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Benzothiadiazole-based dyes that emit red light in solution, solid, and liquid state

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ABSTRACT

In this paper, we report the preparation and red-light-emitting behavior of benzothiadiazole–-tris(alkyloxy)phenylethene dyes. In solution, we observed an efficient red light emission with high fluorescence quantum yields (up to 0.78). With increase in solvent polarity, the emission bands shifted to longer wavelengths accompanied by a large Stokes shift of up to 152 nm. A moderate fluorescence quantum yield of 0.52 could be achieved even in the polar solvent dimethylformamide. Red light emission with good fluorescence quantum yields (up to 0.50) was also observed in the bulk solid, liquid, and film state.

1. Introduction

In recent years, light-emitting dyes have been of much interest in view of their applications in material sciences (e.g., organic light-emitting diodes) and in biological sciences (e.g., bioprobes and biosensors).[1,2] Developing red-light-emitting material is very important because red is one of the three primary colors, and also because red light falls within the biological optical window. Thus, a high emission efficiency is desirable both in solution and in the bulk solid. Till date, a number of red emitting dyes have been reported.[3] For example, boron–dipyrromethenes[4] and perylene diimides[5] are known as superior red-light-emitting dyes. However, these dyes exhibit a small Stokes shift, which results in the reabsorption of the emitted light. A simple strategy for obtaining red light emission is donor–acceptor conjugation, which results in the shifting of the emission band to longer wavelengths. This is accompanied by a large Stokes shift.[6]

Benzothiadiazole dyes are strongly fluorescent both in solution and in the bulk solid.[7,8] In addition, the dyes are strongly electron-accepting.[9] Recently, we reported that benzothiadiazole dyes, which contain electron-donating triphenylamines emit red light.[10] However, in polar solutions, the red emission is quenched by solvation of the polar molecules, and this reduces the emission efficiency.[11] Herein, we report the use of a novel donor, tris(alkyloxy)phenylethene, in a benzothiadiazole-based dye to produce efficient red light emission in nonpolar and polar solutions as well as in the bulk solid, film, and liquid state. We have used tris(alkyloxy)phenylethene as the donor because the three alkyloxy groups behave as electron-donating groups. In addition, the ethylene moiety is a versatile spacer that can be used to expand the π-electron system.[12]

2. Results and discussion

Benzothiadiazole dyes **3a–c** having two tris(alkyloxy)phenylethene moieties were prepared from the coupling reactions of dibromobenzothiadiazole **1** with the corresponding tris(alkyloxy)phenylethenes **2a–c** in the presence of a palladium catalyst (Scheme 1). The synthetic intermediates **2a–c** were prepared by methods described previously.[13] The obtained dyes **3a–c** were identified using spectroscopic methods and elemental analysis.

The dyes **3a** and **3b** bearing methoxy groups and octyloxy groups, respectively, are red solids. With an increase in the alkyl chain length, the melting temperature decreased from 238–240 °C for **3a** to 66–68 °C for **3b**. The melting temperature of dye **3c**, which bears branched 2-ethylhexyloxy groups, decreased below the ambient temperature; consequently, **3c** was a red viscous liquid.

The dyes **3a–c** were soluble in common organic solvents, such as toluene, tetrahydrofuran (THF), and dichloromethane (DCM). The dye **3a**, bearing short alkyl chains, tended to dissolve in polar solvents, such as dimethylformamide (DMF), whereas **3b** and **3c**,

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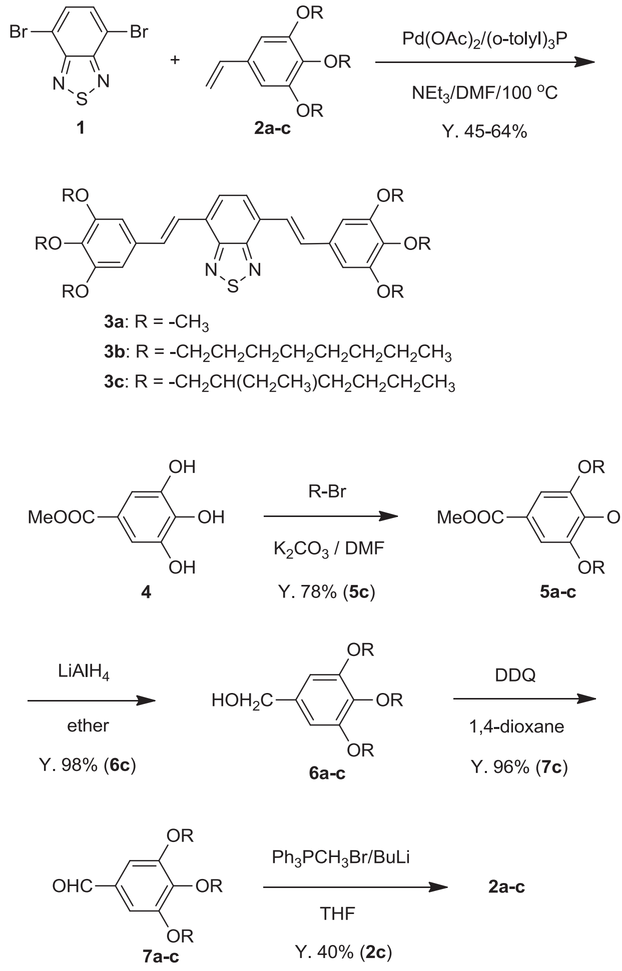

