

Highly dichroic benzo-2,1,3-thiadiazole dyes containing five linearly π -conjugated aromatic residues, with fluorescent emission ranging from green to red, in a liquid crystal guest–host system†

Xuelong Zhang,^b Rumiko Yamaguchi,^c Keiichi Moriyama,^c Masami Kadowaki,^d Takako Kobayashi,^d Tsutomu Ishi-i,^a Thies Thiemann^a and Shuntaro Mataka^{*a}

Received 5th September 2005, Accepted 11th November 2005

First published as an Advance Article on the web 2nd December 2005

DOI: 10.1039/b512493j

A number of fluorescent benzothiadiazole dyes have been synthesised and their optical properties, when dispersed in a liquid crystal host phase, examined. These dyes have five linearly π -conjugated aromatic ring systems (both with and without ethene and 1,3-butadiene spacers). The liquid crystalline host medium, used was the nematic phase of MLC-2039. The emission colours observed ranged from green to red, depending on the unsaturated chains attached at the 4- and 7- positions of the benzo-2,1,3-thiadiazole core. A highly dichroic and efficient fluorescence was observed. The dye 4,7-bis[5-bis(phenylethenyl)thiophen-2-yl]-2,1,3-benzothiadiazole is of particular importance. This is the first example of a dye emitting strong red fluorescence (633 nm). When dispersed in MLC-2039, dichroic ratio values up to 12.3 were obtained.

Introduction

The self-emitting, reflective guest–host (G–H) type liquid crystal displays (LCDs) were suggested as a less energy-consuming display for mobile communication tools.^{1–2} Crucial development of this type of LCD is realized by synthesizing strongly fluorescent dyes with a highly dichroic property and strong emission in the blue–red region.

The dichroic fluorescent dyes were required, in principle, to have a rod-like long molecular structure to associate with the nematic LC host and to exhibit blue–red emission for full-color imaging without quenching by other molecules.^{3–5} A number of compounds such as perylenes,⁶ dilactones,⁷ benzantrones,⁸ naphthaimides⁹ and polyfluorophenazines¹⁰ have been designed and synthesized as fluorescent dichroic dyes, which follow the same guidelines needed for the creation of highly dichroic absorption dyes; however, their dichroic ratios in LC media were unsatisfactory for practical use and their fluorescent colors are mostly restricted to blue-to-orange. Only dichroic oxazine 725 and Nile red were evaluated as real red fluorophores in a G–H LC system;¹¹ however, the dichroic ratios were low.

Recently, we reported highly dichroic fluorescent dyes with a rod-like structure by introducing long flexible side chains to

the *para*-positions of rigid 4,7-diphenyl-2,1,3-benzothiadiazole fluorophore. The dyes in a LC cell containing commercial MLC-2039 host showed high dichroic ratios (up to 9.1) to emit strong fluorescence ranging from blue to yellow, depending on the substituents.¹²

The purpose of this study is to develop highly dichroic fluorescence benzo-2,1,3-thiadiazole-based compounds with emission in the long wavelength region. In principle, an expanding π -conjugation system or intramolecular charge-transfer (ICT) interaction between the electron-withdrawing core and electron-rich side substituents should narrow the HOMO/LUMO energy gap and cause bathchromic shift. Obviously, an expanded π -system along the molecular long axis is beneficial to improve molecular linearity of a dye to control the dichroic property. In this context, the dye molecules in Fig. 1 were designed to have a long π -conjugation system along the molecular long axis by linearly combining the benzene and thiophene rings to the benzothiadiazole-core with/without ethene and 1,3-butadiene spacers. In these dyes, large bathchromic shifts of the absorption and fluorescence spectra were expected due to the long π -conjugation system and ICT interaction between benzo-2,1,3-thiadiazole and the benzene or thiophene rings. Highly dichroic emission was expected also because of the rod-like molecular structure of the dye.

