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Porphyrin hetero-dimer as charge separating system for photocurrent generation†

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Introducing a porphyrin bearing electron acceptor onto a self-assembled monolayer (SAM) using a supramolecular method to form a hetero-dimer increased the photocurrent value compared with using porphyrin without an electron acceptor.

In natural photosynthetic systems, the conversion of light into chemical energy is accomplished by the combined effects of several functional units, each playing a specific role. Antennae are arranged around the reaction centre to capture light energy, and the succeeding excitation energy transfers to the special pair. On receiving this energy, an electron is ejected at the special pair and transferred through the electron transfer chain, ultimately reaching the acceptor. These parts in particular, and the whole system in general, are constructed by the arrangement of chromophore molecules supported in the peptide matrices of biological membranes through the combined use of intermolecular forces.[1]†

In an attempt to develop artificial photosynthetic systems,[2] we attempted to construct a system with the maximum use of intermolecular forces rather than synthesizing complex molecules by covalent bond formation. We have previously developed a unique methodology to afford a complementary coordinated imidazolylporphyrin dimer as a special pair model.[3] Connection of two imidazolylporphyrin units also afforded a giant porphyrin array through which excitation energy was transferred efficiently. Therefore, each porphyrin molecule in a self-assembled monolayer (SAM) prepared on the electrode[4,5] from thiol-substituted porphyrin was capable of growing vertically by the addition of bis(imidazolylporphyrininatoZn(II)). Photocurrent generation was increased significantly by the accumulation of porphyrin chromophores due to the increased efficiency of light absorption because of an antenna effect.[6] Introducing an electron acceptor into the system is crucial for generation and stabilization of charge-separated species.[7] Thus, the next step in developing a more efficient photocurrent generation system was to introduce an appropriate electron acceptor in a form relevant to our system.

Following this reasoning, we designed a new imidazolylporphyrin substituted at the facing meso position by a pyromellitimide group as a strong electron acceptor. The anion radical of pyromellitimide is easily detectable, facilitating the analysis of the charge-separated species by observing the transient absorption spectrum.

The effect of introducing pyromellitimide was apparent from a sharp drop in the fluorescence intensity. The fluorescence of porphyrin **1** was reduced dramatically, to a level of 0.2% compared to that of porphyrin **2** (Fig. 1). The transient absorption spectrum showed the formation of the charge-separated species with an extremely fast time constant of 2 ps, although detailed analysis will be reported elsewhere. As it is known that the fluorescence lifetime of porphyrin **2** is 2.45 ns, we concluded that pyromellitimide accepts electrons efficiently from the complementarily coordinated imidazolylporphyrin dimer as the special pair model. It was therefore expected that porphyrin **1** was an appropriate electron-accepting unit that could be employed on a gold electrode used to investigate the effect of introducing a special pair-electron transfer ensemble into an artificial solar energy conversion system. In order to investigate this theory, a stepwise introduction of porphyrin **1** (or **2**) was accomplished as follows. First, porphyrin **1** (or **2**) was dissolved in nitrobenzene-containing pyridine to dissociate the self-organized dimer into the corresponding monomer. This solution was deposited onto an Au electrode coated with a SAM that had been prepared by soaking the Au electrode in a solution of porphyrin **3**, which was then metalated.[8] Subsequent to this, the pyridine was evaporated off so that the imidazolyl groups in **1** (or **2**) and **3** might mutually coordinate to the Zn in **3** and **1**, respectively, thus adsorbing a coordination-linked hetero-dimer onto the SAM (Scheme 1).[9] Photocurrents were measured by irradiating a 0.5 cm^2 electrode plate with a 150 W Xe lamp through an IR cut-off filter with application of a negative bias voltage (−200 mV *vs* Ag/Ag^+).[10] The plate was immersed in an aq. 0.1 M Na_2SO_4 solution containing 5 mM methylviologen (MV^{2+}) as the electron carrier. The photocurrent values given by electrodes of hetero-dimers **1–3** and **2–3** are summarized in Table 1.

The photocurrent values generated by dimer **1–3** were 3 times larger than those of dimer **2–3** when measured under the same experimental conditions. This increase is ascribed to the incorporation of pyromellitimide as the electron acceptor unit in comparison with dimer **2–3**, which had no electron acceptor.

An alternative (pre-organization) method to incorporate the porphyrin hetero-dimer on an Au surface was also tested. Hetero-dimers were pre-organized first in solution and then adsorbed onto the electrode surface in the same way. For this purpose, a mixture of free base porphyrins **1** (or **2**) and **3** in a 10 : 1 molar ratio was treated with a methanol solution of zinc acetate for 2 hours. In this case, excess **2** was employed to avoid the formation of the **3–3** dimer. After the excess zinc acetate was removed by silica gel chromatography, the solvent was also removed and dichloromethane was added to the residue to make a 1 mM solution with respect to the alkanethiol group. Under these conditions, we expected that the major part of **3** would be

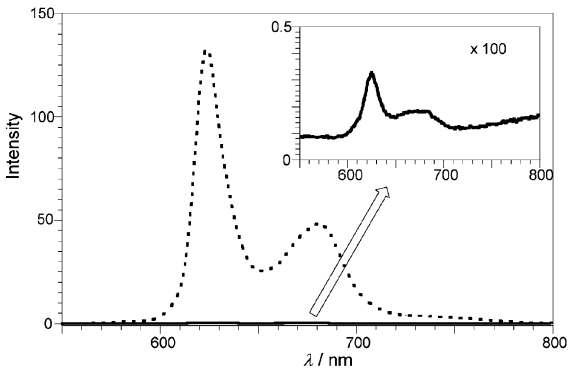

Fig. 1 Fluorescence spectra of **1** (solid line) and **2** (dashed line) in $CHCl_3$. The spectra were measured with the excitation of the Soret band.

