PERKIN 1

Synthesis of novel unsymmetrical squarylium dyes absorbing in the near-infrared region †

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Novel unsymmetrical squarylium dyes which absorb in the near-infrared region were synthesized by a stepwise procedure *via* intermediate 4-substituted 3-hydroxycyclobut-3-ene-1,2-diones. By introducing benz[*c*,*d*]indoline or benzo[*b*]pyran moieties at one end as an electron-donating component, the SQ dyes exhibited their absorption maxima at 739–821 nm with large molar absorption coefficients (log ε = 4.96–5.18) in $CHCl_3$. The X-ray analysis for one of these dyes was also examined to confirm the overall structure of the unsymmetrical SQ dye.

Introduction

Organic near-infrared absorbing dyes (NIR dyes) have been widely investigated in terms of the requirement for optical recording using a Ga–Al–As diode laser (oscillator wavelength; 780–830 nm).[1] Cyanine dyes have attracted much attention because of their advantage of large absorption of light, and a synthetic procedure has been already established. However, they also have disadvantages of formation of dye aggregates, less stability upon exposure to the light, and so on. Thus, it is necessary to develop new molecular skeletons of NIR dyes which have the potential to overcome these problems.

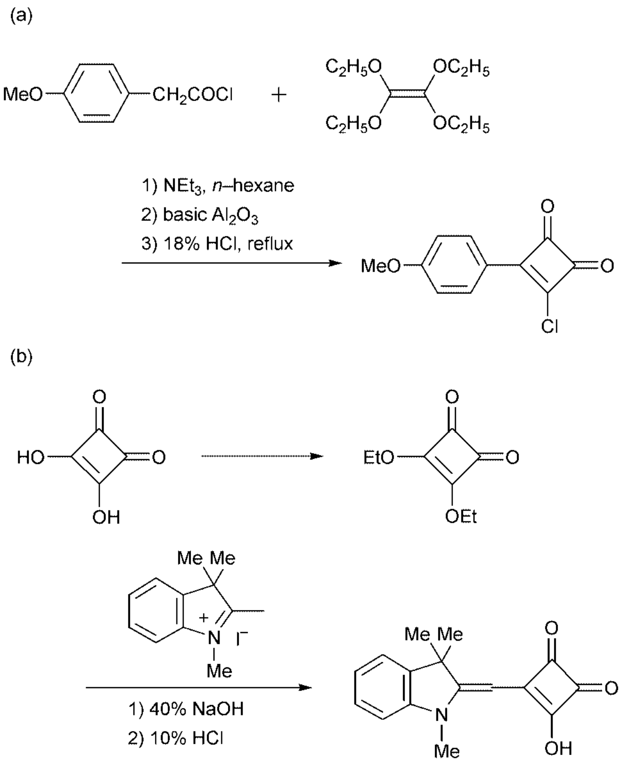
Squarylium (SQ) dye is a 1,3-disubstituted product yielded by condensation of squaric acid (3,4-dihydroxy-1,2-dioxocyclobut-3-ene) with two aromatic or heterocyclic compounds, and belongs to a class of polymethyne dyes such as cyanine dyes. It exhibits an effective light absorption ($\varepsilon > 10^5$ dm^3 mol^{-1} cm^{-1}) and is resistant to photodegradation. Thus, SQ dyes are very attractive for photonics applications such as photoconductors in xerographic devices[2] and organic solar cells[3] as well as optical recording media. The traditional synthesis of SQ dyes, however, affords symmetrical products,[4] and the variation of types of π-conjugation systems is limited. There have been reported only a few examples of NIR SQ dyes, which are limited to symmetrical SQ dyes and their related compounds.[5]

Previously, Law and Bailey reported a stepwise synthesis of unsymmetrical SQ dyes, where the intermediate, 4-aryl-3-hydroxycyclobutene-1,2-dione, was synthesized followed by condensation with another electron-donating aromatic unit.[6] Terpetschnig and Lakowicz also synthesized unsymmetrical SQ dyes by a different method from Law's.[7] To the best of our knowledge, however, no unsymmetrical NIR SQ dyes have so far been reported.

Here we report the stepwise synthesis of a series of novel unsymmetrical SQ dyes absorbing in the NIR region, by using strongly electron-donating heterocyclic components at one end. The X-ray structure for one of these dyes is also reported.

