Efficient Energy Transfer in a Biphenyl-containing Bilayer Membrane

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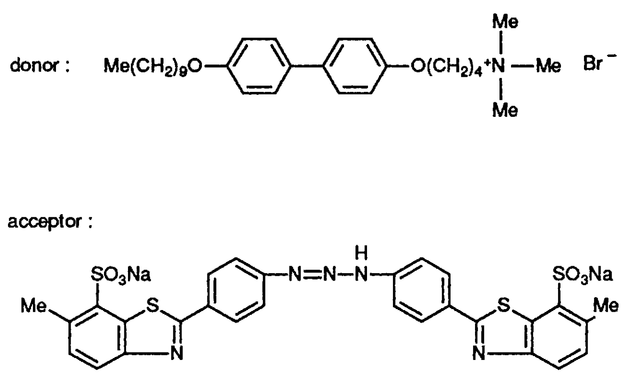
Biphenyl-containing bilayer vesicles of a single-chain ammonium amphiphile exhibit efficient energy transfer from the biphenyl donor to the membrane-bound titan yellow acceptor.

Functionalization of molecular assemblies has been of interest in recent years.[1—7] Synthetic amphiphile vesicles and bilayer lamella are increasingly used as membrane mimetic agents[8] in studies of molecular arrangement, chromophore orientation,[9] and the function of synthetic bilayer membranes. A specific chromophore introduced into the synthetic amphiphile as part of the component molecules will be very useful for obtaining the information at a molecular level.[9,10] Biphenyl in organic compounds is known to be an efficient donor for intramolecular energy transfer in organic solutions,[11] but such behaviour has not been reported for aqueous solutions. We report herein for the first time an energy transfer between biphenyl-containing bilayer membranes and membrane-bound 2,2′-[(diazoamino)-di-*p*-phenylene]bis-(6-methyl-7-benzothiazole sulphonic acid) sodium salt, *i.e.*, titan yellow.

Preparation of the amphiphile 4-(4′-decyloxy-4-biphenyloxy)butyl trimethylammonium bromide (DBBTAB) followed literature procedures.[12,13] This amphiphile forms a stable bilayer aggregate (vesicles and lamella) upon dispersing in a certain volume of distilled water by sonication (Branson B-92, ultrasonicator). Globular vesicles with diameters ranging from 500 to 2000 Å, were obtained by this method (checked by electron microscopy, JEM-2000FX). The vesicles were stable in the pH range 4—10 for weeks, and undergo phase transition at 313.2 K in dilute aqueous solution (*ca.* 1 wt%, Perkin-Elmer, DSC-2C). Fluorescence spectra were recorded (SPEX Fluorolog spectrofluorimeter) using front face angle illumination.

Efficient intermolecular energy transfer has been observed in the DBBTAB vesicle system. The biphenyl-containing single-chain amphiphile DBBTAB, as a donor, was localized in the hydrophobic bilayer of the vesicles and the titan yellow molecules, as acceptors, were sited on the outer charged surface of the DBBTAB vesicles through electrostatic attraction.

Figure 1, curves 1 and 2 show, respectively, the excitation and emission spectra of DBBTAB vesicles (8.0×10^{-4} mol l^{-1}) and titan yellow (1.6×10^{-5} mol l^{-1}) in aqueous



