© 2002 The Chemical Society of Japan Bull. Chem. Soc. Jpn., *75*, 2655–2660 (2002)

Synthesis of *meso*-Substituted Trimethine Cyanine Dyes and Evaluation of Their Sensitivities in Sensitized Photo-Polymerization

Masaru Kimura,* **Hirofumi Mitekura, Tomoko No, and Kazuyoshi Suzuki**

Department of Chemistry, Faculty of Science, Okayama University, Tsushimanaka 3-1-1, Okayama 700-8530

(Received May 20, 2001)

In order to evaluate the role of a substituent in sensitivity enhancement of *meso*-substituted trimethine cyanine dyes as sensitizers for photo-polymerization, we prepared a series of cyanine dyes, 3-ethyl-2-{3-(3-ethyl-3*H*-2-benzothiazolylidene)-2-[2-(4 or 3-X-phenyl)ethenyl]-1-propenyl} benzothiazolium iodide, **1a**–**k** (**a**: X = *p*-NMe$_2$, **b**: X = *p*-OMe, **c**: X = *p*-CH$_3$, **d**: X = H, **e**: X = *p*-Cl, **f**: X = *p*-CF$_3$, **g**: X = *p*-CN, **h**: X = *p*-NO$_2$, **i**: X = *m*-OMe, **j**: X = *m*-CH$_3$, **k**: X = *m*-Cl). The sensitivity for the photo-polymerization tends to be greater for substituents with greater electron-donating ability. In the series, the sensitivity of dye **1a** was 2.1 mJ/cm^2 higher than the other sensitivities. The sensitivities of dye **2** having a 2-(9-julolidinyl)ethenyl group was high: 1.5 mJ/cm^2 and that of dye **3** having a 2-(9-julolidinyl)-1-methylethenyl group was the highest: 0.7 mJ/cm^2, among all dyes tested here.

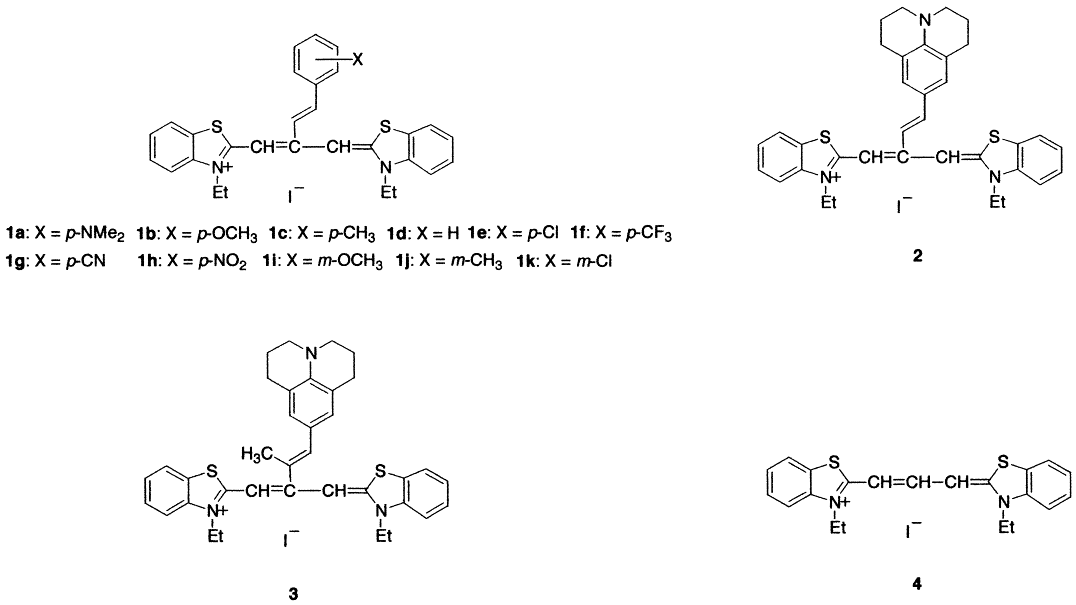
A great number of studies have used polymethine cyanine dyes as sensitizers for silver halide photography.[1] Some polymethine cyanine dyes substituted at the meso position by alkyl or halogen groups are known.[2] These substituents are generally introduced to adjust absorption wavelength and to control aggregation properties.[3] To establish a high sensitive-photosensitized polymerization system for visible light, we investigated the three-component system (TCS) that consists of cyanine dyes and initiators including an electron donor. We found that the sensitivity was increased only in the presence of (*E*)-julolidinylruthenocenylethylene as an electron donor.[4,5] Such findings suggested that, if the dye part and the electron-donating part are combined into one molecule, design of a new type of cyanine dyes stable against photo-irradiation with new functionalities such as an intramolecular charge transfer system would become possible. As for *meso*-substituted trimethine cyanine dyes, their electron-donating power can be controlled by alteration of the substituent on the phenyl of styryl group. We can use such *meso*-substituted trimethine cyanine dyes for evaluation of the role of a substituent in sensitivity enhancement for photo-polymerization. We prepared *p*-substituted cyanine dyes **1a**–**h** or *m*-substituted cyanine dyes **1i**–**k** possessing a cross conjugated π-system composed of the cyanine mother chromophore and the *p*-substituted (X) styryl group (**a**: X = *p*-NMe$_2$, **b**: X = *p*-OMe, **c**: X = *p*-CH$_3$, **d**: X = H, **e**: X = *p*-Cl, **f**: X = *p*-CF$_3$, **g**: X = *p*-CN, **h**: X = *p*-NO$_2$) or the *m*-substituted(X) styryl one (**i**: X = *m*-OMe, **j**: X = *m*-CH$_3$, **k**: X = *m*-Cl). Further, related dyes **2** and **3** having a 2-(9-julolidinyl)ethenyl group and a 2-(9-julolidinyl)-1-methylethenyl group were both prepared, and properties of their absorbance, data of ^{1}H NMR and the results of MO calculation were discussed.[6] Structures of the cyanine dyes **1a**–**k**, **2**, **3**, and **4** are shown in Scheme 1. We would like to discuss the role of the electron-donating substituents on the *meso*-substituted trimethine cyanine dyes in the sensitivity enhancement in photo-polymerization.