Results and discussion

Synthesis of 2,1,3-benzothiadiazole dyes with long and linear π -conjugations on the 4,7 position 1–6

Benzothiadiazole derivatives **1a–b**, **2**, **3**, **4a–c**, **5** and **6** were prepared starting from 4,7-dibromo-2,1,3-benzothiadiazole (**7**)¹³ by using a palladium-mediated coupling reaction as a key step.¹⁴ Yields of the reaction products are given in Scheme 1.

^aInstitute for Materials Chemistry and Engineering, Kyushu University, 6-1 Kasuga-koh-en, Kasuga-shi, Fukuoka, 816-8580, Japan. E-mail: mataka@cm.kyushu-u.ac.jp; Fax: +81-92-583-7894

^bDepartment of Molecular and Material Sciences, Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga-koh-en, Kasuga-shi, Fukuoka, 816-8580, Japan

^cDepartment of Electrical and Electronic Engineering, Akita University, 1-1 Tegata Gakuencho, Akita-shi, Akita, 010-8502, Japan

^dMitsubishi Chemical Group Science and Technology Research Center, Inc., 1000 Kamoshida, Aoba-ku, Yokohama-shi, Kanagawa, 227-8502, Japan

† Electronic supplementary information (ESI) available: synthesis of materials. See DOI: 10.1039/b512493j

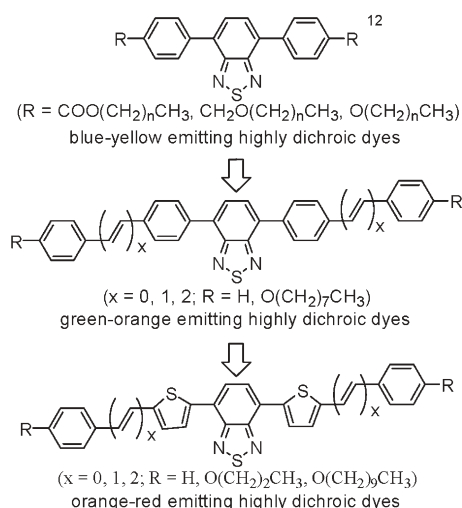
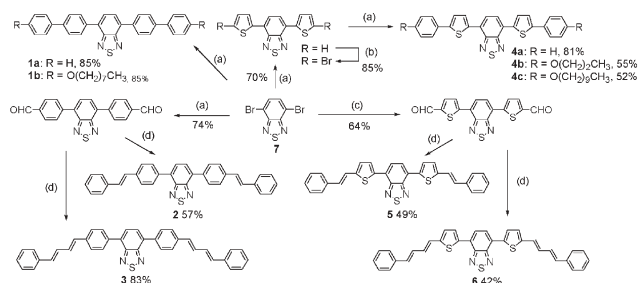


Fig. 1 Molecular design of highly dichroic dyes with long wavelength emission.

Biphenyl-substituted 2,1,3-benzothiadiazole **1a** and **1b** were prepared *via* Suzuki–Miyaura coupling reactions of **7** with the corresponding biphenylboronic acids. Compound **2** having phenyl–ethene–phenyl conjugated π -systems and **3** having π -extended phenyl-1,3-butadiene–phenyl arrays, respectively, were obtained by the coupling reaction¹⁵ of **7** with 4-formylphenylboronic acid, followed by the Wittig reaction¹⁶ of the resulting 4,7-di(4-formylphenyl)-2,1,3-benzothiadiazole. Thiophene derivatives **4–6** were prepared in a similar manner to their benzene analogues **1–3**, as follows. 5-(*p*-Substituted-phenyl)thiophen-2-yl compound **4** was obtained from **7** *via* the sequence of a coupling reaction with (thiophen-2-yl)boronic acid, NBS-bromination, and, again, a coupling reaction with the corresponding (*p*-substituted phenyl)boronic acids.¹⁷ Compound **5**, having ethene spacers, and **6**, having π -extended 1,3-butadiene spacers, respectively, were synthesized by the Wittig reaction of 4,7-bis(5-formylthiophen-2-yl)-2,1,3-benzothiadiazole, which was obtained by the coupling reaction of **7** with (5-formylthiophen-2-yl)boronic acid.¹⁸ In the ¹H NMR spectra of **2**, **3**, **5** and **6**, the spin–spin coupling constants ($J = 13.7$ – 16.5 Hz) of olefinic protons show the all-*trans* conformation of these molecules (see the electronic supplementary information, ESI†).