Results and discussion

Two independent methods for preparing 4-substituted 3-hydroxycyclobut-3-ene-1,2-diones as dye precursors have so far been reported: one is Law's method, a [2 + 2] cycloaddition reaction between arylketenes and tetraethoxyethylene followed by treatment with basic alumina and subsequent acid hydrolysis (Scheme 1, a),[6] and the other is Terpetschnig's method, the reaction of aromatic or heterocyclic compounds with 3,4-diethoxycyclobut-3-ene-1,2-dione followed by acid hydrolysis (Scheme 1, b).[7] We obtained dye precursors **6** and **7** by using different starting materials. The preparation of compounds **6** and **7** is described in Scheme 2. 3,4-Dichlorocyclobut-3-ene-1,2-dione **3**[8] reacted with compounds **1** and **2** under mild conditions (in CH_2Cl_2, rt) to afford intermediates **4** and **5**, respectively. The subsequent acid hydrolysis yielded dye precursors **6** and **7**. Compounds **6a** and **6b** were normally purified by silica gel



Scheme 1 Two synthetic procedures so far reported for preparation of precursors of unsymmetrical SQ dyes. (a) Law's method, and (b) Terpetschnig's method.

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† ^1H NMR data and elemental analyses for compounds **8a** and **8b** are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p1/a9/a907335c/

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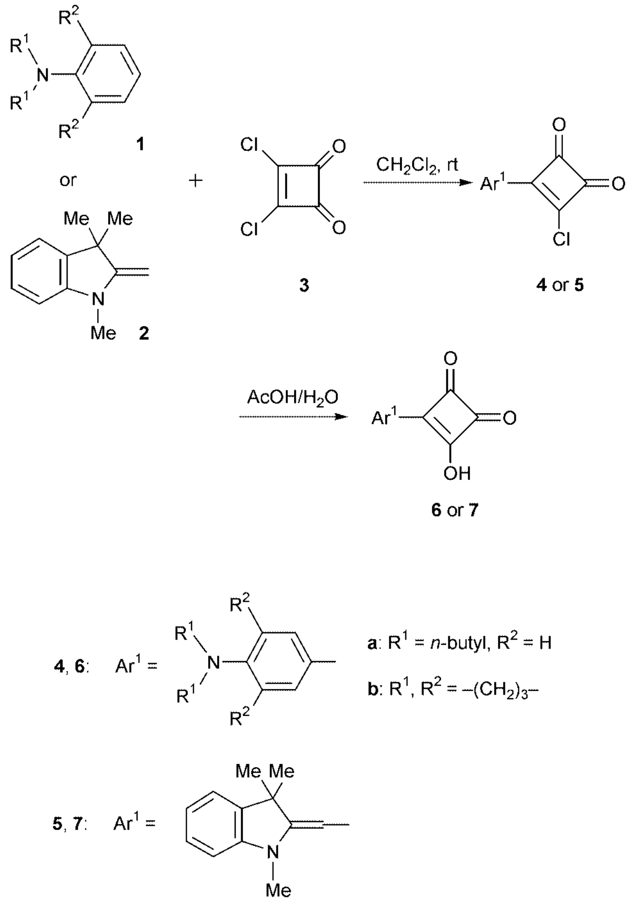
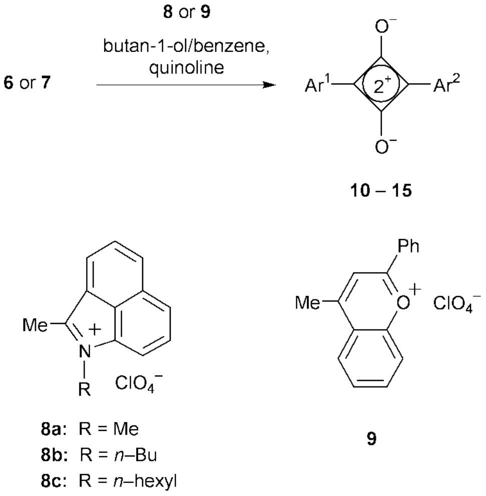


Scheme 2

column chromatography, whereas compound **7** could not be isolated by the same procedure. Purification by reversed-phase column chromatography (octadecyl silicate) enabled compound **7** to be isolated in a pure form. All these intermediates showed two intense peaks of C=O stretchings in their IR spectra at 1763–1774 cm^{-1} and 1675–1716 cm^{-1}, which are characteristic for 4-substituted 3-hydroxycyclobut-3-ene-1,2-diones.[6]



Scheme 3

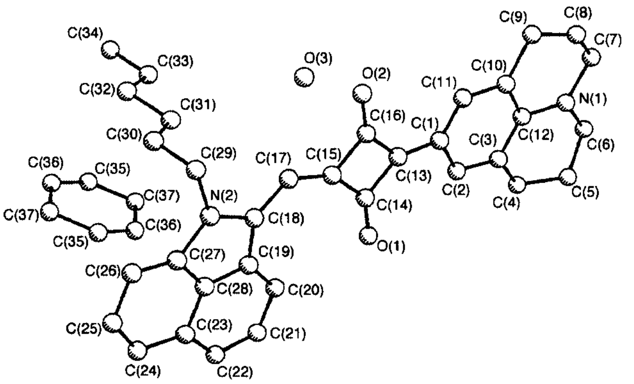


Fig. 1 The PLUTO drawing of **12**. All hydrogen atoms are neglected for clarity.

