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Spectroscopic properties of meso-substituted cyanine dyes: evidences for intramolecular charge transfer from a julolidine moiety as a meso-substituent to the cyanine chromophore

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Abstract

Synthesis and spectral properties of cyanine dyes **1** and **2**, having julolidinylethenyl and α-methyl julolidinylethenyl moieties respectively at the *meso* position, are described. In comparison with planer **1**, the methyl group of the julolidinylethenyl group in **2** prevents the coplanarity of the whole dye system. Their characteristic electronic absorption spectra are analyzed based on the molecular orbital calculations, and the calculations well reproduce the observed data. Analysis of ^{1}H NMR spectrum of **1** indicates that the π-electrons in the julolidinylethenyl group shift toward the cyanine main chromophore through the π-conjugation. Intramolecular charge transfer from the julolidine moiety to the cyanine main chromophore contributes to lightfastness of dyes. These findings make it possible to design a new type of stable cyanine dyes against photoirradiation with new functionalities such as intramolecular charge transfer system.

Keywords: Meso-substituted cyanine; Trimethine cyanine; Julolidinylethenyl group; Electron donor; Intramolecular charge-transfer; New functional dye

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1. Introduction

A great number of investigations have been accomplished by using polymethine cyanine dyes as sensitizer 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 their aggregation property [3].

Cyanine dyes are now used in many applied fields [4] not only silver halide photography, among others, dye-sensitized photopolymers [5], CD-R [6], and dye-sensitized porous semiconductor electrode [7]. In the applied fields, stable dyes against photoirradiation are desirable.

In this paper, we examine the introduction of an electron-donating substituent at meso position in a trimethine cyanine system and evaluate their electronic spectral properties on the basis of the MOPAC calculations. In practice, a julolidinylethenyl group as a strong electron-donor was introduced and the spectral changes are discussed

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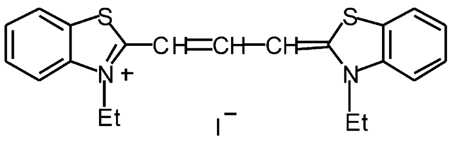
in terms of the coplanarity of the π-conjugation system. The possibility of intramolecular charge transfer from a julolidine moiety to a cyanine main chromophore is analyzed based on the MO calculations and ^{1}H NMR spectra. We discussed the relationship between relative fading rates of dyes by photoirradiation and the coplanarity of the π-conjugation system.

2. Results and discussion

2.1. Syntheses of meso substituted trimethine cyanines *1* and *2*

Meso methyl trimethine cyanine **5** and *meso* ethyl trimethine cyanine **6** are already known [8] and are synthesized in our laboratory. The reaction of 5 with 9-formyljulolidine in ethanol under reflux for 1.5 h in the presence of piperidine as a catalyst gave the corresponding meso-julolidinylethenyl trimethine cyanine **1** [9]. On the other hand, the reaction of **6** with 9-formyljulolidine in toluene/butanol under reflux for 7.5 h in the presence of *p*-toluenesulfonic acid as catalyst gave the corresponding *meso*-julolidinylethenyl trimethine cyanine **2** (Scheme 1).

The corresponding trimethine cyanine 3 synthesized [8] in our laboratory is used to compare their spectral properties.



