Photoinduced energy transfer in mixed self-assembled monolayers of pyrene and porphyrin

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Mixed self-assembled monolayers of pyrene and porphyrin have been prepared to mimic efficient energy transfer in the photosynthetic antenna complex.

X-Ray structural determination of the photosynthetic antenna complex[1] has stimulated many organic chemists to design covalently-linked multichromophores such as linear, circular and dendritic porphyrin oligomers for mimicry of efficient energy transfer (EN) process.[2,3] An alternative strategy involves molecular assembly of chromophores in organized media. Langmuir–Blodgett films and lipid bilayer membranes have been frequently employed to construct light-harvesting systems.[4–10] However, these systems seem to be inapplicable in terms of stability, uniformness and manipulation. In contrast, the use of self-assembled monolayers (SAMs)[11] may be a promising approach to organize chromophores on substrates because of their uniform and well ordered structures. Here, we report the first preparation of mixed SAMs of pyrene **1** and porphyrin **2** on a gold surface (Fig. 1) in which efficient singlet–singlet EN from **1** to **2** has been detected successfully.

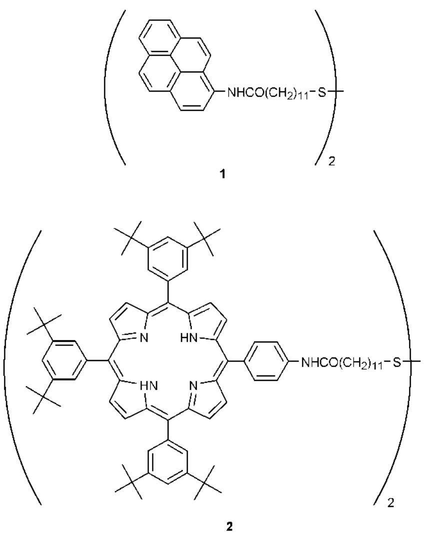
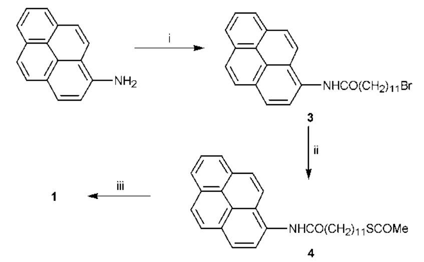


Fig. 1 Molecular structure of pyrene and porphyrin dimers **1** and **2**.

The synthetic route to **1** is shown in Scheme 1. Condensation of 1-aminopyrene with 12-bromododecanoic acid in the presence of 2-chloro-4,6-dimethoxy-1,3,5-triazine afforded **3** in 29% yield. Bromide **3** was converted to disulfide **1** *via* thioesterification with potassium thioacetate and subsequent base deprotection of **4**. Porphyrin disulfide **2** was prepared by following the same procedures as described previously.[12,13] The structures of **1** and **2** were verified by spectroscopic analyses including ^1H NMR and MALDI-TOF mass spectra.†



Scheme 1 *Reagents and conditions*: i, 12-bromododecanoic acid, 2-chloro-4,6-dimethoxy-1,3,5-triazine, THF, 29%; ii, potassium thioacetate,THF–EtOH, 52%; iii, KOH, THF–MeOH, 42%.

Monolayers of mixtures of **1** and **2** were formed by the coadsorption of **1** and **2** onto Au(111) mica substrates (denoted **1**–**2**/Au, where / represents an interface). The coadsorption onto the gold surface was carried out from CH_2Cl_2 solutions containing **1** and **2** with a total concentration of 10 μM [molar ratio of **1**:**2** = (a) 100:0, (b) 90:10, (c) 50:50, (d) 10:90, (e) 0:100] for 20 h to complete mixed SAM formation. After soaking, the gold substrate was washed well with CH_2Cl_2 and dried with a stream of argon. A cyclic voltammetric experiment using **1**–**2**/Au in CH_2Cl_2 containing 0.1 M $Bu^n{}_4NPF_6$ electrolyte with a sweep rate of 50 mV s^{-1} (electrode area, 0.48 cm^2) was performed to estimate the surface coverage (Fig. 2). The adsorbed amount of **1** and **2** on **1**/Au [**1**:**2** = (a) 100:0] and **2**/Au [**1**:**2** = (e) 0:100] was calculated from the charge of the anodic peak of the pyrene and the porphyrin moieties as 2.8×10^{-10} mol cm^{-2} (= 59 Å^2 molecule^{-1})‡ and 1.5×10^{-10} mol cm^{-2} (= 110 Å^2 molecule^{-1}),[12] respectively. These values indicate the formation of the well packed structures of **1** and **2** on the gold surface. However, an attempt to determine the adsorbed amounts of **1** and **2** in the mixed SAMs was