Scheme 1. Preparation of benzothiadiazole-based dyes **3a**–**c**.

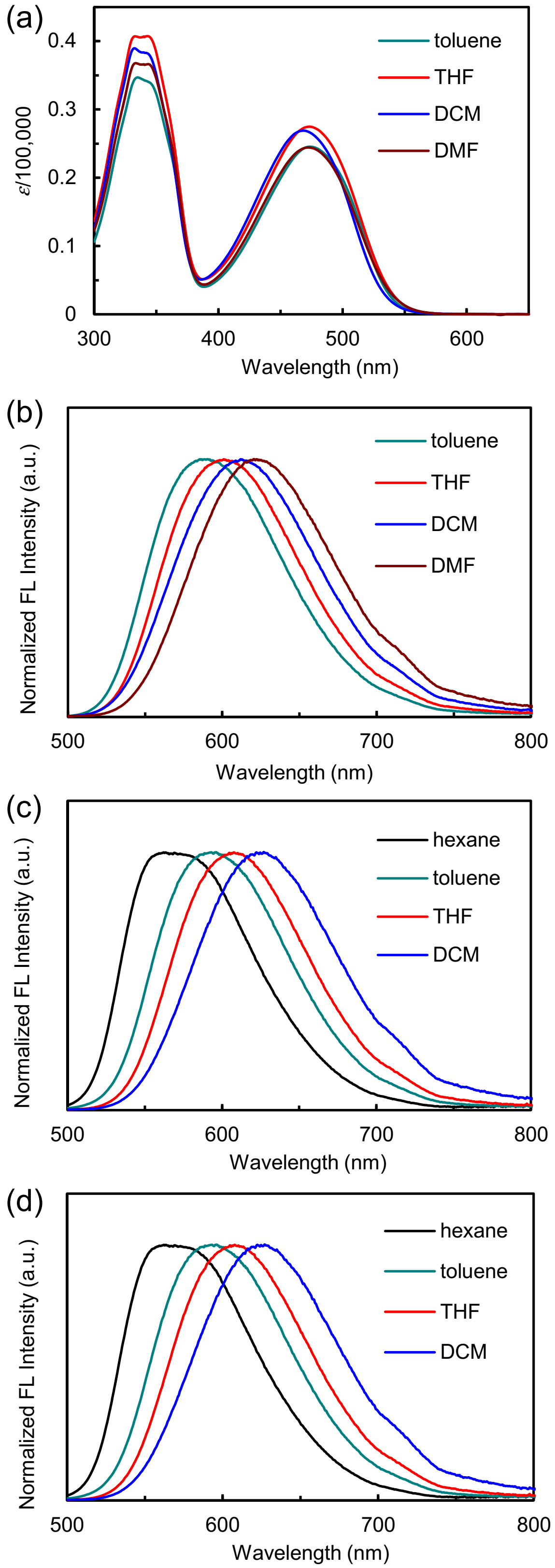

Fig. 1. (a) UV–vis spectra of **3a** at 1×10^{-5} M. Fluorescence spectra of (b) **3a**, (c) **3b**, and, (d) **3c** in 1×10^{-6} M in hexane, toluene, THF, DCM, and DMF excited at 470 nm (**3a**) and 475 nm (**3b** and **3c**).

bearing long alkyl chains, tended to dissolve in nonpolar solvents, such as hexane.

The UV–vis and fluorescence spectra were measured in various solvents (from nonpolar to polar solvents) to investigate the influence of solvent polarity on the optical properties of the benzothiadiazole dyes (Fig. 1 and Table 1). The UV–vis spectra of **3a**, **3b**, and **3c** show absorption bands at around 469–474, 474–478, and 475–479 nm, respectively. These bands would be attributed to the transition of the electron from the electron-donating tris(alkyloxy)phenylethene moiety to the electron-accepting benzothiadiazole moiety (Fig. 1a and Table 1). The absorption bands shifted very slightly depending on the solvent polarity (hexane, toluene, THF, DCM, and DMF). The very weak absorption solvatochromism indicates that the weakly polarized ground state is stabilized in polar solvent media.

