Synthesis and Properties of Bismerocyanines Linked by a 1,8-Naphthylene Skeleton. Novel Solvatochromism Based on Change of Intramolecular Excitonic Coupling Mode

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Abstract: A newly prepared bismerocyanine linked by a 1,8-naphthylene skeleton has two rotational isomers, syn and anti conformers, with respect to orientation of the two merocyanine chromophores. The NMR studies revealed that a polar solvent such as acetonitrile enhanced a preference for the syn conformer to bring about much larger bathochromic shift of the UV/vis absorption band than that of a 1-naphthyl-substituted merocyanine. The INDO/S-CI calculation indicated that the UV/vis absorption bands of the syn and anti conformers are hypsochromically and bathochromically shifted, respectively, compared to that of the 1-naphthylmerocyanine. In accordance with the prediction based on an exciton coupling theory, the anti conformer fluoresces while the syn conformer does not. A polarographic analysis indicated a positive shift of reduction potential and a negative shift of oxidation potential compared to the corresponding value of the 1-naphthylmerocyanine. The shift in the reduction potential of the bismerocyanine relative to the 1-naphthylmerocyanine in acetonitrile was larger than those in chloroform. This was attributed to the difference in the syn/anti ratio.

Introduction

It has been known for a long time that merocyanines, which consist of a formally uncharged conjugate system with a vinylogous amide structure,[1,2] show solvatochromism.[3,4] Solvatochromism of merocyanines is ascribed to the drastic change of a dipole moment on excitation and is related to relative contributions of two canonical forms, nonpolar quinoid and dipolar zwitterionic ones.[5] Merocyanines are important as spectral sensitizers in photographic materials[6] and have attracted much attention also in the field of nonlinear optics[7] and solar energy conversion.[8] Recently, much concern about molecular devices using reversible changes between different states has been shown.[9−13]

Some dyes form aggregates in an aqueous solution and show spectral shifts.[14] *J*-aggregates, which were discovered by Jelly[15] and Scheibe[16] in 1930s, have been characterized by their narrow absorption peak and bathochromic shifts compared to the

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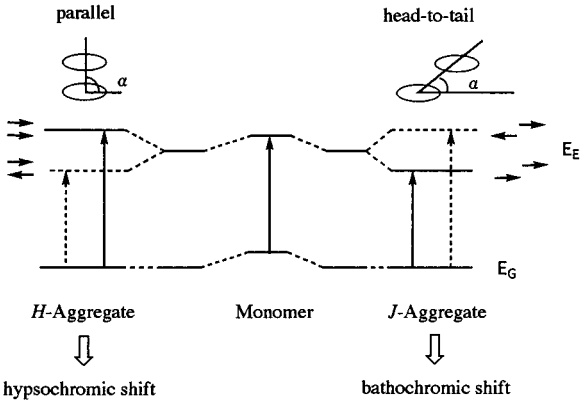

Figure 1. Schematic diagram of the relationship between relative orientation of chromophores and spectral shifts based upon molecular exciton theory.

corresponding monomeric dye. On the contrary, a hypsochromically shifted aggregate is called an *H*-aggregate. Aggregates of polymethine dyes have been of much interest because of their unique photophysical and optical properties.[17] The relationship between relative orientation of chromophores and spectral shifts of a dye aggregate has been explained in terms of molecular exciton theory,[18,19] in which an excited state of a dye aggregate splits into two levels through the coupling of transition dipoles (Figure 1). In a parallel dimer with a large slip angle (α), a transition to the upper state of the two excited states is allowed and hence the absorption of a dimer is hypsochromically shifted compared to that of a monomeric dye. On the other hand, in a head-to-tail dimer with a small slip angle (α), a transition to the lower state is allowed and the absorption undergoes a bathochromic shift.

