

## Molecular Design of Artificial Photosynthesis Based on Synthetic Bilayer Membranes

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Chromophore-containing bilayer membranes are designed as an antenna apparatus in an artificial photosynthetic system. A large Davydov splitting indicating delocalization of excitation energy is found in an azobenzene-containing bilayer membrane. Migrating energy is trapped to so-called "excimer site" within ten picosecond and fluorescence emission from the self-trapped exciton is observed. Excitation energy of a stilbene-containing bilayer membrane is effectively transferred to an energy acceptor bound to the membrane surface. Hopping kinetics of the exciton migration applies very well in the bilayer system. A triplet exciton is also found in a benzophenone-containing bilayer membrane. Strong phosphorescence of the benzophenone chromophore is observed even at room temperature and is efficiently quenched by a small amount of sodium naphthalenesulphonate.

### Introduction

Construction of "artificial photosynthesis" is an attractive subject not only from a practical standpoint of photo-energy conversion but also from biomimetic interest of molecular organizes. A basic conceptual model of our "artificial photosynthesis" is a supramolecular photoreactor composed of three parts of molecular clusters; photo-energy collectors, electron transporting systems, and a center of chemical reaction. Regulation of molecular orientation in the molecular cluster is essential for effective photo-energy transfer and electron transport. Control of molecular distribution is also required for the design of molecular cluster. Effective linkage among the molecular clusters is a final step of assembling procedures. Two-dimensional molecular organizes, such as surface monolayer, Langmuir-Blodgett films, and bilayer membranes, are suitable candidates for the supramolecular photoreactor because of their two-dimensional molecular ordering.

Molecular orientation in the photo-energy collector is focused in this article. Effective photo-energy collection is indispensable in designing an antenna system in the artificial photosynthesis. Extremely efficient energy migration have been observed in organic molecular crystals where the excitation energy is delocalized in the crystal as "exciton". In

spite of this fact, organic molecular crystals are generally considered to have little potential for the antenna system because of its difficulty to couple with reaction center. The excitonic antenna system in designed molecular assemblies was pioneered by Kuhn and Möbius using cyanine dyes embedded in the Langmuir-Blodgett film.<sup>1</sup> In this paper, excitonic antenna systems in chromophore-containing bilayer membranes are discussed.

### 1. Molecular Exciton in Bilayer Assemblies

#### 1.1 Molecular Exciton Theory

Intermolecular interaction is classified by three categories depending on the intensity of the intermolecular coupling force.<sup>2</sup> In the case of strong interaction, intermolecular energy transfer is faster than intramolecular vibrational relaxation from Frank-Condon state. A strong intermolecular interaction at the ground state is observed as Davydov splitting in the absorption spectrum. The rate of intermolecular energy transfer is comparable to the vibrational relaxation in weak-coupling interaction. Spectral shift is not observed, but change of molar absorption coefficient such as hypochromism or hyperchromism is often found. While in the very weak-coupling

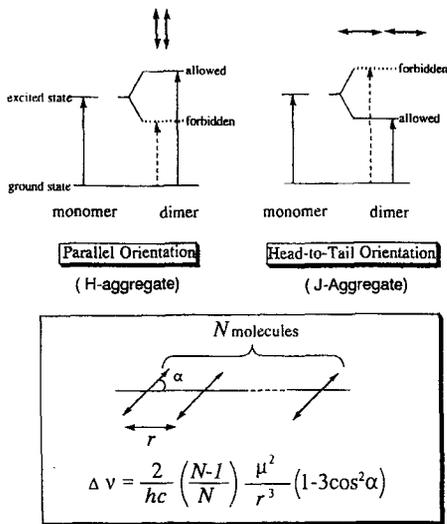


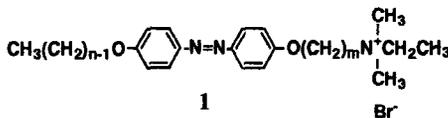
Figure 1. Molecular exciton model proposed by Kasha.

case, excitation energy transfers after the vibrational relaxation. Resonance transfer mechanism based on the dipole-dipole interaction proposed by Förster is applicable to the very weak interaction.

