Synthesis of Near-Infrared Absorbing Bisquarylium Dyes Bearing Unsymmetrically Extended π-Conjugation Structures

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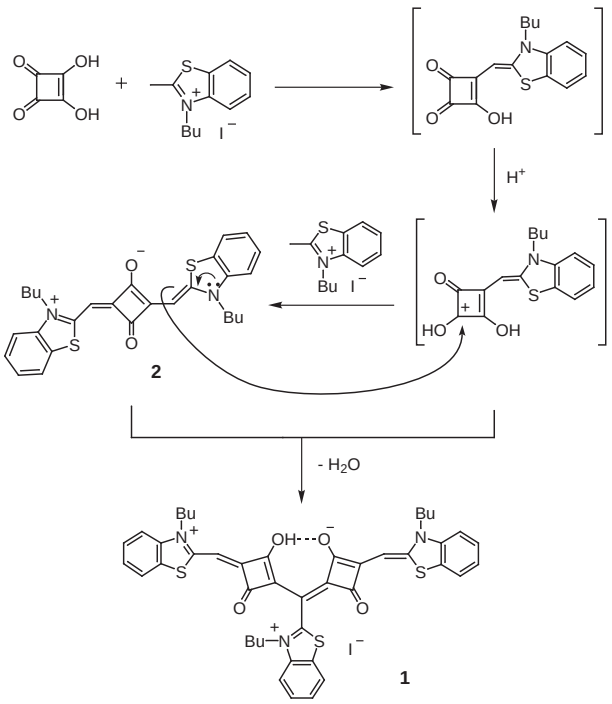
Abstract: Novel cationic bisquarylium dyes **3** and **4** were prepared by the reaction of benzothiazolinosquarylium dye **2** with a series of 4-substituted 3-hydroxy or 3-ethoxycyclobut-3-ene-1,2-diones. These dyes exhibit large and intense absorptions in the near-infrared region with varying absorption maxima in the range of 771 to 815 nm.

Key words:: squarylium dyes, X-ray crystallographic analysis, heterocycles, π-conjugation structures, chromophores

Squarylium (SQ) dyes are 1,3-disubstituted compounds derived from squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione), bearing either aromatic or heterocyclic electron-donating components,[1] and exhibit interesting photochemical properties such as photoconductivity and large and intense light absorption in the visible and/or near-infrared regions. Thus, SQ dyes are applicable to industrial uses such as xerographic photoreceptors,[2] media for optical recording using a diode laser,[3] photoconductive layers in organic solar cells,[4] chemosensors,[5] and so on. However, the traditional synthetic method of SQ dyes can offer only a symmetrical structure bearing the same electron-donating components.[6] From this point of view, the development of synthetic methodology for novel SQ dyes and their related compounds is of much importance for the extension of their utility. Recently, several unsymmetrical SQ dyes have been reported independently,[7–9] and thus, variability of electronic structures of SQ dyes have been widely extended. On the other hand, in the course of our research on the preparation of SQ dyes, we found that a novel cationic SQ homologue **1** is exclusively produced by the reaction of 1-alkyl-2-methylbenzothiazolium and squaric acid in the absence of quinoline which is usually added to obtain a typical SQ dye in an efficient yield.[10] The formation of the cationic dye **1** is achieved by an electrophilic attack of the intermediate on the methine carbon of the SQ dye **2** once formed, as shown in Scheme 1. In contrast to the dye **2**, the dye **1** exhibits a large and intense absorption in the near-infrared region (λ_{max} 797 nm in $CHCl_3$), and the X-ray analysis indicated that this outstanding spectral feature is due to the largely extended π-conjugation structure consisting of two squaryl subunits. If the intermediate is isolated and allowed to attack the SQ dye **2**, it is possible to obtain various cationic SQ derivatives by employing a variety of aromatic/heterocyclic components. In the present paper, we report stepwise synthesis of novel cationic SQ homologues, namely, bisquarylium dyes bearing unsymmetrically extended π-conjugation structures, as shown in Figure 1.



