

# Influence of Molecular Arrangements on the Properties of Polymethine Dye Aggregates

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## Abstract

In order to clarify the properties of interactions between chromophores in polymethine dye aggregates, we prepared polymethine dye dimers in which two chromophores are covalently connected to each other in linear, stack, cross, and brickstone-work modes. The linear and stack dimers were proved to be a J- and an H-aggregate model, respectively, based on the optical analysis. The cross dimer showed the splitting of absorption bands, which was attributed to the splitting of HOMO levels through spiroconjugation-like orbital interactions. The redox potentials of these dimers were different from those of the corresponding monomer.

In order to make a brickstone-work arrangement proposed as a structural model of polymethine dye aggregates on silver halide grains, dimers in which two chromophores are linked by a 1,8-naphthylene skeleton were prepared. The two rotational isomers, *syn* and *anti* conformers, showed some of the typical properties of an H- and a J-aggregate, respectively. The (1,8-naphthylene)-bismero cyanine showed novel solvatochromism based upon change of intermolecular excitonic coupling mode.

The relative arrangement of chromophores in the dimers affects not only transition energies of aggregate bands but also redox potentials of dye aggregates. For a correct understanding of the properties of polymethine dye aggregates, overlapping of orbitals and Coulombic interaction, besides excitonic coupling, must be taken into consideration.

## Introduction

Although aggregates of polymethine dyes are well-known and widely used as spectral sensitizers of silver halide photographic materials, the properties of polymethine dye aggregates remain ambiguous. Usually, a bathochromically-shifted band is called a J-band, while a hypsochromically-shifted one is called an H-band. The relationship between

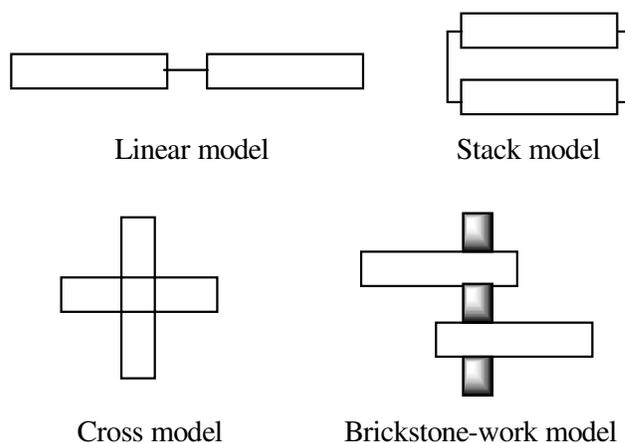


Figure 1. Schematic Diagram of Model Compounds

the relative orientation of chromophores and the spectral shifts has been explained in terms of molecular exciton theory. In this theory, a parallel dimer shows an H-band and a linear dimer shows a J-band.

There is much concern about orbital energy levels of a dye aggregate, since it is widely accepted nowadays that in spectral sensitization an electron of the excited state of a sensitizing dye transfers to a conduction band of a silver halide crystals. Molecular exciton theory can predict spectral shifts of a dye aggregate. However, it is probably unsuitable for prediction of energy levels of a dye aggregate, since the molecular exciton theory is valid only when the interaction between orbitals of constituent molecules is negligible. The effect of chromophore arrangements on the orbital energy levels of aggregates has rarely been demonstrated. This is probably due to the experimental difficulty in preparing a dye aggregate in which the chromophore arrangements and the number of constituent molecules are well defined. The synthesis of model compounds of polymethine dye aggregates by connecting covalently more than two dye moieties seems to be promising, because it provides us with isolated aggregate

models having well-defined structures. In this work, we prepared model compounds in which the chromophore arrangements are fixed in linear, stack, and cross modes and investigated the properties (Figure 1).

### Linear and stack models<sup>1)</sup>

A linear dimer (**1a**) in which the nitrogen atoms of two chromophores are mutually linked by two ethylene chains and a stack dimer (**1b**) connecting by two substituted trimethylene chains were prepared (Figure 2). In this paper, we call a compound which contains two identical chromophores a dimer.