Strong light emission was observed in **3a**–**c** (Fig. 1b–d). The emission bands shifted to longer wavelengths with an increase in the solvent polarity: from 590 nm (toluene) to 624 nm (DMF) in **3a**, from 575 nm (hexane) to 621 nm (DCM) in **3b**, and from 575 nm (hexane) to 622 nm (DCM) in **3c** (Table 1). The wavenumber of the emission bands showed a good correlation with the solvent polarity parameters[14] (E_T^N) of the various solvents (Fig. 2). The bathochromic shift in the fluorescence solvatochromism is attributed to the donor–acceptor character of the dye arising from the electron-accepting benzothiadiazole moiety and the electron-donating tris(alkyloxy)phenylethene moieties. In the polar solvent media, the stabilization of the polarized excited state arising from the donor–acceptor character resulted in the lowering of energy levels and the bathochromic shift. As a result of the bathochromic shift, a large Stokes shift occurred (up to 152 nm in DMF for **3a**). In the

Table 1
Spectral data of **3a**, **3b**, and **3c**

Compd	Solvent	λ_{max} (nm)[a]	ε	λ_{ex} (nm)	λ_{FL} (nm)[b]	Φ_{FL}[c]	$\Delta\lambda$ (nm)
3a	Toluene	474	24,540	470	590	0.76 0.77[d]	116
	THF	474	27,480	470	601	0.72	127
	DCM	469	26,890	470	613	0.70 0.69[d]	144
	DMF	472	24,430	470	624	0.52	152
	Solid			470	629	0.44[d]	
3b	Hexane	474	27,740	475	575 579[e] 598[f]	0.78	101
	Toluene	478	26,710	475	592	0.75 0.76[d]	114
	THF	478	28,650	475	605	0.71	127
	DCM	474	28,330	475	621	0.67 0.69[d]	147
	Solid			475	618	0.50[d]	
	Film	478		475	610	0.31[d]	132
3c	Hexane	475	29,030	475	575 580[e] 598[f]	0.75	100
	Toluene	477	27,310	475	596	0.71 0.72[d]	119
	THF	479	28,040	475	608	0.66	129
	DCM	475	28,000	475	622	0.60	147
	Liquid	485		475	623	0.12[d]	138

[a] 1×10^{-5} M.
[b] 1×10^{-6} M.
[c] Fluorescence quantum yield (Φ_{FL}) relative to fluorescein in ethanol (0.97, ex. 455 nm).
[d] Absolute fluorescence quantum yield (Φ_{FL}).
[e] 1×10^{-3} M.
[f] 1×10^{-2} M.

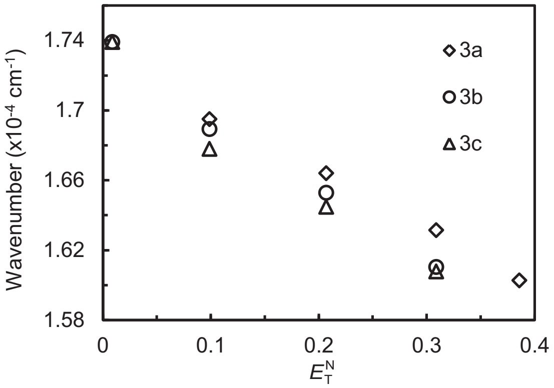

Fig. 2. Correlation of the emission band wavenumber with solvent polarity parameters (E_T^N): correlation coefficient: 0.998 for **3a**, 0.995 for **3b**, and 0.984 for **3c**.

polar solvents DCM and DMF, red light could be emitted with high fluorescence quantum yields (Φ_{FL}) (Fig. 3a and Table 1). The Φ_{FL} values 0.70 (**3a**), 0.67 (**3b**), and 0.60 (**3c**) in DCM are higher than that (0.36) of the benzothiadiazole derivative bearing the triphenylamine donor moiety.[10] In addition, a high Φ_{FL} value of 0.52 in **3a** can be achieved in the more polar solvent DMF. In the polarized excited state, the positive charge may be delocalized among the donor moieties, including the three oxygen atoms, resulting in disturbance of the significant solvation quenching in polar solvent media.

In general, the Φ_{FL} values of **3b**, bearing long alkyl chains, are lower than that of **3a**, bearing short alkyl chains. In addition, the Φ_{FL} values are reduced in **3c** bearing branched alkyl chains (Table 1). These results indicate that the emission efficiency is affected by the length and the branching of the alkyl chains.

