ChemComm

Exchange reaction of a decanethiol self-assembled monolayer with porphyrin disulfides observed by surface plasmon enhanced fluorescence spectroscopy

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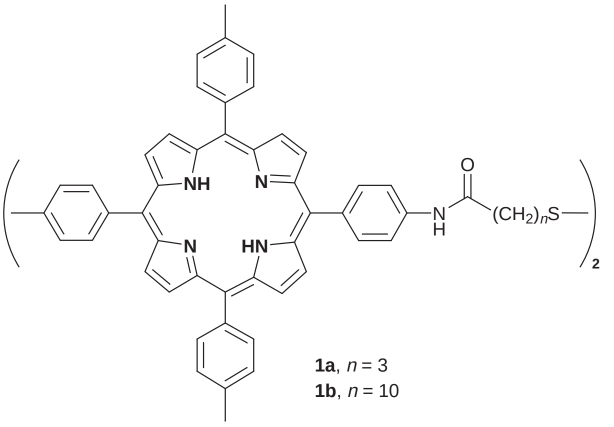
Received (in Cambridge, UK) 27th April 1999, Accepted 8th June 1999

The treatment of a decanethiol SAM with a solution of a porphyrin disulfide gives a SAM inlaid with the porphyrin chromophores adopting J-aggregate-like partially stacked and well oriented structures by site-selective exchange reaction in the SAM.

Molecular exchange in a self-assembly monolayer (SAM) is a fundamental subject of surface science, and experimental[1–4] and theoretical[5] approaches to the reaction process have been developed. Here, we report the exchange reactions of decanethiol SAMs with porphyrin disulfides having trimethylene (**1a**) or decamethylene (**1b**) chains using surface plasmon (SP) enhanced fluorescence spectroscopy.† SP is an effective excitation method for photo-functional molecules on a gold or silver film to give enhanced fluorescence,[6–8] and we employed p-polarization to observe the anisotropy‡ as well as other fluorescence properties.



1a, *n* = 3
1b, *n* = 10

Decanethiol SAMs were prepared by immersion of bare gold films on BK-7 right-angle prisms in a 1 mmol dm^{-3} 1,2-dichloroethane (DCE) solution of decanethiol for 5 h. The resulting decanethiol SAMs were then very carefully immersed into 50 μmol dm^{-3} DCE solutions of **1a** or **1b**, for a suitable time. After carefully washing the surface with DCE, the fluorescence properties were measured by SP excitation in air.[6] Fig. 1 shows changes in the fluorescence properties for the exchange reaction of decanethiol SAMs by **1a** and **1b**, as a function of the immersion time. The remarkable differences demonstrate that the exchange efficiency as well as the motion of the *transplanted* porphyrin chromophores in the SAM depended strongly upon the methylene chain length of **1**.

Very weak fluorescence of the porphyrin with rather large anisotropy was observed independently of the immersion time for **1a** even after a few minutes. This indicates that no exchange reaction with **1a** occurred except for fast exchange in a few minutes. It is well known that decanethiol gives a very tight and densely packed SAM on a flat gold surface. The trimethylene chains of **1a** are too short to penetrate the decanethiol SAM for interaction between the disulfide group and the surface and thus **1a** did not induce an exchange reaction.§

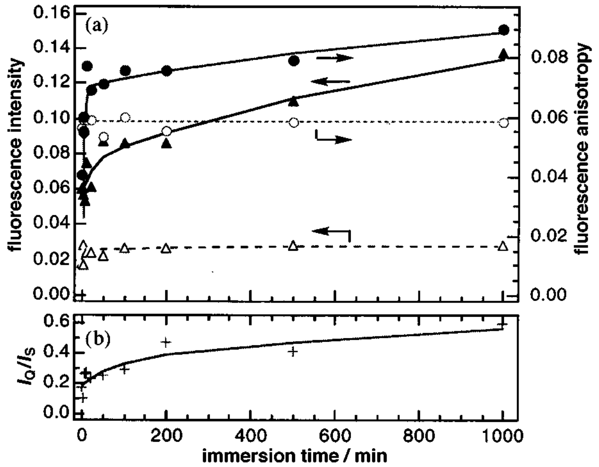


Fig. 1 Changes in the fluorescence properties for the exchange reaction; (a) anisotropy: (○) **1a**, (●) **1b** and intensity (△) **1a**, (▲) **1b**; (b) intensity ratio between the Soret and Q-bands (I_Q/I_S) of the excitation spectrum for **1b**. An almost constant I_Q/I_S value of 1.5 was observed for **1a**.