Scheme 1 Reagents and conditions: (a) arylboronic acid, Pd(PPh₃)₄, 2 M Na₂CO₃, benzene/EtOH; (b) NBS, chloroform; (c) 5-formylthiophene-2-ylboronic acid, Pd(PPh₃)₂Cl₂, 2 M Na₂CO₃, benzene/EtOH; (d) arylmethyltriphenylphosphonium bromide, KOH, DMSO.

Table 1 Absorption and emission properties of 4,7-diaryl-2,1,3-benzothiadiazole derivatives **1–9**

Compound	$\lambda_{\text{max}}^a/\text{nm}$	$\log \epsilon$	$F_{\lambda_{\text{max}}}/\text{nm}^b$	Φ_{FL}^c	Half width/nm
1a	396	4.27	526	0.64	96
1b	406	4.30	551	0.51	102
2	415	4.54	555	0.76	100
3	424	4.62	577	0.70	106
4a	488	4.41	624	0.58 ^d	101
4b	507	4.42	649	0.39 ^d	103
4c	506	4.43	650	0.41 ^d	104
5	516	4.54	647	0.21 ^d	102
6	536	4.57	666	0.06 ^d	104
8a	379	4.00	490	0.77	87
9	446	4.05	573	0.64	102

^a Measured in dichloromethane (1×10^{-5} mmol dm⁻³). ^b Measured in dichloromethane (1×10^{-6} mmol dm⁻³). ^c Fluorescence quantum yield (Φ_{FL}) relative to quinine bisulfate ($\Phi_{\text{st}} = 0.55$). ^d Fluorescence quantum yield (Φ_{FL}) relative to rhodamine B ($\Phi_{\text{st}} = 0.65$).

Optical properties of **1–6**

Absorption and fluorescence spectra data of **1a–b**, **2** and **3** in dichloromethane solution are summarized in Table 1. Both in a solution and in the solid state, **1–3** are strongly fluorescent with high relative quantum yields (0.5–0.8). Large Stokes shifts over 100 nm were characteristic of 4,7-diaryl-2,1,3-benzothiadiazoles^{12, 19} (Table 1).

The biphenyl-substituted 2,1,3-benzothiadiazole dye **1a** showed bathochromic shifts of 17 nm and 36 nm, respectively, in the absorption and fluorescence spectra, compared to the parent compound 4,7-diphenyl-2,1,3-benzothiadiazole (**8a**).¹² Further bathochromic shifts were seen in the spectra of octyloxy derivative **1b** (10 nm and 25 nm, respectively, compared to **1a**), due to the ICT interaction between the electron-withdrawing central benzo-2,1,3-thiadiazole ring and the electron-donating 4'-octyloxybiphenyl groups. In compound **2**, ethene spacers connecting the two benzene rings extended the π -conjugation; therefore, the absorption and fluorescent spectra of **2** showed bathochromic shifts. Further bathochromic-shifts were observed in the spectra of **3**, which has 1,3-butadiene spacers. The molar absorption coefficients increased with the extension of π -conjugations: **1a** (4.27), **2** (4.54) and **3** (4.62).

Comparison of the spectra of **1–3** showed bathochromic shifts of 10 nm for one ethene spacer and 14 nm for one 1,3-butadiene spacer in the absorption, and 15 nm and 25 nm in the fluorescent spectra, respectively.

