Carbazole-containing Bilayer Membranes and Efficient Energy Migration

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Double-chain ammonium amphiphiles containing a carbazole unit undergo spontaneous assembly into bilayer vesicles in which efficient transfer of excitation energy to several acceptors is observed.

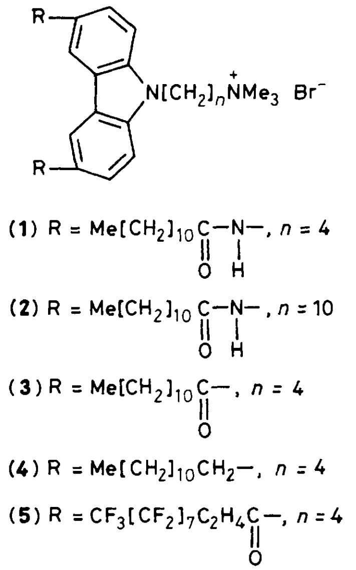
Synthetic bilayer membranes are regular two-dimensional arrays of molecules which are useful for the aggregation of chromophores. We recently observed Davydov splittings of absorption spectra that imply delocalization of excitation energy in aqueous bilayers which contain azobenzene[1] and anthracene[2] chromophores.

The carbazole ring is a principal chromophore in photoconducting polymers[3] and its photophysical properties have been studied extensively.[4] Therefore, it was of interest to prepare carbazole-containing bilayers in which regular chromophore aggregations are anticipated.

Five amphiphilic carbazole derivatives (**1**)—(**5**) were prepared. They all gave transparent aqueous dispersions. Figure 1 shows an electron micrograph obtained of an aqueous dispersion of (**2**). Vesicles of diameters of 400 to 2000 Å are readily seen. The small ones are mostly single-walled (layer width, 50 Å), but the larger ones appear to be double- and triple-walled. The critical micelle concentration determined by the conductivity method was *ca.* 1×10^{-5} M, and the molecular weight was *ca.* 10^8 (laser light scattering technique).[5] The other amphiphiles produced similar bilayer aggregates.

Fluorescence emission spectra of these aqueous bilayers exhibit different patterns. Bilayers of (**1**) and (**2**) show structureless emission at 408 nm, and a similar emission pattern is observed for bilayers of (**3**) at 420 nm. However, bilayers of (**4**) produce typical monomeric emission with maxima at 370 and 386 nm (see Figure 2), in spite of the extensive chromophore stacking. When the two hydrocarbon tails are replaced with fluorocarbon tails, (**5**), broad emission probably due to the excimer[6] is observed at 432 nm. The transformation of monomer emission into excimer emission by introduction of fluorocarbon tails has also been observed for a benzene chromophore in a bilayer of a double-chain ammonium amphiphile.[7]

The intensity of the fluorescence emission decreases on prolonged irradiation with u.v. light. The absorption spectra remain unchanged under the same conditions, and a fluorescence decrease is not observed under an argon atmosphere. Therefore, small amounts of photo-oxidation products must act as efficient quenchers of the carbazole fluorescence,[8] implying efficient migration of excitation energy. In order to confirm this possibility, small amounts of potential quenchers were added to the carbazole bilayers.



(1) $\mathrm{R = Me[CH_2]_{10}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\underset{\underset{\mathrm{H}}{|}}{\mathrm{N}}-,\ n = 4$

(2) $\mathrm{R = Me[CH_2]_{10}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\underset{\underset{\mathrm{H}}{|}}{\mathrm{N}}-,\ n = 10$

(3) $\mathrm{R = Me[CH_2]_{10}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-,\ n = 4$

(4) $\mathrm{R = Me[CH_2]_{10}CH_2}-,\ n = 4$

(5) $\mathrm{R = CF_3[CF_2]_7C_2H_4}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-,\ n = 4$

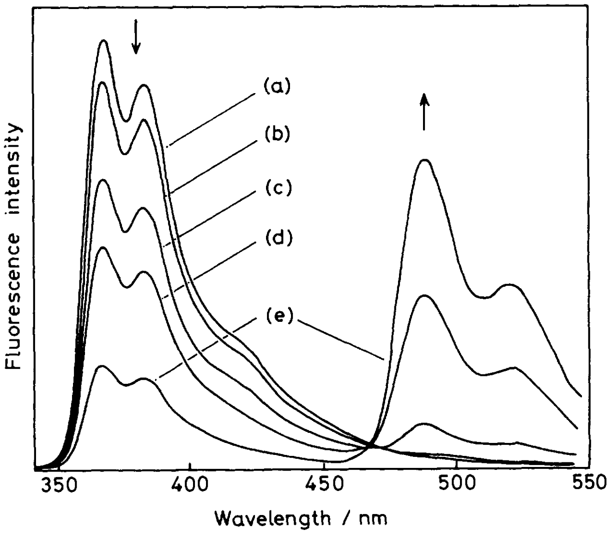


Figure 2. Energy transfer from carbazole bilayer (**4**) to perylene tetracarboxylate: [bilayer (**4**)] = 1.0 × 10^{-4} M, pH 9.1 (carbonate buffer), 20 °C, excitation at 300 nm. Perylene tetracarboxylate concentrations: (a) none, (b) 2.0 × 10^{-10} M, (c) 2.4 × 10^{-9} M, (d) 2.5 × 10^{-8} M, (e) 1.1 × 10^{-6} M.