Kasha proposed "molecular exciton theory" for the strong-coupling case in molecular aggregates.<sup>3</sup> Exciton band splitting is related to the orientational mode (orientation angle  $\alpha$ , distance between dipoles  $r$ , and number of molecules  $N$ ) of the transition moments (Figure.1). In the parallel orientation ( $\alpha=90^\circ$ ) of dimer model, a large hypsochromic shift (blue shift) in the absorption spectrum is predicted. Bathochromic shift (red shift) is the case of the head-to-tail orientation ( $\alpha=0^\circ$ ). Spectral shifts reflecting the orientational geometry of dye molecules are well known as H-aggregate (parallel orientation) and J-aggregate (head-to-tail orientation), respectively.

### 1.2 Spectral Properties of Azobenzene Bilayers

The first finding of the exciton splitting in bilayer assemblies was found in aqueous solutions of azobenzene amphiphiles 1.<sup>4</sup>



Although the absorption maxima of these amphiphiles in ethanol are completely identical (355nm), aqueous solutions show varied absorption spectra. And absorption maximum is strongly dependent on the alkyl chain length. Homologous series of  $m=5$  show a large bathochromic shift to around

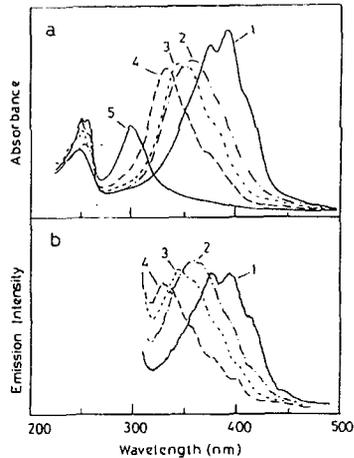


Figure 2. Absorption (a) and excitation (b) spectra of aqueous azobenzene bilayers. (1) $m=12, n=5$ , (2) $m=4, n=12$ , (3) $m=6, n=12$ , (4) $m=10, n=10$ , (5) $m=10, n=8$ .

400nm. Hypsochromic shift to 300nm is found when the difference of the two alkyl chain ( $m-n$ ) is larger than two (Figure.2).

According to the semi-quantitative calculation of the molecular exciton theory, the red shifts and blue shifts relative to the isolated azobenzene chromophore are attributed to the head-to-tail orientation and the parallel orientation in the bilayer membrane, respectively. An X-ray structural analysis of the single crystal proves that the spectral speculation on the chromophore orientation is in fact.<sup>5</sup>

## 2. Exciton Migration in Bilayer Assemblies

### 2-1. Efficient Energy Transfer in Azobenzene Bilayer

Unexpected broad emission with a large Stokes shift is accidentally observed during the course of the photoisomerization experiment.<sup>6</sup> Figure 3 shows time-resolved fluorescence spectra of the bilayer membrane of 1 ( $m=5, n=12$ ). At the early stage of the photoexcitation, a sharp emission with very short life time (ca.10 picosecond) is found at around 470nm. A new emission at around 600nm appears concomitant with the decay of 470nm emission. Because the excitation spectrum monitored at 600nm emission is identical to the absorption spectrum (Figure 2(b)), the peculiar emission of the azobenzene bilayer is ascribable to the exciton emission. The short lived emission is attributed to a free exciton that migrates around in the bilayer membrane and is captured so-called "excimer" site (self-trapped exciton).

