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Photocurrent generation system incorporated with antenna function†

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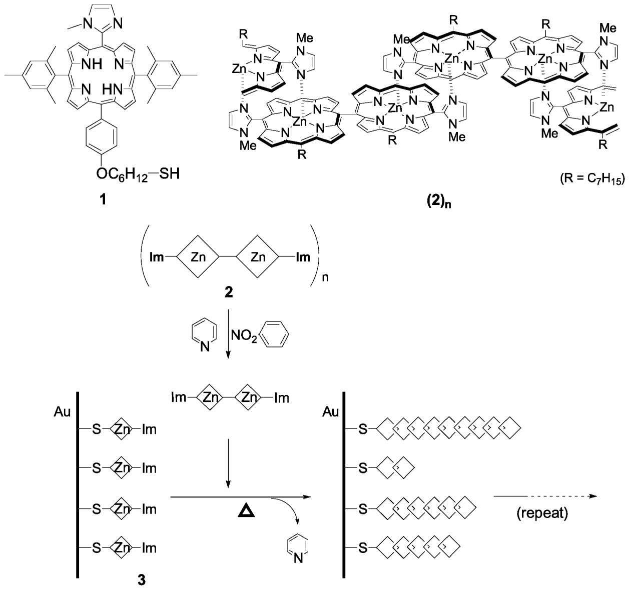
Porphyrin accumulation onto a self-assembled monolayer (SAM) of imidazole-substituted porphyrins by a supramolecular method to form a chain structure leads to significant increase of light absorption in the visible light region and therefore photocurrents.

Recently, the use of self-assembled monolayers (SAMs) of porphyrins on gold electrodes was found to be an efficient method to convert light energy to electric current by photoinduced charge separation on the surface.[1] In these approaches, SAMs have been employed as the key technology because of the easy preparation and the homogeneously developed structure.[2] The use of porphyrin SAMs on gold allows a quantitative determination of the number of porphyrins through monitoring of the number of electrons transferred to gold.[3] At the same time, this approach limits the light absorption only to the single molecular layer and to the narrow range of wavelengths due to the sharp porphyrin Soret band (410–430 nm).[4]

In the natural photosynthetic system, a large number of chlorophylls are arranged around the reaction centre for the capture of light energy, followed by efficient excitation energy transfer to the reaction centre.[5] The use of a simpler light harvesting system combined with the reaction centre could obviate the need for a dense arrangement of the latter unit of high complexity. Such photoelectrical systems may create an improved artificial photosynthetic system.[6] Since we have already developed a unique methodology to obtain a giant porphyrin array by self-coordination of imidazolyl(porphyrinato)zinc(II),[7] each porphyrin monolayer fixed on the electrode surface utilizing Au–S bonds was attempted to be grown into a sequential structure, to bring about an increase of light absorption in the range 350–750 nm and therefore an increase of photocurrent generation.

In order to apply the above principle, imidazolyl-appended porphyrin **1** bearing an ω-mercaptoalkyl substituent was prepared as the first layer molecule on the Au surface.[8] SAM **3** was formed by soaking an Au electrode (1 × 3 cm) into a solution of porphyrin **1** (1.0 mM) followed by metal introduction by using a $Zn(OAc)_2$ solution ($CHCl_3$: MeOH = 10 : 1).[1] The complete metalation was confirmed by disappearance of the absorption band of the free base porphyrin at 500 nm. The surface concentration of porphyrin fixed on the Au electrode was estimated as 3.1×10^{-11} mol cm^{-2} from the anodic peak in the cyclic voltammogram. This value is rather small for a porphyrin SAM, but acceptable given that Au–S bonds are apparently cleaved partly during the metalation step.[9]