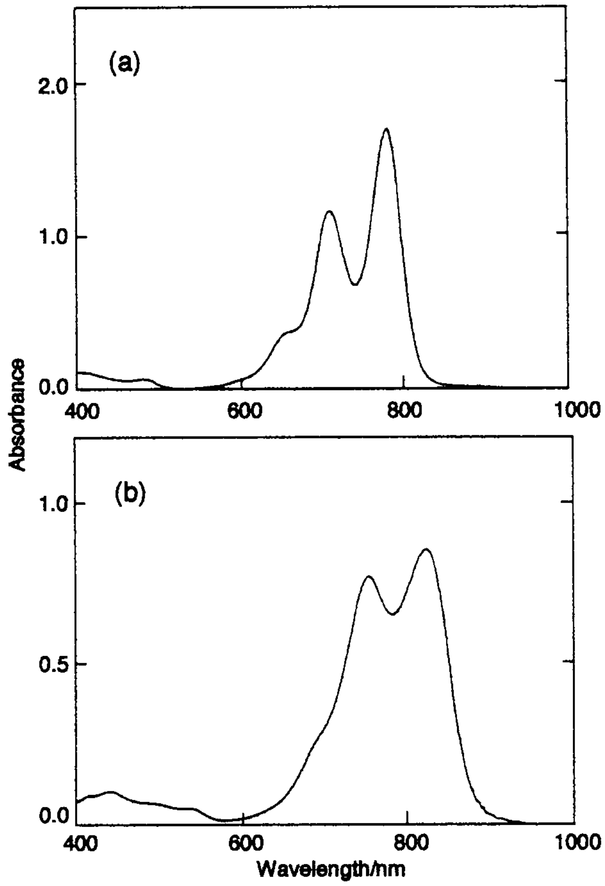
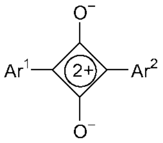


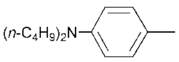
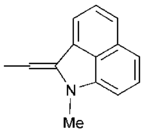
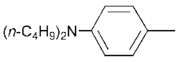
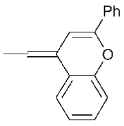
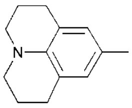
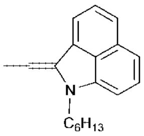
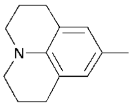
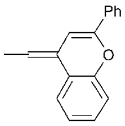
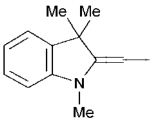
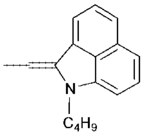
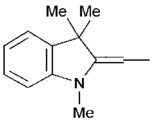
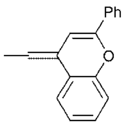
Fig. 2 The UV-vis absorption spectra of (a) **11** and (b) **12** in $CHCl_3$ at 20 °C. The concentrations are 1.7×10^{-5} and 9.4×10^{-6} M, respectively.

The condensation of dye precursors **6** and **7** with various heterocyclic compounds was carried out under azeotropic conditions in a mixed solvent of butan-1-ol and benzene (4 : 1, v/v) containing a small amount of quinoline. The reactions employing *N*-alkylbenz[*c*,*d*]indolium **8** and 4-methyl-2-phenyl-1-benzopyrylium **9** were examined to afford unsymmetrical SQ dyes **10**–**15** in 19–73% yields (Scheme 3). Isolation and purification could be achieved in the usual manner: silica gel column chromatography followed by recrystallization. These dyes, except dye **13**, were characterized by ^{1}H NMR, IR and UV–vis spectra and elemental analyses. Dye **13** exhibited low solubility, and so the structure was confirmed by IR and UV–vis spectra and elemental analysis. The yield and UV–vis spectral data for each dye are shown in Table 1. The X-ray crystallographic analysis for dye **12** was also examined to confirm the structural character of the unsymmetrical SQ dye. The PLUTO drawing is shown in Fig. 1. Two molecules of **12** in the unit cell contain one molecule of benzene and two molecules of water.