Though **1–3** covered the fluorescent color from green to orange, more efficient ICT interaction and π -conjugation were needed to achieve highly dichroic absorption in the long wavelength region and red-color emission based on the 2,1,3-benzothiadiazole system of the rod-like structure. An electron-rich thiophene ring was chosen as a candidate having efficient ICT interaction and a highly planar π -conjugation system, as 4,7-di(2-thienyl)-2,1,3-benzothiadiazole²⁰ (**9**) showed bathochromic shifts of 67 nm and 83 nm, respectively, in the absorption and fluorescent spectra, compared to those of 4,7-diphenyl compound **8a**.¹²

Spectral data of **4a–c**, **5** and **6** in dichloromethane solution are summarized in Table 1. The 5-phenylthiophen-2-yl derivative **4a** absorbed at 488 nm and emitted orange-red

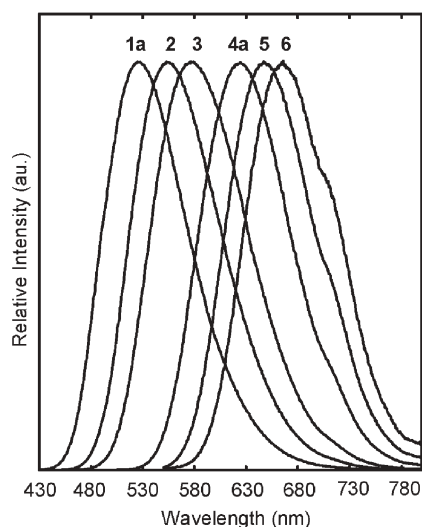


Fig. 2 Fluorescence spectra of 4,7-diary-2,1,3-benzothiadiazoles **1a**, **2**, **3**, **4a**, **5**, and **6** (from left to right) in dichloromethane solution.

fluorescence at 624 nm with a fairly high relative quantum yield of 0.58. Alkoxy groups in **4b–c** caused further red-shifts in the spectra. Compounds **4b** and **4c** emitted red fluorescence at 649 nm and 650 nm, respectively, with quantum yields of around 0.4. In compound **5**, one ethene spacer connecting the thiophene and benzene ring caused the 14 nm and 12 nm bathochromic shifts of the absorption and fluorescence spectra. The values are similar to those of the difference between **2** and **1a**. Compound **5** emitted red light at 647 nm; however, the relative quantum yield is almost one-half (0.21) of those of **4b–c**. Compound **6** having the 1,3-butadiene spacers showed further bathochromic shifts (20 nm and 19 nm, respectively) in the spectra, compared to **5**. The emission of **6** at 666 nm colored magenta; however, the relative quantum yield of **6** was too poor (0.06) to determine the fluorescent dichroic ratio. The 1,3-butadiene spacer may be more probable for molecular movements than the ethene spacer and **6** loses the excitation energy *via* a radiationless process.

Polarized absorption and fluorescence spectra of 1–6 in nematic LC 2039

The polarized absorption and fluorescence spectra of the benzothiadiazole dyes **1a–b**, **2**, **3**, **4a–c**, **5** and **6** in commercial MLC-2039 were measured in a cell, which is coated with a one-directional rubbing of a thin polyimide layer on the surface. Guest dye molecules **1–6** could be assumed to orient themselves parallel to the LC director. Dichroic ratios (N_A and N_F) were measured at concentration of 0.5-wt% for **1–3** and 0.3-wt% for **4–6**, respectively.²¹ Guest dyes **1–6** did not crystallize or demix from the LC host upon irradiation. The nematic mesophase of the host LC was not destabilized by the guest dyes.

The fluorescence maxima of **1a–b**, **2**, **3**, **4a–c**, **5** and **6** in host MLC-2039 showed blue shifts (about 10–20 nm) compared to those in a dichloromethane solution (10^{-5} M), which was supposed to be due to the different polarities of the media (Table 2). The dichroic ratios of **1–6** in MLC-2039 host LC are

Table 2 Spectral and dichroic data of **1–6**, **8a** and **9** in liquid crystalline media MLC-2039