Scheme 1

The mono-substituted squaric acids **5a** and **5b** [Scheme 2(a)] were chosen as candidates for the electrophilic intermediates to obtain the dyes **3a** and **3b**, respectively. These were prepared according to an analogous procedure to the one reported previously [Scheme 2(b)].[9] Although the preparation of **6a**–**c** was also examined according to a similar method, isolation and purification by normal procedures such as column chromatography and recrystallization were not successful except for **6a**: even in the case of **6a**, the optimized yield by using reverse-phase column chromatography of an octadecylsilicate-endocapped stationary phase was only 37%.[9] Instead, the ethyl esters **7a**–**c** were employed as equivalents for **6a**–**c**, each of which was synthesized in a satisfactory yield (50–75%) from **8a**–**c** and 3,4-diethoxy-1,2-dioxocyclobut-3-

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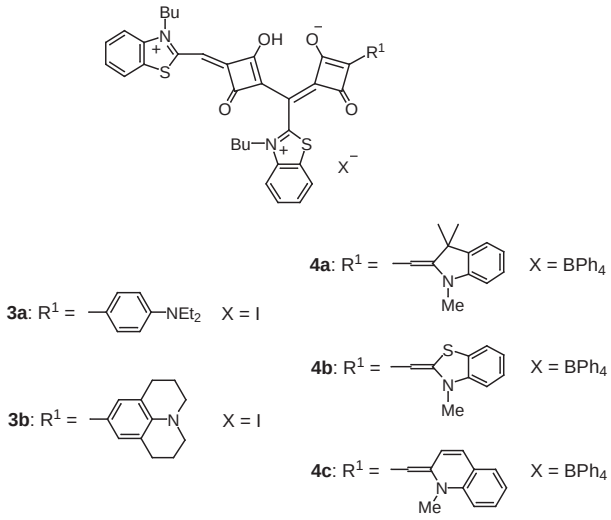


Figure 1 The structures of the bisquarylium dyes **3** and **4**

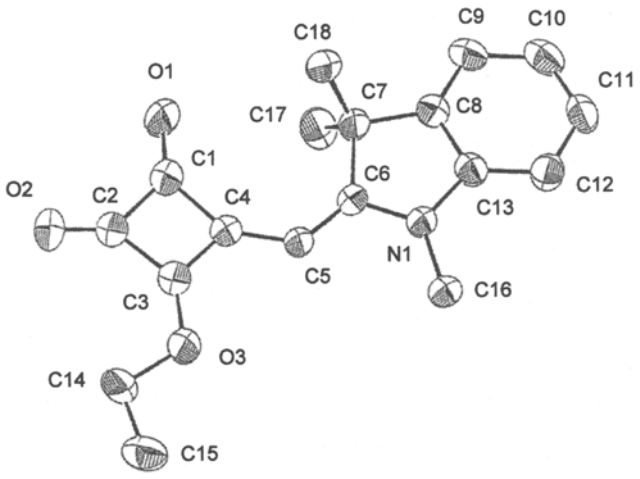
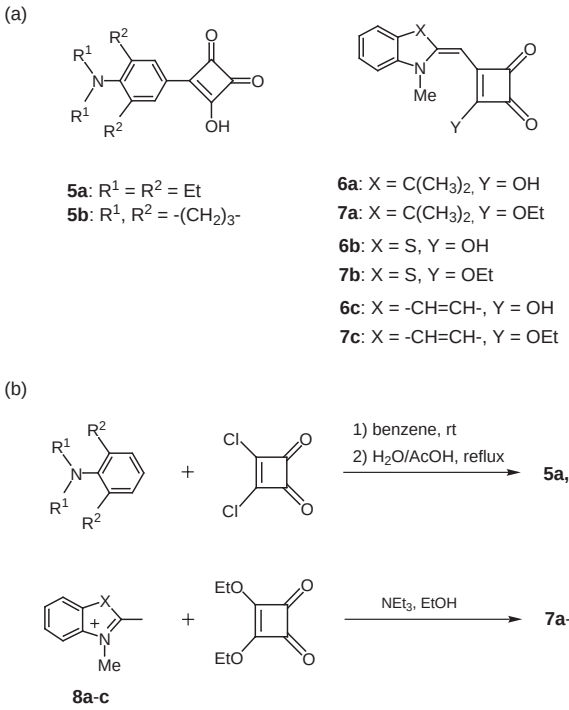