The unsymmetrical SQ dyes prepared here possess their absorption maxima in the NIR region (739–821 nm), although unsymmetrical SQ dyes so far reported have exhibited their absorption in the visible region ($\lambda_{max} < 700$ nm).[6,7] Representative absorption spectra are shown for dyes **11** and **12** in Fig. 2. Typical symmetrical SQ dyes have large molar absorption co-

Table 1 Structures, yields, and UV–vis spectral data for unsymmetrical SQ dyes **10**–**15**

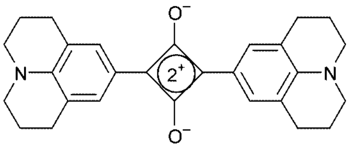


Compd.	Reactants	Ar¹	Ar²	Yield (%)	λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1})[a]
10	**6a** and **8a**			58	729 (4.92) 794 (5.03)
11	**6a** and **9**			20	712 (4.99) 782 (5.18)
12	**6b** and **8c**			71	751 (4.92) 821 (4.96)
13	**6b** and **9**			19	725 (5.01) 800 (5.10)
14	**7** and **8b**			55	720 (4.97) 774 (5.00)
15	**7** and **9**			73	682 (5.02) 739 (4.98)

[a] In $CHCl_3$ at 293 K.

efficients ($\varepsilon > 10^5$ dm^3 mol^{-1} cm^{-1}) with narrow half widths.[9] On the other hand, in the spectra of dyes **11** and **12**, two absorption maxima were observed, and the shapes of the spectra were broad compared to those of symmetrical SQ dyes. A similar tendency was observed in the spectra of dyes **10** and **13**–**15**. These spectral features seem to be characteristic for unsymmetrical SQ dyes in which the electron-donating ability of the one aromatic moiety is very different from that of the other.

Although one might be afraid that the two absorption maxima originate from a mixture of two symmetrical SQ dyes derived from two couplers (in the case of dye **12**, julolidine **1b** and benzindolium **8c**), through coupler exchanges, this possibility can be excluded by the following experimental evidence: the absorption maxima of dyes **16** and **17** in $CHCl_3$ are at 660 nm and 881 nm, respectively, both of which differ from any absorption peaks of **12** described in Table 1. Furthermore, dye **12** possesses a different R_f value on silica gel thin-layer chromatography (benzene–acetone, 5 : 1, v/v, as eluent) from those of dyes **16** and **17** (0.48, 0.32 and 0.65 for **12**, **16** and **17**, respectively), and only one spot on the TLC plate for dye **12** indicated that the isolated dye **12** was a single product. For the other unsymmetrical dyes, overlap of the original spectra and those of coupler-derived SQ dyes was not found and similar results were obtained in the TLC study. Thus, it was confirmed that the two absorption maxima of unsymmetrical SQ dyes prepared here were genuine.



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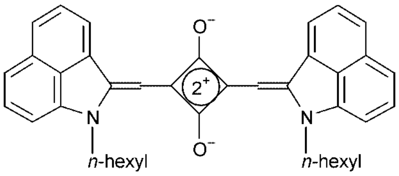

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Conclusion

In conclusion, we achieved the synthesis of novel NIR dyes containing an unsymmetrical squarylium skeleton. The key essence is to introduce heterocyclic components possessing large π-conjugation systems and strong electron-donating properties. The unsymmetrical structure was revealed by the X-ray crystallographic analysis for dye **12**, and this is the first example of a crystal structure analysis of NIR SQ dyes. The results obtained here should stimulate development of synthesis of SQ dyes, aiming at application to optics devices.

Experimental

^{1}H NMR spectra (270 MHz) were recorded on a JEOL JNM-GX 270 spectrometer in $CDCl_3$ and DMSO-d_6 using TMS (0 ppm) and CHD_2SOCD_3 (2.49 ppm) as internal standards, respectively. IR spectra were taken for KBr disks of samples and recorded on a HORIBA FT-200 spectrometer. Mass spectra were obtained by EI and FAB techniques on a Finnigan MAT MS spectrometer. For the FAB-mass spectroscopic measurement, 3-nitrobenzyl alcohol was used as a matrix. Melting points were determined by differential thermal analyses with a RIGAKU TAS 100 analyzer under nitrogen atmosphere (flow rate: 100 mL min^{-1}) using Al_2O_3 as a reference. The temperature-raising rate programmed was 10 °C min^{-1}.