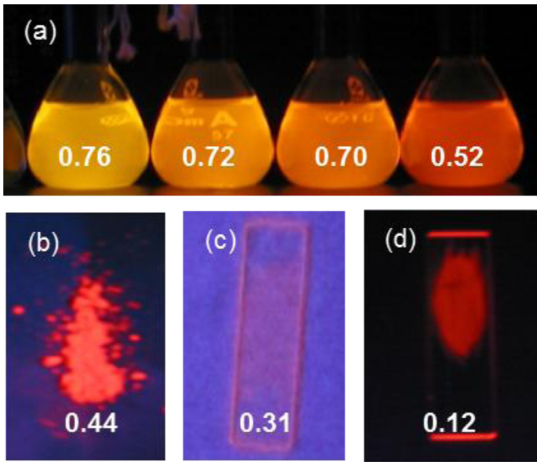

Fig. 3. Fluorescence images of (a) **3a** in toluene, THF, DCM, and DMF (from left to right), (b) **3a** in the bulk solid, (c) **3b** in the film, and (d) **3c** in the bulk liquid under UV light irradiation. The values in the image are fluorescence quantum yields (Φ_{FL}).

Red light emission is also observable in the bulk state (Figs. 3b–d and 4). In the solid state, the emission bands were observed at 629 nm (Φ_{FL} value of 0.44) for **3a**, and at 618 nm (Φ_{FL} value of 0.50) for **3b**. A similar emission was observed at 610 nm (Φ_{FL} value of 0.31) in the film state of **3b**. Interestingly, the red light emission at 623 nm (Φ_{FL} value of 0.12) could be observed in the liquid state of **3c**. These results indicate that these emitting dyes could be used as light-emitting materials both in liquid and in dry-solid systems, such as organic light-emitting diodes.[15]

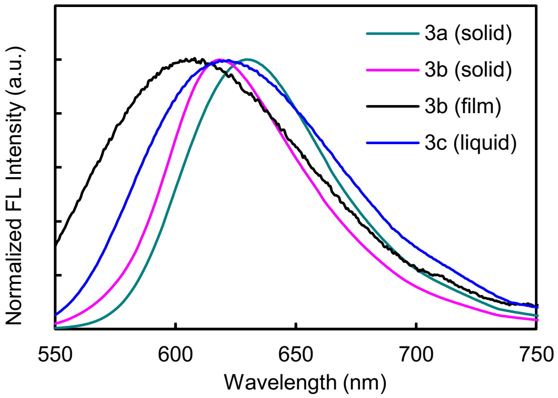

Fig. 4. Fluorescence spectra of **3a**, **3b**, and **3c** in the bulk solid, liquid, and film state excited at 470 nm (**3a**) and 475 nm (**3b** and **3c**).

In the bulk state, the emission bands for **3b** (610–618 nm) and **3c** (623 nm) were observed at longer wavelengths relative to those (575 nm) observed in hexane (1×10^{-6} M). The bathochromic shift is attributed to the aggregation of the **3b** and **3c** molecules. The concentration dependence of the fluorescence spectra in hexane is supportive of the aggregation.[16] At higher concentrations, the emission band of **3b** shifted to longer wavelengths (from 575 to 598 nm) because of facilitated aggregation. The emission band at the higher concentration (1×10^{-2} M) shows good agreement with those of the bulk film and solid states (Fig. 5). We observed a similar trend for the concentration-dependent fluorescence spectra of **3c** (Table 1).

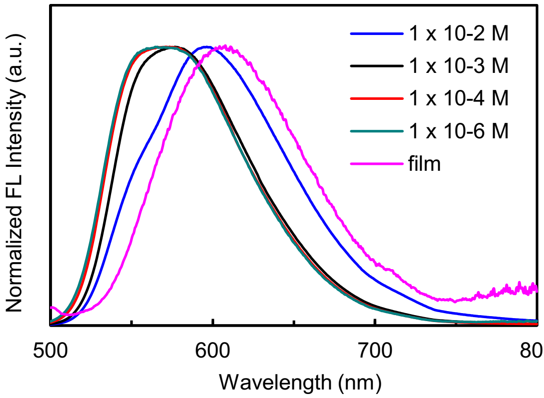

Fig. 5. Fluorescence spectra of **3b** in hexane (1×10^{-6}, 1×10^{-4}, 1×10^{-3}, and 1×10^{-2} M) and in the film state excited at 475 nm.