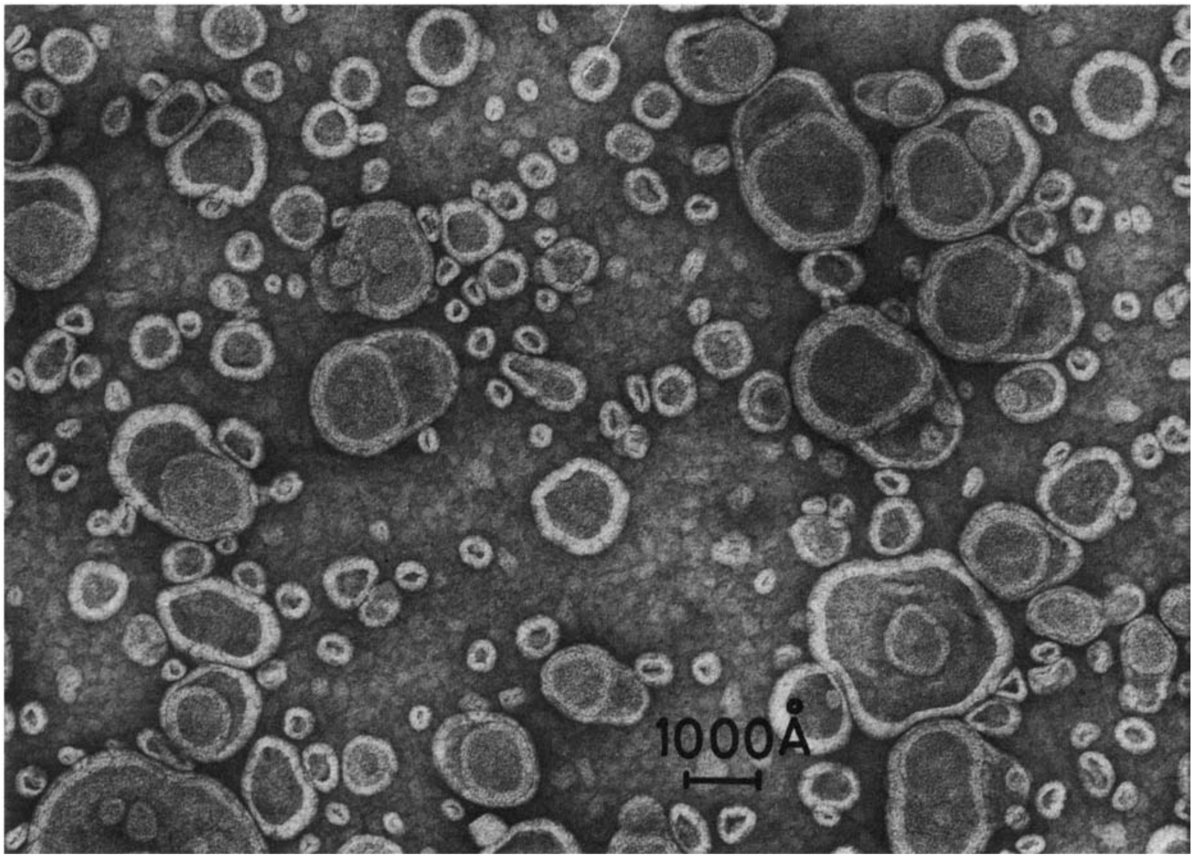
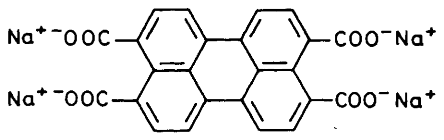
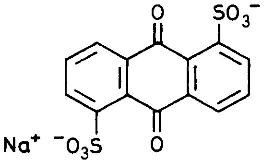


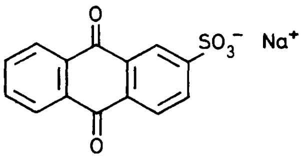
Figure 1. Electron micrograph of a carbazole-containing bilayer membrane (**2**), stained by uranyl acetate.



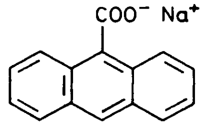
(6)



(7)



(8)



(9)

Figure 2 demonstrates the change in fluorescence spectra of the bilayer of (**4**) by adddition of perylene tetracarboxylate (**6**). The decrease in the carbazole emission is accompanied by an increase in the emission (490 nm and 520 nm) of the perylene. The energy transfer is clearly noticeable at 2×10^{-10} M acceptor.

The hopping number of the excitation energy within its life time was estimated by using an equation[9] that is derived from the analysis by Klöpffer.[10] In the case of the polyanionic acceptors (**6**) and (**7**) the hopping number was *ca.* 10^3, but the monoanionic acceptors gave much larger numbers: 5×10^3 for (**8**), and 7×10^3 for (**9**). The latter values are larger than that found for perylene-doped poly(vinylcarbazole),[9,11] but are smaller than that observed for perylene-doped single crystals of *N*-isopropylcarbazole.[10]

In conclusion, the present results demonstrate that the efficiency of transfer of excitation energy among chromophores in the bilayer assembly is close to that achieved in the single crystal.

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