Compound	$\lambda_{NA, \max}^d$ nm	N_A	$\lambda_{NF, \max}^d$ nm	N_F	l^e	d^f	l/d
1a ^a	380	12.3	510	5.6	22.24	7.81	2.85
1b ^a	410	14.7	540	8.0			
2 ^a	441	11.0	540	10.5	26.89	7.88	3.41
3 ^a	430	12.3	550	12.3	31.34	8.86	3.54
4a ^b	501	9.2	603	10.2	19.93	9.64	2.07
4b ^b	523	11.2	640	9.6			
4c ^b	523	12.2	642	10.2			
5 ^b	527	8.1	633	12.3	26.56	9.25	2.87
6 ^b	543	10.4	656	— ^d	29.78	10.55	2.82
8a ^c	424	3.6	487	2.8	13.63	7.38	1.85
9 ^c	463	4.5	562	4.0	12.48	7.34	1.70

^a Measured by Mitsubishi Co. Ltd., excitations at 350 nm, concentration is 0.5% (w/w). ^b Measured by Akita University, excitations at 360 nm, concentration is 0.3% (w/w). ^c Reported result in ref. 12. ^d Not measured because of the low fluorescence quantum yield. ^e l represents the length of the long axis of the molecule. ^f d represents the diameter of the circumscribed cylinder of the molecule.

shown in Table 2. Fig. 3 exhibits representative polarized absorption and fluorescence normalized spectra of benzene dye **3** (Fig. 3 (a)) and thiophene dye **5** (Fig. 3 (b)) in MLC-2039 media.

The dichroic ratios of the terphenyl-type dye **8a** were low ($N_A = 3.6$ and $N_F = 2.8$) in MLC-2039.¹² In dyes **1–3** having a linearly connected five-aromatic array structure with/without olefinic spacers, higher dichroic ratios were shown for the light-absorption (around 380–430 nm) and light-emission (green to yellow fluorescence around 510–550 nm). Dye **1a**, having a nearly linear five-aromatic array, showed a remarkably high absorption dichroic ratio ($N_A = 12.3$), which is much higher than the requisite minimum ($N_A = 8.0$) for absorption

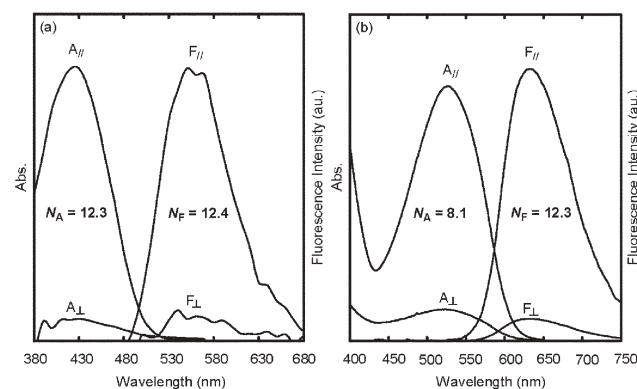


Fig. 3 Polarized absorption and fluorescence spectra of (a) **3** and (b) **5**. Compounds were dissolved in a commercial liquid crystal MLC-2039 at a concentration of 0.5% w/w for **3** and 0.3% w/w for **5**, respectively. Measurement of the polarisation spectra was carried out by irradiation with a tungsten halogen lamp and a black-light blue fluorescent lamp, parallel and perpendicular to the rubbing. The dichroic ratios were determined from the formula: $N_A = A_{||}/A_{\perp}$, $N_F = F_{||}/F_{\perp}$. $A_{||}$ and A_{\perp} are the absorption intensities in the direction parallel and perpendicular to the dye molecules. $F_{||}$ and F_{\perp} are the fluorescence intensities in the direction parallel and perpendicular to the dye molecules.

dichroic dyes in practical use. The value increased up to 14.7 in octyloxyl-substituted dye **1b**. On the other hand, fluorescent dichroic ratios of **1a** and **1b** were low ($N_A = 5.6$ and $N_F = 8.0$, respectively). The reason for this large discrepancy in the absorption and fluorescence dichroic ratios is not known; however, it may reflect the different dipole moments at LUMO and HOMO states of the dye molecule **1**.

