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The synthesis and optical properties of bis-squarylium dyes bearing arene and thiophene spacers

Shigeyuki Yagi*, Taishi Ohta, Nobuo Akagi, Hiroyuki Nakazumi**

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan

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Abstract

A series of arene- and thiophene-bridged bis-squarylium dyes were synthesized using the corresponding bis-squaric acids as precursors and their electronic absorption and fluorescence emission properties were investigated. The arene-bridged, bis-squarylium dyes exhibited electronic absorption in the visible to near-infrared regions. The combination of the pyrene spacer with the benzindoline heterocycles resulted in significantly red-shifted absorption at 770 nm. The arene-bridged dyes were fluorescence emissive to some extent and some compounds exhibited fluorescence emission in the near-infrared region. Thiophene-bridged dyes, in which thiophene-, bithiophene-, and terthiophene spacers were employed, displayed electronic absorption in the near-infrared region from 717 to 807 nm; an increase in the number of thiophene rings in the spacer led to a blue shift of the absorption maxima due to disruption of π-electron conjugation. The thiophene-bridged dyes exhibited fluorescence emission in the near-infrared region, although the fluorescence intensities were much smaller than those of the fluorescent squarylium dye.

Keywords: Squarylium; Arene; Thiophene; NIR dye; Absorption spectra; Fluorescence emission

1. Introduction

Squaryliums, which are also called squaraines, are polymethine dyes with a cyclobutene core in the middle of the π-conjugation systems [1]. Their electronic structures are quite interesting from the scientific and technological viewpoints. Nowadays, squarylium dyes are receiving much attention due to their potential applicability to functional materials suitable for photoenergy conversion devices [2,3], organic electroluminescent devices [4,5], photoreceptors for xerographic devices [6], chemosensory systems [7–9], and so on. Available structures of squarylium dyes, however, have been limited since the conventional synthetic protocol has afforded only symmetrical squarylium frameworks [10]. Such synthetic limitation has been overcome by the development of the stepwise synthesis of unsymmetrical squarylium dyes, where a semi-squarylium (4-aryl-3-hydroxy-3-cyclobutene-1,2-dione) reacts with an electron-rich aromatic or a heterocycle with an activated methyl group to afford unsymmetrical frameworks [11,12]. In this term, we have already reported the synthesis of unsymmetrical squarylium dyes absorbing near-infrared light [12]. Furthermore, we have also reported the syntheses of cationic and neutral methine-bridged bis-squarylium dyes [13–15] and arene-bridged bis-squarylium dyes [16,17]. These synthetic achievements have enabled us to obtain a variety of squaryliums and the related dyes. Here we report the synthesis and light absorption/fluorescence emission properties of bis-squarylium dyes bearing arene and thiophene spacers, employing various arene- and thiophene-bridged bis-squaric acid derivatives as precursors. This is the full paper of the arene- and thiophene-bridged bis-squarylium dyes with extensively conjugated π-electron systems, including some results of

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* Corresponding author. Tel.: +81 72 254 9324; fax: +81 72 254 9910.

** Corresponding author. Tel.: +81 72 254 9320; fax: +81 72 254 9910.

E-mail addresses: yagi@chem.osakafu-u.ac.jp (S. Yagi), nakazumi@chem.osakafu-u.ac.jp (H. Nakazumi).

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two short articles previously reported [16,17]. The detailed synthetic protocols for these dyes are involved.

2. Results and discussion

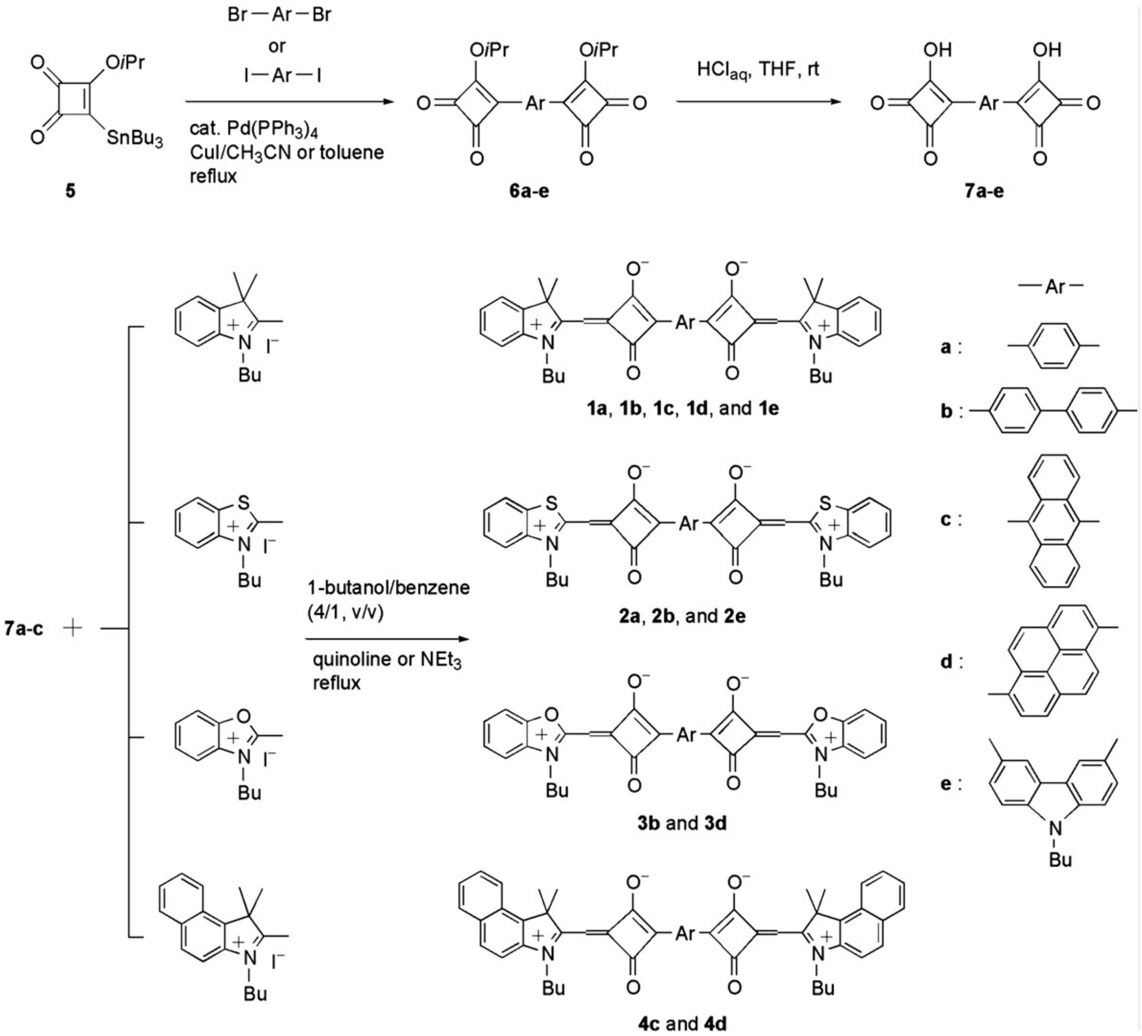
2.1. Arene-bridged bis-squarylium dyes

2.1.1. Synthesis of arene-bridged bis-squarylium dyes

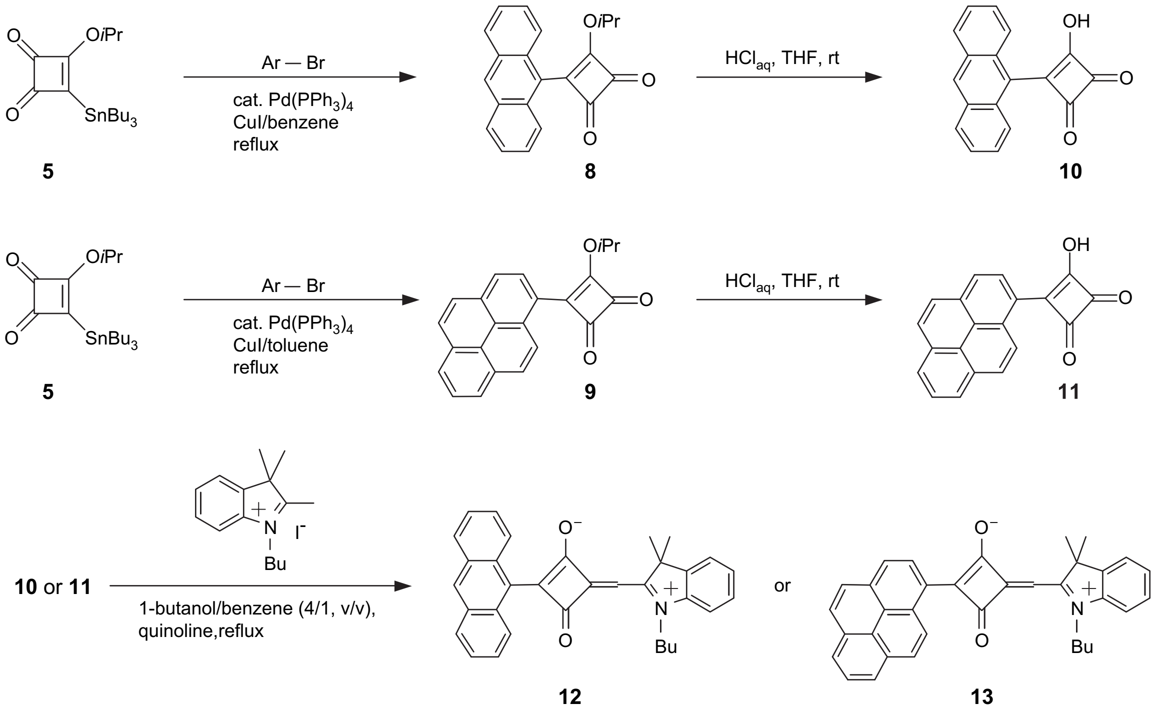
We previously reported the phenylene-bridged (**1a** and **2a**) and biphenylene-bridged (**1b**) bis-squarylium dyes [16]. In the present study, anthracene, pyrene and carbazole skeletons were newly employed as the arene spacers to link two semi-squarylium moieties. In Scheme 1 is shown the synthesis of the bis-squarylium dyes **1**–**4**. In order to prepare the bis-squarylium dyes, the bis-squaric acids **7a**–**e** are required as synthetic precursors. The preparation of the bis-squaric acids **7a** and **7b** were briefly reported in the previous paper [16]. The preparation of anthracene-9,10-bis-squaric acid **7c**, pylene-1,6-bis-squaric acid **7d**, and *N*-butylcarbazole-3,6-bis-squaric acid **7e** is additionally described here (see Section 4 for detailed synthetic procedures of the bis-squaric acids). According to the reported method, the Stille-type Pd-catalyzed cross-coupling reaction of diiodo- or dibromoarene with tributylstannylsquarate **5** [18] afforded the bis-squarates **6a**–**e** in 30–77% yields from the corresponding dihalogenated arenes, which were hydrolyzed under acidic conditions to afford the bis-squaric acids **7a**–**e** in 53–93% yields. These bis-squaric acids were converted to the bis-squarylium dyes by the reaction with a series of heterocyclic methyl quaternary salts such as *N*-butyl-2,3,3-trimethylindolium, *N*-butylbenzothiazolium, *N*-butylbenzoxazolium, and *N*-butylbenzoindolium: under azeotropic conditions (boiled in a mixed solvent of 1-butanol/benzene) as usually employed in squarylium synthesis, the arene-bridged bis-squarylium dyes **1**–**4** were obtained in 11–90% yields.