Our strategy of sequential elongation of the porphyrin was as follows. Compound **2** was dissolved in a 1 : 1 mixture of nitrobenzene and pyridine, in which the multi-porphyrin array was dissociated into monomeric units by competitive coordination of pyridine to the central Zn ion. An aliquot of this solution was applied dropwise to the electrode. Then pyridine was evaporated at 50 °C in a gentle stream of air for 10 min so that the multi-porphyrin sequence might grow on SAM **3**[10] by the development of complementary coordination of the *meso*-imidazolyl ligand to the central Zn(II) (Scheme 1). The Au electrode thus treated was washed thoroughly with CH_2Cl_2 and dried under a stream of nitrogen. When deposition was applied onto bare gold or SAM without metalation, any deposited porphyrin was washed out by the treatment with CH_2Cl_2. The porphyrin remained is therefore linked by strong complementary coordinate bonds between Zn and the imidazolyl groups on removing pyridine.[7] This series of solution application and evaporation was repeated by using gradually increased concentrations of **2** until a satisfactory number of porphyrins were applied, and the electrode finally washed with CH_2Cl_2 and dried. The number of organized porphyrins (*n*) could be controlled by the concentration of **2** in the solution and the number of deposition cycles (ESI†). AFM observation detected long porphyrin assemblies extending from the surface of the electrode. The lengths were not homogeneous and *n* was calculated as a mean value from the absorption area integrated over the range 350–750 nm in $CHCl_3$ employing ε values of **2** in $CHCl_3$. The absorption of visible light was obviously increased by the repeated number of the deposition cycles. Further treatment with a concentrated solution of **2** in nitrobenzene without the addition of pyridine was not effective for the extension. From these results, it is likely that the long porphyrin chains make it difficult to access the surface due to steric hindrance and the low concentration of terminal imidazolyl–Zn. On adding a pyridine-containing solution of **2** for the next deposition cycle, it is also difficult for pyridine to access deep inside of the organized porphyrin chains and coordination bonds are formed to extend preferably at the easily accessible porphyrin chain ends. This may explain the irregular growth of porphyrin chains observed by AFM.



Scheme 1 Schematic representation of **1** and **2**, and preparation of SAM **3**.

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† Electronic supplementary information (ESI) available: synthesis and spectroscopic data for **1**, photoelectrochemical measurement data and further experimental details. See: http://www.rsc.org/suppdata/cc/b2/b201251k/

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Photocurrents were measured by irradiating the electrode plate of area 0.5 cm^2 by a 150 W Xe lamp through an IR cut-off filter with application of negative bias voltage (−200 mV). The plate was immersed in an aqueous 0.1 M Na_2SO_4 solution containing 5 mM methylviologen (MV^{2+}) as the electron carrier. The plot of photocurrent as a function of the irradiating wavelength, *i.e.* the action spectrum (Fig. 1), closely resembles the absorption spectra of the porphyrin-assembled electrode in the whole range of 350–750 nm. Photocurrent quantum efficiencies[11]at the respective absorption peaks were calculated as 0.14% (430 nm), 0.11% (490 nm), 0.10% (580 nm) and 0.26% (650 nm). These values are not large but are reasonable considering that the system is composed only of simple porphyrins without incorporation of either electron donor or acceptor units.[12]

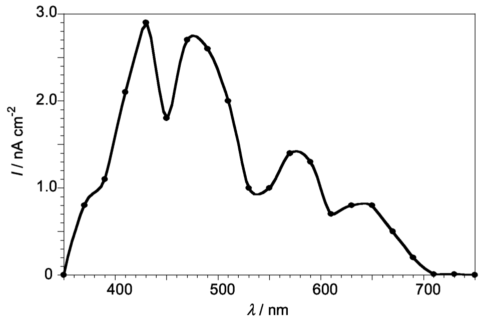

Fig. 1 Action spectrum of electrode (d) described in the legend of Fig. 2; 50 μW cm^{-2}, −200 mV *vs* Ag/AgCl, under N_2, 0.1 M Na_2SO_4, 5 mM MV^{2+}.

In Fig. 2, photocurrent values obtained by SAM **3** and electrodes (a)–(d) obtained as well as other samples, were plotted as a function of the absorption area ($A\lambda$) integrated over the range 350–750 nm. The current value increased uniformly with the increase of the absorption area, showing a sharp increase especially in the range 0–20 $A\lambda$. This drastic increase reveals that the ‘stalactite’ structure extended perpendicularly on the surface is of obvious advantage in the photocurrent generation. It is noteworthy that the photocurrent generation was improved simply by porphyrin chain formation without incorporating any specific electron acceptor or donor groups. The increase comes primarily from the improved efficiency in the absorption of light øenergy and the excitation energy transfer by the accumulated porphyrins. Moreover, effective charge separation and electron/hole transfer along the multi-porphyrin chains may possibly be contributing.