Results and Disucussion

Our strategy for construction of dyes as photo-sensitizers assisted by intramolecular electron transfer is as follows. Electrons involved in the reaction are generated in the half filled LUMO of excited dyes upon irradiation. To initiate the radical reaction, the electrons should attack 2,4,6-tris(trichloromethyl)-1,3,5-triazine **TCT** as radical generator before any deactivation takes place.[7] If an excited dye accommodates an electron in its half filled HOMO, the deactivation process should be blocked by formation of the corresponding radical with filled HOMO. The radical probably has a longer lifetime than the excited dye itself, and the radical should have a high probability of electron transfer to **TCT**.

Cyanine dyes **1a**–**k** were synthesized using the route shown in Chart 1. These dyes were evaluated as regards the role of substituent in sensitivity enhancement for photo-polymerization with related dyes **2**–**4** as follows.

The sensitivities were measured and are listed in Table 1. The order of the sensitivity of the *p*-substituted dyes in the series of dye **1** is **1a** > **1e** > **1c** > **1b** > **1f** > **1d** > **1g** > **1h**. The sensitivities of the *m*-substituted cyanine dyes **1i** and **j** tend to be higher than the corresponding *p*-substituted ones, but **1k** that possesses a Cl atom is less efficient than the corresponding **1e**. The sensitivity for dye **1a** was 2.1 mJ/cm^2, which is the best for the *p*-substituted ones possessing almost the same value of $\lambda_{\max}$ and log ε. The sensitivity for the photopolymerization tends to be greater for substituents with greater electron-donating ability. On the line of this result, dye **2** having a 2-(9-julolidinyl)ethenyl group at the meso position was chosen for evaluating the degree of conjugation between the amino group and the phenyl group. Needless to say, the amino group in the julolidine moiety has a stronger electron-donating ability than the *p*-dimethylamino group in **1a**. Since **2** (1.5 mJ/cm^2) is more sensitive than **1a**, the electron-donating ability of the julolidine moiety should contribute to the sensitivity of cy-



Scheme 1. Structures of cyanine dyes **1a–k**, **2**, **3**, and **4**.

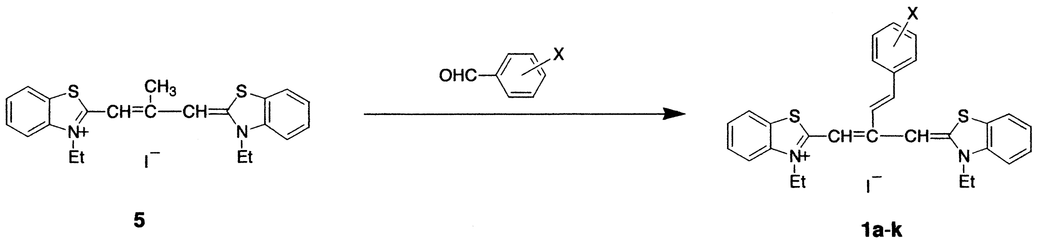


Chart 1.

Table 1. Oxidation–Reduction Potentials[a] of Sensitizing Dyes and Sensitivities of the Potoinitiating System[b] with Sensitizing Dyes

Dye		Potential at peak		Sensitivity/mJ cm^{-2}
		Oxidation potential/V	Reduction potential/V	
1a	p-NMe$_2$	0.68	−0.95	2.1
1b	p-OCH$_3$	0.74	−0.91	20
1c	p-CH$_3$	0.77	−0.91	20
1d	H	0.75	−0.89	43
1e	p-Cl	0.76	−0.89	14
1f	p-CF$_3$	0.79	−0.85	33
1g	p-CN	0.80	−0.86	120
1h	p-NO$_2$	0.81	−0.92	120
1i	m-OCH$_3$	0.77	−0.87	17
1j	m-CH$_3$	0.75	−0.87	10
1k	m-Cl	0.77	−0.87	32
2		0.58	−0.98	1.5
3		0.75	−1.11	0.7
4		0.80	−1.09	7.0

a) In CH_3CN contained 0.1 M n-Bu_4NBF_4 at G.C. electrode at 25 °C. In V vs Ag/AgCl.

b) Composition of the photosensitive layer (parts by weight): matrix polymer (100), polyfunctional monomer (100), TCT (8), sensitizing dye (**1**). In the cases of **2–4**, these absorbances at 540 nm were adjusted at the same value of **1**. Glass filters were used as follows: Y-52 and KL-54 (540 nm).

anine dyes. Actually, cyanine dyes possessing a low oxidation potential are likely to have a higher sensitivity (See Table 1).