As the reference compounds, the unsymmetrical squarylium dyes **12** and **13**, containing anthracene and pyrene moieties, respectively, were also prepared from the corresponding squaric acids **10** and **11**, according to the synthetic protocol shown in Scheme 2.

All the bis-squarylium dyes described here were characterized by ^{1}H NMR, FT-IR, and FAB mass spectra as well as elemental analyses.



Scheme 1.



Scheme 2.

2.1.2. Optical properties of the arene-bridged bis-squarylium dyes

In order to investigate the optical properties of the bis-squarylium dyes, the electronic absorption and fluorescence emission spectra were obtained. Electronic absorption and fluorescence emission spectra of **2b**, **1d**, and **2e** are shown as typical examples in Fig. 1, and the spectral data of the bis-squarylium dyes **1**–**4** are summarized in Table 1. The arene-bridged bis-squaryliums **1**–**4** exhibited absorption maxima at 577–770 nm, which varied with the spacer and also with the heterocycles at both ends of the molecule. As seen in Fig. 1a, the biphenylene-bridged dye **2b** exhibited its absorption in the visible region ($\lambda_{max} = 609$ nm) with relatively narrow absorption bands, whereas the phenylene-bridged dye **2a** exhibited the red-shifted λ_{max} at 685 nm. Similar tendency was found in the comparison between **1a** and **1b** (λ_{max}: 669 and 618 nm for **1a** and **1b**, respectively). This result indicates that the π-conjugation of the biphenylene-bridged dyes is partially disrupted by free C–C bond rotation in the biphenylene spacer. The anthracene- and pyrene-bridged dyes had lower energy gaps of electronic transition compared to the corresponding phenylene- and biphenylene-bridged dyes and exhibited their absorption maxima in near-infrared regions with the absorption bands significantly broadened, as represented by the absorption spectrum of **1d** shown in Fig. 1b. The absorption bands of the reference squarylium dyes **12** and **13** were significantly blue-shifted (λ_{max}: 624 and 629 nm for **12** and **13**, respectively) compared to the corresponding bis-squarylium dyes. Taking this into consideration, in the case of the anthracene- and pyrene-bridged dyes, the arene spacer gave rise to the extension of the π-conjugation system over the whole molecule. As shown in Fig. 1a (for the compound **2e**),

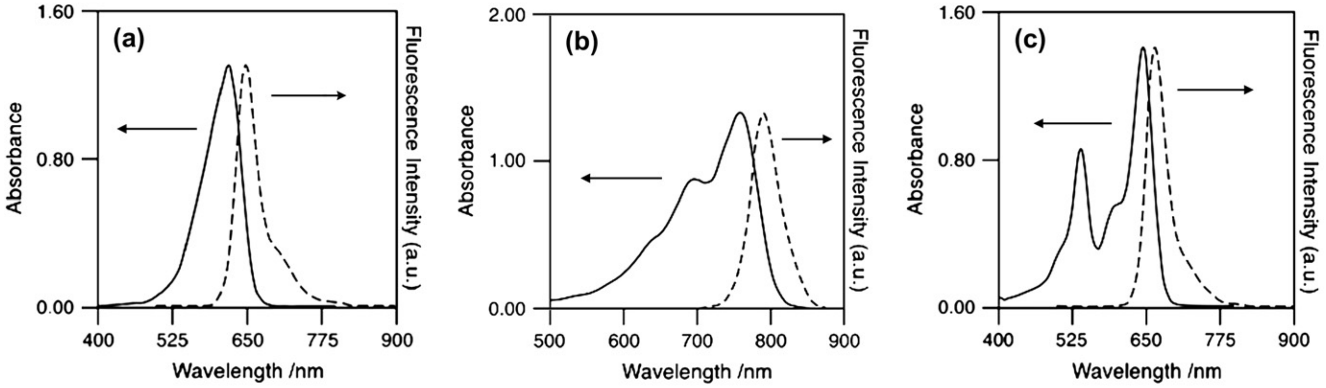


Fig. 1. Electronic absorption (solid) and fluorescence emission (dashed) spectra of (a) **2b**, (b) **1d**, and (c) **2e** in $CHCl_3$ at 298 K. The dye concentrations are adjusted to 10 μM.

Table 1
Electronic absorption and fluorescence emission data of the bis-squarylium dyes **1**–**4** and the reference squarylium dyes **12** and **13**

Compd	Electronic absorption[a]	Fluorescence emission[a]	
	λ_{max}/nm (log [ε/M^{-1} cm^{-1}])	λ_{em}/nm (relative intensity)[b]	Stokes shift/nm
1a	669 (5.3), 635 (4.9)	714 (6.3)	22
1b	618 (5.3)	656 (11)	37
1c	714 (4.8)	820 (0.10)	106
1d	753 (5.1), 692 (4.9)	803 (41)	50
1e	655 (5.3), 538 (5.1)	674 (2.7)	19
2a	685 (5.3), 623 (5.0)	706 (10)	21
2b	609 (5.0)	651 (7.9)	42
2e	646 (5.1), 540 (4.9)	671 (3.5)	25
3b	577 (5.1)	616 (127)	39
3d	708 (4.7), 654 (4.5), 596 (4.4)	731 (23)	23
4c	745 (4.9)	824 (0.10)	79
4d	770 (5.3), 704 (5.1)	790 (18)	20
12	624 (4.5)	686 (0.10)	62
13	629 (5.2), 583 (4.8)	661 (43)	32
BASQ[c]	640 (5.5)	667 (100)	12

[a] The data were obtained in $CHCl_3$ at 298 K.
[b] The fluorescence spectrum of each dye was obtained by excitation at λ_{max}.
[c] 2,4-Bis[4-(*N*,*N*-dibutylamino)phenyl]-1-oxo-3-cyclobutene-3-olate.

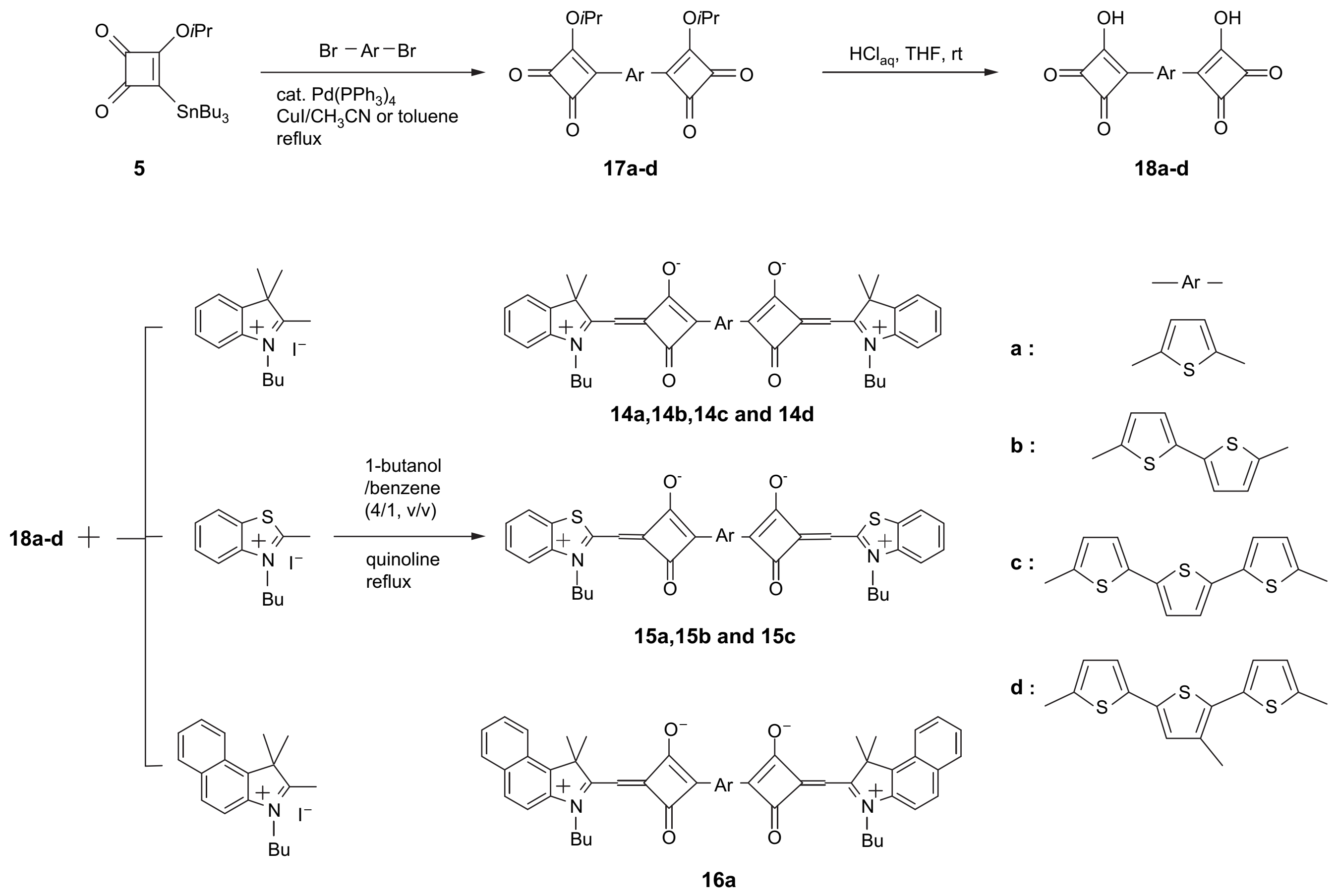
the carbazole-bridged dyes **1e** and **2e** exhibited split absorption bands at ca. 650 and 540 nm: one might see that the carbazole spacer led to generation of two transition moments of the bis-squarylium chromophoric systems.