3. Conclusion

In conclusion, we have demonstrated that red-light-emitting systems could be created by a combination of benzothiadiazole with tris(alkyloxy)phenylethene moieties. The present results provide useful information for strategies on using red-light-emitting material in solution (nonpolar and polar) state as well as in the bulk state (solid and liquid).

4. Experimental

4.1. 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 and on NaCl plate. ^{1}H and ^{13}C NMR spectra were determined in $CDCl_3$ with a JEOL JNM-LA 400 spectrometer. Residual solvent protons and carbons were used as internal standard and chemical shifts (δ) are given relative to tetramethylsilane (TMS). The coupling constants (J) are reported in hertz (Hz). Elemental analysis was performed at the Elemental Analytical Center, Kyushu University. Fast atom bombardment mass spectrometry (FAB-MS) spectra were recorded with a JEOL JMS-70 mass spectrometer with *m*-nitrobenzyl alcohol (NBA) as a matrix. Analytical TLC was carried out on silica gel coated on aluminum foil (Merck $60F_{254}$). Column chromatography was carried out on silica gel (WAKO C300 and KANTO 60N). Gel permeation chromatography (GPC) was performed using a Japan Analytical Industry Co., Ltd LC-918 with a combination of JAIGEL-1H and JAIGEL-2H (20×600 mm) columns eluting with chloroform (3.0 mL min^{-1}). Compounds **2a** and **2b** were prepared according to methods reported previously.[13]

4.2. Spectroscopic measurement

UV–vis spectra were measured in a 1.0 cm width quartz cell at 1.0×10^{-5} M. Fluorescence spectra were measured in a 1.0 cm width quartz cell at 1.0×10^{-6} M. Absolute fluorescence quantum yield was determined by Hamamatsu Photonics C9920-01 Absolute PL Quantum Yield Measurement System.

4.3. Preparation of spin-coating films

Film sample for the measurements of UV–vis and fluorescence spectroscopy was prepared by drop casting and the subsequent spin-coating (2000 rpm, 30 s) from a 1.0×10^{-3} M hexane solution (100 μL×3) on quartz cell (12.5×12.5×45 mm). Film sample for the measurements of absolute fluorescence quantum yields was prepared by drop casting and the subsequent spin-coating (2000 rpm, 30 s) from a 1.0×10^{-3} M hexane solution (20 μL×3) on quartz cell (12.5×12.5×15 mm).

4.4. 4,7-Bis[2-(3,4,5-trimethoxyphenyl)ethenyl]-2,1,3-benzothiadiazole (3a)

To a suspension of **1** (147 mg, 0.5 mmol), **2a** (204 mg, 1.05 mmol), and triethylamine (0.70 mL, 5 mmol) in dry DMF (10 mL) was added a solution of palladium acetate (11.2 mg, 0.05 mmol) and tri(*o*-tolyl)phosphine (31 mg, 0.1 mmol) in dry DMF (2.5 mL) at 100 °C under an argon atmosphere, and the mixture was allowed to stand for 15 h. After the reaction mixture was cooled to 0 °C, it was quenched with aqueous 1.2 N hydrochloric acid solution and extracted with dichloromethane. The organic layer was washed with brine sufficiently, dried over anhydrous magnesium sulfate, and evaporated in vacuo to dryness. The residue was purified by silica gel column chromatography (WAKO C300) eluting with chloroform and by recrystallization from dichloromethane/hexane to give **3a** in 45% yield (118 mg, 0.227 mmol): reddish orange solid; mp 238–240 °C; IR (KBr, cm^{-1}) 3028, 2989, 2934, 2838, 1579, 1509, 1450, 1417, 1341, 1327, 1243, 1132, 994, 966, 835, 655; ^{1}H NMR ($CDCl_3$) δ 3.91 (s, 6H, CH_3), 3.96 (s, 12H, CH_3), 6.88 (s, 4H, ArH), 7.54 (d, J=16.3 Hz, 2H, olefinic H), 7.69 (s, 2H, ArH), 7.97 (d, J=16.3 Hz, 2H, olefinic H); ^{13}C NMR ($CDCl_3$) δ 56.21, 61.01, 104.02, 123.95, 127.05, 129.20, 133.19, 133.32, 138.52, 153.48, 153.93; FAB-MS (positive, NBA) m/z 520 (M^+). Anal. Calcd for $C_{28}H_{28}N_2O_6S$ (520.60): C, 64.60; H, 5.42; N, 5.38. Found: C, 64.36; H, 5.41; N, 5.38.