Dye **3** having a 2-(9-julolidinyl)-1-methylethenyl group at the meso position was chosen for evaluating the degree of conjugation between the julolidine moiety and the cyanine mother π chain for dye **2**. In comparison with planer **2**, the julolidine moiety in **3** prevents coplanarity with the cyanine mother π chain; nevertheless, the sensitivity of **3** (0.7 mJ/cm^2) is higher than that of **2**. Dye **2** forms a fully conjugated π system consisting of a 2-(9-julolidinyl)ethenyl group and a cyanine mother π chain, whereas the full conjugation was blocked by the methyl group in **3**. Analysis of the ^{1}H NMR spectrum of **2** indicates that the π electrons in the julolidinylethenyl group shift toward the cyanine mother chromophore through the π conjugation due to charge transfer in the ground state, but this is not the case for **3**.[6] UV/visible absorption spectra of **2**, **3**, and **4** in methanol at a concentration of 5×10^{-6} mol/L are shown in Fig. 1. The absorption spectrum of **3** is almost equivalent to the trimethine cyanine dye **4**, unlike that of **2**, which is broadened into the longer wavelength range. The λ_{max} values (ε) at each first absorption band in the visible region for **2**, **3**, and **4** are as follows: 560 nm (98,000) for **2**, 559 nm (174,000) for **3**, and 557 nm (153,000) for **4**.

On the basis of the optimized structures of **2–4**, ZINDO MO calculations were performed. The results gave the theoretical electronic transition factors related to the first absorption band in the visible region, as summarized in Table 2. Here, the first absorption bands in the visible region are attributed to the transition from HOMO or NHOMO (Next HOMO) to LUMO in each dye. Judging from the values of oscillator strength (*f*), the observed broad first absorption band consists of two allowed transitions with similar size *f* value in the case of dye **2**. On the other hand, the first excitation of dye **3** from HOMO to LUMO is assigned to forbidden transition by a very small value of *f*. Therefore the observed sharper absorption band for dye **3** consists of an allowed transition and a forbidden transition. Figures 2 and 3 show the frontier molecular orbitals of **2–4** with the *f* value. We assumed that the small *f* value for HOMO-LUMO transition for **3** is attributable to isolation of the two chromophores due to the steric hindrance by the methyl group. We believe these findings imply that there are two types of intramolecular electron transfer modes from the julolidine moiety to the cyanine mother π chain in the excited state as shown in Scheme 2. Both systems contribute to sensitivity enhancement of the cyanine dyes by different modes. In the combined dye system I, the whole molecule is planer and provides two allowed excitations from HOMO to LUMO and NHOMO to LUMO, while the hole generated in HOMO or NHOMO is distributed to the whole molecule. In the combined system II, the whole molecule can not be planer due to steric hindrance of the methyl group on the meso-substituent, limiting excitation from NHOMO to LUMO. An electron may charge the hole generated in NHOMO from HOMO. The radical generated in the mother π chain probably has a longer lifetime than the excited dye **4***, and the radical should have a high probability of electron transfer to **TCT**. It is noteworthy that the sensitivity of **3** is higher than that of **2** under the same absorbencies at 540 nm. Furthermore, Dye **4** is fluorescent, but **2** and **3** are not. These findings are consistent with our concept shown in Scheme 2.

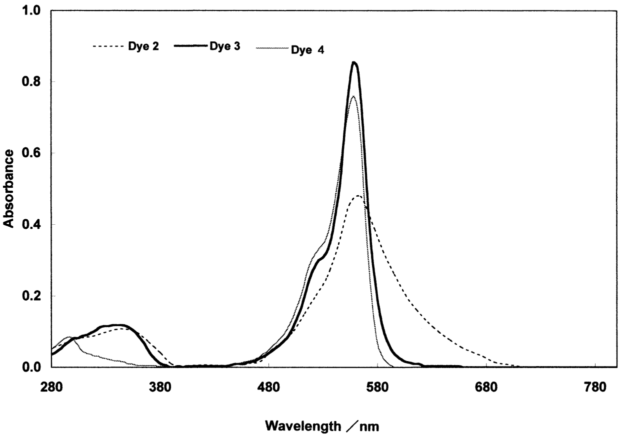


Fig. 1. Absorption spectra of dyes **2–4** (5×10^{-6} M) in methanol.

Experimental

Measurements. Melting points were measured with a Yanagimoto micro melting point apparatus and were uncorrected. ^{1}H (chemical shifts referenced to $CDCl_3$ at δ 7.26) NMR spectra were measured on a Varian VXR-200 spectrometer. IR spectra were on a JASCO FT/IR-5000 spectrometer. UV-vis spectra were recorded on a HITACHI UV-288 spectrophotometer. Cyclic voltammograms were recorded on a Yanaco polarographic analyzer P-1100. High-resolution mass spectral data were obtained on a Hewlett-Packard 5890 SERIES II mass spectrometer.

Materials. 3-Ethyl-2-[3-(3-ethyl-3*H*-2-benzothiazolylidene]-2-methyl-1-propenyl]benzothiazolium iodide **5** was purchased from Hayashibara Biochemical Laboratories, Inc. 2,4,6-Tris(trichloromethyl)-1,3,5-triazine (TCT) was purchased from

Table 2. Observed λ_{max} (ε_{max}) and the Calculated Oscillator Strength *f* and Energy Level of MOs for **2–4**

Dye	Calculated					Observed	
	λ_{max}/nm	*f*	Energy level of MOs/ev			λ_{max}/nm	ε_{max}
			NHOMO	HOMO	LUMO		
2	522	0.943		−9.49	−4.47	600	46,000
	488	1.030	−9.99		−4.47	560	98,000
3	509	0.036		−9.26	−4.43		
	482	1.111	−10.15		−4.43	559	174,000
4	499	1.523		−10.17	−4.67	557	153,000