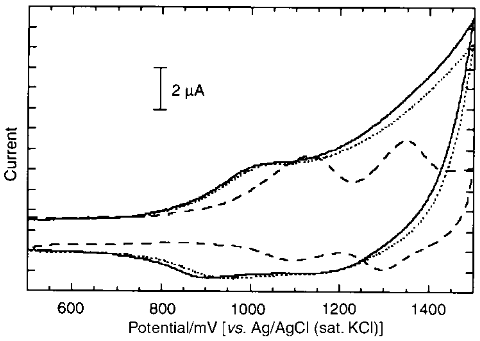


Fig. 2 Cyclic voltammograms of **1**/Au (—), **2**/Au (----), and a mixed SAM of **1** and **2** on a gold surface (·····) from CH_2Cl_2 solution using a molar ratio of 50:50.

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unsuccessful because of the broad wave of the first oxidation due to the pyrene and porphyrin moieties.

Fig. 3 shows absorption spectra of **1** and **2** in CH_2Cl_2 and of **1**–**2**/Au [**1**:**2** = (c) 50:50] using the transmission mode in air.[12] The absorption band of **1** (λ_{max} = 337 nm) and **2** (λ_{max} = 424 nm) on the gold surface is blue- and red-shifted by 7 and 3 nm, respectively, as compared to that of **1** and **2** in CH_2Cl_2. Assuming that the relative ratio of the molar absorption coefficients of **1** and **2** in the mixed SAMs are the same as those in CH_2Cl_2 [**1**: 4.90×10^4 M^{-1} cm^{-1} (λ_{max} = 344 nm); **2**: 1.08×10^6 M^{-1} cm^{-1} (λ_{max} = 421 nm)], the relative ratios of **1**:**2** in the mixed SAMs are estimated as (a) 100:0, (b) 99:1, (c) 94:6, (d) 85:15 and (e) 0:100. The strong π–π interactions of the pyrene moieties compared with the relatively weak interaction between the porphyrin moieties (as a consequence of the bulky tert-butyl groups) may be responsible for the preference of adsorption of **1** over **2** on the gold surface. In addition, the fact that the pyrene molecules occupy about half the surface area of the porphyrins would lead to a thermodynamic preference for pyrene adsorption, since displacement of a porphyrin for two pyrenes results in an extra S–Au interaction.

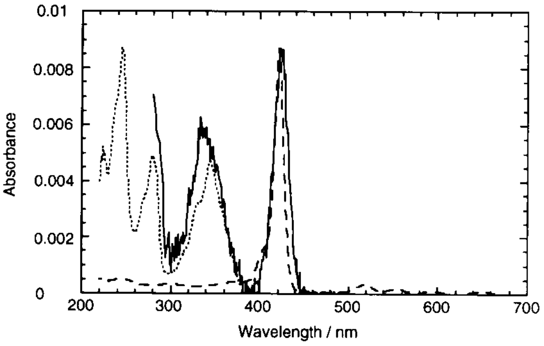

Fig. 3 Absorption spectra of **1** (····) and **2** (----) in CH_2Cl_2 and a mixed SAM of **1** and **2** on a gold surface (—) from CH_2Cl_2 solution using a molar ratio of 50:50. The spectra are normalized for comparison.