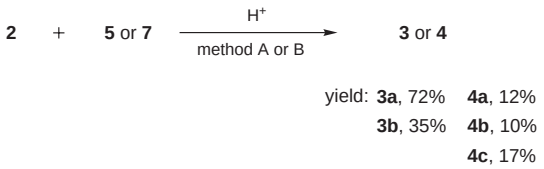
Figure 2 The molecular structure of **7a** (ORTEP drawing). All hydrogen atoms are omitted for clarity

ene according to a similar procedure to Terpetschnig's method [Scheme 2(b)].[8] The structures of these intermediates were confirmed by ^{1}H NMR, IR, and EI or FAB MS spectra as well as elemental analyses. In addition, the structure of **7a** was proved by X-ray crystallographic analysis. As shown in Figure 2, it was confirmed that the ethyloxy and indolinylidenemethyl groups have been introduced at the 3- and 4-positions of the 1,2-dioxo-3-cyclobutene ring, respectively.



Scheme 2 The structures of the intermediates for the preparation of the bisquarylium dyes (a), and the synthetic Schemes (b) of their preparation

As shown in Scheme 3, the reactions of the SQ dye **2** with the mono-substituted squaric acid derivatives **5** and **7** were examined in butan-1-ol/benzene containing HI (Method A) and in butan-1-ol containing H_2SO_4 (Method B) to obtain the dyes **3** and **4**, respectively. For **5a** and **5b**, the reactions with **2** proceeded in 3–4 hours to afford the bisquarylium dyes **3a** and **3b** as iodides in 72 and 35% yields, respectively. The Method A failed to obtain the dyes corresponding to **4a**–**c** from **2** and **7a**–**c**. On the other hand, by the Method B, **7a**–**c** reacted with **2** to afford hydrogensulfates of **4a**–**c**. For convenience of handling, **4a**–**c** were isolated as tetraphenylborates via anion exchange using sodium tetraphenylborate. The total yields of **4a**–**c** from **2** and **7a**–**c** were 12,10, and 17% yields, respectively. Under the conditions of the Method B, the initial reactant mixture of 1 equivalent of **7** and 2 equivalents of **2** with 4 equivalents of H_2SO_4 afforded an optimized yield. One can see that the ethyl esters **7a**–**c** were converted to the intermediate **6a**–**c** in situ by acid-promoted hydrolysis to react with the dye **2**. The cationic bisquarylium dyes **3** and **4** were characterized by ^{1}H NMR, Vis-NIR absorption, IR, and FAB MS spectra as well as elemental analyses.



Scheme 3

A selected region of the ^{1}H NMR spectrum of **4a** in $CDCl_3$ is shown in Figure 3(a). Several signals of the dye skeleton were split into two peaks, as seen for *N*-methyl protons in the indolin component (H^a) and two methine protons (H^d, H^e), although no decoalescence was observed for the signals of the tetraphenylborate anion (not shown).

These split signals were coalesced in DMSO-d_6 solution by raising the temperature to 80 °C as shown in Figure 3(b). Similar results were obtained for the other bisquarylium dyes. Taking it into consideration that the stoichiometry of the dye skeleton and the tetraphenylborate anion is 1:1, conformational isomerization based on some bond rotations slower than the NMR time scale would occur in $CDCl_3$, although the detailed structures of the conformers have not been revealed. Another notable NMR profile is that the signal of the OH proton in the cyclobutene is observed in the quite lower magnetic field (18.3–18.7 ppm) in each dye. This spectral peculiarity originates from high acidity of the proton as well as the magnetic deshielding effect from the negatively charged oxygen in the other cyclobutene ring. In the X-ray structure of the dye **1**,[10] the OH group forms a hydrogen bond with the neighboring oxygen to maintain the planarity of the π-conjugation structure, and in addition, the reported value of pK_a of **1** is 4.9.[5a] Therefore, judging from the ^{1}H NMR spectroscopy, the dyes **3** and **4** also form intramolecular hydrogen bondings to afford similar π-conjugation structures to **1**.