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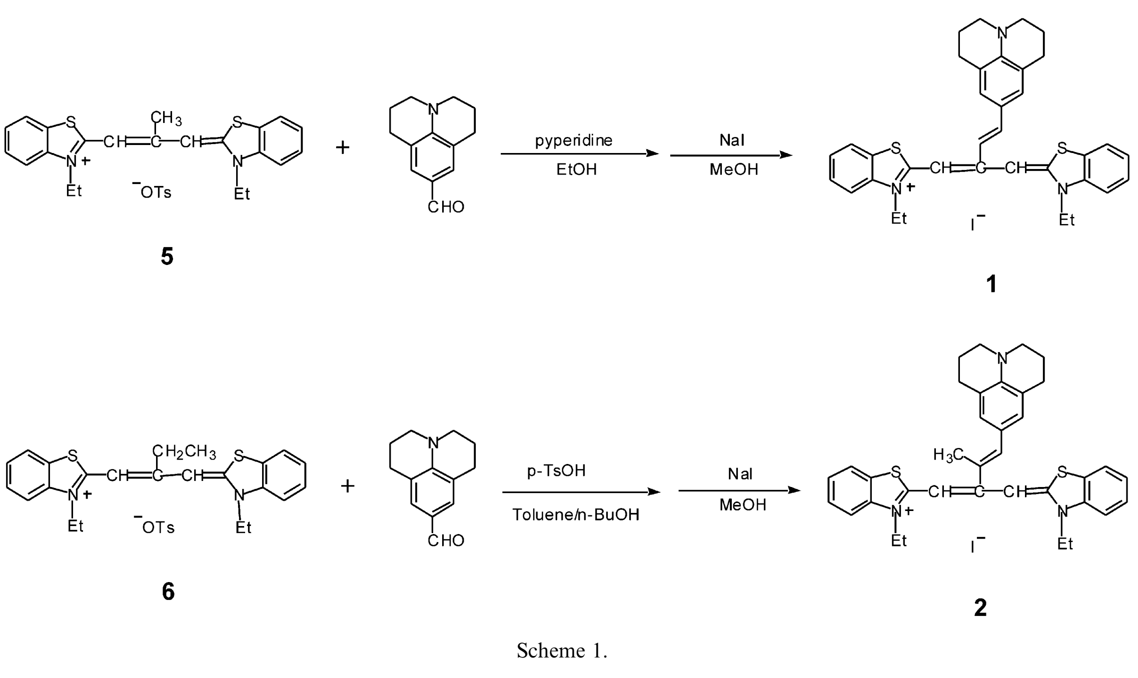
2.2. Visible absorption spectra of trimethine cyanines *1–3*

UV/visible absorption spectra of **1**–**3** in methanol at a concentration of 5×10^{-6} mol dm^{-3} are shown in Fig. 1. The λ_{max} values (ϵ_{max}) at each first absorption band for **1**–**3** are as follows; 560 nm (98,000) for **1**, 559 nm (174,000) for **2** and 557 nm (153,000) for **3**. Shapes of the first absorption bands for **2** and **3** are similar but are different in the UV region. On the other hand, dye **1** shows very broad absorption at the first band and its



Scheme 1.

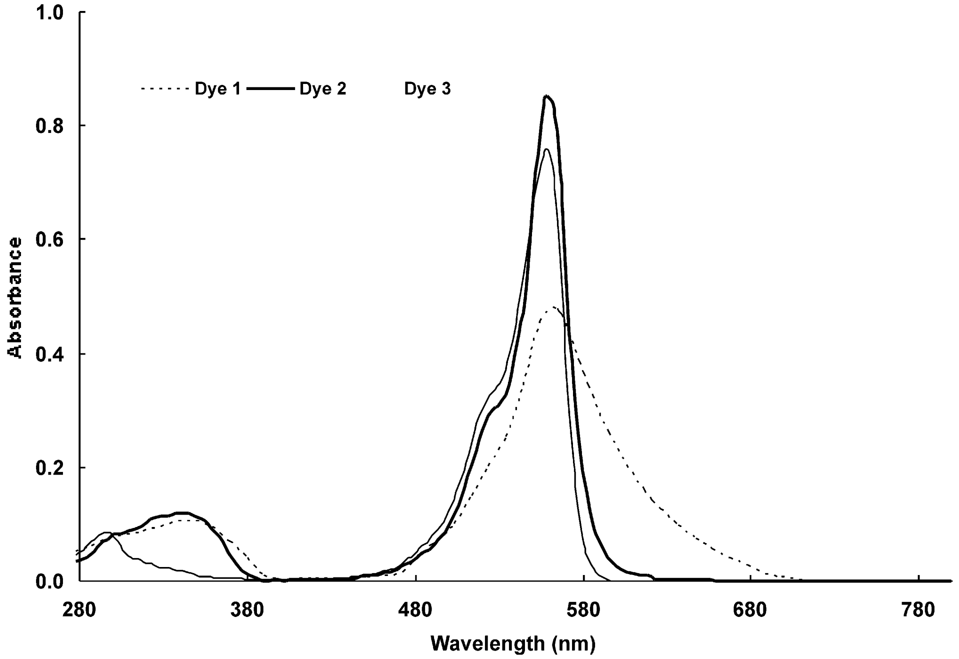


Fig. 1. Absorption spectra of dyes **1**–**3** (5×10^{-6} M) in methanol.