Here we have established a method to grow porphyrin SAMs into a chain structure linked by coordination bonds. The growth is stepwise and controlled easily by the concentration of reagent and the treatment cycle number. The chain structure once formed is resistant under more or less dissociative conditions for the succeeding treatment. In the view of successful elongation of the chain structure by coordination organization, appropriate functional groups may also be introduced at the terminal position of the porphyrin chain.[13] Such structures are interesting not only for artificial photosynthesis, but developing molecular electronic materials, examples of which were reported recently from our laboratory.[14]

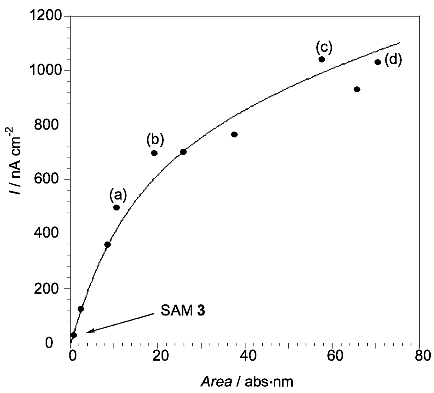

Fig. 2 Plot of photocurrent density of **3** as well as electrodes (a)–(d) and other electrodes as a function of the absorption area integrated over the range 350–750 nm (150 Xe lamp, under N_2). Concentration and repetition cycles are (a) 1 mM and once (n = 2), (b) 0.1 mM and three times, (n = 4), (c) 1 mM and three times (n = 13) and (d) 1 mM and four times (n = 16), respectively.

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Notes and references

1 K. Uosaki, T. Kondo, X.-Q. Zhang and M. Yanagida, *J. Am. Chem. Soc.*, 1997, **119**, 8367; H. Imahori and Y. Sakata, *Eur. J. Org. Chem.*, 1999, 2445; H. Imahori, H. Yamada, Y. Nishimura, I. Yamazaki and Y. Sakata, *J. Phys. Chem. B*, 2000, **104**, 2099.

2 For a review, see:A. Ulman, *Chem. Rev.*, 1996, **96**, 1533.

3 D. A. Offord, S. B. Sachs, M. S. Ennis, T. A. Eberspacher, J. H. Griffin, C. E. D. Chidsey and J. P. Collman, *J. Am. Chem. Soc.*, 1998, **120**, 4478; G. Ashkenasy, G. Kalyuzhny, J. Libman, I. Rubinstein and A. Shanzer, *Angew. Chem.*, 1999, **111**, 1333; G. Ashkenasy, G. Kalyuzhny, J. Libman, I. Rubinstein and A. Shanzer, *Angew. Chem., Int. Ed.*, 1999, **38**, 1257; N. Nishimura, M. Ooi, K. Shimazu, H. Fujii and K. Uosaki, *J. Electroanal. Chem.*, 1999, **473**, 75.

4 H. Imahori, H. Norieda, H. Yamada, Y. Nishimura, I. Yamazaki, Y. Sakata and S. Fukuzumi, *J. Am. Chem. Soc.*, 2001, **123**, 100; H. Imahori, M. Arimura, T. Hanada, Y. Nishimura, I. Yamazaki, Y. Sakata and S. Fukuzumi, *J. Am. Chem. Soc.*, 2001, **123**, 335.

5 G. McDermott, S. M. Prince, A. A. Freer, A. M. Hawthornthwaite-Lawless, M. Z. Papiz, R. J. Cogdell and N. W. Isaacs, *Nature*, 1995, **374**, 517; S. Karrasch, P. A. Bullough and R. Ghosh, *EMBO J.*, 1995, **14**, 631.