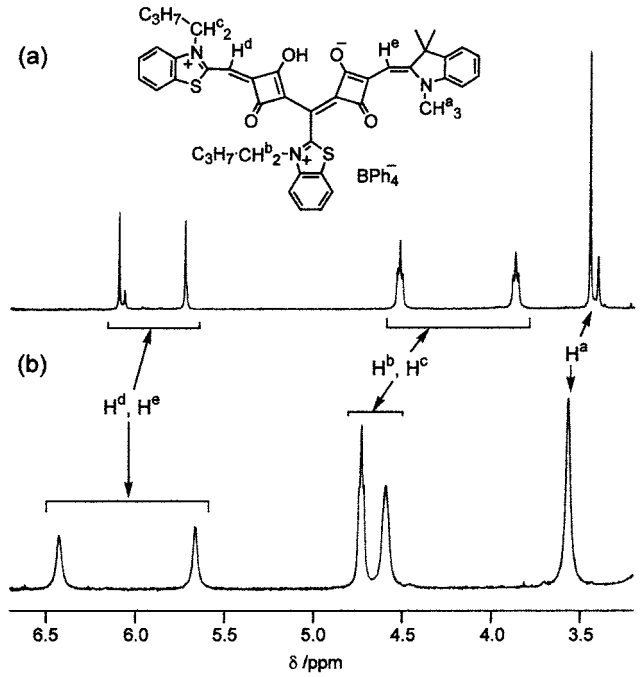


Figure 3 ^{1}H NMR spectra of **4a** (a) in $CDCl_3$ at 23 °C and (b) in DMSO-d_6 at 80 °C

The dye **1** exhibits a large absorption in the near-infrared region, and a similar light-absorbing property was observed for the dyes **3** and **4**, as summarized in the Table. As a typical example, the Vis-NIR spectrum of **4c** is shown in Figure 4, with the reference spectrum of **1**. The values of λ_{max} of the bisquarylium dyes vary from 771 to 815 nm, and the molar absorption coefficient for each dye is $>1 \times 10^5$ mol^{-1} dm^3 cm^{-1}. The λ_{max} and ε are similar to those of **1**, indicating the formation of the cationic SQ homologues. Considering that in the X-ray structure of **1** the benzothiazolium component attached to the methine carbon between two cyclobutene moieties deviates from the π-conjugation plane of the bisquarylium skeleton, the electronic properties of the cationic dyes **3** and **4** are mainly determined by the large π-conjugation system consisting of two unsymmetrically introduced electron-donating components across two cyclobutenes.

Table Absorption Spectral Data[a] of the Bisquarylium Dyes **3** and **4**

Compound	λ_{max} (nm)	ε/mol^{-1} dm^3 cm^{-1}
3a	771	1.04×10^5
3b	815	1.34×10^5
4a	792	2.52×10^5
4b	797	3.05×10^5
4c	812	2.69×10^5

[a] In $CHCl_3$ at 20 °C.

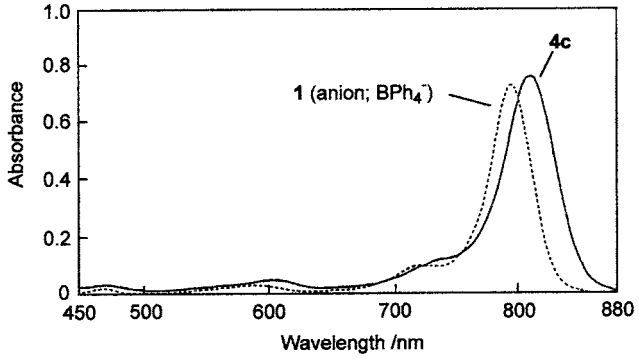


Figure 4 Vis-NIR absorption spectra of **4c** (solid line) and **1** (dashed line) in $CHCl_3$: **4c** = 2.82×10^{-6} M; **1** = 2.06×10^{-6} M

In summary, we have found that the benzothiazolinosquarylium dye **2** reacts with 3-hydroxy and 3-ethoxycyclobut-3-ene-1,2-diones bearing aromatic and heterocyclic substituents at the 4-positions, respectively, to afford novel cationic SQ homologues, namely, bisquarylium dyes. These dyes exhibit large light-absorptions in the near-infrared region. The properties of the dyes varied from the aromatic/heterocyclic components introduced in the π-conjugation systems. Although SQ dyes and their related compounds possess complicated electronic structures and it is not so easy to expect their reaction with various reagents, the present study shows the possibility of preparation of other novel SQ derivatives and, furthermore, should contribute to more understanding of their chemical properties.