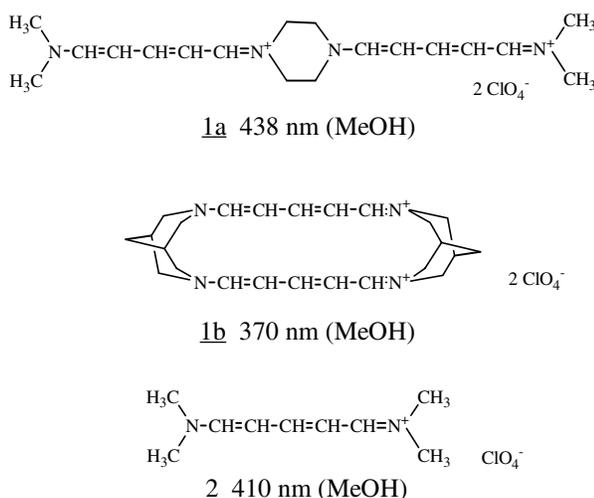


Figure 2. Structures of the linear dimer **1a** and the stack dimer **1b**

The absorption spectra of **1a** in methanol showed a bathochromic shift of 28 nm compared to that of the monomer (**2**), on the other hand, the absorption band of **1b** underwent a hypsochromic shift of 40 nm. The fluorescence of the linear dimer **1a** in methanol was a larger in intensity and a smaller Stokes shift than that of the monomer **2**, while the stack dimer **1b** had a smaller fluorescence in intensity and a larger Stokes shift. These observations are in agreement with a molecular exciton coupling theory, indicating that **1a** and **1b** are suitable for model compounds of J- and H-aggregates, respectively.

The reduction and oxidation potentials for **1a** (E<sub>red</sub> = -1.31 V, E<sub>ox</sub> = 1.09 V) were positively shifted compared to those for the monomer **2** (E<sub>red</sub> = -1.36 V, E<sub>ox</sub> = 0.98 V). These shifts are considered to be due to the Coulombic interaction between the cationic charge of the neighboring cyanine moiety and electrons. The reduction potential of **1b** (E<sub>red</sub> = -1.17 V) was positively shifted, while the oxidation potential (E<sub>ox</sub> = 0.76 V) showed a negative shift compared to those of the monomer **2**. These were observations explained by a combination of the orbital and Coulombic interactions.

### Cross model<sup>2)</sup>

A cross dimer is expected to be a suitable model to investigate orbital interactions, since in molecular exciton theory, an exciton coupling of transition moments that lie perpendicularly to each other will not be observed. A cross dimer (**3**) in which the two cyanine moieties are linked at the center carbon atoms of the two methine chains was prepared (Figure 3). The X-ray crystallographic analysis revealed that the two cyanine moieties are arranged perpendicularly to each other.

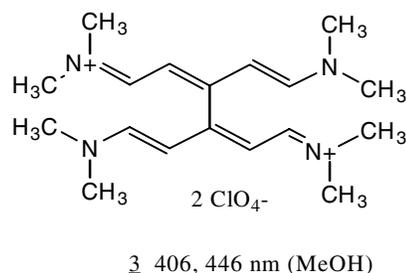


Figure 3. Structure of the cross dimer **3**

The absorption spectrum of **3** in methanol showed the two absorption bands at 446 and 406 nm. Based upon the INDO/S-CI calculation, the band splitting was attributed to the splitting of the HOMO levels through spiroconjugation-like orbital interactions. The reduction potential of **3** (E<sub>red</sub> = -0.90 V) positively shifted with respect to that of the corresponding monomer **2**, while the oxidation potential of **3** (E<sub>ox</sub> = 0.94 V) underwent a negative shift compared to **2**. These shifts were consistent with the calculated molecular orbital energy levels.

### Brickstone-work model<sup>3)</sup>

Brickstone-work models have been proposed for structures of polymethine dye aggregates on silver halide grains. To achieve such a brickstone-work arrangement, biscyanines in which the two cyanine chromophores are linked by a 1,8-naphthylene skeleton were prepared. (1,8-Naphthylene)-biscyanines possess two rotational isomers, *syn* and *anti* isomers, where the two cyanine moieties point in the same or opposite directions with respect to the naphthalene plane, respectively (Figure 4).