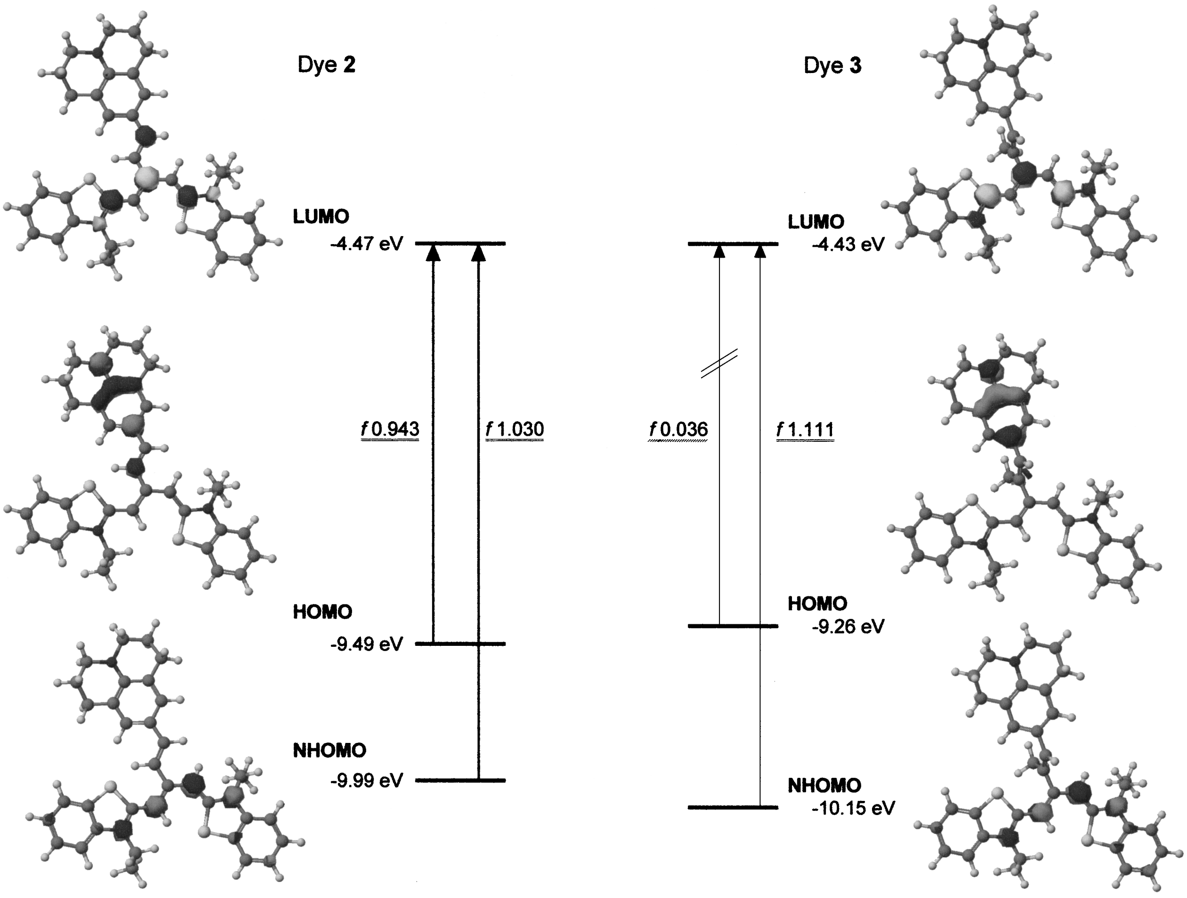


Fig. 2. Frontier molecular orbitals of **2** and **3** with oscillator strength.

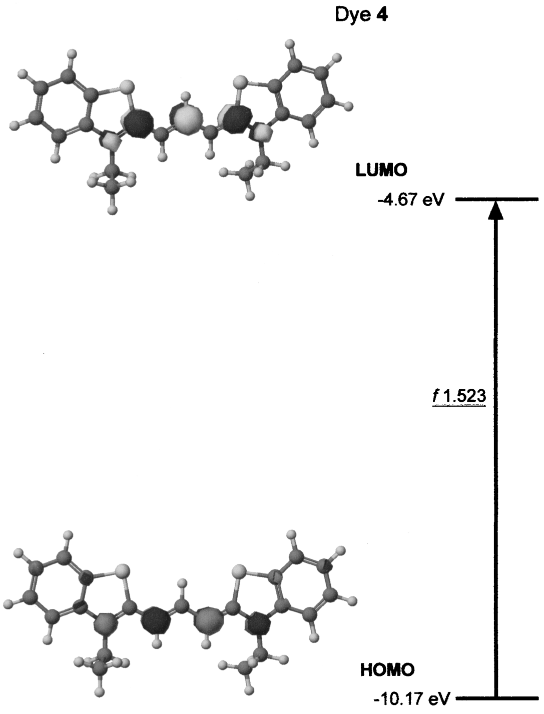
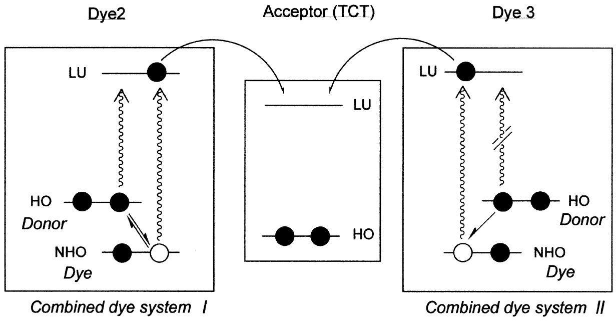


Fig. 3. Frontier molecular orbitals of **4** with oscillator strength.