4.5. 4,7-Bis{2-[3,4,5-tris(octyloxy)phenyl]ethenyl}-2,1,3-benzothiadiazole (3b)

To a suspension of **1** (59 mg, 0.2 mmol), **2b** (203 mg, 0.42 mmol), and triethylamine (0.28 mL, 2.0 mmol) in dry DMF (2 mL) was added a solution of palladium acetate (4.4 mg, 0.02 mmol) and tri(*o*-tolyl)phosphine (12 mg, 0.04 mmol) in dry DMF (1 mL) at 100 °C under an argon atmosphere, and the mixture was allowed to stand for 15 h. After the reaction mixture was cooled to 0 °C, it was quenched with aqueous 1.2 N hydrochloric acid solution and extracted with dichloromethane. The organic layer was washed with brine sufficiently, dried over anhydrous magnesium sulfate, and evaporated in vacuo to dryness. The residue was purified by silica gel column chromatography (WAKO C300) eluting with hexane/dichloromethane (2:1, v/v) and by GPC eluting with chloroform to give **3b** in 64% yield (141 mg, 0.127 mmol): reddish orange solid; mp 66–68 °C; IR (KBr, cm^{-1}) 3034, 2952, 2922, 2851, 1626, 1577, 1505, 1467, 1432, 1389, 1341, 1283, 1243, 1119, 964, 899, 832, 722, 653; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J=6.8 Hz, 18H, CH_3), 1.22–1.42 (m, 48H, CH_2), 1.45–1.56 (m, 12H, $ArOCH_2CH_2CH_2$), 1.77 (quint, J=6.8 Hz, 4H, $ArOCH_2CH_2$), 1.85 (quint, J=6.8 Hz, 8H, $ArOCH_2CH_2$), 4.00 (t, J=6.8 Hz, 4H, OCH_2), 4.06 (t, J=6.8 Hz, 8H, OCH_2), 6.85 (s, 4H, ArH), 7.50 (d, J=16.6 Hz, 2H, olefinic H), 7.66 (s, 2H, ArH), 7.91 (d, J=16.6 Hz, 2H, olefinic H); ^{13}C NMR ($CDCl_3$) δ 14.11 (×2), 22.68, 22.70, 26.13 (×2), 29.31, 29.39 (×2), 29.46, 29.56, 30.35, 31.84, 31.90, 69.22, 73.57, 105.57, 123.47, 126.82, 129.19, 132.67, 133.44, 138.80, 153.35, 153.93; FAB-MS (positive, NBA) m/z 1109 (M^+). Anal. Calcd for $C_{70}H_{112}N_2O_6S$ (1109.71): C, 75.76; H, 10.17; N, 2.52. Found: C, 75.58; H, 10.09; N, 2.71.

4.6. 4,7-Bis{2-[3,4,5-tris(2-ethylhexyloxy)phenyl]ethenyl}-2,1,3-benzothiadiazole (3c)

To a suspension of **1** (88 mg, 0.3 mmol), **2c** (310 mg, 0.63 mmol), and triethylamine (0.41 mL, 3 mmol) in dry DMF (3 mL) was added a solution of palladium acetate (6.6 mg, 0.03 mmol) and tri(o-tolyl) phosphine (18.3 mg, 0.6 mmol) in dry DMF (1.5 mL) at 100 °C under an argon atmosphere, and the mixture was allowed to stand for 15 h. After the reaction mixture was cooled to 0 °C, it was quenched with aqueous 1.2 N hydrochloric acid solution and extracted with dichloromethane. The organic layer was washed with brine sufficiently, dried over anhydrous magnesium sulfate, and evaporated in vacuo to dryness. The residue was purified by silica gel column chromatography (WAKO C300) eluting with chloroform and by GPC eluting with chloroform to give **3c** in 61% yield (258 mg, 0.184 mmol): dark red viscous liquid; IR (NaCl, cm^{-1}) 3035, 2957, 2927, 2872, 1577, 1503, 1463, 1431, 1380, 1325, 1281, 1238, 1119, 1010, 960, 835; ^{1}H NMR (CDCl$_3$) δ 0.92 (t, J=7.3 Hz, 18H, CH$_3$), 0.96 (t, J=7.3 Hz, 18H, CH$_3$), 1.23–1.40 (m, 24H, CH$_2$), 1.40–1.62 (m, 24H, CH$_2$), 1.64–1.86 (m, 6H, CH), 3.83–3.99 (m, 12H, CH$_2$), 6.84 (s, 4H, ArH), 7.51 (d, J=16.6 Hz, 2H, olefinic H), 7.68 (s, 2H, ArH), 7.93 (d, J=16.6 Hz, 2H, olefinic H); ^{13}C NMR (CDCl$_3$) δ 11.18, 11.23, 14.16, 14.19, 23.13, 23.18, 23.71, 23.86, 29.17, 29.34, 30.51, 30.56, 39.68, 40.61, 71.16, 76.05, 104.75, 123.36, 126.88, 129.22, 132.57, 133.61, 138.52, 153.58, 153.96; FAB-MS (positive, NBA) m/z 1109 (M$^+$). HR-FABMS (positive, NBA) m/z 1108.8246 (M$^+$, calcd for $C_{70}H_{112}N_2O_6S$ 1108.8241).