^{1}H NMR spectra were obtained on a JEOL JNM-GX 270 FT-NMR (270 MHz) or a JEOL α-500 FT-NMR (500 MHz) spectrometer, and the chemical shifts are reported in ppm downfield from an internal TMS reference. Vis-NIR spectra were obtained on a Shimadzu UV-3100 spectrometer. IR spectra were recorded on a Horiba

FT-200 spectrometer using KBr pellets. EI mass spectra were obtained on a Shimadzu QP-5000 mass spectrometer. FAB mass spectra were obtained on a Finnigan MAT TSQ-70 mass spectrometer, using 3-nitrobenzyl alcohol as a matrix. Elemental analyses were recorded on a Yanaco CHN-CORDER MT3 recorder.

The preparation of **5b** was reported previously,[9] and **5a** was also prepared in a similar manner to 4-[4-(dibutylamino)phenyl]-3-hydroxy-1,2-dioxocyclobut-3-ene.[9]

4-[4-(Diethylamino)phenyl]-3-hydroxy-1,2-dioxocyclobut-3-ene (5a)

The compound **5a** was obtained from of 4-[4-(diethylamino)phenyl]-3-chlorocyclobut-3-ene-1,2-dione[11] (1.87 g, 7.09 mmol) in 86% yield; mp 220–222 °C (dec.).

IR (KBr): 1763, 1711, 1576 cm^{-1}.

^1H NMR (270 MHz, DMSO-d_6): δ = 1.13 (t, *J* = 7.0 Hz, 6 H, NCH_2CH_3), 3.45 (br, 4 H, NCH_2CH_3), 6.92 (br, 2 H, ArH), 7.89 (d, *J* = 7.3 Hz, 2 H, ArH) (1 H for the hydroxy group was not observed).

FAB MS: *m*/*z*: 246 ($[M + H]^+$).

Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.56; H, 6.16; N, 5.71. Found: C, 68.58; H, 6.22; N, 5.68.

3-Ethoxy-4-(1,3,3-trimethylindolin-2-ylidenemethyl)cyclobut-3-ene-1,2-dione (7a); Typical Procedure

To a dispersed solution of **8a** (3.02 g, 10.0 mmol) in EtOH (20 mL) was added dropwise Et_3N (1.03 g, 10.2 mmol) and an ethanolic solution (20 mL) of 3,4-diethoxycyclobut-3-ene-1,2-dione (1.71 g, 10.1 mmol). The mixture was stirred at r.t. for 2 h under N_2. The solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (CH_2Cl_2 as eluent) followed by recrystallization from benzene–hexane to afford orange crystals of **7a** (2.13 g, 72%); mp 147–148 °C.

IR (KBr): 1772, 1724 cm^{-1}.

^1H NMR (270 MHz, $CDCl_3$): δ = 1.53 (t, *J* = 7.3 Hz, 3 H), 1.63 (s, 6 H), 3.37 (s, 3 H), 4.70 (q, *J* = 7.3 Hz, 2 H), 5.36 (s, 1 H), 6.89 (d, *J* = 7.3 Hz, 1 H), 7.07 (t, *J* = 7.3 Hz, 1 H), 7.25–7.30 (m, 2 H).

EI MS: *m*/*z* (rel. int., %) = 297 (M^+, 75), 212 ($M^+ - 2CO - C_2H_5$, 100).

Anal. Calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71. Found: C, 72.84; H, 6.41; N, 4.50.

3-Ethoxy-4-(1-methylbenzothiazol-2-ylidenemethyl)cyclobut-3-ene-1,2-dione (7b)

The preparation of **7b** was carried out according to that of **7a** using **8b** (1.46 g, 5.07 mmol) and 3,4-diethoxycyclobut-3-ene-1,2-dione (0.860 g, 5.05 mmol) as starting materials. The reaction scale was adjusted to the molar amount of **8b**. The product obtained by silica gel chromatography (CH_2Cl_2 as eluent) was recrystallized from benzene to afford orange crystals of **7b** (1.01 g, 70%); mp 220–223 °C.

IR (KBr): 1765, 1693 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.52 (t, *J* = 7.3 Hz, 3 H), 3.55 (s, 3 H), 4.84 (q, *J* = 7.3 Hz, 2 H), 5.46 (s, 1 H), 7.09 (d, *J* = 7.9 Hz, 1 H), 7.17 (t, *J* = 7.9 Hz, 1 H), 7.35 (t, *J* = 7.9 Hz, 1 H), 7.30 (d, *J* = 7.9 Hz, 1 H).

EI MS: *m*/*z* (%) = 287 (M^+, 34), 202 ($M^+ - 2CO - C_2H_5$, 100).