Both absorption and fluorescence dichroic ratios increased in **2** and **3**, which have the ethene and 1,3-butadiene spacers, respectively, in the aromatic arrays. The values $N_A = 11.0$ and $N_F = 10.5$ obtained for **2**, and $N_A = 12.3$ and $N_F = 12.3$ for **3**, respectively, can be classified in the top level values of low molecular-weight dichroic dyes in host-guest LC systems, reported so far.^{6–10} Red-light emitting dye **4a** has phenylthiophene-2,1,3-benzothiadiazole-thiophene-phenyl arrays and exhibited both high absorption and fluorescence dichroic ratios ($N_A = 9.2$ and $N_F = 10.3$). Introducing propyloxyl chains on the terminal phenyl groups was effective in increasing the dichroic absorption ratio ($N_A = 11.2$) in **4b**, but not the fluorescent one ($N_F = 9.6$). A similar substituent effect was seen in **4c** with longer decyloxyl chains, which showed the dichroic ratios, $N_A = 12.2$ and $N_F = 10.2$, respectively. The ethene spacers in the aromatic array of **5** were advantageous to increase the red-fluorescence dichroic ratio $N_F = 12.5$, though the value of the absorption decreased to $N_A = 8.1$. In compound **6** which has long 1,3-butadiene spacers, the absorption dichroic value was recovered to 10.4, but because of its very weak fluorescence in the MLC-2039 host, the fluorescence dichroic ratio of **6** could not be determined.

The orientation properties of the dyes were evaluated by the l/d ratio, where l and d represent the length of the long axis and the diameter of the circumscribed cylinder of the molecule, respectively (Fig. 4). The l and d values were calculated from the geometry of the most stable conformer by using the Hartree-Fock method with the 6-31G* basis set in the Spartan'04 program (Table 2). Fig. 4 exhibits the relationship between the N values and the l/d ratios in **1–6**, **8a**, **9** and selected comparison compounds of 4,7-di(*p*-methoxyl, *p*-propyloxyl, *p*-butoxyl, and *p*-pentyloxyl substituted phenyl)-2,1,3-benzothiadiazoles (**8b**, **8c**, **8d** and **8e**).¹² It is clear that when a molecule is made slender both by extending its π -system and by introducing alkoxy substituents on the long axis, the higher absorption and fluorescence dichroic ratios are obtained. The increasing N_A and N_F values for the alkoxy substituents are saturated when the chain lengths reached $C_4 \sim C_5$ with $N \approx 9.0$. In the benzothiadiazole dyes **1–6**, the dichroic ratios increased remarkably in value to 12.3, although the l/d ratios are similar to those of alkoxy derivatives **8b–8e**. This result suggests that extending the π -conjugated 2,1,3-benzothiadiazole system with spacers such as 1,4-phenylene, 2,5-thienylene, ethene, and 1,3-butadiene to form a linear fluorophore is a more efficient method to achieve a highly dichroic fluorescent dye than the introduction of long side chains.

Conclusions

Novel benzo-2,1,3-thiadiazole dyes **1–6** having a linear five aromatic array π -conjugation with/without olefinic spacers have been synthesized. Compounds **1–6** exhibit fluorescence