The NMR and X-ray crystallographic analysis exhibited that the biscyanine **4a** having methoxy groups was only the *syn* isomer in solution. In order to raise the population of an *anti* isomer by charge repulsion, we introduced a sulfonate group on each dye moiety. It was revealed that the biscyanine **4b** actually exists as the *anti* isomer in solution (Figure 5).

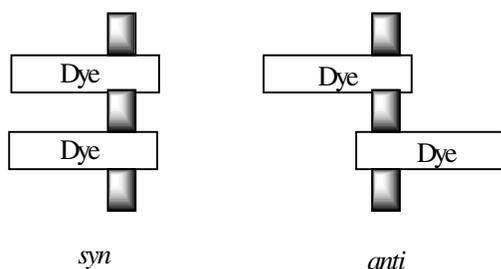


Figure 4. Schematic diagram of the two rotational isomers of (1,8-naphthylene)biscyanines

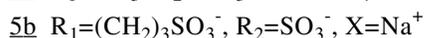
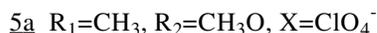
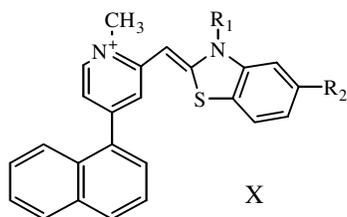
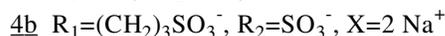
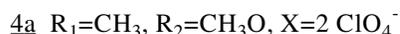
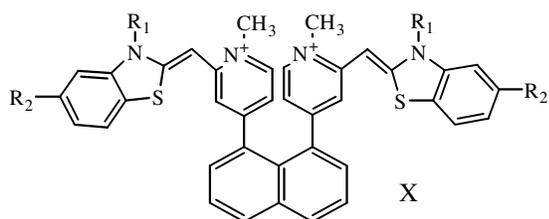


Figure 5. Structures of the (1,8-naphthylene)-biscyanines 4 and the monocyanines 5

The absorption band of the *syn* isomer 4a (453 nm) in dimethylsulfoxide is 8 nm hypsochromically shifted compared to the corresponding monomer 5a (461 nm), while the *anti* isomer 4b (480 nm) showed a bathochromic shift of 26 nm compared to 5b (454 nm).

The reduction potentials of 4a (Ered = -1.12 V) and 4b (Ered = -1.21 V) are positively shifted compared to those of 5a (Ered = -1.31 V) and 5b (Ered = -1.32 V), respectively, and the oxidation potentials of 4a (Eox = 0.97 V) and 4b (Eox = 0.91 V) are comparable to those of 5a (Eox = 0.98 V) and 5b (Eox = 0.93 V). Furthermore, the positive shift of the *syn* isomer 4a (0.19 V) is larger than that of the *anti* isomer 4b (0.11 V). The positive shift of the reduction potentials were explained by the difference in Coulombic and orbital interactions between the two cyanine moieties.

## Merocyanine model<sup>4)</sup>

Although many kinds of cyanines form J-aggregates in silver halide emulsions, few examples of merocyanine J-aggregates have been reported. In order to clarify the properties of merocyanine aggregates, bimerocyanine (6) in which two merocyanine chromophores were linked by a 1,8-naphthylene skeleton was prepared (Figure 6).

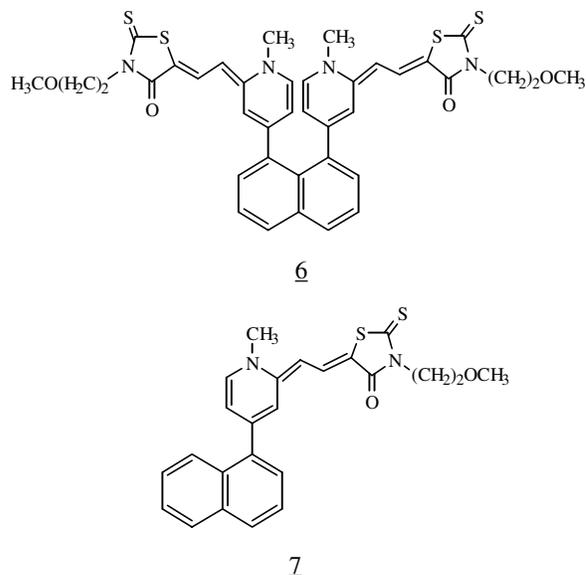


Figure 6. Structures of the (1,8-naphthylene)-bimerocyanine 6 and the monomerocyanine 7