Anal. Calcd for $C_{15}H_{13}NO_3S \cdot 0.25H_2O$: C, 61.73; H, 4.66; N, 4.80. Found: C, 61.52; H, 4.40; N, 4.52.

3-Ethoxy-4-(2*H*-dihydoro-1-methyquinolin-2-ylidenemethyl)-cyclobut-3-ene-1,2-dione (7c)

For the preparation of **7c**, compound **8c** (2.28 g, 8.10 mmol) and 3,4-diethoxycyclobut-3-ene-1,2-dione (1.36 g, 7.99 mmol) were employed, and the reaction scale was adjusted to the molar amount of **8c**. The product obtained by silica gel chromatography (CH_2Cl_2 as eluent) was recrystallized from benzene to afford reddish orange crystals of **7c** (1.68 g, 75%); mp 216–218 °C.

IR (KBr): 1762, 1686 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.51 (t, *J* = 7.3 Hz, 3 H), 3.68 (s, 3 H), 4.86 (q, *J* = 7.3 Hz, 2 H), 5.27 (s, 1 H), 7.23 (d, *J* = 7.3 Hz, 1 H), 7.34–7.37 (m, 2 H), 7.40–7.55 (m, 2 H), 8.54 (d, *J* = 9.8 Hz, 1 H).

EI MS: *m*/*z* (%) = 281 (M^+, 51), 196 ($M^+ - 2CO - C_2H_5$, 100).

Anal. Calcd for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.37; N, 4.98. Found: C, 72.94; H, 5.26; N, 4.57.

Dye 3a; Typical Procedure

Method A: A stirred solution of **2** (508 mg, 1.04 mmol) and **5a** (245 mg, 1.00 mmol) in a mixture of butan-1-ol–benzene (40 mL, 4:1, v/v) was heated in an oil bath kept at 120 °C in the presence of HI (2 equiv, supplied as hydroiodic acid) for 3 h. After cooling, EtOH (50 mL) was added to the reaction mixture, and the solution was allowed to stand for 24 h. The resulting solid was separated by filtration and purified by silica gel column chromatography (CH_2Cl_2 as eluent) to afford solid **3a** (610 mg, 72%). The dye **3b** was similarly prepared.

IR (KBr): 1747, 1602 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6, 80 °C): δ = 0.79 (t, *J* = 7.3 Hz, 3 H), 0.94 (t, *J* = 7.3 Hz, 3 H), 1.14 (t, *J* = 6.9 Hz, 6 H), 1.26 (sext, *J* = 7.3 Hz, 2 H), 1.44 (sext, *J* = 7.3 Hz, 2 H), 1.78–1.84 (m, 4 H), 3.44 (q, *J* = 6.9 Hz, 4 H), 4.74–4.69 (m, 4 H), 6.63 (s, 1 H), 6.77 (d, *J* = 8.2 Hz, 2 H), 7.60 (t, *J* = 7.8 Hz, 1 H), 7.73 (t, *J* = 7.8 Hz, 1 H), 7.81 (d, *J* = 8.2 Hz, 2 H), 7.87 (t, *J* = 7.8 Hz, 1 H), 7.96 (t, *J* = 7.8 Hz, 1 H), 8.04 (d, *J* = 7.8 Hz, 1 H), 8.20 (d, *J* = 7.8 Hz, 1 H), 8.39 (d, *J* = 7.8 Hz, 1 H), 8.47 (d, *J* = 7.8 Hz, 1 H), 18.31 (br, 1 H).

FAB MS: *m*/*z* = 716 ($[M - I]^+$).

Anal. Calcd for $C_{42}H_{42}IN_3O_4S_2 \cdot H_2O$: C, 58.53; H, 5.15; N, 4.88. Found: C, 58.72; H, 5.10; N, 4.92.

Dye 3b

Yield: 35%.

IR (KBr): 1747, 1610 cm^{-1}.

^1H NMR (DMSO-d_6, 23 °C): δ = 0.75 (t, *J* = 7.3 Hz, 3 H), 0.90 (t, *J* = 7.3 Hz, 3 H), 1.22 (m, 2 H), 1.41 (m, 2 H), 1.75 (m, 4 H), 1.84 (m, 4 H), 2.65 (m, 4 H), 3.37 (m, 4 H), 4.70 (m, 2 H), 4.77 (m, 2 H), 6.68 (s, 1 H), 7.35–8.60 (m, 10 H) (the broad signal assigned to OH is at ca. 18.5–19.0 ppm).