Although many kinds of cyanines form *J*-aggregates in aqueous solutions or in silver halide emulsions, few examples of merocyanine *J*-aggregates have been reported.[20−22] Making use of Langmuir−Blodgett techniques, Kuhn et al. revealed that

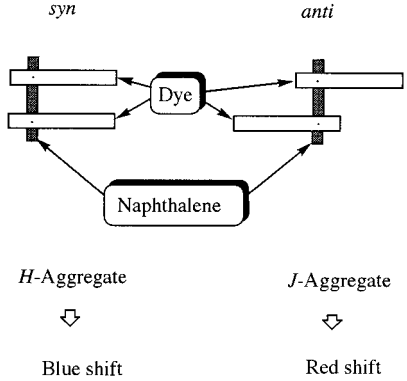

Figure 2. Schematic diagram of two rotational isomers of a biscyanine linked by a 1,8-naphthylene skeleton.

merocyanines having long alkyl chains aggregate in monomolecular layers and show aggregate bands.[21] Recently, Nüesch et al. observed *H*- and *J*-aggregates of merocyanines in metal oxide films made of TiO_2, Al_2O_3, or ZrO_2.[22] Upon the basis of X-ray crystallographic analysis of single crystals and scanning force microscopy (SFM) analysis of monolayers, a brickstonework model was proposed as a structure of merocyanine *J*-aggregates.[23] Absorption bands of hypothetical merocyanine aggregates were calculated with the exciton coupling theory to suggest that *H*- and *J*-aggregates have large (ca. 90°) and small slip angles (ca. 30°), respectively.[24]

There is much concern about orbital energy levels of a dye aggregate, since today it is widely accepted that in spectral sensitization of photographic emulsions an electron of the excited state of a sensitizing dye transfers to a conduction band of a silver halide crystal.[9,25] However, little is known about orbital energy levels of a dye aggregate. This is probably due to the experimental difficulty in isolating a dye aggregate in which the mode of a chromophore arrangement and the number of constituent molecules are well defined. Many examples of biscyanines[26−28] and a few bismerocyanines[29] in which more than two chromophores were covalently linked have been reported. Although some of these bismerocyanines with two chromophores linked by a polymethylene chain to each other showed aggregate absorption bands, the chromophore arrangements remained ambiguous. Recently, biscyanines linked by a 1,8-naphthylene skeleton were prepared by our group and the effects of the relative orientation of two chromophores on the spectral shifts and the redox potentials were investigated.[28] The two rotational isomers, the syn and anti conformers, of (1,8-naphthylene)biscyanines showed such spectral shifts as to be expected for *H*- and *J*-aggregate models, respectively (Figure

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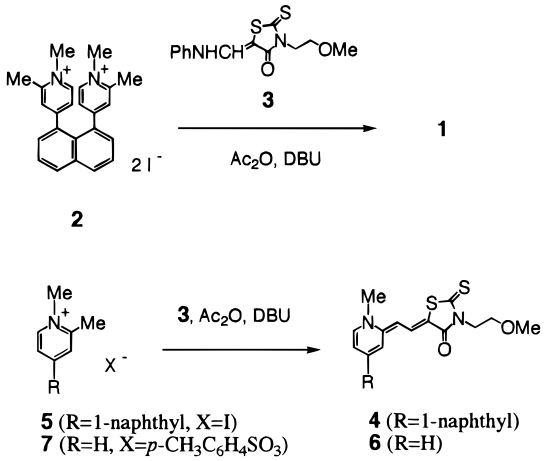
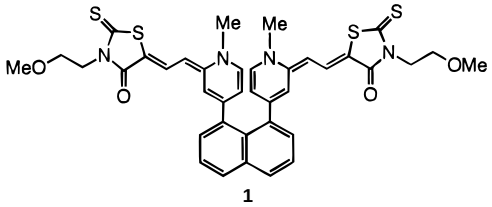
Scheme 1



5 (R=1-naphthyl, X=I)
7 (R=H, X=*p*-$CH_3C_6H_4SO_3$)

4 (R=1-naphthyl)
6 (R=H)

2). Accordingly, the 1,8-naphthylene linkage is expected to be suitable also for making model compounds of merocyanine aggregates. In this paper, we describe the synthesis of (1,8-naphthylene)bismerocyanine **1** and its novel solvatochromism and pronounced shifts in redox potentials. We account for these properties of the bismerocyanine in terms of a change in the chromophore arrangement by rotational isomerization.



1

Results and Discussion

Synthesis. The bismerocyanine linked by a 1,8-naphthylene skeleton **1** having rhodanine nuclei was prepared from 4,4′-(1,8-naphthylene)bispyridinium **2** and enamine **3** in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and acetic anhydride (Scheme 1). Similarly, 1-naphthyl-substituted monomerocyanine **4** and prototypical monomerocyanine **6** were prepared from 4-(1-naphthyl)pyridinium and pyridinium salts, **5** and **7**, respectively.