Fluorescence emission properties of the bis-squarylium dyes were also investigated. As typical examples, the fluorescence emission spectra of the bis-squaryliums **2b**, **1d**, and **2e** are shown in Fig. 1, and the emission data for all the arene-bridged dyes are summarized in Table 1. The arene-bridged bis-squaryliums **1**–**4** were fluorescent to some extent, although the emission intensity was relatively weak compared to a fluorescent bis(*N*,*N*-dialkylanilino)squarylium dye (BASQ). The emission maxima of the phenylene-, biphenylene-, and carbazole-bridged dyes were observed in the red region, and the dye **3b** was highly fluorescent. Interestingly, the anthracene- and pyrene-bridged dyes (**1c**, **1d**, **3d**, **4c**, and **4d**) exhibited fluorescence emission in the near-infrared region ($\lambda_{em} = 731$–824 nm), although with lower intensity.

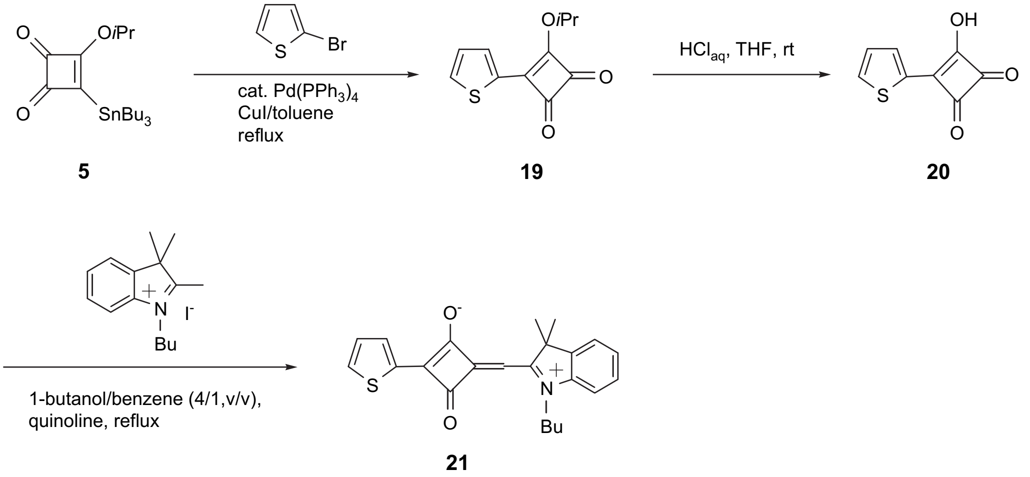
2.2. Thiophene-bridged bis-squarylium dyes

2.2.1. Synthesis of the thiophene-bridged bis-squarylium dyes

As shown in Scheme 3, the thiophene-, bithiophene-, and terthiophene-bridged bis-squarylium dyes were synthesized in



Scheme 3.



Scheme 4.

a similar way to the preparation of the arene-bridged bis-squaryliums, using 2,5-dibromothiophene, 5,5′-dibromo-2,2′-bithiophene, and 5,5″-dibromo-2,2′:5′,2″-terthiophene as starting materials. In the same way as described above, the Stille-type Pd-catalyzed cross-coupling reaction of these dibrominated thiophene derivatives with tributylstannylsquarate **5** afforded the bis-squarates **17a–d** in 26–59% yields, which were converted by acid hydrolysis to the bis-squaric acids **18a–d** in 59–93% yields. The reaction of these bis-squaric acids with 1-butyl-2,3,3-trimethylindolium iodide and 1-butylbenzothiazolium iodide under azeotropic conditions in 1-butanol/benzene afforded the thiophene-, bithiophene-, and terthiophene-bridged bis-squarylium dyes **14** and **15** in 22–53% yields. For the mono-thiophene-bridged dye, the benzindolino derivative **16a** was also synthesized in 11% yield. As a reference compound, the unsymmetrical squarylium dye with thiophene and indoline moieties at both ends of the cyclobutene core was also synthesized according to Scheme 4. All these compounds gave satisfactory analytical data in ^{1}H NMR, FT-IR, and FAB mass spectra as well as elemental analyses.

2.2.2. *Optical properties of thiophene-bridged bis-squarylium dyes*

In Fig. 2 are shown electronic absorption spectra of thiophene-bridged bis-squarylium dyes **14a**, **15a**, and **16a** in CHCl$_3$, and the optical data of all the thiophene-bridged bis-squarylium dyes are summarized in Table 2. When the thiophene ring was used as the spacer, the absorption maxima of the dyes were significantly shifted to the near-infrared region, compared to the phenylene-bridged dyes with the corresponding heterocycle moieties. In particular with the benzindolium heterocycle, the mono-thiophene-bridged dye **16a** exhibited significantly red-shifted electronic absorption, showing its absorption maximum at 807 nm. As observed in the phenylene- and carbazole-bridged dyes, the absorption bands of the mono-thiophene-bridged dyes were split into two, indicating that the multiple electronic transitions were obtained. On the other hand, in the case of the bithiophene- and terthiophene-bridged dyes, the increase in the number of the thiophene rings in the spacer afforded broadened and blue-shifted absorption bands, as shown in Fig. 3. As discussed in the biphenylene-bridged

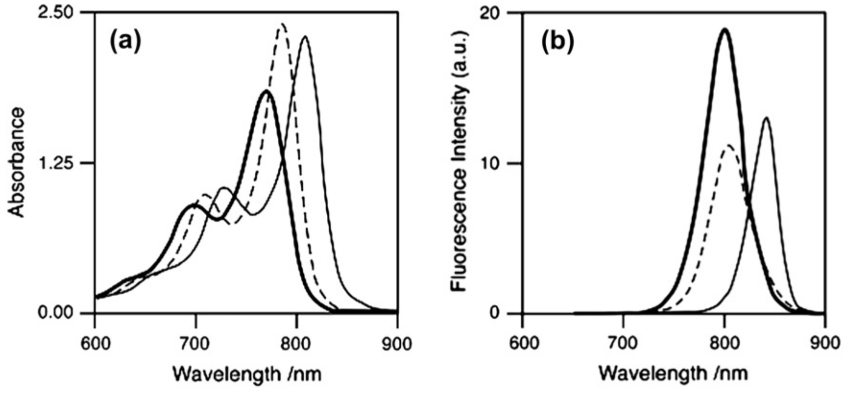


Fig. 2. (a) Electronic absorption and (b) fluorescence emission spectra of **14a** (dashed), **15a** (bold), and **16a** (solid) in CHCl$_3$ at 298 K. The dye concentrations are adjusted to 10 μM.

Table 2
Electronic absorption and fluorescence emission data of the thiophene-, bithiophene-, and terthiophene-bridged bis-squarylium dyes **14–16** and the reference squarylium dye **21**

Compd	Electronic absorption[a]	Fluorescence emission[a]	
	λ_{max}/nm (log [ε/M^{-1} cm^{-1}])	λ_{em}/nm (relative intensity)[b]	Stokes shift/nm
14a	785 (5.4), 708 (5.0)	803 (1.8)	18
14b	771 (5.1), 705 (5.0)	802 (9.6)	33
14c	735 (5.1), 695 (5.1)	792 (9.6)	57
14d	723 (5.0), 681 (5.0)	779 (7.2)	56
15a	772 (5.2), 696 (4.8)	797 (3.2)	25
15b	725 (4.9), 687 (5.0)	792 (14)	67
15c	717 (5.0), 784 (5.0)	778 (12)	57
16a	807 (5.4), 728 (5.0)	825 (2.2)	18
21	554 (4.9)	578 (4.0)	22
BASQ[c]	640 (5.5)	667 (100)	12

[a] The data were obtained in $CHCl_3$ at 298 K.

[b] The fluorescence spectrum of each dye was obtained by excitation at λ_{max}.

[c] 2,4-Bis[4-(*N*,*N*-dibutylamino)phenyl]squarane.

dyes, the bond rotation between neighboring thiophene rings should give rise to partial disruption of the π-conjugation over the whole molecule. This is also supported by the fact that the ^{1}H NMR signal of the β-protons of the thiophene rings of the bi- and terthiophene dyes **14b** and **14c** shifted upfield by 0.16–0.18 ppm, compared to the β-proton of the thiophene spacer of **14a**. In the case of **14d**, introduction of the methyl group to the 3′-position of the terthiophene spacer brought about the blue shift of the λ_{max} by 12 nm, compared to **14c**. This might be because the disruption of the π-conjugation in the terthiophene spacer is more considerable than that in **14c**. Interestingly, the reference unsymmetrical dye **21** exhibited its λ_{max} at 554 nm, and therefore, linking of two semi-squarylium subunits by the mono- and oligo-thiophene spacers is quite effective on extension of the π-conjugation systems, resulting in construction of near-infrared absorbing chromophores.