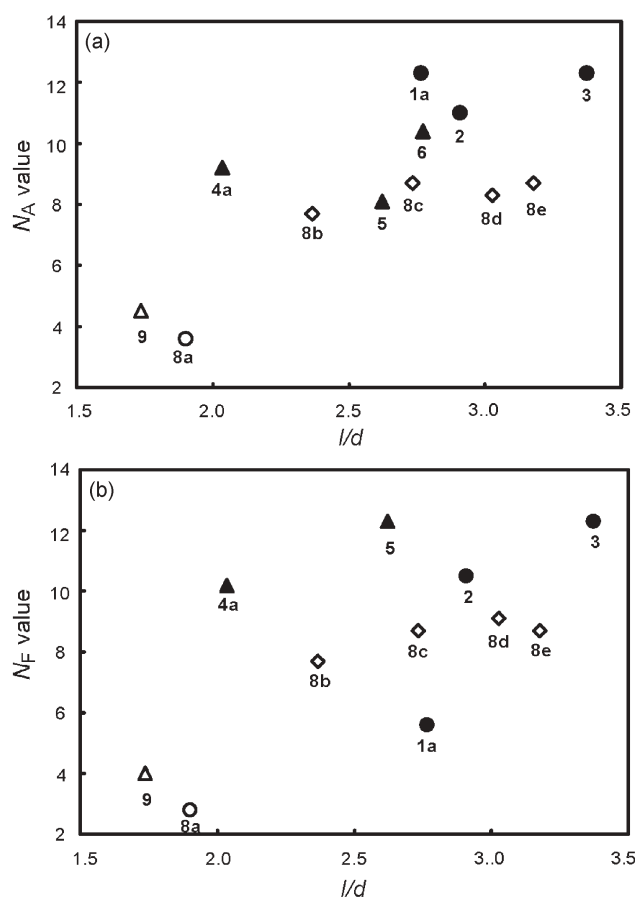


Fig. 4 Relationship between dichroic ratio (N) and l/d ratio of compounds **1–9**. (a) Absorption dichroic ratio vs. l/d ratio; (b) Fluorescence dichroic ratio vs. l/d ratio. (c) l represents the length of the long axis of the molecule. (d) d represents the diameter of the circumscribed cylinder of the molecule.

from green to magenta in dichloromethane. The relative quantum yields of **1–3** with 1,4-phenylene spacers are high (0.5–0.8). Dye **4** and **5** with 2,5-thienylene spacers show relative quantum yields in the range 0.2–0.6 as a red fluorescent dye. The relative quantum yield of **6** was poor. The molecules **1–5** act as highly fluorescent dichroic guest dyes in the MLC-2039 host, in which colors from green to red are emitted. It should be noted that extending the π -conjugation system along the long axis of the dye molecule is an effective approach to improve dichroic properties with green-to-red color emission. The electron-rich thiophene ring in **4–6** caused a large long wavelength shift, not only in the absorption, but also in fluorescence spectra, which is useful for achieving efficient red-emission. Compound **5** is the first example of the dye having a high dichroic ratio up to $N_F = 12.3$ and strong fluorescence in the real red region ($F_{L \max} = 633 \text{ nm}$) in MLC-2039 liquid crystal.

Experimental

General. All melting points are uncorrected. IR spectra were recorded on a JASCO FT/IR-470 plus Fourier Transform

Infrared Spectrometer and measured as KBr pellets. ^1H NMR spectra were determined in CDCl_3 or CD_2Cl_2 with a JEOL EX-270 spectrometer. Residual solvent protons were used as internal standard and chemical shifts (δ) are given relative to tetramethylsilane (TMS). The coupling constants (J) were reported in Hz. Elemental analysis was performed at the Elemental Analytical Center, Kyushu University. EI-MS spectra were recorded with a JEOL JMS-70 mass spectrometer at 70 eV using a direct inlet system. FAB-MS spectra were recorded with a JEOL JMS-70 mass spectrometer with *m*-nitrobenzyl alcohol (NBA) as a matrix. UV-Vis spectra were measured on a JASCO V-570 spectrophotometer in a 1 cm width cell. Fluorescence spectra were measured on a HITACHI F-4500 fluorescence spectrophotometer in a 1 cm width cell. Gel permeation chromatography (GPC) was performed with a Japan Analytical Industry LC-908 using JAIGEL-1H column (20×600 mm) and JAIGEL-2H column (20×600 mm) eluting with chloroform (3.0 mL min^{-1}). Analytical TLC was carried out on silica gel coated on aluminum foil (Merck 60 F₂₅₄). Column chromatography was carried out on silica gel (Wako C-300). THF and toluene were distilled from sodium and benzophenone under an argon atmosphere. DMSO, benzene, and chloroform were dried over 4 Å molecular sieve. Compound **7** was prepared according to a method reported previously.¹²

Acknowledgements

R. Y. and K. M. thank Professor Dr. S. Sato of the Department of Electrical and Electronic Engineering, Akita University, and M. K. and T. K. are grateful to Dr. S. Maeda of the Optoelectronic Materials Laboratory, Mitsubishi Chemical Group Science and Technology Research Center, Inc., for helpful discussions.

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