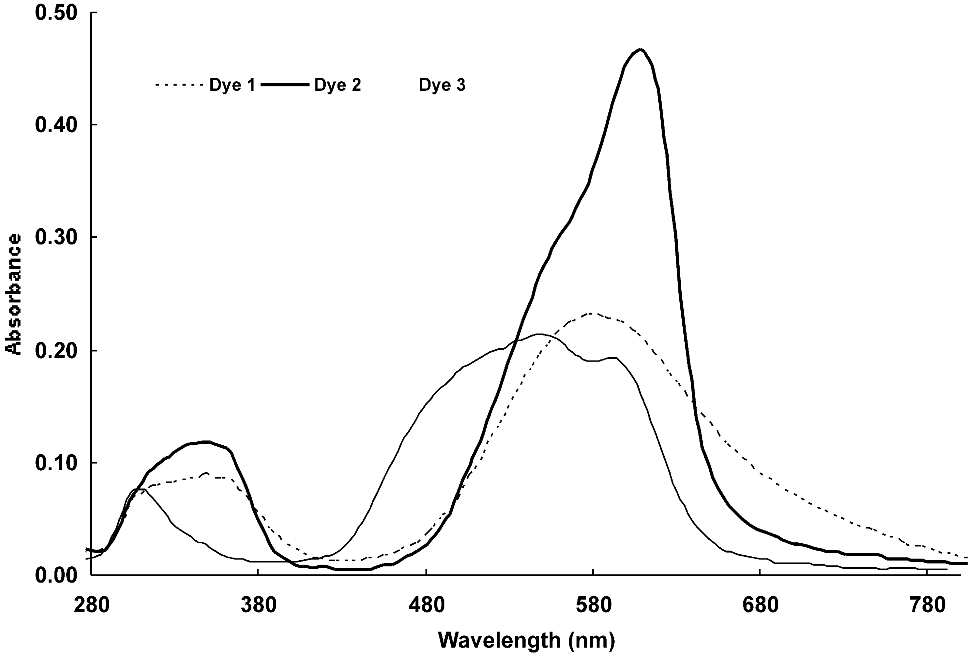


Fig. 2. Absorption spectra of dyes **1**–**3** in thin film.

second band around 350 nm is similar to that of **2**. The second band probably arises from the julolidinylethenyl group, which is a common side chain for **1** and **2**. The λ_{max} values of these three dyes are equivalent but the ϵ_{max} value of dye **1** is smaller than those of the other two.

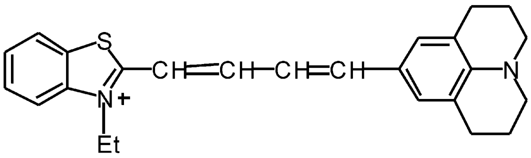
To elucidate these differences in absorption spectra in connection with their substituent effects, we evaluated their absorption spectra by conducting MOPAC calculations to estimate their optimized structure. The optimized three-dimensional structures of **1** and **2** are obtained by the combination of MM2 and MOPAC PM3 calculations as shown in Fig. 3. The configuration of two benzothiazole rings is *trans* in each case. In comparison with planer **1**, the methyl group in **2** prevents the coplanarity of the whole dye system. Consequently, the julolidinylethenyl group in **2** can not form full π-conjugation with the cyanine main chromophore. The optimized structure of **3** is completely planer π-conjugated system.

On the basis of the optimized structures, ZINDO MO calculations were performed and gave the theoretical electronic transition factors related to the first absorption band in the visible region as summarized in Table 1. From the results of Table 1, the first absorption bands in the visible region are attributed to the transition from HOMO or NHOMO to LUMO in each dye. Judging from the values of oscillator strength (*f*), the broad first absorption band consists of two allowed transitions with similar size *f* value in the case of dye **1**. On the other hand, the first excitation of dye **2** from HOMO to LUMO is assigned to forbidden transition by a very small value of *f*. Therefore the sharper absorption band for dye **2** consists of an allowed transition and a forbidden transition. We assumed that the small *f* value for HOMO-LUMO transition for **2** is attributable to isolation of the two chromophores due to the steric hindrance by the methyl group.