The bimerocyanine showed *syn* - *anti* isomerism. The isomer ratio of *syn* : *anti* for 6 in various solvents indicated that a polar solvent such as acetonitrile enhanced a preference for the *syn* isomer (*syn* : *anti* = 90 : 10 in  $\text{CD}_3\text{CN} + 2\%\text{CD}_3\text{OD}$ , *syn* : *anti* = <5 : 95 in  $\text{CDCl}_3$ ). This solvent effect on the *syn* / *anti* ratio is in accordance with a difference of the dipole moments between the *syn* and *anti* isomer. The AM1 calculations indicated that the dipole moments of the *syn* and *anti* isomer were 17.0 and 8.0 D, respectively. The *syn* isomer must be more stable than the *anti* one in a relatively polar solvent.

The absorption band of 6 in chloroform (568 nm) was bathochromically shifted compared to that of the corresponding monomer 7 (551 nm), while the absorption band of 6 in acetonitrile (516 nm) underwent a hypsochromic shift compared to 7 (550 nm). The absorption spectra in methylene chloride-methanol showed both the bathochromic and hypsochromic bands compared to that of the corresponding monomer 7, and that the hypsochromic band becomes intense with increasing the methanol fraction. This solvatochromism of 6 was interpreted by the change of the *syn* / *anti* ratio based on the INDO/S-CI calculations and the NMR analysis.

The reduction potentials of **6** in both acetonitrile ( $E_{red} = -1.41$  V) and methylene chloride ( $E_{red} = -1.49$  V) were positively shifted compared to those of **7** ( $E_{red} = -1.55$  V in  $\text{CH}_3\text{CN}$ ,  $E_{red} = -1.56$  V in  $\text{CH}_2\text{Cl}_2$ ), while the oxidation potentials of **6** ( $E_{ox} = 0.30$  V in  $\text{CH}_3\text{CN}$ ,  $E_{ox} = 0.46$  V in  $\text{CH}_2\text{Cl}_2$ ) shifted negatively compared to **7** ( $E_{ox} = 0.37$  V in  $\text{CH}_3\text{CN}$ ,  $E_{ox} = 0.49$  V in  $\text{CH}_2\text{Cl}_2$ ). These potential shifts are in accordance with expectations based on the orbital interaction between the two merocyanine moieties. The difference of the reduction potentials between **6** and **7** in acetonitrile (0.14 V) was larger than that in methylene chloride (0.07 V). This result indicates that the reduction potentials of **6** are affected by the *syn* / *anti* ratio.

### Conclusions

In order to clarify the properties of interactions between chromophores in polymethine dye aggregates, polymethine dye dimers were synthesized, in which two chromophores are covalently connected to each other in linear, stack, and cross modes. The spectral shifts of linear and stack models were in agreement with those based upon the molecular exciton theory. The absorption band splitting of the cross dimer was attributed to the splitting of the degenerate HOMO levels through spiroconjugation-like orbital interactions, indicating that orbital interactions as well as exciton couplings play an important role in dye aggregates. The redox potentials of cyanine dimers positively shifted compared to those of the corresponding monomer, which was explained by a combination of Coulombic and orbital

interactions. The relative arrangement of chromophores affects not only transition energies of aggregate bands but also redox potentials of dye aggregates: overlapping of orbitals and Coulombic interaction, besides excitonic coupling, must be taken into consideration for a correct understanding of the properties of the polymethine dye aggregates.

### References

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### Biography

Takashi Katoh was born in 1964 and received his Master's degree in 1989 from the University of Tokyo. In 1989 he joined Fuji Photo Film Co., and received his Doctor's degree in 1996 from the University of Tokyo for this work under Prof. Renji Okazaki. His research interest is in supramolecular chemistry in spectral sensitization. He is a member of the Chemical Society of Japan and the American Chemical Society.