† Electronic supplementary information (ESI) available: synthesis and spectroscopic data of **1**, **2**, photoelectrochemical measurement data and experimental details. See http://www.rsc.org/suppdata/cc/b3/b300456b/

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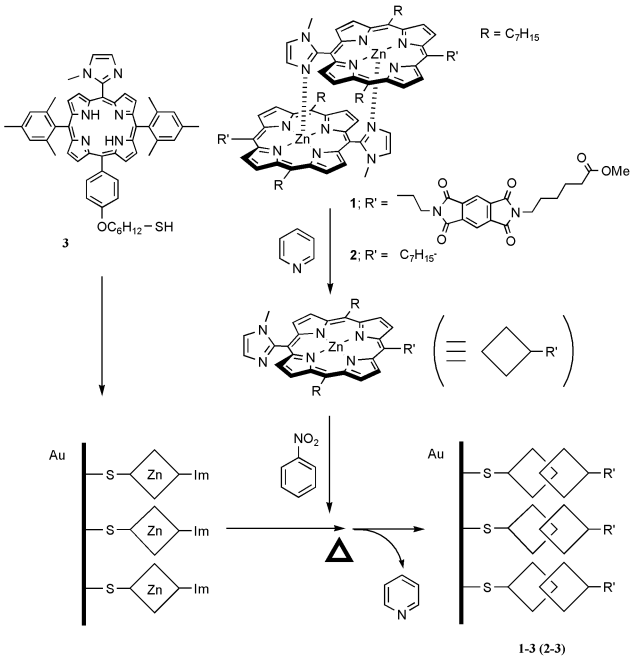
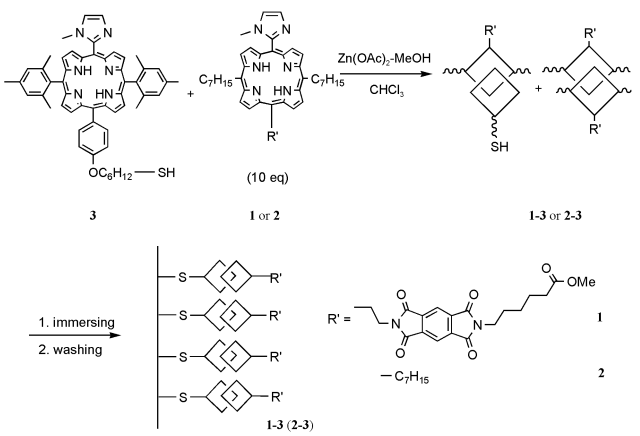


Scheme 1 Schematic representation of **1** and **2** and the stepwise introduction method onto SAM **3**.

Table 1 Photocurrent values of electrodes (**1–3** and **2–3**); 150 Xe lamp, −200 mV *vs* Ag/Ag^+,[10] 0.1 M Na_2SO_4, 5 mM MV^{2+}

Hetero-dimerized electrode	Photocurrent (nA cm^{-2})	
	under N_2	under O_2
1–3	145	230
2–3	44	75

converted to the hetero-dimer **1–3** or **2–3**. TOF-mass spectra supported this reasoning. Plates of gold electrodes were immersed in this solution under nitrogen at room temperature for 36 hours to obtain modified electrodes (Scheme 2). The surface modification of the gold substrate by the molecule was confirmed by UV-visible absorption spectroscopy. Photocurrent values measured under nitrogen in the same way for this stepwise introduction method were 160 and 35 nA for **1–3** and **2–3**, respectively. The photocurrent value of dimer **1–3** was 5 times larger than that of dimer **2–3**. Although the pre-organization method gave a larger photocurrent value ratio, the



Scheme 2 Schematic representation of the pre-organized method.

use of an excess amount of free base porphyrin was required to avoid the formation of the homo-dimer that contains terminal dithiol moieties. Thus, we found that the stepwise growth of chromophoric units was preferable because it was more convenient and had wider applicability to introduce various terminal moieties into the SAM.

The scheme of this photocurrent generation system may be summarized as follows. Excitation of dimeric porphyrin, as the hetero-dimer, induces rapid electron transfer to pyromellitimide, and then methyl viologen (and/or oxygen) in the solution takes the electron away from pyromellitimide to leave a cation radical on the dimeric porphyrin moiety. The cationic charge is neutralized by the electron flow from one of the terminal electrodes and the other terminal accepts an electron from viologen to complete the electron flow cycle. The facile introduction of the required set of chromophores can be achieved with less synthetic effort, providing an attractive way to expand the horizons of research into artificial photosynthesis further into real applications. The method presented in this paper is unique as it allows a special pair arrangement or antenna chains to be obtained by self-coordination when combined with formation of a porphyrin array.[6] We are interested in introducing combination and further developed functional groups, and such systems are under active investigation.[11]

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