Benzindolium **8** was obtained by the reported procedure.[10] ^{1}H NMR data and elemental analyses for **8a** and **8b** are available as supplementary materials. Benzopyrylium **9** was prepared according to the reported procedure.[11] Dyes **16**[12] and **17**[5d] were obtained by the usual procedure[4] from julolidine (2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline) and benzindolium **8c**, respectively.

4-(*N*,*N*-Dibutylaminophenyl)-3-chlorocyclobut-3-ene-1,2-dione 4a

A mixture of **1a** (2.05 g, 9.98 mmol) and **3** (2.26 g, 15.0 mmol) in CH_2Cl_2 (20 mL) was stirred for 24 h at ambient temperature. The solvent was removed by a rotary evaporator, and the residue was purified by silica gel column chromatography (benzene as eluent) to afford **4a** as a yellow solid; yield, 22%; mp 80 °C; ^{1}H NMR ($CDCl_3$) δ 0.98 (t, $J = 7.3$ Hz, 6H), 1.39 (sextet, $J = 7.3$ Hz, 4H), 1.63 (quintet, $J = 7.3$ Hz, 4H), 3.40 (t, $J = 7.3$ Hz, 4H), 6.76 (d, $J = 9.2$ Hz, 2H), 8.13 (d, $J = 9.2$ Hz, 2H); IR (KBr) 1795, 1759 cm^{-1} (C=O); EI-MS *m*/*z* 319 (M$^+$, 100%), 321 (M$^+$ + 2, 26%); Anal. Calcd for $C_{18}H_{22}NO_2Cl$: C, 67.60; H, 6.93; N, 4.38%. Found: C, 67.79; H, 7.00; N, 4.45%.

4-(2,3,6,7-Tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-yl)-3-chlorocyclobut-3-ene-1,2-dione 4b

A mixture of **1b** (1.73 g, 9.98 mmol) and **3** (1.81 g, 12.0 mmol) in CH_2Cl_2 (20 mL) was stirred for 24 h at ambient temperature. The solvent was removed by a rotary evaporator, and the residue was purified by silica gel column chromatography (CH_2Cl_2 as eluent) followed by recrystallization from $CHCl_3$ to afford **4b** as an orange solid; yield, 39%; mp 208 °C (decomp.); ^{1}H NMR ($CDCl_3$) δ 1.98 (quintet, $J = 6.1$ Hz, 4H), 2.77 (t, $J = 6.1$ Hz, 4H), 3.37 (t, $J = 6.1$ Hz, 4H), 7.69 (s, 2H); IR (KBr) 1774, 1749 cm^{-1} (C=O); EI-MS *m*/*z* 231 ([M − 2CO]$^+$, 100%), 233 ([M − 2CO]$^+$ + 2, 31%), 287 (M$^+$, 30%), 289 (M$^+$ + 2, 9.7%); Anal. Calcd for $C_{16}H_{14}NO_2Cl$: C, 66.79; H, 4.90; N, 4.87%. Found: C, 66.30; H, 4.61; N, 5.22%.

4-(1,3,3-Trimethylindolin-2-ylidenemethyl)-3-chlorocyclobut-3-ene-1,2-dione 5

To a stirred solution of **3** (3.04 g, 20.2 mmol) in benzene was added dropwise a solution of 1,3,3-trimethyl-2-methyleneindoline (3.46 g, 20.0 mmol). The reaction mixture was stirred for 20 min at ambient temperature. An orange precipitate was formed, which was separated by filtration. Purification by silica gel column chromatography (dichloromethane as eluent) followed by recrystallization from $CHCl_3$ afforded **5** as an orange solid; yield, 47%; mp 239 °C (decomp.); ^{1}H NMR ($CDCl_3$) δ 1.65 (s, 6H), 3.52 (s, 3H), 5.53 (s, 1H), 7.03 (d, $J = 7.3$ Hz, 1H), 7.18 (t, $J = 7.3$ Hz, 1H), 7.35 (m, 2H); IR (KBr) 1764, 1726 cm^{-1} (C=O); EI-MS *m*/*z* 231 ([M − 2CO − CH$_3$]$^+$, 100%), 233 ([M − 2CO − CH$_3$]$^+$ + 2, 33%), 231 ([M − 2CO]$^+$, 70%), 233 ([M − 2CO]$^+$ + 2, 24%), 287 (M$^+$, 28%), 289 (M$^+$ + 2, 11%); Anal. Calcd for $C_{16}H_{14}NO_2Cl$: C, 66.79; H, 4.90; N, 4.87. Found: C, 66.98; H, 4.74; N, 4.96%.

