structure. Linear rate constants are connecting the different positions of the hole on the different chromophores (For Details see text.).

stage 2 of the chain is neglected. The kinetic scheme yields the following expression for the current:

$$j = g\,A[1 + (\frac{1}{k_e} \cdot \exp(-\frac{\Delta\mu^o_{1,2}}{kT}) + \frac{1}{k_{2f}})\;x \tag{2}$$

$$x(\varkappa_1 + \varkappa_i\,A\,\exp(-\frac{\Delta\mu^o_{i,1}}{kT}))]^{-1}$$

where $A = (\frac{k_{1f}}{\varkappa_i + k_{1f}})$.

We have assumed here a Boltzmann-type expression for the ratio of the rate constants for backward and forward reaction, i.e. $\frac{k_{2r}}{k_{2f}} = \exp(-\frac{\Delta\mu^o_{1,2}}{kT})$ where $\Delta\mu^o_{1,2}$ is the difference in the electrochemical standard redox potential between stages 1 and 2. Assuming plausible values for the deactivation reactions $\varkappa_i = 10^9\ s^{-1}$, and $\varkappa_1 = 10^8$ for recombination via the singlet route (4) and provided that the reaction steps are sufficiently downhill, one can simplify considerably the above expression. $\varkappa_1$ is probably less than $10^8\ s^{-1}$ due to the fatty acid barrier in the present system. However, this barrier also makes k_{1f} and thus the factor A small in equation (2) thus leading to the fairly small current yield Y = 0.3.

For a discussion of the current flow according to the scheme in Fig. 5 let us consider first a properly designed layer structure without the barrier in Fig. 1 and with suitable differences in the standard redox potentials. With the above typical values for $\varkappa_i$, $\varkappa_1$ and k_e it is sufficient to make the differences in standard redox potentials for the consecutive electron transfer steps about 0.3 eV downhill in order to eliminate the influence of the back reactions, i.e. of k_{1r} and k_{2r}, on the current yield. According to equation (2) this is achieved since in this case $\varkappa_i A \exp(-\frac{\Delta\mu^o_{i,1}}{kT}) << \varkappa_1$ and $(k_{2f})^{-1} >> (k_e)^{-1} \exp(-\frac{\Delta\mu^o_{1,2}}{kT})$ so that equation (2) is simplified to yield.

$$j = g \left(\frac{k_{1f}}{k_{1f} + \varkappa_i}\right) \left(\frac{k_{2f}}{k_{2f} + \varkappa_1}\right) \qquad (3)$$

The transition from eqn. (2) to eqn. (3) shows that in such a network of linear rate constants the influence of the back reactions can be suppressed without having to search for an unknown specific kinetic trick that is often assumed to be necessary for this purpose. The appropriate downhill difference in the standard redox potentials of the order of 0.3 eV between consecutive stages eliminates by virtue of the Boltzmann factor the influence of the back reactions. A corresponding reasoning as given above making use of a large ratio of forward over backward rate constant leads also from eqn. (2) to eqn. (3) when the first forward reaction does not take place from a vibrationally relaxed state. Such an ultra fast reaction has been discussed by Jortner (15).

Returning to our present structure we can ascertain in eqn. (2) that escape from recombination is satisfactorily achieved for the hole in our present structure. The escape via k_{2f}, i.e. hole transfer from the anthracene layer to the perylene crystal surface, is about 0.4 eV downhill (see above). The room temperature hole diffusion coefficient in the neat anthracene and perylene crystals is of the order of $2 \times 10^{-2} cm^2 s^{-1}$ corresponding to a transfer time of about 10^{-12} s between isoenergetic nearest neighbor molecules. Insertion of, e.g., $k_{2f} = 10^{12} s^{-1}$ and of the other values given above into equation (2) shows that recombination is negligible in our present structure. However, k_{1f} is even smaller than $\varkappa_i$ (see above) leading to the low current yield Y = 0.3 which is essentially controlled by the branching ratio A in the present system. It is clear from equations (1) and (2) that the conversion efficiency can be improved in a structure with a faster first electron transfer step, i.e. in the absence of the barrier and with a greater downhill value for $\Delta\mu^o_{i,1}$.

SUMMARY AND OUTLOOK

We have found both by experiments and model calucations that a molecular layer structure assembled by the Langmuir-Blodgett technique can function as light to electrical energy converter. Downhill electron-hole separation has been achieved through a sequence of 3 molecular layers with suitable differences in their electronic levels. One of the main problems is the realisation of a sufficiently short distance between the chromophores in the consecutive layers that allows for very fast electron or hole transfer. The performance of presently feasible molecular systems as photovoltaic devices is not competitive in comparison to inorganic devices. However molecular layer structures are very promising model systems.

The reaction center of bacterial photosynthesis is a functioning molecular model system for converting light into electrical energy. The recently identified ground state structure (16) shows some surprising features. The center to center and also edge to edge distances appear to be very similar for electron transfer from the special pair, the primary donor, to two chlorophyll B monomers representing the first potential acceptors in two different electron transfer chains. However, according to all the available experimental evidence only one particular monomer of these two and thus only one of the two electron transfer chains is populated via the excited special pair. The origin of this selectivity in the reaction mechanism is not known. In the present state of relative ignorance one is forced to speculate here since a conventional model of a simple electron transfer reaction is apparently not sufficient to explain the ultrafast (a few ps) primary electron transfer reaction that is directed only towards one of the two adjacent bacteriochlorophyll monomers. One can think of more complicated reactions, for example an ultrarapid molecular motion in the excited state of the special pair, which could decrease the distance between one of the two bacteriochlorophyll molecules in the special pair and the bacteriochlorophyll monomer in the active branch, accompanied by ultrafast electron transfer only into this branch. It is an open and speculative question at present whether such complicated reaction mechanisms beyond simple electron transfer do occur at all and whether they are perhaps even essential for efficient light to electric power conversion in a molecular machine.

Considering the already known complexity of the molecular machine in the ground state (16) and the many open questions concerning the dynamics it appears worthwhile and necessary to investigate in addition in vitro systems to gain further insight into the dynamics of light driven electron-hole separation and to obtain optimization criteria for the conversion process. In particular, a variation in the intermolecular distances and in the orientations with a fixed set of chromophores in the electron transfer chain appears to be of great importance. Such variations appear feasible in suitable molecular structures assembled with the Langmuir-Blodgett technique.

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