4.7. Methyl 3,4,5-tris(2-ethylhexyl)benzoate (5c)

To a solution of 1-bromo-2-ethylhexane (11.4 mL, 66 mmol) and **4** (3.68 g, 20.0 mmol) in dry DMF (100 mL) was added potassium carbonate (24.8 g, 180 mmol) under an argon atmosphere, and heated at 70 °C for 27 h. The reaction mixture was quenched by addition of water and neutralized with cold aqueous 1 N hydrochloric acid solution. The mixture was extracted with dichloromethane, washed with water sufficiently, dried over anhydrous magnesium sulfate, and evaporated in vacuo to dryness. The residue was purified by silica gel column chromatography (WAKO C300) eluting with hexane/dichloromethane (2:1, v/v) to give **5c** in 78% (8.16 g, 15.67 mmol) as pale yellow oil: IR (NaCl, cm^{-1}) 3100, 2958, 2928, 2873, 2860, 2731, 1722 ($\nu_{C=O}$), 1588, 1460, 1432, 1334, 1217; 1108, 766; ^{1}H NMR (CDCl$_3$) δ 0.90 (t, J=7.3 Hz, 9H, CH$_3$), 0.93 (t, J=7.3 Hz, 9H, CH$_3$), 1.27–1.36 (m, 12H, CH$_2$), 1.40–1.60 (m, 12H, CH$_2$), 1.65–1.80 (m, 3H, CH), 3.85–3.95 (m, 6H, OCH$_2$), 3.90 (s, 3H, COOMe), 7.25 (s, 2H, ArH); ^{13}C NMR (CDCl$_3$) δ 11.12, 11.20, 14.13, 14.17, 23.09, 23.14, 23.64, 23.81, 29.10, 29.29, 30.43, 30.50, 39.55, 40.60, 52.14 (COOCH$_3$), 71.16, 75.88, 107.29, 124.50, 142.15, 153.0, 167.07 (C=O); FAB-MS (positive, NBA) m/z 520 (M$^+$). Anal. Calcd for $C_{32}H_{56}O_5$ (520.78): C, 73.80; H, 10.84. Found: C, 73.92; H, 10.71.

4.8. 1,2,3-Tris(2-ehtylhexyloxy)-5-hydroxymethylbenzene (6c)

To a suspension of lithium aluminum hydride (380 mg, 10 mmol) in dry ether (10 mL) was added dropwise **5c** (2.60 g, 5.0 mmol) in dry ether (10 mL) at 0 °C under an argon atmosphere, and stirred at room temperature for 1 h. The reaction mixture was quenched by addition of ethyl acetate. The resulting mixture was poured into cold water carefully, and neutralized with cold aqueous 1 N sulfuric acid solution. The mixture was extracted with dichloromethane, washed with brine and water, dried over anhydrous magnesium sulfate, and evaporated in vacuo to dryness. The residue was purified by silica gel column chromatography (WAKO C300) eluting with hexane/dichloromethane (1:2, v/v) to give **6c** in 98% (2.41 g, 4.88 mmol) as colorless oil: IR (NaCl, cm^{-1}) 3366 (ν_{OH}), 3054, 2958, 2927, 2872, 1591, 1505, 1436, 1381, 1331, 1231, 1121, 1015; ^{1}H NMR (CDCl$_3$) δ 0.90 (t, J=7.6 Hz, 9H, CH$_3$), 0.93 (t, J=7.3 Hz, 9H, CH$_3$), 1.26–1.36 (m, 13H, CH$_2$ and OH), 1.37–1.60 (m, 12H, CH$_2$), 1.63–1.80 (m, 3H, CH), 3.77–3.88 (m, 6H, OCH$_2$), 4.59 (d, J=5.9 Hz, 2H, ArCH$_2$), 6.55 (s, 2H, ArH); ^{13}C NMR (CDCl$_3$) δ 11.11, 11.21, 14.14, 14.19, 23.11, 23.18, 23.69, 23.77, 29.09, 29.32, 30.47 (×2), 39.56, 40.55, 65.80 (CH$_2$OH), 71.05, 75.91, 104.52, 135.91, 137.21, 153.50; FAB-MS (positive, NBA) m/z 492 (M$^+$). Anal. Calcd for $C_{31}H_{56}O_4$ (492.77): C, 75.56; H, 11.45. Found: C, 75.73; H, 11.49.