Scheme 2. The concept of intramolecular electron transfer in terms of HOMO (HO), LUMO (LU), and Next HOMO (NHO) energy levels.

Midori Kagaku Co., Ltd. The polymer for measurement of photographic sensitivity was used as matrix polymer: polyacrylate caboset XPD-2000 (B.F. Goodrich, MW 30,000, and acid value 75). As a poly-functional monomer, pentaerythrithol triacrylate (PETA) was purchased from Shin Nakamura Kagaku Kogyo Co., Ltd.

Synthesis. Preparation of 3-Ethyl-2-{3-(3-ethyl-*3H*-2-benzothiazolylidene)-2-[2-(4-dimethylaminophenyl)ethenyl]-1-propenyl}benzothiazolium Iodide **1a**: *p*-Dimethylaminobenzaldehyde (0.186 g, 1.25 mmol) was added to a mixture of **5** (0.206 g, 0.407 mmol), piperidine (1.0 mL), and $CHCl_3$/EtOH (v/v = 1/1)

(30 mL), then the mixture was heated on an oil bath for 24 h with continuous stirring under covering. After cooling, the mixture was evaporated under reduced pressure, then **1a** was obtained as green powder in 70% yield (0.182 g, 0.286 mmol) with recrystallization from methanol. ^{1}H NMR (200 MHz, in DMSO) δ 1.41 (6H, t, J = 7 Hz), 3.02 (6H, s), 4.49 (4H, q, J = 7 Hz), 6.65 (2H, s), 6.81 (2H, d, J = 9 Hz), 7.08 (1H, d, J = 16 Hz), 7.25 (1H, d, J = 16 Hz), 7.35 (2H, t, J = 7.4 Hz), 7.56 (2H, t, J = 8 Hz), 7.62 (2H, d, J = 9Hz), 7.76 (2H, d, J = 8 Hz), 7.93 (2H, t, J = 7.4 Hz); IR (KBr) 2987, 1487, 1460, 1406, 1361, and 743 cm^{-1}; UV (MeOH) $\lambda_{\max}$ 559 nm (log ε = 4.79); mp 237–241 °C (lit, 247–248 °C)[8]; HRMS (FAB) Found: *m*/*z* 510.2041. Calcd for $C_{31}H_{32}N_3S_2$: M$^+$, 510.7380.

Preparation of 3-Ethyl-2-{3-(3-ethyl-3*H*-2-benzothiazolylidene)-2-[2-(4-methoxyphenyl)ethenyl]-1-propenyl}benzothiazolium Iodide 1b: *p*-Methoxybenzaldehyde (0.145 g, 1.07 mmol) was added to a mixture of **5** (0.210 g, 0.416 mmol), piperidine (1.0 mL), and $CHCl_3$/EtOH (v/v = 1/1) (30 mL), then the mixture was heated on an oil bath for 24 h with continuous stirring while covered. After cooling, the mixture was evaporated under reduced pressure. The mixture was dissolved methanol and extracted with hexane. The methanol layer was evaporated reduced pressure, then **1b** was obtained as dark green needles in 39% yield (0.102 g, 0.179 mmol) with recrystallization from ethanol. ^{1}H NMR (200 MHz, in DMSO) δ 1.41 (6H, t, J = 7.1 Hz), 3.84 (3H, s), 4.51 (4H, q, J = 7.1 Hz), 6.72 (2H, s), 7.08 (2H, d, J = 8.5 Hz), 7.23 (2H, s), 7.36 (2H, t, J = 7.4 Hz), 7.57 (2H, t, J = 8.2 Hz), 7.76 (2H, d, J = 8.5 Hz), 7.78 (2H, d, J = 8.2 Hz), 7.94 (2H, d, J = 7.4 Hz); IR (KBr) 3001, 1495, 1460, 1406, and 745 cm^{-1}; UV (MeOH) $\lambda_{\max}$ 559 nm (log ε = 5.03); mp 241–243 °C; HRMS (FAB) Found: *m*/*z* 497.1725. Calcd for $C_{30}H_{29}N_2OS_2$: M$^+$, 497.6961.

Preparation of 3-Ethyl-2-{3-(3-ethyl-3*H*-2-benzothiazolylidene)-2-[2-(4-tolyl)ethenyl]-1-propenyl} benzothiazolium Iodide 1c: *p*-Tolualdehyde (0.220 g, 1.83 mmol) was added to a mixture of **5** (0.215 g, 0.424 mmol), piperidine (1.0 mL), and $CHCl_3$/EtOH (v/v = 1/1) (30 mL), then the mixture was heated on an oil bath for 24 h with continuous stirring while covered. After cooling, the mixture was evaporated under reduced pressure, then was obtained **1c** as black powder in 57% yield (0.147 g, 0.241 mmol) with recrystallization from methanol. ^{1}H NMR (200 MHz, in $CDCl_3$) δ 1.52 (6H, t, J = 7 Hz), 2.48 (3H, s), 4.71 (4H, q, J = 7 Hz), 6.82 (2H, s), 7.25 (2H, d, J = 6.5 Hz), 7.35–7.53 (10H, m), 7.58 (2H, d, J = 6.5 Hz); IR (KBr) 2911, 1652, 1492, 1460, 1406, and 743 cm^{-1}; UV (MeOH) $\lambda_{\max}$ 559 nm (log ε = 4.96); mp 237–239 °C; HRMS (FAB) Found: *m*/*z* 481.1778. Calcd for $C_{30}H_{29}N_2S_2$: M$^+$, 481.6967.