Structures. The ^{1}H NMR spectrum of the bismerocyanine **1** in CD_2Cl_2 at 298 K showed two sets of sharp signals (Figure 3). Warming of the sample solution caused a broadening of signals, indicating that **1** exists as a mixture of two isomers in CD_2Cl_2. The assignment of the anti conformers was confirmed on the basis of the appearance of the cross peaks between the 3- and 5-positions of the pyridine rings and between the 5-position of the pyridine rings and the β-position of the methine chain protons in the ROESY spectrum. The isomer ratio of syn:anti in various solvents indicated that a polar solvent such as acetonitrile enhanced a preference for the syn conformer (Table 1). This solvent effect on the syn/anti ratio of **1** is in accordance with a difference of the dipole moments between the syn and anti conformers. The dipole moments of **1** (syn) and **1** (anti) calculated with the AM1 method[30] using the MM2[31]-optimized structures were 17.0 and 8.0 D, respectively. The syn isomer must be more stabilized than the anti isomer in a relatively polar solvent. The coupling constants of the methine

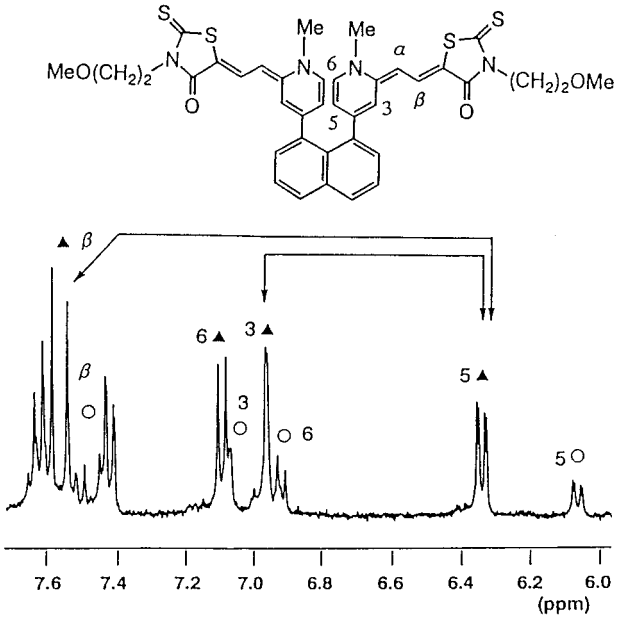


Figure 3. ^{1}H NMR spectrum of (1,8-naphthylene)bismerocyanine **1** in CD_2Cl_2 at 298 K. ○ and ▲ stand for the syn and anti conformers, respectively. The arrows indicate the cross peaks of ROESY.

Table 1. Solvent Effect on the Syn/Anti Ratio of (1,8-Naphthylene)bismerocyanine **1**

solvents	ET(30) (kcal mol^{-1})[a]	syn:anti[b]
$CDCl_3$	39	<5:95
CD_2Cl_2	41	24:76
DMSO-d_6	45	52:48
CD_3CN + 2% CD_3OD	46	90:10

[a] Values for $CHCl_3$, CH_2Cl_2, DMSO, CH_3CN, and CH_3OH in ref 3. [b] Determined by ^{1}H NMR at 298 K.

chain protons were 13 Hz, indicating all-trans conformations of the methine chains. The variable-temperature ^{1}H NMR spectra of **1** in DMSO-d_6 revealed the coalescence temperature to be 338 K and the free energy of the rotational isomerization was calculated to be 75 kJ mol^{-1}.[32]

UV/Vis Absorption Spectra. The absorption band of the bismerocyanine **1** in $CHCl_3$ (568 nm) was bathochromically shifted compared to that of the corresponding monomerocyanine **4** (551 nm), while the absorption band of **1** in acetonitrile (516 nm) underwent a hypsochromic shift compared to **4** (550 nm) (Figure 4). The absorption spectra of **1** in CH_2Cl_2−methanol showed both the hypsochromic and bathochromic bands and that the hypsochromic band becomes intense with increasing the methanol fraction (Figure 5). The pronounced solvatochromism makes a striking contrast with very slight solvatochromic shifts of the corresponding monomerocyanines **4** and **6**. The shape of the absorption band of **1** was independent of the concentration, indicating that the spectral shifts were not caused by intermolecular aggregation. The solvatochromism of **1** was interpreted by the change of the syn/anti ratio, which was supported by the INDO/S-CI calculation[33] and the NMR study described above. The calculation using the MM2-