4-(*N*,*N*-Dibutylaminophenyl)-3-hydroxycyclobut-3-ene-1,2-dione 6a

A solution of **4a** (704 mg, 2.2 mmol) in AcOH–water (4 : 1, v/v, 9 mL) was stirred at reflux for 4 h. After cooling, the precipitate was separated by filtration, and stirred in ether–hexane (1 : 1, v/v, 20 mL) for 30 min. Filtration afforded **6a** as a yellow solid; yield, 83%; mp 253 °C (decomp.); ^{1}H NMR (DMSO-d_6) δ 0.90 (t, $J = 7.3$ Hz, 6H), 1.31 (sextet, $J = 7.3$ Hz, 4H), 1.48 (m, 4H), 3.40 (m, 4H), 6.85 (d, $J = 7.9$ Hz, 2H), 7.32 (d, $J = 7.9$ Hz, 2H) (the OH proton was not observed); IR (KBr) 1763, 1716 cm^{-1} (C=O); FAB-MS *m*/*z* 302 ([M + H]$^+$); Anal. Calcd for $C_{18}H_{23}NO_3 \cdot 0.5H_2O$: C, 69.65; H, 7.79; N, 4.51. Found: C, 70.45; H, 7.73; N, 4.48%.

4-(2,3,6,7-Tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-yl)-3-hydroxycyclobut-3-ene-1,2-dione 6b

A solution of **4b** (905 mg, 3.4 mmol) in AcOH–water (4 : 1, v/v, 30 mL) was stirred at reflux for 4 h. After cooling, the precipitate was separated by filtration, and stirred in ether (100 mL) for 30 min. Filtration afforded **6b** as a yellow solid; yield, 81%; mp 248 °C (decomp.); ^{1}H NMR (DMSO-d_6) δ 1.86 (quintet, $J = 6.1$ Hz, 4H), 2.69 (t, $J = 6.1$ Hz, 4H), 3.26 (t, $J = 6.1$ Hz, 4H), 7.40 (s, 2H) (the OH proton was not observed); IR (KBr) 1763, 1716 cm^{-1} (C=O); EI-MS *m*/*z* 213 ([M − 2CO]$^+$, 100%), 269 (M$^+$, 61%); Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.07; H, 5.43; N, 4.93%.

4-(1,3,3-Trimethylindolin-2-ylidenemethyl)-3-hydroxycyclobut-3-ene-1,2-dione 7

A solution of **5** (2.23 g, 7.75 mmol) in AcOH–water (4 : 1, v/v, 22 mL) was stirred at reflux for 5 h. After cooling, the precipitate was separated by filtration. Purification by ODS column chromatography (Nakalai Tesque, inc., Cosmosil 75C$_{18}$-OPN, MeOH–water (2 : 1, v/v) as eluent) followed by recrystallization from CH_2Cl_2 afforded **7** as a yellow solid; yield, 37%; mp 205 °C (decomp.); ^{1}H NMR ($CDCl_3$) δ 1.55 (s, 6H), 3.34 (s, 3H), 5.45 (s, 1H), 7.01 (d, $J = 7.3$ Hz, 1H), 7.11 (t, $J = 7.3$ Hz, 1H), 7.25 (t, $J = 7.3$ Hz, 1H), 7.38 (t, $J = 7.3$ Hz, 1H) (the OH proton was not observed); IR (KBr) 1764, 1726 cm^{-1} (C=O); EI-MS *m*/*z* 198 ([M − 2CO − CH$_3$]$^+$, 100%), 269 (M$^+$, 28%); Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.43; H, 5.55; N, 5.19%.

General procedure for unsymmetrical SQ dyes: preparation of 10

A mixture of **6a** (151 mg, 0.501 mmol), **8a** (141 mg, 0.501 mmol) and quinoline (84 mg, 0.65 mmol) in butan-1-ol–benzene (4 : 1, v/v, 20 mL) was heated at reflux for 4 h with removal of water by using a Dean–Stark distillation apparatus. After cooling, the solvent was removed by a rotary evaporator, and the residue was purified by silica gel column chromatography (CH_2Cl_2–methanol, 30 : 1, as eluent). Recrystallization from benzene afforded a crystal of **10**.