### 2-2. Kinetic Evidence of Exciton Migration

Absorption spectrum of stilbene amphiphile 2 in ethanol shows a typical pattern of *trans* stilbene (dashed line in Figure

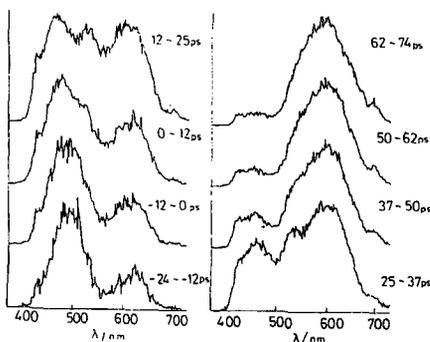
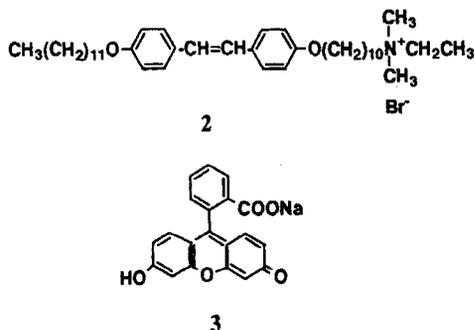


Figure 3. Time-resolved fluorescence spectra of azobenzene bilayer membrane ( $m=5, n=12$ ).

4), whereas a large hypsochromic shift is observed for a transparent aqueous dispersion. This shift is apparently attributed to the parallel orientation of the stilbene chromophore. Red-shifted structured fluorescence is ascribable to be the free exciton. Broad emission from self-trapped exciton is not detected. As shown in Figure 4, fluorescence of the free exciton is quenched efficiently by an anionic energy acceptor 3, and the emission of 3 appears at 530nm.



Plots of  $I_0/I$  against the acceptor concentration (where  $I_0$  and  $I$  are the fluorescence intensity of the donor in the absence and presence of the acceptor molecule, respectively) is known to be Stern-Volmer plot. A straight line of Stern-Volmer plot indicates that the quenching process is diffusion controlled. The slope of the plot gives Stern-Volmer constant that is the product of the donor's life time and the quenching rate constant. A large value ( $1.8 \times 10^7$ ) of the Stern-Volmer constant of this experiment suggests that the quenching rate is extremely faster than the diffusion rate of the acceptor molecule even if the life time of the donor is estimated to be one nanosecond.

Klöpper proposed quenching kinetics based on the exciton diffusion for organic molecular crystals.<sup>7</sup> In this mechanism,

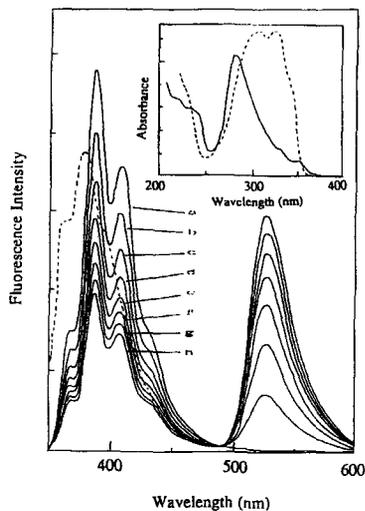


Figure 4. Absorption (inserted) and fluorescence spectra of stilbene bilayer membrane. acceptor concentration: (a) 0M, (b) 9.8nM, (c) 20nM, (d) 30nM, (e) 39nM, (f) 49nM, (g) 59nM, (h) 68nM.

quenching efficiency  $Q$  ( $Q=I_0/I - 1$ ) is proportional to the trapping probability, which is given by a product among the jumping probability during the life time, the capturing probability by the acceptor site, and the molar ratio of the acceptor molecule. If the capturing probability is unity and only acceptor site acts as energy trap (no self-trapped exciton), the quenching kinetics is expressed in a simple equation

$$Q = nc(1-F) = n'c \quad (1)$$

where  $c$  is the acceptor concentration (mol/mol),  $n$  is the hopping number of the exciton,  $F$  is the returning probability to the starting point in the random walk process of the exciton hopping. A straight line with the slope of 1.0 and the intercept ( $\log n'$ ) of 3.0 in the double-logarithmic plots of eq.1 strongly indicates that the stilbene exciton hops around the bilayer membrane more than 1000 times within its lifetime (Fig.5).<sup>8</sup>

### 2-3. Triplet Exciton

Benzophenone is a well known chromophore having a strong phosphorescence emission. An excitonic spectral shift is also found in an aqueous bilayer solution of a benzophenone amphiphile 4. Absorption maximum drastically shifts from 268nm to 292nm at around 50°C which corresponds the crystal-to-liquid crystal phase transition temperature ( $T_c$ ) measured by the differential scanning calorimetry (51.5°C). The later absorption maximum is similar to the isolated chromophore in an ethanol solution. A strong chromophore interaction is promoted by the ordered molecular packing at lower temperature than  $T_c$ .