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(31) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

(32) The rotational barrier was estimated based on eq 1, where $\Delta\nu$ is the chemical shift difference between the individual rotameric signals of methyl groups and T_c is the coalescence temperature: Gunther, F. *NMR Spectroscopy: An Introduction*; John Wiley and Sons: New York, 1980; p 180.

$$\Delta G^{\ddagger}\ (\mathrm{J\ mol^{-1}}) = 19.14T_c(9.97 + \log(T_c/\Delta\nu)) \qquad (1)$$

(33) Ridley, J.; Zerner, M. *Theor. Chim. Acta (Berlin)* **1973**, *32*, 111.

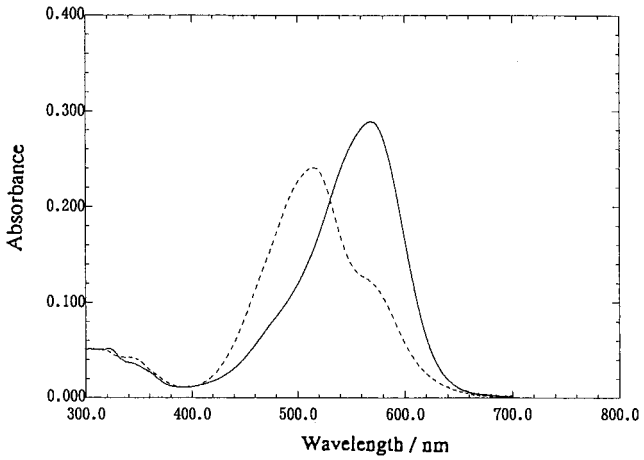

Figure 4. UV/vis absorption spectra of (1,8-naphthylene)bismerocyanine **1** in chloroform (—) and acetonitrile (···) at 298 K (3.0×10^{-6} mol dm^{-3}).

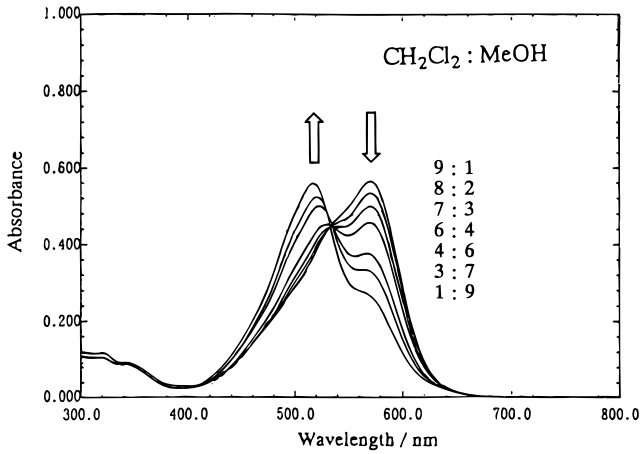

Figure 5. UV/vis spectral changes of **1** in various ratios of dichloromethane and methanol at 298 K (1.0×10^{-5} mol dm^{-3}).

Table 2. UV/Vis Absorption Spectra of (1,8-Naphthylene)bismerocyanines **1** (syn) and **1** (anti) and 1-Naphthylmerocyanine **4** Calculated with the INDO/S-CI Method

compd[a]	λ_{max} (nm)	f[b]	transition character[c]
1 (syn)	460	0.06	−0.45(H→L) + 0.33(H→L+1) − 0.36(H→L+2)
	397	2.06	−0.58(H→L+1)+0.60(H−1→L)
1 (anti)	456	1.15	−0.87(H→L)+0.36(H−1→L+1)
	450	0.39	+0.80(H→L+1)−0.46(H−1→L)
4	422	1.16	0.94(H→L)

[a] The MM2-optimized structures were used. [b] Oscillator strength. [c] H and L stand for HOMO and LUMO, respectively.

optimized structure of **1** indicated that the syn and anti conformers showed hypsochromically and bathochromically shifted absorption bands compared to that of **4**, respectively (Table 2).[34] Accordingly, the hypsochromic shift of **1** observed on increasing the polarity of the solvent is attributed to the increase of the syn conformer population. The relationship between the relative orientation of chromophores and the calculated spectral shifts of **1** agreed with that expected by molecular exciton theory. The calculated orientation of the transition dipole moments of **1** was along the long axis of the merocyanine moieties. This suggests that the spectral shifts of **1** are based on an excitonic coupling between the two merocyanine moieties.