FAB MS: *m*/*z* = 740 ($[M - I]^+$).

Anal. Calcd for $C_{44}H_{42}IN_3O_4S_2 \cdot H_2O$: C, 59.66; H, 5.01; N, 4.74. Found: C, 59.73; H, 4.98; N, 4.78.

Dye 4a; Typical Procedure

Method B: A butan-1-ol solution (40 mL) of **7a** (0.297 g, 1.00 mmol) containing H_2SO_4 (4 mmol) was heated at 120 °C for 2 h. To the mixture was added **2** (977 mg, 2.00 mmol) in a single portion, and the mixture was stirred at the same temperature for 6 h. After cooling, the solvent was removed by distillation at reduced pressure, and the residue was washed with a small amount of H_2O. The crude product was purified by silica gel column chromatography (CH_2Cl_2–MeOH, 15:1, v/v, as eluent), and recrystallized from EtOH–hexane. The crystals were dissolved in CH_2Cl_2 (10 mL), and to the solution was added dropwise a MeOH solution (4 mL) of sodium tetraphenylborate (102 mg, 0.298 mmol). The mixture was

stirred at 60 °C for 1 h. After cooling, the solvent was removed by evaporation, and the residue was washed with a small amount of H_2O and recrystallized from CH_2Cl_2–hexane to afford crystals of **4a** (126 mg, 12%). The dyes **4b** and **4c** were similarly prepared.

IR (KBr): 1749, 1558 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6, 80 °C): δ = 0.76 (t, *J* = 7.3 Hz, 3 H), 0.94 (t, *J* = 7.3 Hz, 3 H), 1.22 (sext, *J* = 7.3 Hz, 2 H), 1.44 (sext, *J* = 7.3 Hz, 2 H), 1.60 (s, 6 H), 1.76–1.82 (m, 4 H), 3.57 (s, 3 H), 4.59 (br, 2 H), 4.73 (m, 2 H), 5.66 (s, 1 H), 6.43 (s, 1 H), 6.77 (t, *J* = 7.3 Hz, 4 H), 6.91 (t, *J* = 7.3 Hz, 8 H), 7.16–7.21 (m, 9 H), 7.29 (br, 1 H), 7.35 (t, *J* = 7.8 Hz, 1 H), 7.45 (d, *J* = 7.8 Hz, 1 H), 7.53 (br, 1 H), 7.66 (t, *J* = 7.8 Hz, 1 H), 7.87 (t, *J* = 7.8 Hz, 1 H), 7.92 (d, *J* = 7.8 Hz, 1 H), 7.96 (t, *J* = 7.8 Hz, 1 H), 8.11 (br, 1 H), 8.41 (d, *J* = 7.8 Hz, 1 H), 8.48 (d, *J* = 7.8 Hz, 1 H), 18.67 (br, 1 H).

FAB MS: *m*/*z* = 740 ($[M – BPh_4]^+$).

Anal. Calcd for $C_{68}H_{62}BN_3O_4S_2$: C, 77.04; H, 5.89; N, 3.96. Found: C, 76.60; H, 5.76; N, 3.98.

Dye 4b
Yield: 10%.

IR (KBr): 1743, 1579 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6, 80 °C): δ = 0.77 (t, *J* = 7.3 Hz, 3 H), 0.95 (t, *J* = 7.3 Hz, 3 H), 1.20 (sext, *J* = 7.3 Hz, 2 H), 1.44 (sext, *J* = 7.3 Hz, 2 H), 1.73–1.79 (m, 4 H), 3.92 (s, 3 H), 4.44 (m, 2 H), 4.69 (m, 2 H), 6.15 (m, 2 H), 6.77 (t, *J* = 7.3 Hz, 4 H), 6.90 (t, *J* = 7.3 Hz, 8 H), 7.19 (m, 8 H), 7.38–7.47 (m, 2 H), 7.54–7.58 (m, 2 H), 7.74–7.82 (m, 3 H), 7.91 (br, 1 H), 7.96–98 (m, 2 H), 8.33 (br, 1 H), 8.42 (br, 1 H), 18.56 (br, 1 H).