Table 1
Observed λ_{max} (ε_{max}) for **1**–**3**, and the calculated oscillator strength *f* and energy level of MOs for **1**–**4**

	Calculated					Observed	
Dye	λ_{max} (nm)	*f*	Energy level of MOs (ev)			λ_{max} (nm)	ε_{max}
			NHOMO	HOMO	KYNI		
1	522	9.943		−9.49	−4.47	600	46,000
	488	1.030	−9.99		−4.47	560	98,000
2	509	0.036		−9.26	−4.43		
	482	1.111	−10.15	−10.17	−4.43	559	174,000
3	499	1.523			−4.67		
4	551	1.867		−9.60	−4.72	557	153,000

A model compound **4** only for the calculations and dye **3** were chosen as two constituents for dyes **1** and **2**. The energy level of HOMO for **4** is higher (0.57 eV) than that of **3**, but the LUMO level for **4** is lower only by 0.05 eV than that of **3**.



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From these findings, the cyanine main chromophore 3 plays important role in the electronic transition in the visible region for both dyes **1** and **2**. The julolidinylethenyl group in **1** acts as a substituent contributing to the first electronic absorption as the cyanine main chromophore, but that in **2** does not contribute to the first electronic absorption.

2.3. NMR spectra

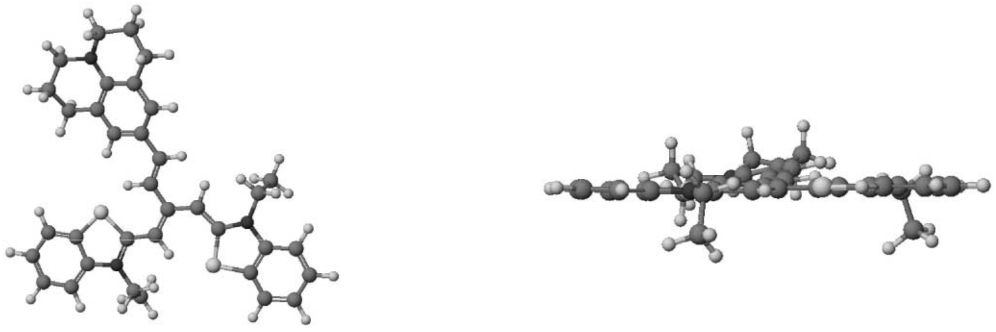
The extent of π-conjugation of the cyanine main chromophore with julolidinylethenyl group can be evaluated from the ^{1}H NMR spectra of **1** and **2** which are shown in Fig. 4. The trimethine cyanine **3** shows chemical shifts of the protons unperturbed by julolidinylethenyl group. The methine proton peak at 7.65 ppm in **2** shifts to 7.34 ppm in **1**. On the contrary, all of the julolidinylethenyl proton peaks in 1 shift to downfield by 0.15–0.21 ppm in comparison with those in **2**. This indicates that the π-electrons in the julolidinylethenyl group shift toward the cyanine main chromophore through the π-conjugation.

The methylene protons of the *N*-ethyl group of **2** shows geminal coupling ($J = 15.0$ Hz) which indicates that the whole molecule does not freely rotate due to sterically hindered *meso*-substituent preventing the rotation of the N-ethyl substituent. In the cases of **1** and **3**, these *geminal* coupling are not observed.

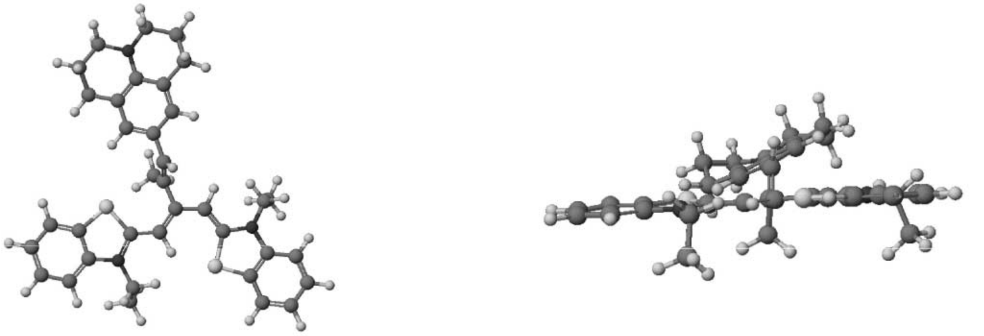
These observations are consistent with results from the visible absorption spectra discussed before.