Table 3. UV/Vis Absorption Maxima, Half-Widths, Fluorescence Maxima, Relative Intensities, and Stokes Shifts of (1,8-Naphthylene)bismerocyanine **1** and Monomerocyanine **4**

		absorption		fluorescence[a]		
compds	solvents	λ_{max} (nm)	half-width (cm^{-1})	λ_{max} (nm)	relative intensity	Stokes shift (cm^{-1})
1	$CHCl_3$	566	2950	646	1.34	2130
	CH_3CN	516				
4	$CHCl_3$	551	2740	638	1.0 (standard)	2480
	CH_3CN	550	2230	582		1010

[a] Excitation at absorption maxima at 298 K.

The calculated absorption bands of **1** (syn) consist of an intense transition at 397 nm ($f = 2.06$, f is an oscillator strength) and a weak one at 460 nm ($f = 0.06$). The weak band of **1** (syn) corresponds to the theoretically forbidden transition to a lower excited state of an *H*-aggregate, and the splitting of the excited state was calculated to be 0.43 V. The calculated absorption bands of **1** (anti) consist of an intense transition at 456 nm ($f = 1.15$) and a weak one at 450 nm ($f = 0.39$), indicating that the excitonic coupling of **1** (anti) is only 0.036 V. The difference in the exciton coupling between **1** (syn) and **1** (anti) is explained by the orientation of dipole moments of the merocyanine moieties. In **1** (syn) the two merocyanine moieties point in the same direction, which strengthens the transition dipole moment. On the other hand, in **1** (anti), the two merocyanine moieties point in the reverse direction to minimize the transition dipole moment. This explains why the exciton coupling of **1** (anti) is smaller than that of **1** (syn).

Fluorescence Spectra. The relative intensity of the fluorescence of **1** in $CHCl_3$, in which only the anti isomer exists, was larger than that of **4**, and the Stokes shift of **1** in $CHCl_3$ (2130 cm^{-1}) was smaller than that of **4** (2480 cm^{-1}). On the other hand, **1** in CH_3CN, in which the syn/anti ratio was 90:10, did not fluoresce (Table 3). These observations agree with those expected from molecular exciton theory:[18,35] An *H*-aggregate is expected to show weaker fluorescence than a monomer because an internal conversion from an upper excited state to a lower one occurs immediately and fluorescence from a lower excited state is theoretically forbidden (Figure 1). The anti isomer of **1** shows such spectral features of a *J*-aggregate as a bathochromic shift and a smaller Stokes shift compared with the corresponding monomerocyanine. On the other hand, the syn isomer of **1** indicates such features of an *H*-aggregate as a hypsochromic shift and a decrease of fluorescence. Therefore, the anti and syn isomers of **1** correspond to model compounds for minimum units of the *J*- and *H*-aggregates of merocyanine dyes. The anti isomer of **1** shows broader absorption band than that of **4** (Table 3). Usually, a *J*-aggregate is known to exhibit a sharper absorption band compared to that of a monomer.[36] This narrowing was attributed to the delocalization of excitons over the aggregate, and the width of a *J*-band was theoretically shown to decrease as the number of molecules constituting the *J*-aggregate increases.[37] It is considered that the narrowing of the absorption band is not necessarily obvious for the bismero-

(34) Usually the INDO/S-CI calculation underestimates the absorption wavelength for organic dyes. Adachi, M.; Nakamura, S. *Dyes Pigm.* **1991**, *17*, 287. It was reported that the INDO/S-CI method is useful to predict the spectral shifts of organic dye aggregates. Thompson, M. A.; Zerner, M. C. *J. Am. Chem. Soc.* **1988**, *110*, 606. Adachi, M.; Yoneyama, M.; Nakamura, S. *Langmuir* **1992**, *8*, 2240. Adachi, M.; Nakamura, S. *J. Phys. Chem.* **1994**, *98*, 1796. Mizuguchi, J.; Rihs, G.; Karfunkel, H. R. *J. Phys. Chem.* **1995**, *99*, 16217.