Structured emission typical of benzophenone

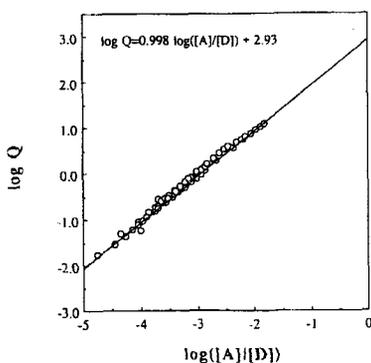


Figure 5. Double-logarithmic plots of quenching factor  $Q$  vs. molar ratio  $c([A]/[D])$ . Sixty-three data were obtained at various donor concentration.

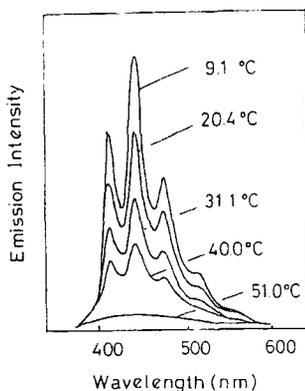
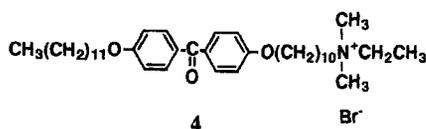


Figure 6. Temperature dependence of phosphorescence of benzophenone bilayer membrane.

phosphorescence is surprisingly observed even in the aqueous solution without deaeration procedure. Since the phosphorescence emission is intense below  $T_c$ , the peculiar emission is ascribable to the triplet exciton of the benzophenone. Thermal deactivation process of the triplet energy is assumed to be suppressed at the crystalline state. Results of an efficient phosphorescence quenching by a triplet energy acceptor (sodium naphthalene-2-sulphonate) follow the exciton hopping kinetics and the hopping number of the triplet

exciton is estimated to be about 1100.<sup>9</sup>

### Concluding Remarks

Remarkable Davydov splitting in the absorption spectrum and a satisfactory fitting of energy transfer to the "exciton" hopping kinetics proposed for organic molecular crystals are the definitive evidence for "exciton" formation and migration in self-assembling bilayer membranes in aqueous solution. These findings are quite significant not only for construction of an efficient antenna apparatus but also for creative novel aspects of photochemistry of molecular assemblies in general.

### Acknowledgment

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### References

1. e.g., Möbius, D., *Ber. Bunsenges. Phys. Chem.*, **82**, 848-858 (1978).
2. e.g., Kasha, M., *Radiation Research*, **20**, 55-71 (1963).
3. Kasha, M., "Spectroscopy of the Excited State", Ed. by B.D. Bartolo, Plenum Press, New York, 1976, pp. 337-363.
4. Shimomura, M., Ando, R., Kunitake, T., *Ber. Bunsenges. Phys. Chem.*, **87**, 1134-1143 (1983).
5. Okuyama, K., Watanabe, H., Shimomura, M., Hirabayashi, K., Kunitake, T., Kajiyama, T., Yasuoka, N., *Bull. Chem. Soc. Jpn.*, **59**, 3351-3356 (1986).
6. Shimomura, M., Kunitake, T., *J. Am. Chem. Soc.*, **109**, 5175-5183 (1987).
7. Klöpffer, K., *J. Chem. Phys.*, **50**, 1689-1694 (1969).
8. Shimomura, M., *Annual Report of Iwatani Memorial Foundation*, **11**, 45-49 (1988).
9. Kimizuka, N., Kawanaka, T., Shimomura, T., Kunitake, T., *Polym. Prep. Jpn.*, **35**, 397 (1986).