2.4. Solid state spectra of dyes 1–3

The absorption spectra of dyes **1**–**3** in the solid state (thin film) are shown in Fig. 2. Thin films of each dye were prepared by spin coating method with the same conditions and equal molar solutions.



1 (Top View) **1 (Side View)**



2 (Top View) **2 (Side View)**

Fig. 3. Optimized structures of **1** and **2** from the top view and the side view of π-plane.

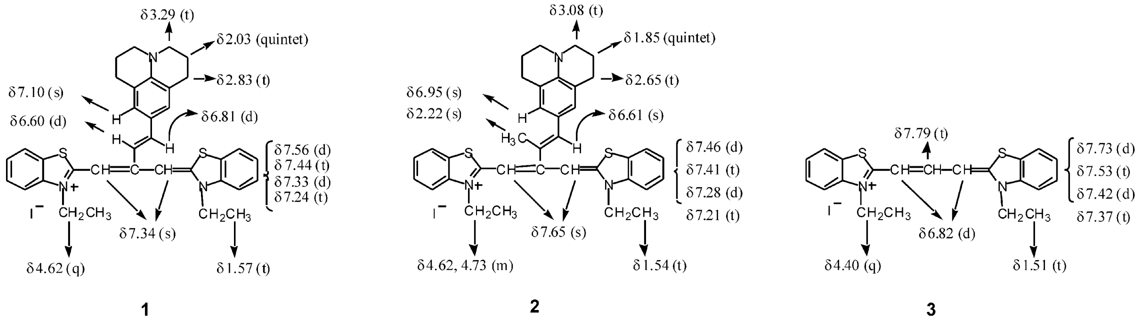


Fig. 4. Structural assignments of protons in **1**–**3** by ^{1}H NMR.

The absorption bands for **3** in solid state broaden compared to those in solution. The sharp absorption band at 560 nm in solution shifts to around 600 nm in the solid state and the new broad band appears around 500 nm. As dye **3** itself has a completely planar π-plane, the band broadening can not be explained in terms of planarity in the solid state. The band broadening is probably attributable to aggregate such as H-type and J-like types. In the case of dye **1**, the absorption bands are similar in both cases but shifts to longer wavelength from 560 nm to 580 nm in the solid state.

In the case of dye **2** in the solid state, a bathochromic shift by 40 nm and strong absorption around 590 nm are observed in comparison with those of **1** and **3**. In the solid state, dye **2** having a bulky moiety is not favorable for molecular stacking resulting in the lack of change in the absorption band in comparison with that of **3**.

2.5. Effect of the julolidine moiety on the light fastness

The relationship between the color fading rates and cyanine dyes **1**, **2**,and **3** are shown in Fig. 5. The extent of fading was estimated by the ratio, A/A_0 where A_0 was the original absorbance. The values A_0 and A were measured at the λ_{max} of each dye. In the presence of 2,4,6-tris(trichloromethyl)-1,3,5-triazine (TCT) as an electron-acceptor, both meso-substituted dyes **1** and **2** show better lightfastness than plain dye **3** in the first stage of the irradiation time. It is noteworthy that the julolidine moiety worked effectively as an intramolecular electron donor to stabilize the dyes, but julolidine itself (the same concentration with dye **3**) did not play a role in light fastness as an intermolecular electron donor as shown in the case of - - -●- - - (3/TCT/Julolidine). The photopolymerization system with cyanine dyes as photo-sensitizers show photo-fading in the presence of 2, 4, 6-tris (trichloromethyl)-1, 3, 5-triazine TCT as a radical initiator due probably to generation of radicals of the dyes. An established mechanism is not yet known, but the stabilization mechanism for cyanine dyes in the presence of electron donors is thought to be as follows. Upon irradiation, the electron in the excited dye probably transfers to TCT acting as an electron accepting radical generator. As a result, the radical of the dye is formed which should be sensitive to surrounding conditions such as oxygen in the