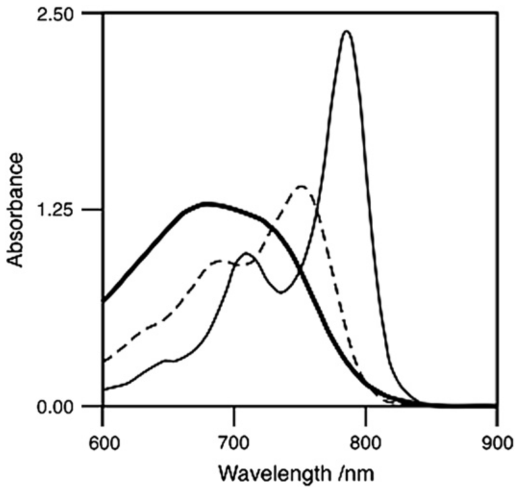


Fig. 3. Comparison of electronic absorption spectra among mono-thiophene-bridged **14a** (solid), bithiophene-bridged **14b** (dashed), and terthiophene-bridged **14c** (bold). The spectra were obtained in $CHCl_3$ at 298 K, and the dye concentrations were adjusted to 10 μM.

Fluorescence emission properties of the thiophene-bridged dyes were also investigated. The emission spectra of the mono-, bi-, and terthiophene-bridged dyes **14a**, **14b**, and **14c** are displayed in Fig. 2b. The data for the other dyes are also summarized in Table 2. Although the mono-thiophene-bridged dyes exhibited emission with narrow halfwidths in the near-infrared region (797–825 nm), the intensities were modest. On the other hand, the bi- and terthiophene-bridged dyes also exhibited their emission maxima in the near-infrared region (778–802 nm), and their intensities were relatively larger, compared to the mono-thiophene-bridged dyes.

3. Conclusions

The synthesis of bis-squarylium dyes bearing a variety of arene and thiophene spacers is described here. These dyes exhibited the large and intense electronic absorption ranging from the visible to the near-infrared region, and some of them were fluorescent emissive. In the arene-bridged dyes, employing extensively conjugated spacers such as anthracene and pyrene allowed us to obtain the near-infrared absorbing dyes, especially in combination with the benzindolium heterocycles. The bis-benzoxazolino dyes with the biphenylene spacer **3b** exhibited exceptionally intense emission in the visible region ($\lambda_{em} = 616$ nm). In the thiophene-bridged dyes, the mono-thiophene spacer was most effective to obtain the red-shifted absorption because the bond rotation between the thiophene rings in the bi- and terthiophene spacers disrupted the π-conjugation over the whole molecules. All the thiophene-bridged dyes exhibited fluorescence emission in the near-infrared region, although the fluorescence intensities were much smaller than the typical fluorescent squarylium dye BASQ. In conclusion, the present study demonstrated that a wide range of combination of the spacer with the heterocycles afforded a variety of electronic structures of bis-squarylium π-conjugation systems. Further development of squarylium-based chromophoric systems and the applications are currently going on.

4. Experimental

4.1. General

^{1}H NMR spectra were obtained on a Jeol JNM GX-270 or a Jeol JNM LA-400 spectrometer, using TMS as an internal standard (0.00 ppm). IR spectra were obtained as KBr pellets on a Shimadzu FT-IR 8400S spectrometer. Electronic absorption spectra were obtained on a Shimadzu UV-3100 spectrometer. Fluorescence emission spectra were obtained on a Shimadzu RF-5000 spectrometer. MALDI-TOF mass analyses were performed on a Shimadzu Kratos KOMPACT MALDI2 spectrometer, using shinapinic acid as a matrix. FAB mass analyses were performed on a Finnigan MAT

TSQ-70 spectrometer, using 3-nitrobenzylalcohol as a matrix. Elemental analyses were performed on a Yanaco CHN CORDER MT-3 analyzer. Melting points were recorded on a Yanaco MP-21 apparatus.

For preparation of the bis-squarylium dyes and their precursors, commercially available starting materials and reagents were used without purification: 1,4-diiodobenzene, 4,4′-diiodobiphenyl, 9,10-dibromoanthracene, 1-bromopyrene, 2,5-dibromothiophene 2-bromothiophene, and squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione) were purchased from Tokyo Chemical Industry co., Ltd. 1,6-Dibromopyrene [19], *N*-butyl-3,6-diiodocarbazole [20], 5,5′-dibromo-2,2′-bithiophene [21,22], 5,5″-dibromo-2,2′:5′,2″-terthiophene [23], and 5,5″-dibromo-3′-methyl-2,2′:5′,2″-terthiophene [21,22] were prepared according to the reported procedures. The methyl quaternary salts were obtained by *N*-alkylation of commercially available 2,3,3-trimethylindolenine, 2-methylbenzothiazole, 2-methylbenzoxazole, and 2,3,3-trimethyl-4,5-dibenzo-3*H*-indole.

*4.2. Preparation of the arene-bridged bis-squarate **6***

*4.2.1. 4,4′-Bis[3-(1-methylethyloxy)-1,2-dioxo-3-cyclobuten-4-yl]biphenyl **6b**: typical procedure for preparation of the bis-squarate **6***

A mixture of 4,4′-diiodobiphenyl (2.0 g, 4.9 mmol), **5** (4.3 g, 10 mmol), $Pd^0(PPh_3)_4$ (0.96 g, 0.83 mmol) and CuI (0.36 g, 1.9 mmol) in acetonitrile (40 mL) was heated at reflux overnight. After cooling, chloroform was added, and insoluble materials were removed by filtration. The solid on a filter was washed with hexane. The filtrate and washing were combined, and the solvent was removed to dryness on a rotary evaporator. The residue was purified by silica gel column chromatography (chloroform as eluent), followed by recrystallization from chloroform to afford **6b** (1.04 g, 2.4 mmol) as a yellow solid.

Yield 53%; mp 212–213 °C (dec); ^{1}H NMR ($CDCl_3$) δ 8.15 (d, 4H, $J = 8.6$ Hz), 7.78 (d, 4H, $J = 8.6$ Hz), 5.65 (heptet, 2H, $J = 6.5$ Hz), 1.59 (d, 12H, $J = 5.9$ Hz); MALDI-TOF MS *m/z* 430 ($[M]^+$). Anal. Calcd for $C_{26}H_{22}O_6$: C, 72.55; H, 5.15%. Found: C, 72.28; H, 5.15%.

*4.2.2. 1,4′-Bis[3-(1-methylethyloxy)-1,2-dioxo-3-cyclobuten-4-yl]benzene **6a***

The bis-squarate **6a** was prepared in a similar way to the preparation of **6b**, using 1,4-diiodobenzene as the starting material.

Yield 77%; mp 214–215 °C; ^{1}H NMR ($CDCl_3$) δ 8.16 (s, 4H), 5.65 (heptet, 2H, $J = 6.2$ Hz), 1.58 (d, 12H, $J = 6.2$ Hz); FAB MS *m/z* 355 ($[M]^+$); Anal. Calcd for $C_{20}H_{18}O_6 \cdot H_2O$: C, 64.51; H, 5.41%; Found: C, 64.22; H, 5.02%.

*4.2.3. 9,10-Bis[3-(1-methylethyloxy)-1,2-dioxo-3-cyclobuten-4-yl]anthracene **6c***

The bis-squarate **6c** was prepared in a similar way to the preparation of **6b**, using 9,10-dibromoanthracene as the starting material.

Yield 60%; mp 240–241 °C (dec); ^{1}H NMR ($CDCl_3$) δ 7.83 (m, 4H), 7.62 (m, 4H), 5.59 (m, 2H, $J = 6.0$ Hz), 1.48 (d, 12H, $J = 6.0$ Hz); FAB MS *m/z* 454 ($[M]^+$); Anal. Calcd for $C_{28}H_{22}O_6 \cdot 0.5H_2O$: C, 72.56; H, 5.00%; Found: C, 72.06; H, 4.60%.

*4.2.4. 1,6-Bis[3-(1-methylethyloxy)-1,2-dioxo-3-cyclobuten-4-yl]pyrene **6d***

The bis-squarate **6d** was prepared in a similar way to the preparation of **6b**, using 1,6-dibromopyrene as the starting material.

Yield 30%; mp > 250 °C (dec); ^{1}H NMR ($CDCl_3$) δ 8.93 (d, 2H, $J = 9.2$ Hz), 8.60 (d, 2H, $J = 7.8$ Hz), 8.32 (d, 2H, $J = 9.2$ Hz), 8.26 (d, 2H, $J = 9.2$ Hz), 5.82 (m, 2H), 1.65 (d, 12H); FAB MS *m/z* 479 ($[M + 1]^+$); Anal. Calcd for $C_{30}H_{22}O_6$: C, 75.30; H, 4.63%. Found: C, 75.31; H, 4.41%.

*4.2.5. 1-Butyl-3,6-bis[3-(1-methylethyloxy)-1,2-dioxo-3-cyclobuten-4-yl]carbazole **6e***

The bis-squarate **6e** was prepared in a similar way to the preparation of **6b**, using *N*-butyl-3,6-diiodocarbazole as the starting material.

Yield 38%; mp > 250 °C (dec); ^{1}H NMR ($CDCl_3$) δ 8.85 (s, 2H), 8.27 (d, 2H, $J = 8.6$ Hz), 7.54 (d, 2H, $J = 8.5$ Hz), 5.69 (m, 2H), 4.38 (t, 2H, $J = 7.1$ Hz), 1.90 (m, 2H), 1.63 (d, 12H, $J = 6.3$ Hz), 1.13 (m, 2H), 0.97 (t, 3H, $J = 7.1$ Hz); FAB MS *m/z* 499 ($[M]^+$); Anal. Calcd for $C_{30}H_{29}NO_6$: C, 72.13%; H, 5.85%; N, 2.80%. Found: C, 71.81%; H, 5.89%; N, 2.41%.