(35) Cooper, W.; Liebert, N. B. *J. Photogr. Sci. Eng.* **1972**, *16*, 25.

(36) Similar broadening was observed for biscyanines linked by a 1,8-naphthylene skeleton. See ref 28.

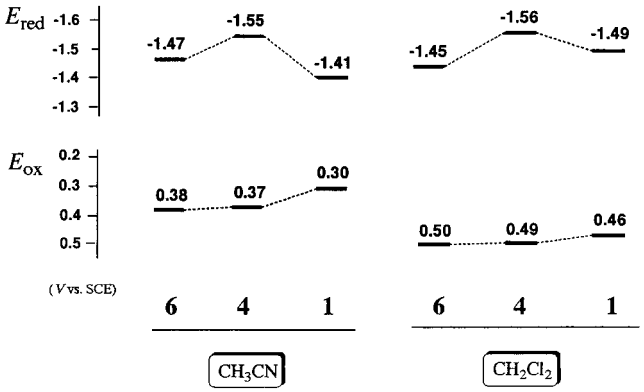

Figure 6. Redox potentials of (1,8-naphthylene)bismerocyanine **1** and monomerocyanines **4** and **6** measured with polarography.

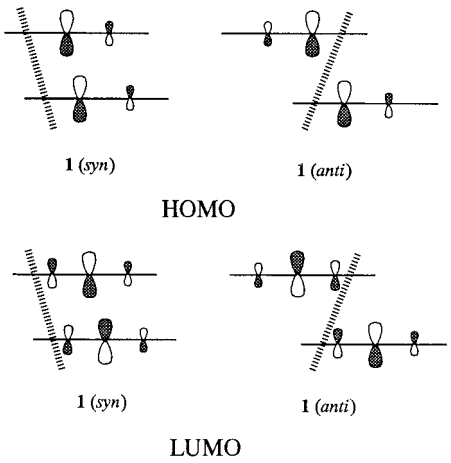

Figure 7. Schematic diagram of the orbital relationships of the HOMOs and LUMOs of (1,8-naphthylene)bismerocyanines, **1** (syn) and **1** (anti).

cyanine **1**, in which only two merocyanine moieties are placed close together. The fluctuation of the relative orientation of the merocyanine moieties in **1**, which is not so rigidly restricted as in a large aggregate or in a single crystal, is possibly an additional factor for the broadening.

Redox Potentials. To examine the effect of the chromophore arrangement on the redox potentials of a merocyanine aggregate, the redox potentials of **1**, **4**, and **6** in CH_3CN or CH_2Cl_2 were measured. The reduction potentials of **1** in both CH_3CN and CH_2Cl_2 were positively shifted compared to those of **4**, while the oxidation potentials of **1** shifted negatively (Figure 6). These potential shifts are in accordance with expectations based on orbital interaction between the two merocyanine moieties. The HOMO of **1** is derived from the antibonding combinations of the merocyanine moieties and the LUMO of **1** from the bonding combination of the LUMOs of the merocyanine moieties (Figure 7). Accordingly, the HOMO level is destabilized and the LUMO level is stabilized by orbital interaction.

The difference between the oxidation potentials of **4** in CH_3CN and that in CH_2Cl_2 was 0.12 V, which was comparable to the difference observed for **1** (0.16 V). While the difference between the reduction potential of **4** in CH_3CN and that in CH_2Cl_2 was small enough to ignore the solvent effect. The difference of the reduction potentials between **1** and **4** in CH_3CN (0.14 V) was larger than that in CH_2Cl_2 (0.07 V). This result indicates that the reduction potentials of **1** are affected by the syn/anti ratio.

Conclusion

A newly prepared bismerocyanine linked by a 1,8-naphthylene skeleton has two rotational isomers, syn and anti conformers, with respect to orientation of two merocyanine chromophores. The syn and the anti conformers were found to have a hypsochromic and a bathochromic absorption, respectively, compared to a 1-naphthyl monomerocyanine. A polar solvent such as acetonitirile enhanced a preference for the syn conformer, causing a hypsochromic shift. The pronounced solvatochromism based on the change in an excitonic coupling mode makes a striking contrast with very slight solvatochromic shift of the corresponding monomerocyanine. The changes of chromophore arrangements of the two merocyanine moieties also induced the positive shift of reduction potential of the bismerocyanine.