Preparation of 3-Ethyl-2-[3-(3-ethyl-3*H*-2-benzothiazolylidene)-2-(2-phenylethenyl)-1-propenyl]benzothiazolium Iodide 1d: *p*-Benzaldehyde (0.262 g, 2.47 mmol) was added to a mixture of **5** (0.206 g, 0.406 mmol), piperidine (1.0 mL), and $CHCl_3$/EtOH (v/v = 1/1) (30 mL), then the mixture was heated on an oil bath for 24 h with continuous stirring while covered. After cooling, the mixture was evaporated under reduced pressure, then was obtained **1d** as dark green powder in 63% yield (0.152 g, 0.256 mmol) with recrystallization from ethanol. ^{1}H NMR (200 MHz, in $CDCl_3$) δ 1.25 (6H, t, J = 7 Hz), 4.71 (4H, q, J = 7 Hz), 6.94 (2H, s), 7.21–7.30 (4H, m), 7.35 (2H, d, J = 8.5 Hz), 7.44–7.57 (7H, m), 7.68 (2H, d, J = 8.5 Hz); IR (KBr) 2990, 1642, 1487, 1205, and 791 cm^{-1}; UV (MeOH) $\lambda_{\max}$ 559 nm (log ε = 5.00); mp 242–243 °C; HRMS (FAB) Found: *m*/*z* 467.1615. Calcd for $C_{29}H_{27}N_2S_2$: M$^+$, 467.6702.

Preparation of 3-Ethyl-2-{3-(3-ethyl-3*H*-2-benzothiazolylidene)-2-[2-(4-chlorophenyl)ethenyl]-1-propenyl}benzothiazolium Iodide 1e: *p*-Chlorobenzaldehyde (0.156 g, 1.11 mmol) was added to a mixture of **5** (0.220 g, 0.435 mmol), piperidine (1.0 mL), and $CHCl_3$/EtOH (v/v = 1/1) (30 mL), then the mixture was heated on an oil bath for 24 h with continuous stirring while covered. After cooling, the deposited crystal was filtrated, then the mixture was evaporated under reduced pressure. Recrystallization from ethanol/CH_2Cl_2 gave **1e** as black needles in 67% yield (0.184 g, 0.292 mmol). ^{1}H NMR (200 MHz, in DMSO) δ 1.41 (6H, t, J = 7 Hz), 4.51 (4H, q, J = 7 Hz), 6.79 (2H, s), 7.24 (1H, d, J = 17 Hz), 7.34 (2H, t, J = 7.4 Hz), 7.39 (2H, d, J = 8 Hz), 7.46 (1H, d, J = 17 Hz), 7.59 (2H, d, J = 8.4 Hz), 7.81 (2H, t, J = 8 Hz), 7.84 (2H, d, J = 8.4 Hz), 7.95 (2H, d, J = 7.4 Hz); IR (KBr) 2926, 1495, 1462, 1392, and 732 cm^{-1}; UV (methanol) $\lambda_{\max}$ 558 nm (log ε = 4.99); mp 256–257 °C; HRMS (FAB) Found: *m*/*z* 501.1230. Calcd for $C_{29}H_{26}ClN_2S_2$: M$^+$, 502.1149.

Preparation of 3-Ethyl-2-{3-(3-ethyl-3*H*-2-benzothiazolylidene)-2-[2-(4-trifluoromethylphenyl)ethenyl]-1-propenyl}-benzothiazolium Iodide 1f: *p*-(Trifluoromethyl)benzaldehyde (0.301 g, 1.72 mmol) was added to a mixture of **5** (0.206 g, 0.407 mmol), piperidine (1.0 mL), and $CHCl_3$/EtOH (v/v = 1/1) (30 mL), then the mixture was heated on an oil bath for 24 h with continuous stirring while covered. After cooling, the mixture was evaporated under reduced pressure, then **1f** was obtained as green needles in 35% yield (0.0954 g, 0.144 mmol) with recrystallization from methanol. ^{1}H NMR (200 MHz, in DMSO) δ 1.42 (6H, t, J = 7.6 Hz), 4.50 (4H, q, J = 7.6 Hz), 6.77 (2H, s), 7.36 (1H, d, J = 7.2 Hz), 7.37 (2H, t, J = 7.5 Hz), 7.58 (2H, t, J = 7.5 Hz), 7.60 (1H, d, J = 7.2 Hz), 7.80 (2H, d, J = 7.5 Hz), 7.89 (2H, d, J = 7.8 Hz), 7.96 (2H, d, J = 7.5 Hz), 8.03 (2H, d, J = 7.8 Hz); IR (KBr) 3024, 1485, 1460, 1408, 1112, and 748 cm^{-1}; UV (MeOH) $\lambda_{\max}$ 560 nm (log ε = 5.00); mp 259–260 °C; HRMS (FAB) Found: *m*/*z* 535.1505. Calcd for $C_{30}H_{26}F_3N_2S_2$: M$^+$, 535.6681.