The very weak fluorescence observed for **1a** is probably attributed to the very small numbers of porphyrin-linked trimethylenethiol groups attached on the gold surface at defects in the decanethiol SAM. Because the porphyrin-linked trimethylene thiols have capped the defects, no further exchange reaction can occur.

In sharp contrast to **1a**, significant increases of fluorescence intensity and anisotropy were observed for **1b** at an initial immersion time of 50 min. These changes demonstrate effective exchange by **1b**, and the resulting porphyrin-linked decanethiols in the SAM are gradually ordered and lose their freedom of motion as the exchange reaction proceeds. The increase of the anisotropy can be rationalized by the increase of π–π stacking of the porphyrin chromophores which causes a characteristic change in the absorption spectrum. This is reflected in the SP enhanced fluorescence excitation spectra shown in Fig. 2.

The Q-bands increased strikingly with increased the immersion time.¶ It is well known that the π–π stacking of porphyrins

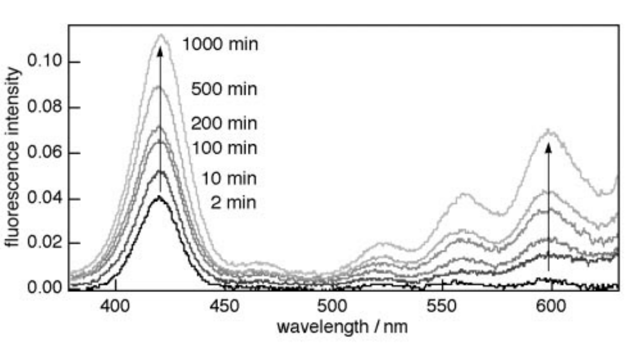


Fig. 2 Changes in the SP enhanced fluorescence excitation spectra for the exchange reaction of a decanethiol SAM with a 50 μmol dm^{-3} DCE solution of **1b** (λ_{em} = 725 nm; λ_{ex} = 425 nm).

reduces the intensity of the Soret band and that the relative ratio between the Soret and Q-bands (I_Q/I_S) increases.[9] Therefore, the changes in the excitation spectra demonstrate that the initially formed monomeric porphyrin-linked decanethiols in the SAM gradually change to a stacked structure as the exchange reaction proceeds. Because the excitation spectrum after 1000 min immersion shows maxima of the Soret bands at 420 and 470 nm, the porphyrin chromophores seem to adopt partially stacked structures similar to J-aggregates.[9] The increase of the fluorescence anisotropy is attributable to the increase of well oriented stacked structures which are more inflexible than the monomeric porphyrin chromophores.

Two possible mechanisms are presumed for the gradual stacking; (i) lateral migration of the porphyrin-linked decanethiol units exchanged at random in the SAM,|| or (ii) site-selective exchange reaction nearby initially exchanged porphyrin-linked decanethiols. We have carried out the successive exchange reaction using a zinc complex of **1b** (**1b**–Zn) followed by **1b**. A decanethiol SAM was immersed into a 50 μmol dm^{-3} DCE solution of **1b**–Zn for 3 min and the resulting SAM showed characteristic fluorescence of the Zn–porphyrin (Fig. 3). This SAM was then immersed into a 50 μmol dm^{-3} DCE solution of **1b** for 30 s. After this treatment, the fluorescence of the Zn–porphyrin completely disappeared and was replaced by fluorescence of the free-base porphyrin (Fig. 3). This demonstrates fluorescence resonance energy transfer (FRET) from the Zn–porphyrin chromophores to the neighboring free-base porphyrin chromophores which have a lower singlet excitation energy than that of the Zn–porphyrin.** Because the efficiency of FRET is highly dependent upon the distance between the donor and acceptor, the free-base porphyrin chromophores must be exchanged nearby the Zn–porphyrin chromophores. The small numbers of initially exchanged porphyrin chromophores are likely to disturb the surrounding decanethiol SAM so leading to active sites, or act to increase the local concentration of **1b** by π–π interactions.