*4.3. Preparation of the arene-bridged bis-squaric acid **7***

*4.3.1. 4,4′-Bis(3-hydroxy-1,2-dioxo-3-cyclobuten-4-yl)-biphenyl **7b**: typical procedure for preparation of the bis-squaric acid **7***

A mixture of **6b** (0.25 g, 0.58 mmol) and 18 wt% HCl_{aq} (4 mL) in THF (60 mL) was heated at 60 °C for 2 days. The solvent was removed on a rotary evaporator, and the residue was washed with chloroform and ether and purified by recrystallization from THF to afford **7b** (106 mg, 0.31 mmol) as a yellow solid.

Yield 53%; mp > 250 °C (dec); ^{1}H NMR (DMSO-d_6) δ 8.15 (d, 4H, $J = 8.6$ Hz), 7.78 (d, 4H, $J = 8.6$ Hz) (the OH protons were not observed due to rapid proton exchange with residual water); MALDI-TOF MS (negative mode) *m/z* 344 ($[M - 2]^-$). Anal. Calcd for $C_{20}H_{10}O_6$: C, 69.37; H, 2.91%. Found: C, 69.01; H, 2.77%.

*4.3.2. 1,4-Bis(3-hydroxy-1,2-dioxo-3-cyclobuten-4-yl)benzene **7a***

The bis-squaric acid **7a** was prepared in a similar way to the preparation of **7b**, using **6a** as the starting material.

Yield 79%; mp > 250 °C (dec); ^{1}H NMR (DMSO-d_6) δ 8.00 (s, 4H) (the OH protons were not observed due to rapid proton exchange with residual water); MALDI-TOF MS (negative mode) *m/z* 268 ($[M - 2]^-$). Anal. Calcd for $C_{14}H_6O_6 \cdot 2.5H_2O$: C, 53.34; H, 3.52%. Found: C, 53.43; H, 3.27%.

*4.3.3. 9,10-Bis(3-hydroxy-1,2-dioxo-3-cyclobuten-4-yl)anthracene **7c***

The bis-squaric acid **7c** was prepared in a similar way to the preparation of **7b**, using **6c** as the starting material.

Yield 74%; mp 218–220 °C (dec); ^{1}H NMR (DMSO-d_6) δ 7.94 (m, 4H), 7.44 (m, 4H) (the OH protons were not observed due to rapid proton exchange with residual water); FAB MS *m/z* 370 ([M]$^+$); Anal. Calcd for $C_{22}H_{10}O_6 \cdot 1.5H_2O$: C, 66.50; H, 3.29%. Found: C, 66.72; H, 2.92%.

*4.3.4. 1,6-Bis(3-hydroxy-1,2-dioxo-3-cyclobuten-4-yl)pyrene **7d***

The bis-squaric acid **7d** was prepared in a similar way to the preparation of **7b**, using **6d** as the starting material.

Yield 89%; mp > 250 °C (dec); ^{1}H NMR (DMSO-d_6) δ 8.47 (d, 2H, $J = 9.2$ Hz), 8.27 (d, 2H, $J = 8.3$ Hz), 8.13 (d, 2H, $J = 8.3$ Hz), 8.06 (d, 2H, $J = 8.2$ Hz); FAB MS *m/z* 394 ([M]$^+$); Anal. Calcd for $C_{24}H_{10}O_6 \cdot 2H_2O$: C, 66.98; H, 3.28%. Found: C, 66.61; H, 2.72%.

*4.3.5. 1-Butyl-3,6-bis(3-hydroxy-1,2-dioxo-3-cyclobuten-4-yl)carbazole **7e***

The bis-squaric acid **7e** was prepared in a similar way to the preparation of **7b**, using **6e** as the starting material.

Yield 93%; mp > 250 °C (dec); ^{1}H NMR (DMSO-d_6) δ 8.83 (s, 2H), 8.28 (d, 2H, $J = 8.6$ Hz), 7.51 (d, 2H, $J = 8.6$ Hz), 4.38 (t, 2H, $J = 7.3$ Hz), 1.93–1.62 (m, 2H), 1.46–1.37 (m, 2H), 0.94 (t, 3H, $J = 7.3$ Hz); FAB MS *m/z* 415([M]$^+$). Anal. Calcd for $C_{24}H_{17}NO_6$: C, 69.39; H, 4.12; N, 3.37%. Found: C, 69.01; H, 4.15; N, 3.56%.

*4.4. Preparation of the arene-bridged bis-squarylium dyes **1–4***

The typical synthetic protocol for the preparation of the bis-squarylium dyes **1–4** was shown previously in the literature [16], where the characterization of **1a** and **1b** and **2a** and **2b** was also described in detail. The characterization of the other dyes is shown here.

*4.4.1. The bis-squarylium dye **1c***

Yield 14%; mp > 250 °C (dec); ^{1}H NMR (CDCl$_3$, 45 °C) δ 8.43–8.40 (m, 4H), 7.58–7.55 (m, 4H), 7.53–7.49 (m, 6H), 7.66–7.43 (m, 2H), 6.59 (s, 2H), 4.45 (t, 4H, $J = 7.8$ Hz), 1.95–1.96 (m, 16H), 1.55–1.49 (m, 4H), 1.06 (t, 6H, $J = 7.8$ Hz); IR (KBr) 1558, 1612 cm^{-1}; FAB MS *m/z* 764 ([M]$^+$); Anal. Calcd for $C_{52}H_{48}N_2O_4 \cdot 0.5H_2O$: C, 80.70; H, 6.38; N, 3.62%. Found: C, 80.31; H, 6.23; N, 3.50%.

*4.4.2. The bis-squarylium dye **1d***

Yield 31%; mp > 250 °C (dec); ^{1}H NMR (CDCl$_3$, 45 °C) δ 10.07 (d, 2H, $J = 8.4$ Hz), 9.43 (d, 2H, $J = 8.4$ Hz), 8.22 (m, 4H), 7.27–7.54 (m, 8H), 6.51 (s, 2H), 4.35 (t, 4H, $J = 7.6$ Hz), 1.97 (m, 4H), 1.95 (s, 12H), 1.54 (m, 4H), 1.05 (t, 6H, $J = 7.6$ Hz); IR (KBr) 1549, 1609 cm^{-1}; FAB MS *m/z* 789 ([M + 1]$^+$); Anal. Calcd for $C_{54}H_{48}N_2O_4 \cdot H_2O$: C, 80.37; H, 6.25; N, 3.47%. Found: C, 80.61; H, 6.02; N, 3.28%.

*4.4.3. The bis-squarylium dye **1e***

Yield 33%; mp > 250 °C (dec); ^{1}H NMR (CDCl$_3$, 25 °C) δ 9.19 (s, 2H), 8.56 (d, 2H, $J = 8.6$ Hz), 7.48 (d, 2H, $J = 8.6$ Hz), 7.52–7.33 (m, 8H), 6.36 (s, 2H), 4.29 (m, 6H), 1.97–1.90 (m, 18H), 1.59–1.43 (s, 6H), 1.06–0.95 (m, 9H); IR (KBr) 1541 cm^{-1}; FAB MS *m/z* 809 ([M]$^+$); Anal. Calcd for $C_{54}H_{55}N_3O_4 \cdot H_2O$: C, 78.33; H, 6.94; N, 5.07%. Found: C, 77.88; H, 6.70; N, 4.97.

*4.4.4. The bis-squarylium dye **2e***

Yield 28%; mp > 230–232 °C (dec); ^{1}H NMR (CDCl$_3$, 25 °C) δ 9.03 (s, 2H), 8.45 (d, 2H, $J = 8.6$ Hz), 7.82 (d, 2H, $J = 7.9$ Hz), 7.53 (m, 2H), 7.45 (m, 6H), 6.43 (s, 2H), 4.36 (m, 6H), 1.95–1.90 (m, 6H), 1.58–1.50 (m, 6H), 1.04 (t, 6H, $J = 7.3$ Hz), 0.98 (t, 3H, $J = 7.3$ Hz); IR (KBr) 1562, 1601 cm^{-1}; MALDI-TOF MS (*m/z*) 790 ([M + 1]$^+$); Anal. Calcd. for $C_{48}H_{43}N_3O_4S_2 \cdot 2H_2O$: C, 69.79; H, 5.74; N, 5.09%. Found: C, 69.74; H, 5.83; N, 5.21%.

*4.4.5. The bis-squarylium dye **3b***

Yield 40%; mp > 250 °C (dec); ^{1}H NMR (CDCl$_3$) δ 8.39 (d, 4H, $J = 8.6$ Hz), 7.81 (m, 2H), 7.71 (d, 4H, $J = 8.6$ Hz), 7.51 (m, 4H), 7.41 (m, 2H), 6.13 (s, 2H) 4.28 (t, 4H, $J = 7.3$ Hz), 1.99–1.88 (m, 4H), 1.47–1.36 (m, 4H), 1.02 (t, 6H, $J = 7.3$ Hz); IR (KBr) 1559 cm^{-1}; FAB MS *m/z* 689 ([M + 1]$^+$); Anal. Calcd for $C_{44}H_{36}N_2O_6 \cdot 3H_2O$: C, 71.15; H, 5.70; N, 3.77%. Found: C, 70.56; H, 5.51; N, 3.74%.

*4.4.6. The bis-squarylium dye **3d***

As this compound exhibited low solubility in any solvents, it could not be characterized by ^{1}H NMR spectroscopy.

Yield 17%; mp > 250 °C (dec); IR (KBr) 1562 cm^{-1}; FAB MS *m/z* 736 ([M]$^+$); Anal. Calcd for $C_{48}H_{36}N_2O_6 \cdot 2H_2O$: C, 74.60; H, 5.22; N, 3.62%. Found: C, 74.61; H, 5.42; N, 3.71%.

