Photophysical and Photochemical Studies of the Synthetic Bilayer Membranes, III. Ternary Energy Transfer from Biphenyl-containing Bilayer Vesicles Cascading through Titan Yellow to Fluorescein Sodium

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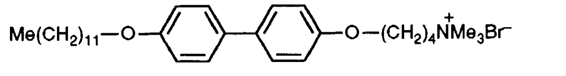
A biphenyl-containing bilayer vesicle aqueous solution conducts ternary energy transfer from the biphenyl donor cascading through titan yellow to the fluorescein sodium acceptor.

An important function of biological membranes is to organize molecules in their environments. Photochemical and photophysical studies of bilayers have arisen in relation to attempts to develop artificial photosynthetic systems.[1,2] Energy transfer in *in vivo* photosynthesis is largely dependent on the precise location of chlorophyll molecules in the chloroplast.[3] Synthetic vesicles have properties similar to biomembranes and are currently being studied as model systems of photosynthesis.[4–5] Binary intermolecular efficient energy transfer has been reported in vesicle aqueous solutions.[7,8] The amphiphile,



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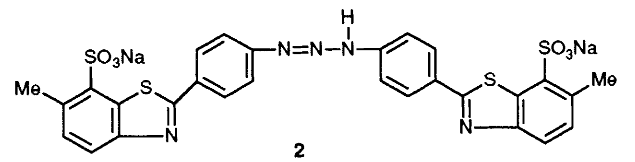

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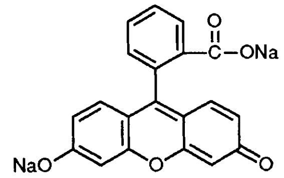

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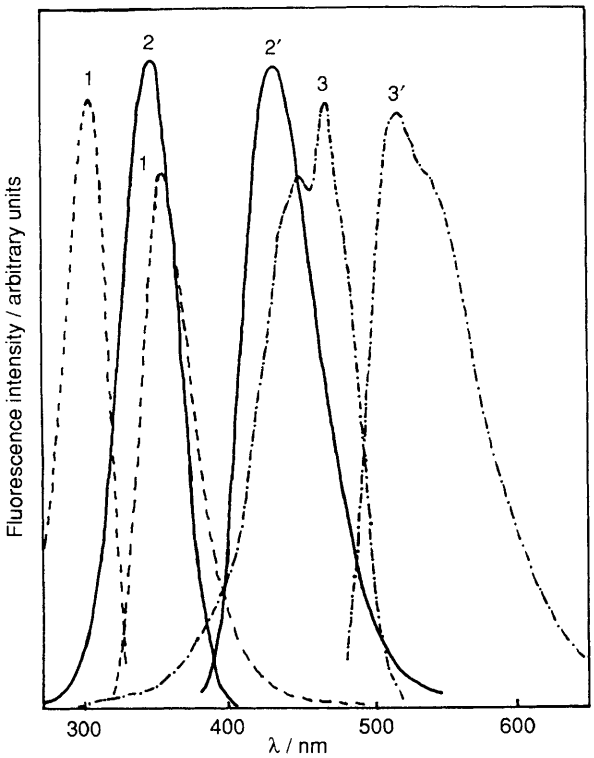

Fig. 1 Excitation spectra of 1 biphenyl intercalated in 8.0×10^{-4} mol l^{-1} stoichiometric **1** vesicles monitored at 350 nm; (2) **2** aqueous solution (4.0×10^{-5} mol l^{-1}) monitored at 420 nm; (3) sodium aqueous solution (4.0×10^{-6} mol l^{-1}) monitored at 540 nm. Emission spectra of (1′) biphenyl intercalated in 8.0×10^{-4} mol l^{-1} vesicles excited at 295 nm; (2′) **2** aqueous solution (4.0×10^{-5} mol l^{-1}) excited at 365 nm; (3′) fluorescence in sodium aqueous solution (4.0×10^{-6} mol l^{-1}) excited at 460 nm.

4-(4′-decyloxy-4-biphenyloxy)butyltrimethylammonium bromide **1** could form stable globular vesicles in dilute aqueous solution.[9] These vesicles have exhibited binary efficient energy transfer from biphenyl donor to the membrane-bound titan yellow **2** acceptor.[10] Recently, it has been discovered that the biphenyl chromophores develop a pronounced coplanar conformation and form face-to-face aggregates in the bilayer vesicles.[11] In this communication, we report ternary efficient transfer from the biphenyl-containing bilayer vesicles of **1** cascading through titan yellow to fluorescein sodium **3**.