Steady-state corrected fluorescence spectra of **1** and **2** in CH_2Cl_2 were measured with the excitation wavelength at 340 and 427 nm, respectively, and were compared with those of **1**/Au and **2**/Au. The fluorescence spectrum of **2**/Au is essentially the same as that of **2** in CH_2Cl_2 as shown in Fig. 4.[12] Fluorescence emission of **1** in Fig. 4 overlaps well with absorption of **2** in Fig. 3. Thus, it is expected that excitation of the pyrene moiety as an antenna chromophore may lead to efficient singlet–singlet EN from the pyrene to the porphyrin in the SAMs. Unfortunately, however, the emission of **1**/Au was too weak to be detected. No detectable fluorescence from the pyrene or the porphyrin moiety was observed in **1**–**2**/Au under steady state irradiation. Then, time-resolved, single-photon counting fluorescence studies were made for **1**–**2**/Au§ [**1**:**2** = (a) 100:0, (b) 90:10, (c) 50:50, (d) 10:90, (e) 0:100) as well as for **1** and **2** in solutions with an excitation wavelength at 280 nm, where the light is mainly absorbed by the pyrene moiety. In each case the decay of the fluorescence intensity at 385 nm and/or 720 nm (due to the singlet excited states of the pyrene and the porphyrin, respectively) could be monitored. The decay curve could be fitted as single exponential except for **1** at 385 nm in CH_2Cl_2. The fluorescence lifetimes of **1**/Au at 385 nm (23 ps) and **2**/Au at 720 nm (40 ps) were much shorter than those of **1** [7.4 ns (30%), 3.2 ns (70%)] and **2** (8.1 ns) in CH_2Cl_2. This indicates that the excited singlet states of the pyrene and the porphyrin are quenched by the gold surface through EN, as reported previously.[12] The fluorescence lifetimes of the pyrene moiety in **1**–**2**/Au at 385 nm decreased with an increase in the relative ratio of the porphyrin to the pyrene [(a) 23 ps, (b) 20 ps, (c) 11 ps, (d) 8.8 ps].¶ The fluorescence lifetimes of the porphyrin moiety in **1**–**2**/Au at 720 nm also decreased with an increase in the relative ratio of the porphyrin to the pyrene [(b) 92 ps, (c) 88 ps, (d) 60 ps, (e) 40 ps]. A likely explanation for these observations is that efficient EN (> 62%) occurs from the excited singlet state of the pyrene to the porphyrin, followed by energy transfer among the porphyrins.[14]

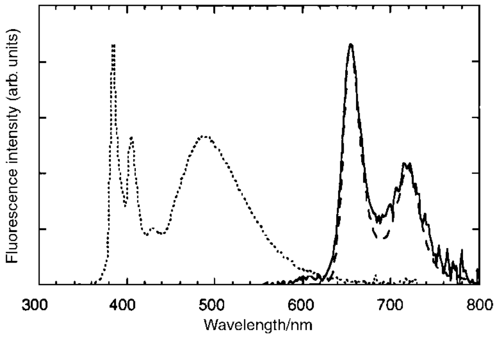

Fig. 4 Fluorescence spectra of **1** (····) and **2** (----) in CH_2Cl_2 and a SAM of **2** on a gold surface (—) with excitation at 340 nm for **1** and 427 nm for **2**. The spectra are normalized for comparison.

In conclusion, we have developed the first mixed self-assembled monolayers of pyrene and porphyrin in which efficient singlet–singlet EN takes place from the pyrene to the porphyrin. Further improvement on the ability of harvesting the light may be made by choosing a suitable couple of different chromophores which absorb visible light extensively.

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Notes and references

† *Selected data* for **1**: δ_H(270 MHz; $CDCl_3$) 7.7–8.3 (m, 20H), 2.68 (t, *J* 8 Hz, 4H), 2.58 (t, *J* 8 Hz, 4H), 2.0–1.0 (m, 36H); *m/z* (MALDI-TOF; positive mode) 862 ($M + H^+$).

‡ Densely packed monolayer films are known to retard ion transport and electrochemical accessibility. Since pyrene is a planar aromatic molecule, the pyrene moiety of **1** may be densely packed owing to the strong π–π stacking in the monolayers. Thus, the real value of surface coverage may be larger, as compared to the estimated value using cyclic voltammetry.

§ For the time-resolved fluorescence measurements, gold substrates were prepared by a vacuum deposition technique with titanium (50–100 Å) and gold (200–1000 Å) in sequence onto a Si(100) wafer (Sumitomo Sitix Corp.).

¶ Monomer emission (*ca.* 400 nm) as well as excimer emission (*ca.* 500 nm) were observed for **1** in CH_2Cl_2, as shown in Fig. 4. The fluorescence lifetimes of **1**–**2**/Au at 500 nm also decreased with an increase in the relative ratio of the porphyrin to the pyrene.

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