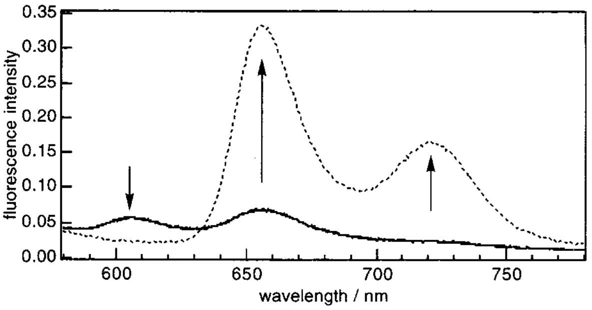


Fig. 3 The fluorescence spectra of the decanethiol SAM exchanged by a 50 μmol dm^{-3} DCE solution of **1b**–Zn for 3 min before (——) and after (- - - -) successive treatment with a 50 μmol dm^{-3} DCE solution of **1b** for 30 s (λ_{ex} = 420 nm).

We have demonstrated that the treatment of a decanethiol SAM with **1b** gives a SAM inlaid with the porphyrin chromophores adopting J-aggregate-like partially stacked and well oriented structures by site-selective exchange reaction.

This work was supported by a Grant-in Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan (A. I. and T. M.), and Research Area of 'Fields and Reactions' in PRESTO Project of JST Corporation (A. I.), NEDO (A. I.), and the Kansai Research Foundation (A. I.).

Notes and references

† The porphyrin disulfides were synthesized and purified by reported procedures (T. Akiyama, H. Imahori and Y. Sakata, *Chem. Lett.*, 1994, 1147). A 50 nm gold film was directly evaporated on the hypotenuse face of a 15 × 15 × 15 mm BK-7 right-angle prism at a pressure of $< 6 \times 10^{-4}$ Pa, rinsed with 1,2-dichloroethane (DCE) and dried in class-100 air.

‡ The degree of polarization (r) of the β bands are calculated by the fluorescence intensities at parallel ($I_{\parallel}$) and perpendicular ($I_{\perp}$) polarizer configurations as $r = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + 2I_{\perp})$.

§ The inefficient exchange reaction of **1a** may also be a consequence of **1a** having an odd number of methylene units. This may result in steric or kinetic barriers such as unfavorable orientation of the porphyrin chromophores of **1a** initially adsorbed in the decanethiol SAM.

¶ The fluorescence excitation spectrum of a porphyrin SAM by SP excitation shows enormous magnification of the Q-bands compared with the absorption and excitation spectra by direct photoirradiation on the surface due to the field enhancement effect which is much more considerable for the wavelength region of the Q-bands than that of the Soret-band.[6]

|| The treatment of a bare gold surface with a mixture of **1b** and **1b**–Zn gave a SAM containing both of the chromophores in the same ratio as in the original mixture which suggests similar exchange rates for **1b** and **1b**–Zn. Consequently, we can rule out the possibility that the initially exchanged Zn–porphyrin-linked decanethiol units may be selectively forced out by added **1b** resulting in disappearance of the fluorescence.

** The changes in the fluorescence properties of the decanethiol SAM after 5 min immersion in a solution of **1b** were observed in air. After 15 h, small increases in the anisotropy and enhancement of the Q-bands were barely observed. This suggests that the lateral migrations of the porphyrin-linked decanethiols in the decanethiol SAM proceed slowly in air.

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Communication 9/03334C