The sample solution was prepared by the sonication method.[9] The fluorescence spectra were recorded (SPEX Fluorolog spectrofluorimeter) using front face angle illumination.

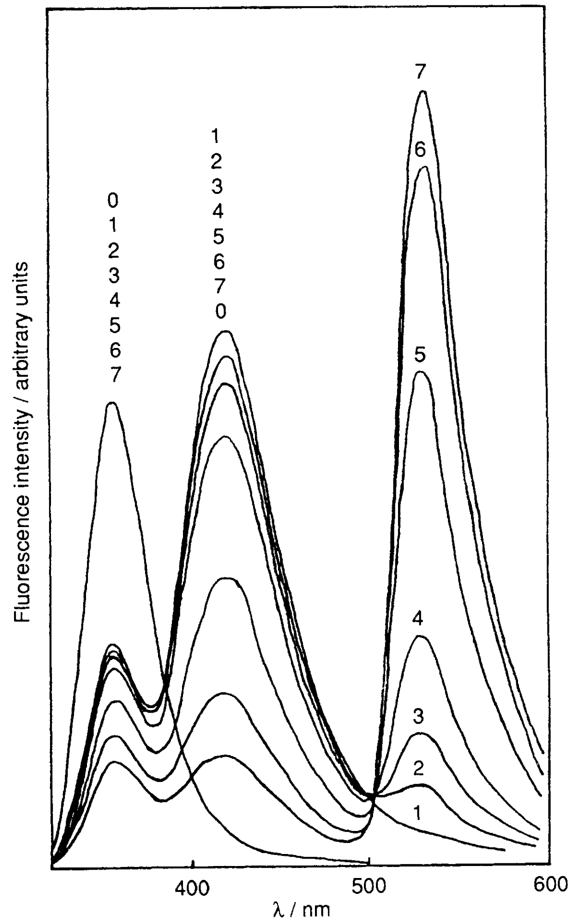

Fig. 2 Ternary energy transfer from biphenyl-containing bilayer cascading through from **2** to **3**. Concentration of **1** vesicle and that of **2** are fixed at 8.0×10^{-4} and 4.0×10^{-5} mol l^{-1}, respectively. Concentrations of fluorescein sodium: 1, none; 2, 5.0×10^{-7}; 3, 1.0×10^{-6}; 4, 2.0×10^{-6}; 5, 4.0×10^{-6}; 6, 7.0×10^{-6}; 7, 1.0×10^{-5} mol l^{-1}; 0, emission spectrum of **1** vesicles (8.0×10^{-4} mol l^{-1}). The scale of the ordinate is the same as that of Fig. 1.

Fig. 1 shows the excitation and emission spectra of **1** vesicle, **2** and **3** in aqueous solution, respectively. Good overlap between the emission spectrum (1′) of the biphenyl chromophore in **1** vesicles, with excitation spectrum (2) of **2**, and the good overlap between emission spectrum (2′) and the **2** with the excitation spectrum (3) of fluorescein sodium suggest possible Forster-type sequential excitation energy transfer from the biphenyl cascading through **2** to **3**.

Fluorescence spectra of the **1–2–3** system in aqueous solutions with **1** concentration fixed at 8.0×10^{-4} mol l^{-1} and **2** concentration at 4×10^{-5} mol l^{-1}, and **3** at various concentrations, excited at 305 nm, are shown in Fig. 2. It is found that the fluorescence intensities of biphenyl and **2** decrease, respectively, and that of fluorescein sodium increases with increased concentration of **3**, indicating the cascade excitation energy transfer from biphenyl through **2** to **3**. The changes in the fluorescence spectra of the biphenyl and **2** are a function of the concentration of **3**. The excitation of the mixture of vesicles, **2** and **3** in aqueous solution at 305 nm resulted in an increase in the emission intensity, centred at 530 nm of fluorescein sodium and a decrease in the emission intensity, centred at 355 and 420 nm, of the biphenyl in **1** vesicles and vesicle-bound **2**, respectively. These observations reveal that the mixture system of vesicle aqueous solution conducts ternary energy transfer from biphenyl cascading through **2** to **3**.