Preparation of 3-Ethyl-2-{3-(3-ethyl-3*H*-2-benzothiazolylidene)-2-[2-(4-cyanophenyl)ethenyl]-1-propenyl}benzothiazolium Iodide 1g: *p*-Cyanobenzaldehyde (0.141 g, 1.08 mmol) was added to a mixture of **5** (0.199 g, 0.394 mmol), piperidine (1.0 mL), and $CHCl_3$/EtOH (v/v = 1/1) (30 mL), then the mixture was heated on an oil bath for 24 h with continuous stirring while covered. After cooling, the mixture was evaporated under reduced pressure, then **1g** was obtained as black needles in 26% yield (0.0635 g, 0.102 mmol) with recrystallization from methanol. ^{1}H NMR (200 MHz, in DMSO) δ 1.41 (6H, t, J = 7 Hz), 4.52 (4H, q, J = 7 Hz), 6.76 (2H, s), 7.38 (1H, d, J = 16 Hz), 7.38 (2H, t, J = 8.4 Hz), 7.58 (2H, t, J = 8.4 Hz), 7.67 (1H, d, J = 16 Hz), 7.80 (2H, d, J = 8.4 Hz), 7.96 (2H, d, J = 8.4 Hz), 7.96 (2H, d), 8.00 (2H, d); IR (KBr) 2992, 2240, 1495, 1462, 1386, and 743 cm^{-1}; UV (MeOH) $\lambda_{\max}$ 560 nm (log ε = 4.91); mp 250–251 °C; HRMS (FAB) Found: *m*/*z* 492.1599. Calcd for $C_{30}H_{26}N_3S_2$: M$^+$, 492.6797.

Preparation of 3-Ethyl-2-{3-(3-ethyl-3*H*-2-benzothiazolylidene)-2-[2-(4-nitrophenyl)ethenyl]-1-propenyl}benzothiazolium Iodide 1h: *p*-Nitrobenzaldehyde (0.153 g, 1.01 mmol) was added to a mixture of **5** (0.181 g, 0.357 mmol), piperidine (1.0 mL), and $CHCl_3$/EtOH (v/v = 1/1) (30 mL), then the mixture was heated on an oil bath for 24 h with continuous stirring under covering. After cooling, the mixture was evaporated under reduced pressure, then was obtained **1h** as black needles in 34% yield (0.0777 g, 0.121 mmol) with recrystallization from methanol. ^{1}H NMR (200 MHz, in DMSO) δ 1.42 (6H, t, J = 7 Hz), 4.53 (4H, q, J = 7 Hz), 6.78 (2H, s), 7.38 (2H, t, J = 7.9 Hz), 7.40 (1H, d, J = 18 Hz), 7.59 (2H, t, J = 7.9 Hz), 7.70 (1H, d, J = 18 Hz), 7.80 (2H, d, J = 7.9 Hz), 7.96 (2H, d, J = 7.9 Hz), 8.08 (2H, d, J = 8.8 Hz), 8.37 (2H, d, J = 8.8 Hz); IR (KBr) 2992, 1597, 1495, 1462, 1392, 1340, 845, and 745 cm^{-1}; UV (MeOH) $\lambda_{\max}$ 560 nm (log ε = 4.96); mp 271–272 °C; HRMS (FAB) Found: m/z 512.1456. Calcd for $C_{29}H_{26}N_3O_2S_2$: M$^+$, 512.6678.

m-Substituted cyanine dyes **1i**–**k** were prepared by a similar method for *p*-substituted cyanine dyes **1a**–**h**.

3-Ethyl-2-{3-(3-ethyl-3*H*-2-benzothiazolylidene)-2-[2-(3-methoxyphenyl)ethenyl]-1-propenyl}benzothiazolium Iodide 1i: 39% yield, recrystallization from ethanol; ^{1}H NMR (200 MHz, in DMSO) δ 1.41 (6H, t, J = 7 Hz), 3.83 (3H, s), 4.51 (4H, d, J = 6 Hz), 6.74 (2H, s), 7.33–7.44 (8H, m), 7.57 (2H, t, J = 8 Hz), 7.78 (2H, d, J = 8 Hz), 7.96 (2H, d, J = 8 Hz); IR (KBr) 3001, 1495, 1460, 1406, and 745 cm^{-1}; UV (MeOH) $\lambda_{\max}$ 559 nm (log ε = 5.03); mp 241–243 °C; HRMS (FAB) Found: m/z 497.69614. Calcd for $C_{30}H_{29}N_2OS_2$: M$^+$, 497.6961.

3-Ethyl-2-{3-(3-ethyl-3*H*-2-benzothiazolylidene)-2-[2-(3-tolyl)ethenyl]-1-propenyl}benzothiazolium Iodide 1j: 57% yield, recrystallization from methanol: ^{1}H NMR (200 MHz, in DMSO) δ 1.41 (6H, t, J = 7 Hz), 2.39 (3H, s), 4.51 (4H, q, J = 7 Hz), 6.74 (2H, s), 7.25–7.40 (6H, m), 7.56 (4H, d, J = 12 Hz), 7.68 (2H, d, J = 7.8 Hz), and 7.95 (2H, d, J = 7.8 Hz); IR (KBr) 3046, 1485, 1460, 1408, and 748 cm^{-1}; UV (MeOH) $\lambda_{\max}$ 558.4 nm (log ε = 5.03); mp 255–256 °C; HRMS (FAB) Found: m/z 481.69674. Calcd for $C_{30}H_{29}N_2S_2$: M$^+$, 481.6967.

3-Ethyl-2-{3-(3-ethyl-3*H*-2-benzothiazolylidene)-2-[2-(3-chlorophenyl)ethenyl]-1-propenyl}benzothiazolium Iodide 1k: 67% yield, recrystallization from ethanol/CH_2Cl_2; ^{1}H NMR (200 MHz, in DMSO) δ 1.41 (6H, t, J = 7 Hz), 4.49 (4H, q, J = 7 Hz), 6.75 (2H, s), 7.39 (2H, d, J = 7.6 Hz), 7.50–7.62 (6H, m), 7.75–7.81(3H, d, m), 7.95 (3H, t, J = 7.6 Hz); IR (KBr) 2956, 1485, 1460, 1408, and 748 cm^{-1}; UV (methanol) $\lambda_{\max}$ 558.8 nm (log ε = 5.01); mp 252–253 °C; HRMS (FAB) Found: m/z 501.11492. Calcd for $C_{29}H_{26}ClN_2S_2$: M$^+$, 502.1149.