6 G. Steinberg-Yfrach, P. A. Liddell, S.-C. Hung, A. L. Moore, D. Gust and T. A. Moore, *Nature*, 1997, **385**, 239; D.-L. Jiang and T. Aida, *J. Am. Chem. Soc.*, 1998, **120**, 10895; A. Nakano, A. Osuka, I. Yamazaki, T. Yamazaki and Y. Nishimura, *Angew. Chem.*, 1998, **110**, 3172; A. Nakano, A. Osuka, I. Yamazaki, T. Yamazaki and Y. Nishimura, *Angew. Chem., Int. Ed.*, 1998, **37**, 3023; D. Kuciauskas, P. A. Liddell, S. Lin, T. E. Johnson, S. J. Weghorn, J. S. Lindsey, A. L. Moore, T. A. Moore and D. Gust, *J. Am. Chem. Soc.*, 1999, **121**, 8604; R. K. Lammi, A. Ambroise, T. Balasubramanian, R. W. Wagner, D. F. Bocian, D. Holten and J. S. Lindsey, *J. Am. Chem. Soc.*, 2000, **122**, 7579.

7 Y. Kobuke and M. Hiyaji, *J. Am. Chem. Soc.*, 1994, **116**, 4111; Y. Kobuke and H. Miyaji, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 3563; K. Ogawa and Y. Kobuke, *Angew. Chem., Int. Ed.*, 2000, **39**, 4070.

8 The porphyrin **1** was prepared as follows. Treatment of 5-mesityldipyrromethane, *p*-[(6-acetylthio)hexyloxy]benzaldehyde and *N*-methylimidazolecarboxyaldehyde with trifluoroacetic acid (TFA) in chloroform under N_2 afforded the corresponding free-base porphyrin, which was isolated through a column chromatograph packed with silica ($CHCl_3$–acetone), then metalated in a $Zn(OAc)_2$ solution and recrystalized from $CHCl_3$–MeOH. The hydrolysis of this porphyrin followed by demetalation afforded porphyrin **1** (yield = 7%).

9 H. M. Schessler, D. S. Karpovich and G. J. Blanchard, *J. Am. Chem. Soc.*, 1996, **118**, 9645.

10 H. Byrd, E. P. Suponeva, A. B. Bocarsly and M. E. Thompson, *Nature*, 1996, **380**, 610; Y-S. Kim, K. Liang, K.-Y. Law and D. G. Whitten, *J. Phys. Chem.*, 1994, **98**, 984; J. Wienke, T. J. Schaafsma and A. Goossens, *J. Phys. Chem. B*, 1999, **103**, 2702; M. Lahav, T. Gabriel, A. N. Shipway and I. Willner, *J. Am. Chem. Soc.*, 1999, **121**, 258.

11 A. Aoki, Y. Abe and T. Miyashita, *Langmuir*, 1999, **15**, 1463.

12 H. Imahori, H. Norieda, S. Ozawa, K. Ushida, H. Yamada, T. Azuma, K. Tamaki and Y. Sakata, *Langmuir*, 1998, **14**, 5335; H. Imahori, H. Norieda, Y. Nishimura, I. Yamazaki, K. Higuchi, N. Kato, T. Motohiro, H. Yamada, K. Tamaki, M. Arimura and Y. Sakata, *J. Phys. Chem. B*, 2000, **104**, 1253.

13 M. Fujihira, K. Nishiyama and H. Yamada, *Thin Solid Films*, 1985, **132**, 77; Y. Sakata, H. Tatemitsu, E. Bienvenue and P. Seta, *Chem. Lett.*, 1988, 1625; T. J. Meyer, *Acc. Chem. Res.*, 1989, **22**, 163; P. Bonñote, J.-E. Moser, R. Humphry-Baker, N. Vlachopoulos, S. M. Zakeeruddin, L. Walder and M. Grätzel, *J. Am. Chem. Soc.*, 1999, **121**, 1324; D. M. Kaschak, J. T. Lean, C. C. Waraksa, G. B. Saupe, H. Usami and T. E. Mallouk, *J. Am. Chem. Soc.*, 1999, **121**, 3435.

14 K. Ogawa, T. Zhang, K. Yoshihara and Y. Kobuke, *J. Am. Chem. Soc.*, 2002, **124**, 22.