Compound 10. Yield 58%; mp 199 °C (decomp.); ^{1}H NMR ($CDCl_3$) δ 0.98 (t, $J = 7.3$ Hz, 6H), 1.39 (sextet, $J = 7.3$ Hz, 4H), 1.64 (quintet, $J = 7.3$ Hz, 4H), 3.41 (t, $J = 7.3$ Hz, 4H), 3.78 (s, 3H), 6.33 (s, 1H), 6.71 (d, $J = 9.2$ Hz, 2H), 7.14 (d, $J = 7.9$ Hz, 1H), 7.50 (t, $J = 7.9$ Hz, 1H), 7.61 (d, $J = 7.9$ Hz, 1H), 7.85 (t, $J = 7.9$ Hz, 1H), 7.98 (d, $J = 7.9$ Hz, 1H), 8.29 (d, $J = 9.2$ Hz, 2H), 9.36 (br s, 1H); IR (KBr) 1605, 1583 cm^{-1} (C=O); FAB-MS *m*/*z* 464 (M$^+$); Anal. Calcd for $C_{31}H_{32}N_2O_2$: C, 80.14; H, 6.94; N, 6.03%. Found: C, 80.16; H, 6.98; N, 5.89%.

Compound 11. Benzene–acetone (7 : 1, v/v) was used as eluent for silica gel column chromatography. Further purification was carried out by recrystallization from benzene–hexane; yield 20%; mp 197 °C (decomp.); ^{1}H NMR (CDCl$_3$) δ 0.99 (t, $J = 7.3$ Hz, 6H), 1.40 (sextet, $J = 7.3$ Hz, 4H), 1.60–1.71 (m, 4H), 3.44 (t, $J = 7.3$ Hz, 4H), 6.74 (d, $J = 8.5$ Hz, 2H), 6.92 (s, 1H), 7.40 (dt, $J = 1.2$ and 7.9 Hz, 1H), 7.48–7.65 (m, 5H), 8.12 (dd, $J = 1.2$ and 7.9 Hz, 1H), 8.21–8.24 (m, 2H), 8.36 (d, $J = 8.5$ Hz, 2H), 9.58 (s, 1H); IR (KBr) 1622, 1595 cm^{-1} (C=O); FAB-MS *m*/*z* 503 (M$^+$); Anal. Calcd for $C_{34}H_{33}NO_3$: C, 81.08; H, 6.60; N, 2.78%. Found: C, 81.36; H, 6.45; N, 2.87%.

Compound 12. Benzene–acetone (5 : 1, v/v) was used as eluent for silica gel column chromatography. Further purification was carried out by recrystallization from benzene; yield 71%; mp 181 °C (decomp.); ^{1}H NMR (CDCl$_3$) δ 0.88 (t, $J = 7.3$ Hz, 3H), 1.25–1.48 (m, 6H), 1.87 (quintet, $J = 7.3$ Hz, 2H), 1.98 (quintet, $J = 6.1$ Hz, 4H), 2.80 (t, $J = 6.1$ Hz, 4H), 3.38 (t, $J = 6.1$ Hz, 4H), 4.20 (t, $J = 7.3$ Hz, 2H), 6.36 (s, 1H), 7.10 (d, $J = 7.9$ Hz, 1H), 7.50 (t, $J = 7.9$ Hz, 1H), 7.60 (d, $J = 7.9$ Hz, 1H), 7.86 (t, $J = 7.9$ Hz, 1H), 7.94 (s, 2H), 7.97 (d, $J = 7.9$ Hz, 1H), 9.26 (br s, 1H); IR (KBr) 1595, 1581 cm^{-1} (C=O); FAB-MS *m*/*z* 502 (M$^+$); Anal. Calcd for $C_{34}H_{34}N_2O_2$: C, 81.24; H, 6.82; N, 5.57%. Found: C, 81.62; H, 6.77; N, 5.24% (the elemental analysis was carried out after the sample had been thoroughly dried *in vacuo*).

Compound 13. This compound was purified by washing with DMF followed by ether, due to low solubility. The ^{1}H NMR spectrum could not be obtained; yield 19%; mp 246 °C (decomp.); IR (KBr), 1614, 1597 cm^{-1} (C=O); FAB-MS *m*/*z* 471 (M$^+$); Anal. Calcd for $C_{32}H_{25}NO_3$: C, 81.51; H, 5.34; N, 2.97%. Found: C, 81.13; H, 5.16; N, 2.92%.