*4.4.7. The bis-squarylium dye **4c***

Yield 33%; mp > 250 °C (dec); ^{1}H NMR (CDCl$_3$) δ 8.45–8.43 (m, 4H), 8.25 (d, 2H, $J = 8.8$ Hz), 8.05–8.01 (m, 4H), 7.72 (d, 2H, $J = 8.8$ Hz), 7.63–7.53 (m, 8H), 6.66 (s, 2H), 4.57 (t, 4H, $J = 7.8$ Hz), 2.21 (s, 12H), 2.01 (quintet, 4H, $J = 7.8$ Hz), 1.53 (m, 4H), 1.07 (t, 6H, $J = 7.8$ Hz); IR (KBr) 1558 cm^{-1}; FAB MS *m/z* 864 ([M]$^+$); Anal. Calcd for $C_{60}H_{52}N_2O_4 \cdot 2H_2O$: C, 79.97; H, 6.26; N, 3.11%. Found: C, 80.16; N, 5.99; H, 3.05%.

*4.4.8. The bis-squarylium dye **4d***

Yield 11%; mp > 250 °C (dec); ^{1}H NMR (CDCl$_3$, 25 °C) δ 10.07 (d, 2H, $J = 8.8$ Hz), 9.43 (d, 2H, $J = 8.8$ Hz), 8.28–8.20 (m, 6H), 7.97 (m, 4H), 7.94 (d, 2H, $J = 8.8$ Hz), 7.71 (t, 2H, $J = 7.8$ Hz), 7.60 (t, 2H, $J = 7.8$ Hz), 6.57 (s, 2H), 4.47 (t, 2H, $J = 7.8$ Hz), 2.21 (s, 12H), 1.98 (m, 4H), 1.56 (m, 4H), 1.06 (t, 6H, $J = 7.8$ Hz); IR (KBr) 1558 cm^{-1}; FAB MS *m/z* 888 ([M]$^+$); Anal. Calcd for $C_{62}H_{52}N_2O_4 \cdot H_2O$: C, 82.09; H, 6.00; N, 3.09%. Found: C, 82.19; N, 5.75; H, 2.98%.

4.5. Synthesis of the reference compounds **12** and **13**

4.5.1. 9-[3-(1-Methylethyloxy)-1,2-dioxo-3-cyclobuten-4-yl]anthracene **8**

A mixture of 9-bromoanthracene (0.51 g, 2.0 mmol), **5** (1.8 g, 4.2 mmol), $Pd^0(PPh_3)_4$ (0.27 g, 0.23 mmol), CuI (0.090 g, 0.47 mmol) in benzene (4 mL) was heated at reflux for 18 h under N_2. After cooling, $CHCl_3$ was added, and the insoluble materials were removed by filtration. The filtrate was evaporated, and the residue was purified by silica gel column chromatography ($CHCl_3$ as eluent) to obtain **8** (0.18 g, 0.57 mmol) as a yellow solid.

Yield 29%; mp 156–157 °C (dec); ^{1}H NMR ($CDCl_3$, 25 °C) δ 8.62 (s, 1H), 8.07 (d, 2H, $J = 7.3$ Hz), 7.80 (d, 2H, $J = 8.8$ Hz), 7.52–7.60 (m, 4H), 5.62 (hept, 1H, $J = 6.3$ Hz), 1.49 (d, 6H, $J = 6.3$ Hz); FAB MS *m/z* 316 ([M]$^+$); Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10%. Found: C, 80.11; H, 5.08%.

4.5.2. 1-[3-(1-Methylethyloxy)-1,2-dioxo-3-cyclobuten-4-yl] pyrene **9**

This compound was obtained by a similar procedure to the preparation of **8**. Toluene was used as a solvent.

Yield 49%; mp 179–181 °C (dec); ^{1}H NMR ($CDCl_3$, 25 °C) δ 8.84 (d, 1H, $J = 9.2$ Hz), 8.60 (d, 1H, $J = 7.9$ Hz), 8.22 (m, 5H), 8.09 (m, 2H), 5.82 (hept, 1H, $J = 6.3$ Hz) 1.64 (d, 6H, $J = 6.3$ Hz); FAB MS *m/z* 340 ([M]$^+$); Anal. Calcd for $C_{23}H_{16}O_3$: C, 81.16; H, 4.74%. Found: C, 81.36; H, 4.82%.

4.5.3. 9-(3-Hydroxy-1,2-dioxo-3-cyclobuten-4-yl)anthracene **10**

To a solution of **8** (0.32 g, 1.0 mmol) in THF (40 mL) was added 18 wt% HCl (4 mL), and the mixture was heated at reflux for 4 h. After cooling, the solvent was removed by evaporation, and the residue was washed with ether several times. Recrystallization from THF afforded **10** (0.20 g, 0.73 mmol) as a yellow solid.

Yield 73%; mp 213–215 °C (dec); ^{1}H NMR (DMSO-d_6, 25 °C) δ 8.57 (s, 1H), 8.02 (d, 2H, $J = 9.2$ Hz), 7.88 (d, 2H, $J = 8.6$ Hz), 7.47–7.56 (m, 4H); FAB MS *m/z* 294 ([M]$^+$); Anal. Calcd for $C_{18}H_{10}O_3$: C, 78.83; H, 3.68%. Found: C, 79.21; H, 3.48%.

4.5.4. 1-(3-Hydroxy-1,2-dioxo-3-cyclobuten-4-yl) pyrene **11**

This compound was obtained by a similar procedure to the preparation of **10**.

Yield 15%; mp 230–232 °C (dec); ^{1}H NMR (DMSO-d_6, 25 °C) δ 9.53 (d, 1H, $J = 9.3$ Hz), 9.00 (d, 1H, $J = 8.3$ Hz), 8.18 (m, 7H); FAB MS *m/z* 298 ([M]$^+$); Anal. Calcd for $C_{20}H_{10}O_3 \cdot 2H_2O$: C, 71.85; H, 4.22%. Found: C, 71.47; H, 4.51%.

4.5.5. The unsymmetrical squarylium dye **12**

A mixture of **10** (0.054 g, 0.20 mmol) and 1-butyl-2,3,3-trimethylindolium iodide (0.20 g, 0.58 mmol) in a 1-butanol/benzene mixture (4/1, v/v, 25 mL) was heated at reflux for 4 h in the presence of quinoline (1 mL). After cooling, the solvent was removed on a rotary evaporator, and the residue was dissolved in chloroform. Addition of ether afforded a precipitate, which was collected by filtration and purified by silica gel column chromatography ($CHCl_3$/methanol, 20/1, v/v, as eluent) followed by recrystallization from hexane–$CHCl_3$–methanol to afford **12**.

Yield 47%; mp > 250 °C (dec); ^{1}H NMR ($CDCl_3$, 25 °C) δ 8.50 (s, 1H), 8.38 (d, 2H, $J = 8.8$ Hz), 8.00 (d, 2H, $J = 7.8$ Hz), 7.59–7.44 (m, 7H), 7.36 (d, 1H, $J = 7.8$ Hz), 6.62 (s, 1H), 4.44 (t, 2H, $J = 7.8$ Hz), 1.96 (m, 8H), 1.56 (sext, 2H, $J = 7.8$ Hz) 1.06 (t, 3H, $J = 7.8$ Hz); IR (KBr) 1568, 1595 cm^{-1}; FAB MS *m/z* 471 ([M]$^+$); Anal. Calcd for $C_{33}H_{29}NO_2 \cdot CHCl_3$: C, 69.10; H, 5.12; N, 2.37%. Found: C, 69.12; H, 5.16; N, 2.50%.

4.5.6. The unsymmetrical squarylium dye **13**

This compound was prepared by a similar method to the preparation of **12**.

Yield 39%; mp > 250 °C (dec); ^{1}H NMR ($CDCl_3$, 25 °C) δ 9.98 (d, 1H, $J = 9.3$ Hz), 9.44 (d, 1H, $J = 8.3$ Hz), 8.18 (m, 7H), 7.46 (m, 4H), 6.53 (s, 1H), 4.36 (t, 2H, $J = 7.8$ Hz), 1.61 (m, 10H), 1.05 (t, 3H, $J = 7.8$ Hz); IR (KBr) 1734, 1606, 1558 cm^{-1}; FAB MS *m/z* 495 ([M]$^+$); Anal. Calcd for $C_{35}H_{29}NO_2 \cdot 0.5H_2O$: C, 83.31; H, 5.99; N, 2.78%. Found: C, 83.74; H, 5.41; N, 2.64%.

4.6. Preparation of the thiophene-bridged bis-squarate **17**

4.6.1. 2,5-Bis[3-(1-methylethyloxy)-1,2-dioxo-3-cyclobuten-4-yl]thiophene **17a**: typical procedure for preparation of the bis-squarate **17**

A mixture of 2,5-dibromothiophene (0.51 g, 2.1 mmol) was dissolved in 5 mL of acetonitrile, and then, **5** (2.0 g, 4.6 mmol), $Pd^0(PPh_3)_4$ (0.27 g, 0.23 mmol) and CuI (0.090 g, 0.48 mmol) were added, and the mixture was heated at reflux for 17 h. After cooling, chloroform was added, and insoluble materials were removed by filtration. The solvent was removed to dryness on a rotary evaporator. The residue was purified by silica gel column chromatography (chloroform as eluent), followed by recrystallization from chloroform to afford **17a** (0.29 g, 0.80 mmol) as a yellow solid.

Yield 38%; mp 173–175 °C (dec); ^{1}H NMR ($CDCl_3$) δ 7.94 (s, 2H), 5.64 (heptet, 2H, $J = 6.3$ Hz), 1.59 (d, 12H, $J = 6.3$ Hz); IR (KBr) 1606, 1777 cm^{-1}; FAB MS *m/z* 360 ([M]$^+$). Anal. Calcd for $C_{18}H_{16}O_6S \cdot 0.5H_2O$: C, 58.53; H, 4.64%. Found: C, 58.37; H, 4.44%.