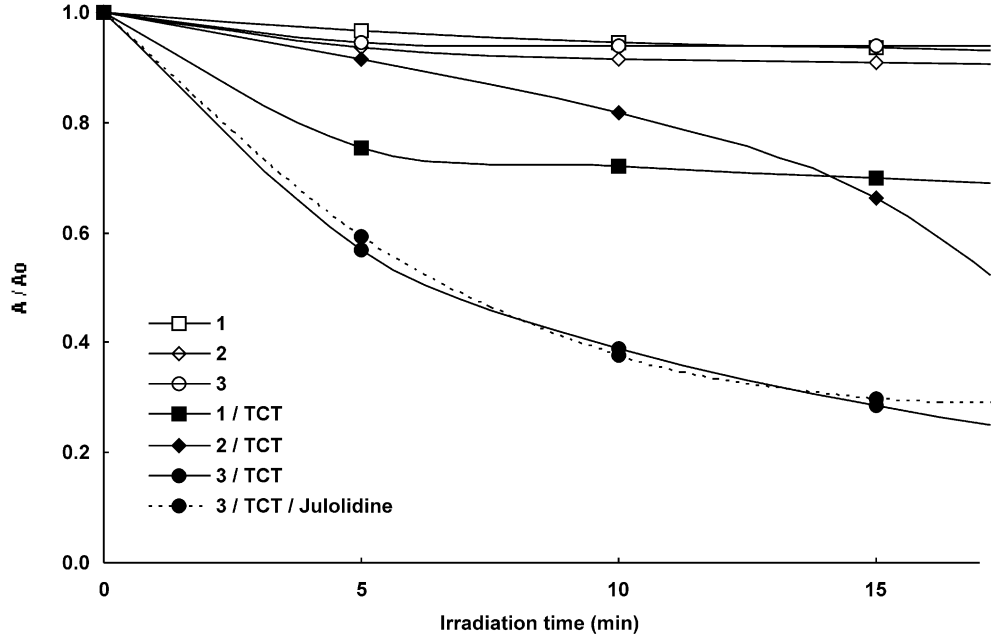


Fig. 5. Absorbance changes at the λ_{max} of dyes **1**–**3** in ethanol vs. time by irradiation with visible light.

reaction system. If an excited dye possessing an electron donating substituent like a julolidine moiety, tan electron from the donating group may transfer to the dye bases SOMO (HOMO) yielding a more stable configuration resembling the ground state of the dye. The julolidine moiety does effect the stability, sterically hinders attack of oxygen on the molecule. These findings imply that intramolecular electron-transfer from the julolidine moiety to the cyanine main chromophore contributes to light fastness of cyanine dye **2**.

3. Experimental

3.1. General

The ^{1}H NMR spectra were measured on a Jeol JNM-AL 300 spectrometer for solutions in deuteriochloroform with tetramethylsilane as internal standard; δ values are in ppm and coupling constants values in Hz. Mass spectra were recorded on a Perkin-Elmer Sciex API III spectrometer by the ESI method. The UV/visible spectra were measured on a Hitachi U-3400 spectrometer. Melting points were determined on a Yanagimoto micro melting point apparatus without correction. Elemental analyses were conducted with a Perkin-Elmer 2400-type analyzer.

2,4,6-tris (trichloromethyl)-1,3,5-triazine (TCT) was purchased from Midori Kagaku Co., Ltd. and Julolidine was purchased from Aldrich. Photo-irradiating test was performed in ethanol at a concentration of 1.0×10^{-6} mol dm^{-3} (Dye **1–3**), 1.0×10^{-4} mol dm^{-3} (TCT) and 1.0×10^{-6} mol dm^{-3} (julolidine, in case of **3**). The solutions were bubbled with a nitrogen gas before irradiation. The light was irradiated by a 150 W xenon arc lamp through a Toshiba Y-43 filter.

*3.2. Preparation of meso alkyl substituted trimethine cyanins **5** and **6***

A mixture of 3-ethyl-2methylbenzotiazolium *p*-toluenesulfonate (0.1 mol) and triethyl orthoacetate (0.2 mol) in pyridine was refluxed. After 1h, the mixture was cooled to room temperature and added ethyl acetate. The precipitate was filtered to give *meso* methyl trimethine cyanine **5**. In case of *meso* ethyl trimethine cyanine **6**, triethyl orthoacetate was replace by triethyl orthopropionate.