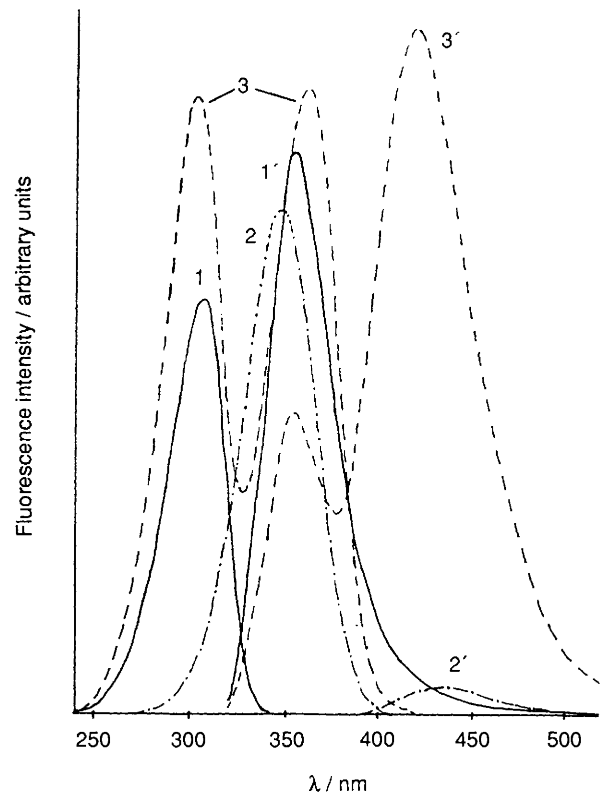


Figure 1. Excitation and emission spectra of various solutions of DBBTAB vesicles (8.0×10^{-4} mol l^{-1}; curves 1 and 1′), titan yellow (1.6×10^{-5} mol l^{-1}; curves 2 and 2′), and DBBTAB vesicles (8.0×10^{-4} mol l^{-1}) plus titan yellow (1.6×10^{-5} mol l^{-1}; curves 3 and 3′). Curves 1, 2, and 3 are excitation spectra monitored at 375 nm, (1), and 437 nm, (2) and (3). Curves 1′, 2′, 3′ are emission spectra, excitation at 295 nm.

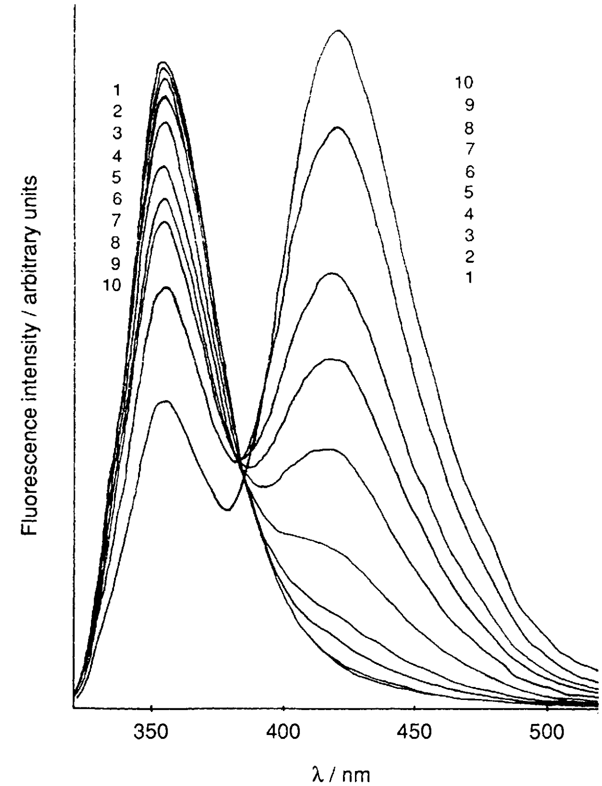


Figure 2. Energy transfer from a biphenyl-containing DBBTAB bilayer to a membrane-bound titan yellow acceptor at different concentrations of titan yellow. Concentration of DBBTAB vesicles, 8.0×10^{-4} mol l^{-1}. Excitation at 295 nm. Titan yellow concentration: (1) none, (2) 8.0×10^{-8}, (3) 8.0×10^{-7}, (4) 1.6×10^{-6}, (5) 4.0×10^{-6}, (6) 8.0×10^{-6}, (7) 1.2×10^{-5}, (8) 1.6×10^{-5}, (9) 2.4×10^{-5}, (10) 4.0×10^{-5} mol l^{-1}, respectively.