4.6.2. 5,5′-Bis[3-(1-methylethyloxy)-1,2-dioxo-3-cyclobuten-4-yl]-2,2′-bithiophene **17b**

This compound was prepared by a similar method to the preparation of **17a**, using 5,5′-dibromo-2,2′-bithiophene as the starting material.

Yield 59%; mp 228–230 °C (dec); ^{1}H NMR ($CDCl_3$) δ 7.82 (d, 2H, $J = 4.3$ Hz), 7.46 (d, 2H, $J = 4.3$ Hz), 5.62 (heptet, 2H, $J = 6.3$ Hz), 1.58 (d, 12H, $J = 6.3$ Hz); FAB MS *m/z* 442 ([M]$^+$). Anal. Calcd for $C_{22}H_{18}O_6S_2$: C, 59.72; H, 4.10%. Found: C, 59.68; H, 3.98%.

4.6.3. *5,5″-Bis[3-(1-methylethyloxy)-1,2-dioxo-3-cyclobuten-4-yl]-2,2′:5′2″-terthiophene* ***17c***

This compound was prepared by a similar method to the preparation of **17a**, using 5,5″-dibromo-3′-methyl-2,2′:5′,2″-terthiophene as the starting material.

Yield 30%; mp 219–221 °C (dec); ^{1}H NMR ($CDCl_3$) δ 7.81 (d, 2H, $J = 4.4$ Hz), 7.34 (d, 2H, $J = 3.9$ Hz), 7.31 (s, 2H), 5.60 (heptet, 2H, $J = 6.3$ Hz) 1.57 (d, 12H, $J = 6.3$ Hz); FAB MS *m/z* 524 ($[M]^+$). Anal. Calcd for $C_{26}H_{20}O_6S_3$: C, 59.52; H, 3.84%. Found: C, 59.16; H, 3.84%.

4.6.4. *5,5″-Bis[3-(1-methylethyloxy)-1,2-dioxo-3-cyclobuten-4-yl]-3′-methyl-2,2′:5′2″-terthiophene* ***17d***

This compound was prepared by a similar method to the preparation of **17a**, using 5,5″-dibromo-3′-methyl-2,2′:5′,2″-terthiophene as the starting material.

Yield 26%; mp 235–237 °C (dec); ^{1}H NMR ($CDCl_3$) δ 7.85 (d, 1H, $J = 3.9$ Hz), 7.81 (d, 1H, $J = 3.9$ Hz), 7.34–7.31 (m, 2H), 7.19 (s, 1H), 5.61 (m, 2H) 2.49 (s, 3H), 1.57 (d, 12H, $J = 5.9$ Hz); FAB MS *m/z* 539 ($[M + 1]^+$). Anal. Calcd for $C_{27}H_{22}O_6S_3 \cdot H_2O$: C, 59.21; H, 4.23%. Found: C, 59.21; H, 3.78%.

4.7. *Preparation of the thiophene-bridged bis-squaric acid* ***18***

4.7.1. *2,5-Bis(3-hydroxy-1,2-dioxo-3-cyclobuten-4-yl)thiophene* ***18a****: typical procedure for preparation of the bis-squarate* ***18***

A mixture of **17a** (0.29 g, 0.80 mmol) and 18 wt% HCl_{aq} (1 mL) in THF (10 mL) was heated at 60 °C for 20 h. The solvent was removed on a rotary evaporator, and the residue was washed with ether to afford **17a** (0.19 g, 0.70 mmol) as an orange solid. This compound was used in the next step without further purification.

Yield 88%; mp > 250 °C (dec); ^{1}H NMR (DMSO-d_6) δ 7.57 (s, 2H) (the OH protons were not observed due to rapid proton exchange with residual water); IR (KBr) 1602, 1789 cm^{-1}; FAB MS *m/z* 276 ($[M]^+$). Anal. Calcd for $C_{12}H_4O_6S \cdot H_2O$: C, 48.98; H, 2.06%. Found: C, 49.16; H, 2.03%.

4.7.2. *5,5′-Bis(3-hydroxy-1,2-dioxo-3-cyclobuten-4-yl)-2,2′-bithiophene* ***18b***

This compound was prepared by a similar method to the preparation of **18a**, using **17b** as the starting material.

Yield 90%; mp 218–221 °C (dec); ^{1}H NMR (DMSO-d_6) δ 7.43 (d, 2H, $J = 5.9$ Hz), 7.41 (d, 2H, $J = 3.9$ Hz) (the OH protons were not observed due to rapid proton exchange with residual water); FAB MS (negative mode) *m/z* 356 ($[M - 2]^-$). Anal. Calcd for $C_{16}H_6O_6S_2 \cdot 2H_2O$: C, 48.73; H, 2.56%. Found: C, 49.16; H, 2.03%.

4.7.3. *5,5″-Bis(3-hydroxy-1,2-dioxo-3-cyclobuten-4-yl)-2,2′:5′2″-terthiophene* ***18c***

This compound was prepared by a similar method to the preparation of **18a**, using **17c** as the starting material.

Yield 59%; mp 208–210 °C (dec); ^{1}H NMR (DMSO-d_6) δ 7.44 (d, 2H, $J = 4.0$ Hz), 7.40 (d, 2H, $J = 3.6$ Hz), 7.35 (s, 2H) (the OH protons were not observed due to rapid proton exchange with residual water); IR (KBr) 1569, 3434 cm^{-1}; FAB MS (negative mode) *m/z* 439 ($[M - 1]^-$). Anal. Calcd for $C_{20}H_8O_6S_3 \cdot 2H_2O$: C, 50.41; H, 2.53%. Found: C, 49.89; H, 2.14%.

4.7.4. *5,5″-Bis(3-hydroxy-1,2-dioxo-3-cyclobuten-4-yl)-3′-methyl-2,2′:5′2″-terthiophene* ***18d***

This compound was prepared by a similar method to the preparation of **18a**, using **17d** as the starting material.

Yield 93%; mp 211–213 °C (dec); ^{1}H NMR ($CDCl_3$) δ 7.41 (d, 1H, $J = 3.9$ Hz), 7.35 (d, 1H, $J = 4.0$ Hz), 7.26 (d, 1H, $J = 3.9$ Hz), 7.22 (d, 1H, $J = 4.0$ Hz), 7.19 (s, 1H), 2.32 (s, 3H) (the OH protons were not observed due to rapid proton exchange with residual water); FAB MS (negative mode) *m/z* 453 ($[M]^-$). Anal. Calcd for $C_{21}H_{10}O_6S_3 \cdot 1.5H_2O$: C, 52.38; H, 2.72%. Found: C, 52.20; H, 3.20%.

4.8. *Preparation of the thiophene-bridged bis-squarylium dyes* ***14–16***

The thiophene-bridged bis-squarylium dyes **14–16** were prepared according to a similar method to obtain the bis-squarylium dyes **1–4** [16].

4.8.1. *The bis-squarylium dye* ***15a****: typical procedure for preparation of the bis-squarylium dyes* ***14–16***

A mixture of **18a** (0.055 mg, 0.20 mmol) and 1-butyl-2-methylbenzothiazolium iodide (0.20 g, 0.60 mmol) in a 1-butanol/benzene mixture (4/1, v/v, 15 mL) was heated at reflux for 6 h in the presence of quinoline (0.5 mL). After cooling, the solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (CH_2Cl_2/methanol, 20/1, v/v, as eluent) followed by recrystallization from hexane–CH_2Cl_2–methanol to afford **15a** (31 mg, 0.048 mmol).

Yield 24%; mp > 237–239 °C (dec); ^{1}H NMR ($CDCl_3$) δ 7.94 (s, 2H), 7.84 (d, 2H, $J = 7.8$ Hz), 7.77 (t, 2H, $J = 7.8$ Hz), 7.59 (d, 2H, $J = 7.3$ Hz), 7.49 (t, 2H, $J = 7.3$ Hz), 6.45 (s, 2H), 4.89 (t, 4H, $J = 7.3$ Hz), 1.87 (m, 4H), 1.53 (m, 4H), 1.05 (t, 6H, $J = 7.3$ Hz); IR (KBr) 1605 cm^{-1}; FAB MS *m/z* 650 ($[M]^+$). Anal. Calcd for $C_{36}H_{30}N_2O_4S_3 \cdot H_2O$: C, 64.65; H, 4.82; N, 4.19%. Found: C, 64.78; H, 4.76; N, 4.11%.

4.8.2. *The bis-squarylium dye* ***14a***

Yield 43%; mp > 250 °C (dec); ^{1}H NMR ($CDCl_3$) δ 8.05 (s, 2H), 7.50 (d, 2H, $J = 7.3$ Hz), 7.45 (t, 2H, $J = 7.4$ Hz), 7.39 (t, 2H, $J = 7.4$ Hz), 7.28 (d, 2H), 6.37 (s, 2H), 4.28 (t, 4H, $J = 8.0$ Hz), 1.87 (m, 4H), 1.85 (s, 12H), 1.37 (m, 4H), 1.01 (t, 6H, $J = 8.4$ Hz); IR (KBr) 1575, 1624 cm^{-1}; FAB MS *m/z* 670 ($[M]^+$); Anal. Calcd. for $C_{42}H_{42}N_2O_4S \cdot H_2O$: C, 73.23; H, 6.44; N, 4.07%. Found: C, 73.39; H, 6.35; N, 4.03%.