4.9. 1,2,3-Tris(2-ehtylhexyloxy)-5-formylbenzene (7c)

To a solution of **6c** (2.11 g, 4.26 mmol) in dry 1,4-dioxane (26 mL) was added DDQ (1.02 g, 4.5 mmol) at 0 °C under an argon atmosphere, and stirred at room temperature for 2 h. The reaction mixture was evaporated in vacuo to dryness. The residue was suspended in dichloromethane (10 mL), then the insoluble hydroquinone was removed by filtration and washed with dichloromethane. The combined filtrates were evaporated in vacuo to dryness. The residue was purified by silica gel column chromatography (KANTO 60N) eluting with hexane/dichloromethane (7:3, v/v) to give **7c** in 96% (2.01 g, 4.10 mmol) as pale yellow oil: IR (NaCl, cm^{-1}) 3086, 2958, 2928, 2873, 2860, 1696 ($\nu_{C=O}$), 1584, 1496, 1462, 1439, 1382, 1329, 1228, 1139, 1117; ^{1}H NMR (CDCl$_3$) δ 0.90 (t, J=7.3 Hz, 9H, CH$_3$), 0.92 (t, J=7.3 Hz, 9H, CH$_3$), 1.25–1.38 (m, 12H, CH$_2$), 1.38–1.60 (m, 12H, CH$_2$), 1.63–1.82 (m, 3H, CH), 3.87–3.99 (m, 6H, OCH$_2$), 7.26 (s, 2H, ArH), 9.84 (s, 1H, CHO); ^{13}C NMR (CDCl$_3$) δ 11.11, 11.18, 14.13, 14.17, 23.08, 23.13, 23.60, 23.78, 29.07, 29.27, 30.38, 30.48, 39.50, 40.61, 71.27, 76.00, 107.28, 131.29, 143.71, 153.67, 191.48 (C=O); FAB-MS (positive, NBA) m/z 490 (M$^+$). Anal. Calcd for $C_{31}H_{54}O_4$ (490.76): C, 75.87; H, 11.09. Found: C, 75.69; H, 11.02.

4.10. 1,2,3-Tris(2-ehtylhexyloxy)-5-ethenylbenzene (2c)

To a suspension of methyltriphenylphosphonium bromide (1.78 g, 5 mmol) in dry THF (25 mL) was added dropwise 1.57 M butyllithium hexane solution (3.03 mL, 5 mmol) at −78 °C for 10 min under an argon atmosphere and allowed to stand for 30 min. The white suspension was changed to yellow suspension. Then, **7c** (1.96 g, 10 mmol) in dry THF (2.5 mL) was added dropwise for 5 min at −78 °C. The mixture was warmed up to room temperature and allowed to stand for 3 h. The reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with water, dried over anhydrous magnesium sulfate, and evaporated in vacuo to dryness. The residue was purified by silica gel column chromatography (WAKO C300) eluting with hexane/dichloromethane (9:1, v/v) to give **2c** in 40% (494 mg, 1.01 mmol): colorless oil; IR (NaCl, cm^{-1}) 3087, 2927, 2872, 2860, 1578, 1503, 1463, 1434, 1416, 1380, 1326, 1235, 1118, 1012, 985, 899, 833; ^{1}H NMR (CDCl$_3$) δ 0.90 (t, J=6.8 Hz, 9H, CH$_3$), 0.93 (t, J=7.6 Hz, 9H, CH$_3$), 1.25–1.37 (m, 12H, CH$_2$), 1.39–1.60 (m, 12H, CH$_2$), 1.66–1.78 (m, 3H, CH), 3.79–3.89 (m, 6H, OCH$_2$), 5.17 (d, J=10.7 Hz, 1H, olefinic H), 5.63 (d, J=17.6 Hz, 1H, olefinic H), 6.60 (s, 2H, ArH), 6.61 (dd, J=10.7, 17.6 Hz, 1H, olefinic H); ^{13}C NMR (CDCl$_3$) δ 11.13, 11.21, 14.12, 14.18, 23.12, 23.18, 23.69, 23.81, 29.13, 29.33, 30.52 (×2), 39.61, 40.57, 71.08, 75.99, 104.05, 112.61, 132.67, 137.05, 138.03, 153.39; FAB-MS (positive, NBA) m/z 488 (M$^+$). Anal. Calcd for $C_{32}H_{56}O_3$ (488.79): C, 78.63; H, 11.55. Found: C, 78.48; H, 11.38.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.08.066. These data include MOL files and InChiKeys of the most important compounds described in this article.

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