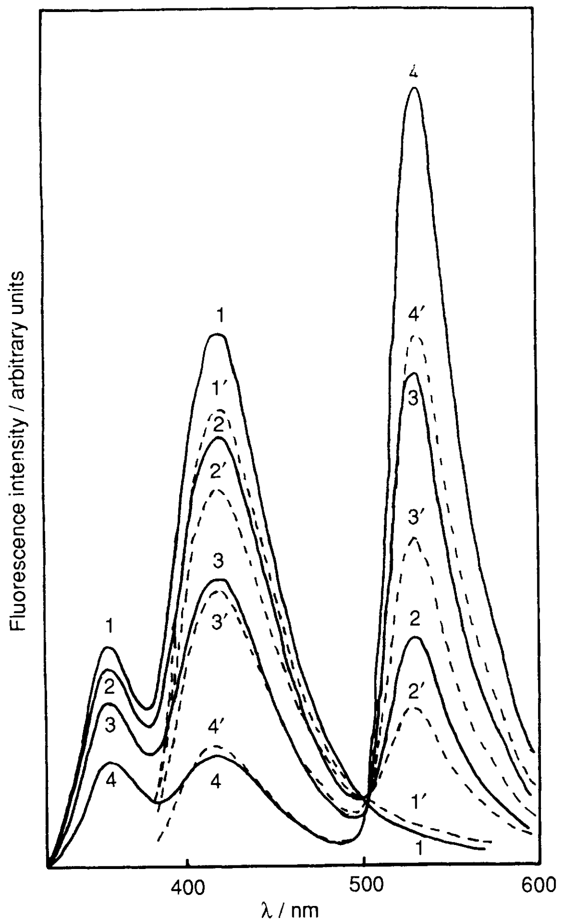

Fig. 3 Fluorescence spectra of **1–2–3** (—) excited at 305 nm and **2–3** (- - -) excited at 365 nm. **1** vesicles and **2** at fixed concentration 8.0 × 10^{-4} and 4.0 × 10^{-5} mol l^{-1}, respectively. Fluorescein sodium concentration: 1, none; 2, 2.0 × 10^{-4}; 3, 4.0 × 10^{-6}; 4, 1.0 × 10^{-5} mol l^{-1} (1′–4′ represent the **2–3** system). The scale of the ordinate is the same as that of Fig. 1.

In the same sample solution, excitation at 365 nm results in binary energy transfer from membrane-bound **2** to **3**, as shown in Fig. 3. In this figure, the spectra regarding the ternary energy transfer are also displayed for comparison. It is found that the fluorescence intensity in the ternary energy transfer system is stronger than the corresponding intensity of the binary energy transfer system. This result shows that the efficiency of the ternary transfer system is higher than that of the binary energy transfer system. Considering the preferable interaction of the sulfonate anionic group on **2** to the alkyltrimethylammonium cationic group on the surface of the **1** vesicles,[12] partly free dispersion of **2** in the solution is reasonably negligible. Therefore, the above findings reflect that the vesicle-bound **2** accepts a photon from the bilayer (excited at 305 nm) more effectively than from direct irradiation (excited at 365 nm). This implies that the energy migration in the bilayer aggregate is important[11] and gains the energy transfer from the biphenyl to the membrane-bound titan yellow. Theoretical support for this consideration has recently been put forward.[13]

In conclusion, this work demonstrates the efficient ternary transfer of excitation energy from biphenyl-containing bilayer vesicles cascading through **2** to **3**. Ternary energy transfer resulted in extending the wavelength region for excitation and enhancing the efficiency of the energy transfer.

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References

1 J. H. Fendler, *Membrane Mimetic Chemistry*, Wiley-Interscience, New York, 1982, p. 492–505.
2 K. Monserrat and M. Gratzel, *J. Chem. Soc., Chem. Commun.*, 1981, 1183.
3 G. Porter, *Proc. R. Soc. London, Ser. A*, 1978, **362**, 281; *Pure Appl. Chem.*, 1978, **5**, 263.
4 J. H. Fendler, *Acc. Chem. Res.*, 1980, **13**, 7.
5 H. Ringsdorf, B. Schlarb and J. Venzmer, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 113.
6 T. Kunitake, Y. Okahata, M. Shimomura, S. Yasunami and K. Takarabe, *J. Am. Chem. Soc.*, 1981, **103**, 5401.
7 N. Nakashima, N. Kimizuka and T. Kunitake, *Chem. Lett.*, 1985, 1817.
8 T. Nomura, J. R. Escabi-Perez, J. Sunamoto and J. H. Fendler, *J. Am. Chem. Soc.*, 1980, **102**, 1484.
9 G. Li, Z. Wang, Y. Tian and Y. Liang, *Chem. J. Chin. Univ.*, 1989, **10**, 1024.
10 G. Li, Y. Tian and Y. Liang, *J. Chem. Soc., Chem. Commun.*, 1990, 889.
11 G. Li, Y. Tian and Y. Liang, *J. Phys. Chem.*, submitted for publication.
12 Yongchi Tian, *J. Phys. Chem.*, in the press.
13 I. Yamazaki, N. Tamai and T. Yamazaki, *J. Phys. Chem.*, 1990, **94**, 516.