FAB MS: *m*/*z* = 731 ($[M + H – BPh_4]^+$).

Anal. Calcd for $C_{65}H_{56}BN_3O_4S_3 \cdot 0.5H_2O$: C, 73.71; H, 5.42; N, 3.97. Found: C, 73.46; H, 5.24; N, 4.00.

Dye 4c
Yield: 17%.

IR (KBr): 1749, 1633 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6, 80 °C): δ = 0.77 (t, *J* = 7.3 Hz, 3 H), 0.93 (t, *J* = 7.3 Hz, 3 H), 1.22 (sext, *J* = 7.3 Hz, 2 H), 1.42 (sext, *J* = 7.3 Hz, 2 H), 1.69–1.79 (m, 4 H), 3.32 (s, 3 H), 4.33 (br, 2 H), 4.71 (br, 2 H), 6.00 (s, 1 H), 6.08 (s, 1 H), 6.77 (t, *J* = 7.3 Hz, 4 H), 6.91 (t, *J* = 7.3 Hz, 8 H), 7.18–7.21 (m, 8 H), 7.33–7.62 (m, 4 H), 7.78–7.87 (m, 4 H), 7.94 (t, *J* = 7.8 Hz, 1 H), 8.00 (br, 1 H), 8.15 (br, 1 H), 8.35–8.37 (m, 1 H), 8.45 (d, *J* = 7.8 Hz, 1 H), 8.85 (br, 1 H), 18.67 (br, 1 H).

FAB MS: *m*/*z* = 724 ($[M – BPh_4]^+$).

Anal. Calcd for $C_{67}H_{58}BN_3O_4S_2$: C, 77.07; H, 5.60; N, 4.02. Found: C, 76.71; H, 5.62; N, 3.88.

X-Ray Crystallographic Analysis of 7a
Formula: $C_{18}H_{19}NO_3$, molecular weight: 297.35, crystal system: triclinic, space group: $P\bar{1}$, cell constants: *a* = 9.508(2) Å, *b* = 11.657(1) Å, *c* = 7.3640(6) Å, α = 97.091(8)°, β = 101.29(1)°, γ = 82.01(1)°, volume: 788.7(2) $Å^3$, *Z* = 2, d_{calcd} = 1.252 g cm^{-3}, unique reflections: 1694 ($I > 5.00\sigma(I)$), final *R* = 0.048, R_W = 0.083.

Selected bond lengths (Å): N1–C6, 1.362(7); N1–C13, 1.406(7); O1–C1, 1.207(7); O2–C2, 1.211(7), O3–C3, 1.317(7); C1–C2, 1.529(9); C1–C4, 1.496(8); C2–C3, 1.461(8); C3–C4, 1.391(8); C4–C5, 1.411(7); C5–C6, 1.369(8); C6–C7, 1.532(7); C7–C8, 1.513(8); C8–C9, 1.376(8); C8–C13, 1.385(8); C9–C10, 1.390(9); C10–C11, 1.370(9); C11–C12, 1.385(8); C12–C13, 1.381(8).

Selected bond angles (°): C6–N1–C13, 111.7(4); C6–N1–C16, 125.0(5); C13–N1–C16, 123.1(5); O1–C1–C2, 134.2(6); O1–C1–C4, 137.0(6); C2–C1–C4, 88.8(5); O2–C2–C1, 136.3(6); O2–C2–C3, 137.9(6); C1–C2–C3, 85.8(5); O3–C3–C2, 136.4(5); O3–C3–C4, 127.8(5); C2–C3–C4, 95.8(5); C1–C4–C3, 89.6(5); C1–C4–C5, 144.2(5); C3–C4–C5, 126.1(5); C4–C5–C6, 131.7 (5); N1–C6–C5, 120.8(5); N1–C6–C7, 108.3(4); C5–C6–C7, 130.8(5).

A single crystal of **7a** suitable for X-ray crystallographic analysis was obtained by slow evaporation of a saturated solution of **7a** in benzene. All reflection data were collected on a Rigaku AFC5-R diffractometer using graphite monochromated Mo-K_α radiation. Intensity data were collected in the range of $3 < 2\theta < 55°$ by using the ω-2θ scan technique. The structure was solved by a direct method and refined by a full-matrix least-squares procedure. All non-hydrogen atoms were refined with anisotropic thermal parameters. In all calculations, the TEXSAN program was used.

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