*3.3. Preparation of 3-Ethyl-2-[2-(3-ethyl-3H-benzothiazol-2-ylidenemethyl)-4-(2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-9-yl)-buta-1,3-dienyl]-benzothiazol-3-ium iodide **1***

A mixture of *meso* methyl trimethine cyanine **5** (2.75 g, 5 mmol), 9-formyljulolidine (1.2 g, 6 mmol) and piperidine (0.5 g) in ethanol was refluxed for 1 h. After cooling at room temperature, diisopropylether (75 ml) was added, and stirred. Then the solvent was removed. The crude oil was dissolved in methanol (20 ml) and the mixture was stirred at 60 °C. To the solution, a mixture of sodium iodide (1.5 g, 10 mmol) and methanol (5 ml) was added dropwise. After the mixture was stirred for 0.5 h at 60 °C, it was allowed to cool down to room temperature. The precipitate was filtered to give **1** as dark green solid (47%), m.p. 248–249 °C; δ_H (CDCl$_3$) 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): λ_{max} 560 nm ($\log\epsilon=4.99$).

*3.4. Preparation of 3-Ethyl-2-[2-(3-ethyl-3H-benzothiazol-2-ylidenemethyl)-3-methyl-4-(2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-9-yl)-buta-1,3-dienyl]-benzothiazol-3-ium iodide **2***

A mixture of meso ethyl trimethine cyanine **6** (1.0 g, 1.77 mmol), 9-formyljulolidine (0.428 g, 2.2 mmol), and *p*-toluenesulfonic acid (30 mg), dissolved in toluene (20 ml) and butanol (4 ml) was heated by using a Dean–Stark trap for 8 h. After cooling, the mixture was poured into water and extracted with chloroform. The combined organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The crude oil was dissolved in methanol (25 ml) and the mixture was stirred at 60 °C. To the solution, a mixture of sodium iodide (0.53 g, 3.5 mmol) and methanol (2 ml) was added dropwise. After the mixture was stirred for 0.5 h at 60 °C, it was allowed to cool down to room temperature. The precipitate was filtered to give **2** as brass solid (65%), m.p. 212–213 °C; δ_H ($CDCl_3$) 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): λ_{max} 559 nm ($\log\epsilon=5.24$).

*3.5. Preparation of 3-Ethyl-2-[3-(3-ethyl-3H-benzothiazol-2-ylidene)-propenyl]-benzothiazol-3-ium iodide **3***

A mixture of 3-ethyl-2methylbenzotiazolium iodide (0.1 mol) and triethyl orthoformate (0.2 mol) in pyridine was refluxed. After 1h, the mixture was cooled to room temperature and the precipitate was filtered. The product was recrystalized from methanol to give 3 as purple solid (86%), m.p. 267–269 °C; δ_H ($CDCl_3$) 7.79 (1H, t, $J=12.6$), 7.73 (2H, d, $J=7.8$), 7.53 (2H, t, $J=7.8$), 7.42 (2H, d, $J=7.8$), 7.37 (2H, t, $J=7.8$), 6.82 (2H, d, $J=12.6$), 4.40 (4H, q, $J=7.2$), 1.51 (6H, t, $J=7.2$). UV (methanol): λ_{max} 557 nm ($\log\epsilon=5.18$).

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References

[1] Tani T. Photographic sensitivity. Oxford University Press; 1995.
[2] Mishra A, Behera RK, Behera PK, Mishra BK, Behera GB. Cyanines during the 1990s: a review. Chem Rev 2000; 100:1973–2011.
[3] James TH. The theory of the photographic process. 4th Ed. New York: Macmillan Publishing Co; 1977.
[4] Yasui S. Shikizai Kyoukai-shi 1987;60:212.
[5] Koseki K, Yamaoka T, Mitekura H, Yasui S. Polymer Preprint Japan 1994;43:792.
[6] Hayami M, Okazaki T, Chen P. Photostabilizing effects of singlet oxgen quenchers on long wavelength cyanine dyes. Journal of the Association for Advancement of Science & Technology 1997;45:51–61.
[7] Sayama K, Hara K, Ohga Y, Shinpou A, Suga S, Arakawa H. Significant effects of the distance between the cyanine dye skeleton and the semiconductor surface on the photoelectrochemical properties of dye-sensitized porous semiconductor electrodes. New J Chem 2001;25:200–2.
[8] (a) Venkataraman K. The chemistry of synthetic dyes. Academic Press, 1952;II:1143. (b) ibid 1971;IV:212.
[9] Wladyslaw M. Chem. Stosowana 1961;5:311–316 (Chem. Abstr., 1962; 56: 4902a).