Experimental Section

General Method. The following spectroscopic and analytical instruments were used: UV, Shimadzu UV-3100PC; ^{1}H NMR, Bruker ARX-300 or ARX-600 (reference to TMS); IR, JASCO IR-810; MS, JEOL DX-303; redox potential, Yanaco P-1100 (reference to a saturated calomel electrode (SCE)). A dropping mercury working and a rotating Pt working electrode were used for a reduction and an oxidation potential measurement, respectively, and 0.1 mol dm^{-3} Pr_4NClO_4 was used as a supporting salt.

3-(2-Methoxyethyl)-2-thioxothiazolidin-4-one,[38] 4,4′-(1,8-naphthylene)bis(1,2-dimethylpyridinium) diiodide (**2**),[39] 1,2-dimethyl-4-(1-naphthyl)pyridinium iodide (**5**),[39] and 1,2-dimethylpyridinium *p*-toluenesulfonate (**7**)[40] were prepared by the reported method.

5-(Anilinomethylene)-3-(2-methoxyethyl)-2-thioxothiazolidin-4-one (3). A solution of 3-(2-methoxyethyl)-2-thioxothiazolidin-4-one (1.0 g, 5.2 mmol) and *N*,*N*′-diphenylformamidine (1.0 g, 5.1 mmol) in ligroin (5 mL) was stirred at 110 °C for 1 h. After cooling, the precipitates were filtered off and washed with ligroin to afford **3** (1.2 g, 81%) as orange crystals: mp 158 °C; ^{1}H NMR ($CDCl_3$, 298 K) δ 3.07 (s, 3H), 3.72 (t, 2H, J = 6 Hz), 4.25 (t, 2H, J = 6 Hz), 6.72 (d, 1H, J = 14 Hz), 7.08 (d, 2H, J = 8 Hz), 7.15 (t, 1H, J = 8 Hz), 7.38 (t, 2H, J = 8 Hz), 8.00 (d, 1H, J = 14 Hz); IR (KBr) 1690, 1630, 1580, 1500, 1380, 1300, 1275, 1182, 1100, 975 cm^{-1}. Calcd for $C_{13}H_{14}N_2O_2S_2$: C, 53.04; H, 4.79; N, 9.52. Found: C, 52.85; H, 4.97; N, 9.34.

4,4′-(1,8-Naphthylene)bis[1-methyl-2-[2-[3-(2-methoxyethyl)-4-oxo-2-thioxothiazolidin-5-ylidene]ethylidene]pyridine] (1). To a solution of **2** (0.1 g, 0.17 mmol) and **3** (0.16 g, 0.54 mmol) in CH_3CN (10 mL) was added DBU (0.1 g, 0.86 mmol) and acetic anhydride (0.1 g, 0.98 mmol), and the mixture was stirred at room temperature for 2 h. After addition of methanol (10 mL), about a half-volume of the solvent was removed under reduced pressure. The precipitates were filtered off and dissolved into methanol and dichloromethane. The solvent was removed under reduced pressure until crystals appeared. The precipitates were filtered off and washed with methanol to afford **1** (50 mg, 40%) as purple crystals: mp 295−297 °C (dec); λ_{max} (CH_2Cl_2) 566 nm (ϵ = 79 000); ^{1}H NMR (CD_2Cl_2, 300 K) syn conformer δ 3.30 (s, 6H), 3.38 (s, 6H), 3.65 (t, 4H, J = 8 Hz), 4.23 (t, 4H, J = 7 Hz), 4.70 (d, 2H, J = 13 Hz), 6.08 (d, 2H, J = 7 Hz), 6.93 (d, 2H, J = 7 Hz), 7.11 (s, 2H), 7.50 (d, 2H, J = 13 Hz), 7.55 (d, 2H, J = 7 Hz), 7.66 (t, 2H, J = 7 Hz), 8.07 (d, 2H, J = 7 Hz); anti conformer δ 3.32 (s, 6H), 3.38 (s, 6H), 3.65 (t, 4H, J = 8 Hz), 4.23 (t, 4H, J = 7 Hz), 4.83 (d, 2H, J = 13 Hz), 6.37 (d, 2H, J = 7 Hz), 6.98 (d, 2H, J = 1 Hz), 7.11 (d, 2H, J = 7 Hz), 7.43 (d, 2H, J = 7 Hz), 7.58 (d, 2H,