4.8.3. *The bis-squarylium dye* ***14b***

Yield 53%; mp > 250 °C (dec); ^{1}H NMR ($CDCl_3$) δ 7.89 (d, 2H, *J* = 3.9 Hz), 7.49 (d, 2H, *J* = 7.3 Hz), 7.45 (d, 2H, 3.9 Hz), 7.43 (t, 2H, *J* = 7.8 Hz), 7.37 (t, 2H, *J* = 7.3 Hz), 7.24 (m, 2H), 6.32 (s, 2H), 4.26 (t, 4H, *J* = 7.5 Hz), 1.87 (m, 4H), 1.85 (s, 12H), 1.49 (m, 4H), 0.88 (t, 6H, *J* = 7.5 Hz); IR (KBr) 1563, 1616 cm^{-1}; FAB MS *m/z* 752 ([M]$^+$); Anal. Calcd. for $C_{46}H_{44}N_2O_4S_2 \cdot 1.5H_2O$: C, 70.83; H, 6.07; N, 3.59%. Found: C, 71.03; H, 5.76; N, 3.54%.

4.8.4. *The bis-squarylium dye* ***14c***

Yield 22%; mp > 250 °C (dec); ^{1}H NMR ($CDCl_3$) δ 7.87 (d, 2H, *J* = 4.4 Hz), 7.50 (d, 2H, *J* = 6.8 Hz), 7.45 (t, 2H, *J* = 6.8 Hz), 7.38 (t, 2H, *J* = 6.8 Hz), 7.34 (d, 2H, *J* = 4.4 Hz), 7.28 (s, 2H), 7.25 (d, 2H, *J* = 6.8 Hz), 6.32 (s, 2H), 4.26 (t, 4H, *J* = 7.8 Hz), 1.88 (m, 4H), 1.85 (s, 12H), 1.49 (m, 4H), 1.02 (t, 6H, *J* = 7.3 Hz); IR (KBr) 1645 cm^{-1}; FAB MS (*m/z*) 835 ([M + 1]$^+$); Anal. Calcd. for $C_{50}H_{46}N_2O_4S_3 \cdot 2H_2O$: C, 68.94; H, 5.79; N, 3.22%; Found: C, 69.10; H, 5.30; N, 3.33%.

4.8.5. *The bis-squarylium dye* ***14d***

Yield 26%; mp > 250 °C (dec); ^{1}H NMR ($CDCl_3$) δ 7.94 (d, 1H, *J* = 4.3 Hz), 7.87 (d, 1H, *J* = 3.9 Hz), 7.49–7.52 (m, 2H), 7.42–7.46 (m, 2H), 7.36 (d, 1H, *J* = 4.0 Hz), 7.32 (d, 1H, *J* = 4.0 Hz), 7.22–7.25 (m, 4H), 7.15 (s, 1H), 6.31 (s, 2H), 4.25 (t, 4H, *J* = 7.5 Hz), 2.52 (s, 3H), 1.85–1.86 (m, 16H), 1.49–1.55 (m, 4H), 1.02 (t, 6H, *J* = 7.5 Hz); IR (KBr) 1538 cm^{-1}; FAB MS *m/z* 848 ([M]$^+$); Anal. Calcd. for $C_{51}H_{48}N_2O_4S_3 \cdot H_2O$: C, 70.64; H, 5.81; N, 3.23%. Found: C, 70.39; H, 5.41; N, 3.33%.

4.8.6. *The bis-squarylium dye* ***15b***

Yield 33%; mp > 250 °C (dec); ^{1}H NMR ($CDCl_3$) δ 7.83 (d, 2H, *J* = 7.8 Hz), 7.75 (d, 2H, *J* = 4.4 Hz), 7.61 (t, 2H, *J* = 7.8 Hz), 7.51 (m, 4H), 7.37 (d, 2H, *J* = 3.7 Hz), 6.44 (s, 2H), 4.40 (t, 4H, *J* = 7.8 Hz), 1.90 (quint, 4H), 1.54 (m, 4H), 1.04 (t, 6H, *J* = 7.3 Hz); IR (KBr) 1588 cm^{-1}; FAB MS *m/z* 732 ([M]$^+$); Anal. Calcd. for $C_{40}H_{32}N_2O_4S_4 \cdot 2H_2O$: C, 62.48; H, 4.72; N, 3.64%. Found: C, 62.64; H, 4.17; N, 3.45%.

4.8.7. *The bis-squarylium dye* ***15c***

Yield 31%; mp 235–237 °C (dec); ^{1}H NMR ($CDCl_3$) δ 7.82 (d, 2H, *J* = 7.8 Hz), 7.76 (d, 2H, *J* = 3.9 Hz), 7.60 (t, 2H, *J* = 6.8 Hz), 7.51–7.47 (m, 4H), 7.29–7.21 (m, 4H), 6.42 (s, 2H), 4.38 (t, 4H), 1.91 (m, 4H), 1.26 (m, 4H), 1.04 (t, 6H, *J* = 7.3 Hz); IR (KBr) 1645 cm^{-1}; FAB MS *m/z* 814 ([M]$^+$); Anal. Calcd. for $C_{44}H_{34}N_2O_4S_5 \cdot 3H_2O$: C, 60.81; H, 4.64; N, 3.22%. Found: C, 60.49; H, 4.60; N, 3.22%.

4.8.8. *The bis-squarylium dye* ***16a***

Yield 11%; mp 221–224 °C (dec); ^{1}H NMR ($CDCl_3$) δ 8.24 (d, 2H, *J* = 8.7 Hz), 8.07(s, 2H), 8.01–7.99 (m, 4H), 7.70 (t, 2H, *J* = 7.8 Hz), 7.58 (t, 2H, *J* = 7.8 Hz), 7.47 (d, 2H, *J* = 9.3 Hz), 6.42 (s, 2H), 4.41 (t, 4H, *J* = 7.8 Hz), 2.11 (s, 12H), 1.93 (quint, 4H, *J* = 7.3 Hz), 1.53 (m, 4H), 0.88 (t, 6H, *J* = 6.8 Hz); IR (KBr) 1560, 1620 cm^{-1}; FAB MS *m/z* 771 ([M + 1]$^+$); Anal. Calcd. for $C_{50}H_{46}N_2O_4S \cdot 1.25CH_2Cl_2$: C, 70.18; H, 5.57; N, 3.19%. Found: C, 70.07; H, 5.57; N, 3.07%.

4.9. *Synthesis of the reference compound* ***21***

4.9.1. *2-[3-(1-Methylethyloxy)-1,2-dioxo-3-cyclobuten-4-yl]thiophene* ***19***

A mixture of 2-bromothiophene (0.32 g, 2.0 mmol), **5** (1.8 g, 4.2 mmol), $Pd^0(PPh_3)_4$ (0.27 g, 0.23 mmol), CuI (0.090 g, 0.47 mmol) in benzene (4 mL) was heated at reflux for 18 h under N_2. After cooling, $CHCl_3$ was added, and the insoluble materials were removed by filtration. The filtrate was evaporated, and the residue was purified by silica gel column chromatography ($CHCl_3$ as eluent) to obtain **19** (0.41 g, 1.1 mmol) as a red solid.

Yield 57%; mp 222–223 °C (dec); ^{1}H NMR ($CDCl_3$, 25 °C) δ 7.89 (d, 1H, *J* = 3.7 Hz), 7.80 (t, 1H, *J* = 5.9 Hz), 7.27 (d, 1H, *J* = 3.9 Hz), 5.62 (hept, 1H, *J* = 6.3 Hz), 1.49 (d, 6H, *J* = 6.1 Hz); FAB MS *m/z* 222 ([M]$^+$); Anal. Calcd for $C_{11}H_{10}O_3S$: C, 59.44; H, 4.53%. Found: C, 59.92; H, 4.64%.

4.9.2. *2-(3-Hydroxy-1,2-dioxo-3-cyclobuten-4-yl)thiophene* ***20***

To a solution of **19** (0.10 g, 0.44 mmol) in THF (60 mL) was added 6 wt% HCl (6 mL), and the mixture was heated at reflux for 84 h. After cooling, the solvent was removed on a rotary evaporator, and the residue was washed with ether several times. Recrystallization from THF afforded **20** (0.84 g, 0.38 mmol) as a reddish orange solid.

Yield 87%; mp 183 °C (dec); ^{1}H NMR (DMSO-d_6, 25 °C) δ 7.67 (d, 1H, *J* = 5.4 Hz), 7.53 (d, 1H, *J* = 3.5 Hz), 7.17 (t, 1H, *J* = 3.9 Hz) (the OH protons were not observed due to rapid proton exchange with residual water); FAB MS *m/z* 180 ([M]$^+$); Anal. Calcd for $C_8H_4O_3S$: C, 53.33; H, 2.24%. Found: C, 53.60; H, 2.31%.

4.9.3. *The unsymmetrical squarylium dye* ***21***

A mixture of **20** (0.054 g, 0.30 mmol) and 1-butyl-2,3,3-trimethylindolium iodide (0.30 g, 0.90 mmol) in a 1-butanol/benzene mixture (5/1, v/v, 6 mL) was heated at reflux for 4 h in the presence of quinoline (1 mL). After cooling, the solvent was removed on a rotary evaporator, and the residue was dissolved in a small amount of chloroform. Addition of ether afforded a precipitate, which was collected by filtration. Purification of the precipitate by silica gel column chromatography ($CHCl_3$/methanol, 20/1, v/v, as eluent) followed by recrystallization from hexane–$CHCl_3$–methanol afforded **12** (0.037 g, 0.099 mmol).

Yield 33%; mp 236 °C (dec); ^{1}H NMR ($CDCl_3$, 25 °C) δ 7.97 (d, 1H, *J* = 3.9 Hz), 7.65 (d, 1H, *J* = 4.9 Hz), 7.51–7.37 (m, 3H), 7.29–7.22 (m, 2H), 6.34 (s, 1H), 4.27 (t, 2H, *J* = 7.6 Hz), 1.91–1.82 (m, 8H), 1.55–1.47 (m, 2H), 1.01 (t, 3H, *J* = 7.3 Hz); IR (KBr) 1568, 1595 cm^{-1}; FAB MS *m/z* 377 ([M]$^+$); Anal. Calcd. for $C_{23}H_{23}NO_2S \cdot 2H_2O$: C, 66.80; H, 6.58; N, 3.39%. Found: C, 66.75; H, 6.42; N, 3.54%.

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