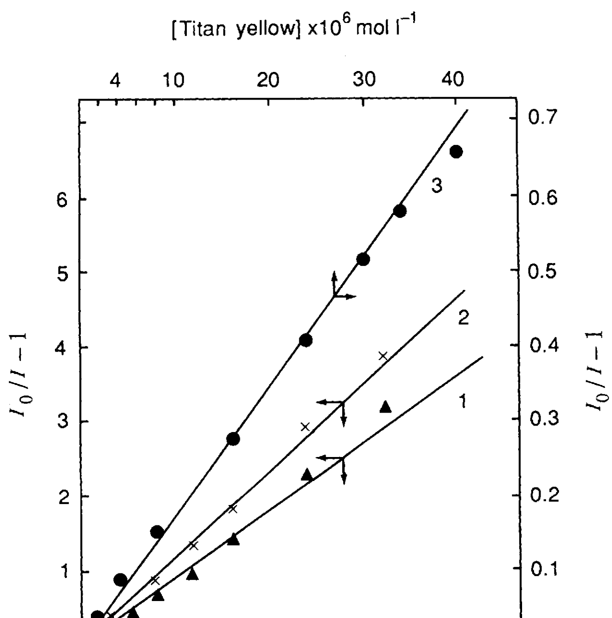


Figure 3. Stern–Volmer plot of biphenyl containing DBBTAB vesicles. (1) Sodium anthraquinone-2-sulphonate. (2) Sodium anthraquinone-2,7-disulphonate. (3) Titan yellow.

solution. These spectra are similar to those in alcohol except for the slight red shift of the corresponding band. Overlap of the emission spectrum at 355 nm of the biphenyl chromophore in DBBTAB vesicles with the excitation spectrum at 348 nm of titan yellow suggests possible Förster-type intermolecular energy transfer from the biphenyl chromophore in DBBTAB vesicles to membrane-bound titan yellow. Such energy transfer is observed in the presence of DBBTAB vesicles and titan yellow molecules, as illustrated in Figure 1, curve 3. The excitation of the mixture of DBBTAB vesicles and titan yellow in aqueous solution at 295 nm (where direct energy absorption by titan yellow is very small) resulted in an increase in the emission intensity, centred at 420 nm, of titan yellow

(1.6×10^{-5} mol l^{-1}) and a decrease in the emission intensity, centred at 355 nm, of the biphenyl in DBBTAB vesicles (8.0×10^{-4} mol l^{-1}). In alcohol solution, however, no energy transfer was observed under the same conditions. This result indicates that bilayer vesicles formed in aqueous solution play a decisive role in the efficient energy transfer process. Factors contributing to the occurrence of energy transfer are the specific molecular orientation of the bilayer membrane and the order aggregation of membrane-forming amphiphile molecules, as well as the organization of surrounding molecules. The results also provide evidence for the proposed morphology of DBBTAB vesicles.[13]

Figure 2 shows the changes in the fluorescence spectra of the DBBTAB vesicles as a function of the concentration of titan yellow. The fluorescence intensity of the biphenyl emission of DBBTAB vesicles (8.0×10^{-4} mol l^{-1}), which gives a broad peak centred at 355 nm, gradually decreases as the concentration of titan yellow increases. The fluorescence intensity of the emission peak, centred at *ca.* 420 nm, of the titan yellow increases with concentration up to *ca.* 5×10^{-5} mol l^{-1}, then starts to decrease. This decrease is probably due to inner filtering.[6]

It is clear that the titan yellow molecules quench the fluorescence of the biphenyl chromophore in the DBBTAB vesicles. This follows the Stern–Volmer relationship over the concentration range studied (0—2×10^{-5} mol l^{-1}), as shown in Figure 3, plot 1, see equation (1). I_0 and I are the emission intensities of DBBTAB vesicles in the absence and presence of titan yellow, respectively, and K_{SV} is the Stern–Volmer quenching constant. The slope of the Stern–Volmer plot gives K_{SV} 1.75×10^4 mol^{-1} dm^3. Other compounds such as sodium anthraquinone-2-sulphonate and sodium anthraquinone-2,7-disulphonate have a similar quenching effect on the 355 nm emission intensity of biphenyl, as shown in Figure 3 (plots 1 and 2) and also obey the Stern–Volmer equation [K_{SV} 1.85×10^5 mol^{-1} dm^3 and K_{SV} 2.35×10^5 mol^{-1} dm^3, respectively].

$$I_0/I - 1 = K_{SV}\,[\text{titan yellow}] \qquad (1)$$

In conclusion, the present work demonstrates the efficient transfer of excitation energy through the biphenyl chromophore introduced in a bilayer assembly to membrane-bound titan yellow molecules. The synthetic bilayer membrane has similar functions to the complex liposomes, but is readily manipulated and functionalized. Thus, specific chromophore-containing bilayers will have many applications in research.

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