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J = 13 Hz), 7.63 (t, 2H, J = 7 Hz), 8.07 (d, 2H, J = 7 Hz); IR (KBr) 3420, 1640, 1520, 1418, 1296, 1258, 1210, 1180, 1118, 1058, 780 cm^{-1}; MS m/z 741 (M^+). Calcd for $C_{38}H_{36}N_4O_4S_4 \cdot H_2O$: C, 60.08; H, 5.01; N, 7.38. Found: C, 59.81; H, 4.85; N, 7.33.

1-Methyl-4-(1-naphthyl)-2-[2-[3-(2-methoxyethyl)-4-oxo-2-thioxothiazolidin-5-ylidene]ethylidene]pyridine (4). To a solution of **5** (0.12 g, 0.33 mmol) and **3** (0.15 g, 0.51 mmol) in CH_3CN (10 mL) were added DBU (0.1 g, 0.86 mmol) and acetic anhydride (0.1 g, 0.98 mmol), and the mixture was stirred at room temperature for 2 h. After addition of methanol (10 mL), the solvent was removed under reduced pressure until crystals appeared. The precipitates were filtered off and dissolved into methanol and dichloromethane. The solvent was removed under reduced pressure until crystals appeared. The precipitates were filtered off and washed with methanol to afford **4** (61 mg, 43%) as purple crystals: mp 197−200 °C (dec); λ_{max} (CH_2Cl_2) 551 nm (ϵ = 57 700); ^{1}H NMR (DMF-d_7, 298 K) δ 3.30 (s, 3H), 3.60 (t, 2H, J = 7 Hz), 3.94 (s, 3H), 4.24 (t, 2H, J = 7 Hz), 5.34 (d, 1H, J = 13 Hz), 6.88 (d, 1H, J = 7 Hz), 7.6−7.8 (m, 4H), 7.90 (s, 1H), 8.0−8.3 (m, 5H); IR (KBr) 1640, 1560, 1520, 1418, 1260, 1218, 1180, 1120, 1060, 780 cm^{-1}; MS m/z 434 (M^+). Calcd for $C_{24}H_{22}N_2O_2S_2 \cdot H_2O$: C, 63.77; H, 5.31; N, 6.19. Found: C, 64.04; H, 5.49; N, 6.05.

1-Methyl-2-[2-[3-(2-methoxyethyl)-4-oxo-2-thioxothiazolidin-5-ylidene]ethylidene]pyridine (6). To a solution of **7** (0.56 g, 2.0 mmol) and **3** (0.60 g, 2.0 mmol) in CH_3CN (10 mL) was added DBU (0.36 g, 3.1 mmol) and acetic anhydride (0.40 g, 3.9 mmol), and the mixture was stirred at room temperature for 12 h. After addition of methanol (10 mL), the solvent was removed under reduced pressure until crystals appeared. The precipitates were filtered off and dissolved into methanol and dichloromethane. The solvent was removed under reduced pressure until crystals appeared. The precipitates were filtered off and washed with methanol to afford **6** (0.26 g, 46%) as purple crystals: mp 205 °C; λ_{max} (DMSO) 548 nm (ϵ = 87 200); ^{1}H NMR (DMSO-d_6, 298 K) δ 3.30 (s, 3H), 3.60 (t, 2H, J = 7 Hz), 3.75 (s, 3H), 4.20 (t, 2H, J = 7 Hz), 5.22 (d, 1H, J = 13 Hz), 6.75 (t, 1H, J = 5 Hz), 7.52 (t, 1H, J = 5 Hz), 7.80−90 (m, 2H), 7.95 (d, 1H, J = 5 Hz); IR (KBr) 1650, 1570, 1500, 1420, 1260, 1240, 1150, 1120, 1060, 830 cm^{-1}; MS m/z 308 (M^+). Calcd for $C_{14}H_{16}N_2O_2S_2$: C, 54.52; H, 5.23; N, 9.09. Found: C, 54.67; H, 5.29; N, 9.26.

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