Cyanine Dyes 2, 3, and 4 Were Prepared by the Method in Ref. 6. **2**: mp 248–249 °C; ^{1}H NMR ($CDCl_3$) δ 7.56 (2H, d, J = 7.8), 7.44 (2H, t, J = 7.8), 7.34 (2H, s), 7.33 (2H, d, J = 7.8), 7.24 (2H, t, J = 7.8), 7.10 (2H, s), 6.81 (1H, d, J = 16.2), 6.60 (1H, d, J = 16.2), 4.62 (4H, q, J = 7.1), 3.29 (4H, t, J = 5.7), 2.83 (4H, t, J = 6.3), 2.03 (4H, quintet, J = 5.7, 6.3), 1.57 (6H, t, J = 7.1); $C_{35}H_{36}IN_3S_2$ requires C, 60.95; H, 5.26; N, 6.09%. Found: C, 60.75; H, 5.29; N, 6.08%; (M − I)$^+$ 562. UV (methanol): $\lambda_{\max}$ 560 nm (log ε = 4.99).

3: mp 212–213 °C; ^{1}H NMR ($CDCl_3$) δ 7.65 (2H, s), 7.46 (2H, d, J = 7.8), 7.41 (2H, t, J = 7.8), 7.28 (2H, d, J = 7.8), 7.21 (2H, t, J = 7.8), 6.95 (2H, s), 6.61 (1H, s), 4.73 (2H, m, J = 7.2, 15.0), 4.62 (2H, m, J = 7.2, 15.0), 3.08 (4H, t, J = 5.7), 2.65 (4H, t, J = 6.3), 1.85 (4H, quintet, J = 5.7, 6.3), 1.54 (6H, t, J = 7.2); $C_{36}H_{38}IN_3S_2$ requires C, 61.44; H, 5.44; N, 5.97%. Found: C, 60.58; H, 5.51; N, 5.85%; (M − I)$^+$ 577. UV (methanol): $\lambda_{\max}$ 559 nm (log ε = 5.24).

Measurement of Photographic Sensitivity. The photosensitive layer was prepared by coating a 2-ethoxyethanol solution of the photosensitive composition onto a grained aluminum plate, this dried to form an 1–2 μm thick layer. Furthermore, an aqueous solution of poly(vinyl alcohol) was coated on it in order to eliminate inhibition of polymerization by oxygen. The photographic sensitivity (E, mJ/cm^2) was measured by counting the minimum exposing light intensity after exposing the photosensitive layer through a 21 step tablet (Kodak no. 2 step tablet) with a 150 W xenon arc lamp. An appropriate glass filter allowed selection of the wavelength of the exposing light. In this paper, combinations of Toshiba Y-52 and KL-54 (540 nm light) were used. The exposed photosensitive layer was developed in an aqueous alkaline solution, and the plate was toned by printing ink. The sensitivity was defined as the minimum E for polymerization of the layer, and is calculated as

$$E = I_0 \times T \times t$$

where I_0 is the incident light intensity (mJ/cm^2 s), T is the transmittance of the step at which the photosensitive layer begins to be polymerized, and t is exposure time(s).

Computational Methods.[9] The transition metal INDO/S formalism (ZINDO) calculation was carried out using MOPAC. Several starting geometries were used for the geometry optimization to ensure that the optimized structure corresponds to a minimum obtained by PM3.

This investigation was partially supported by Grants-in-Aid for Scientific Research from Hayashibara Biochemical Laboratories, Inc. We thank the Okayama NMR Center for NMR spectra, recorded on a Varian VXR-500 spectrometer, and we appreciate encouragement and discussion with Dr. M. Hayami of Hayashibara Biochemical Laboratories.

References

1 T. Tani, "Photographic Sensitivity," Oxford University Press, London (1995).

2 A. Mishra, R. K.Behera, B. K.Mishra, and G. B.Behera, *Chem. Rev.*, **100**, 1973 (2000).

3 T, H. James, "The Theory of the Photographic Process," 4th ed, Macmillan Publishing Co., New York (1977).

4 a) M. Kimura, H. Mitekura, T. Fujie, and T. No, *Bull. Chem. Soc. Jpn.*, **75**, 1159 (2002). b) M. Kimura, T. Fujie, and M. Sakaguchi, *ITE Letters*, **2**, 518 (2001).

5 a) S. Yasui, H. Mitekura, K. Koseki, and T. Yamaoka, *Koubunshi Ronbunsyu*, **51**, 801 (1994). b) H. Mitekura, N. Oga, S. Yasui, K. Koseki, and T. Yamaoka, *Koubunshi Ronbunsyu*, **52**, 582 (1995). c) M. Harada, Y. Takimoto, N. Noma, and Y. Shirota, *J. Photopolym. Sci. Technol.*, **4**, 51 (1991).

6 H. Mitekura, T. No, K, Suzuki, K. Satake, and M. Kimura, *Dyes Pigm.*, **54**, 113 (2002).

7 G. Buhr, R. Dammel, C. R. Lindley, *Polym. Mater. Sci. Eng.*, **61**, 269 (1989)

8 M. Wladyslaw, *Chem. Stosow.*, **5**, 311 (1961).

9 D. R. Kanis, M. A. Ratner, and T. J. Marks, *J. Am. Chem. Soc.*, **114**, 10338 (1992).