Compound 14. CH_2Cl_2–AcOEt (5 : 1, v/v) was used as eluent for silica gel column chromatography. Further purification was carried out by recrystallization from CH_2Cl_2–hexane; yield 55%; mp 196 °C (decomp.); ^{1}H NMR (CDCl$_3$) δ 0.99 (t, $J = 7.3$ Hz, 3H), 1.49 (sextet, $J = 7.3$ Hz, 2H), 1.97 (quintet, $J = 7.3$ Hz, 2H), 1.82 (s, 6H), 3.67 (s, 3H), 4.11 (t, $J = 7.3$ Hz, 3H), 6.04 (s, 1H), 6.25 (s, 1H), 6.95 (d, $J = 7.9$ Hz, 1H), 7.07 (d, $J = 7.9$ Hz, 1H), 7.21 (dt, $J = 1.2$ and 7.9 Hz, 1H), 7.32–7.42 (m, 2H), 7.45–7.51 (m, 2H), 7.80 (t, $J = 7.9$ Hz, 1H), 7.89 (d, $J = 7.9$ Hz, 1H), 9.06 (d, $J = 7.9$ Hz, 1H); IR (KBr) 1600 cm^{-1}; EI-MS *m*/*z* 474 (M$^+$); Anal. Calcd for $C_{32}H_{30}N_2O_2$: C, 80.98; H, 6.37; N, 5.90%. Found: C, 81.32; H, 6.47; N, 6.00%.

Compound 15. CH_2Cl_2–MeOH (50 : 1, v/v) was used as eluent for silica gel column chromatography. Further purification was carried out by recrystallization from EtOH; yield 80%; mp 262 °C (decomp.); ^{1}H NMR (CDCl$_3$) δ 1.80 (s, 6H), 3.86 (s, 3H), 6.30 (s, 1H), 6.74 (s, 1H), 7.29–7.36 (m, 2H), 7.40–7.58 (m, 8H), 8.02 (d, $J = 7.9$ Hz, 1H), 8.11 (m, 2H), 9.02 (s, 1H); IR (KBr) 1598 cm^{-1}; EI-MS *m*/*z* 471 (M$^+$); Anal. Calcd for $C_{32}H_{25}NO_3$: C, 81.51; H, 5.34; N, 2.97%. Found: C, 81.03; H, 5.26; N, 2.65%.

X-Ray structural analysis ‡

A single crystal of **12** suitable for the X-ray crystallographic analysis was obtained as a clathrate by recrystallization from a benzene solution of **12** in hexane by slow solvent diffusion. All data were collected on a Rigaku AFC-5R diffractometer. The final refinement converged with the unweighted and weighted agreement factor 0.123 and 0.091, respectively. The structure is not of sufficient quality to allow discussion of bond lengths and angles. There were so few reflections that it was not meaningful to refine anisotropic thermal parameters, and the five carbon atoms in the *N*-hexyl group of **12** were disordered in the crystal.

Crystal data: $C_{34}H_{34}N_2O_2\cdot H_2O\cdot 0.5(C_6H_6)$, molecular weight 559.73, triclinic, space group: $P\bar{1}$, cell parameters: $a = 14.427(6)$ Å, $b = 15.199(6)$ Å, $c = 7.498(3)$ Å, $\alpha = 98.72(3)°$, $\beta = 99.51(3)°$, $\gamma = 106.61(3)°$, $V = 1519(2)$ Å^3, $Z = 2$, $D_{calc} = 1.224$ g cm^{-3}, unique reflections 3825, final $R = 0.123$, $R_w = 0.091$.

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‡ CCDC reference number 207/388. See http://www.rsc.org/suppdata/p1/a9/a907335c/ for crystallographic files in .cif format.

References

1 (*a*) M. G. Clark, *Chem. Ind.*, 1985, 258; (*b*) M. Emmelius, G. Pawlowski and W. Vollmann, *Angew. Chem.*, *Int. Ed. Engl.*, 1989, **28**, 1445; (*c*) J. Fabian, H. Nakazumi and M. Matsuoka, *Chem. Rev.*, 1992, **92**, 1197.

2 K.-Y. Law, *Chem. Rev.*, 1993, **93**, 449 and references therein.

3 (*a*) V. Y. Merritt and H. Hovel, *J. Appl. Phys. Lett.*, 1976, **29**, 414; (*b*) D. L. Morel, K. Ghosh, T. Feng, E. L. Stogryn, P. E. Purwin, R. F. Shaw and C. Fishman, *J. Appl. Phys. Lett.*, 1978, **32**, 495.

4 (*a*) A. Trebs and K. Jacob, *Angew. Chem.*, *Int. Ed. Engl.*, 1965, **4**, 694; (*b*) for a review, see, G. Maahs and P. Hegenberg, *Angew. Chem.*, *Int. Ed. Engl.*, 1966, **5**, 888.

5 (*a*) JP 58 217588/1983 (*Chem. Abstr.*, 1984, **100**, 193532q); (*b*) JP 61 167680/1986 (*Chem. Abstr.*, 1987, **106**, 50042t); (*c*) JP 62 187087/1987 (*Chem. Abstr.*, 1988, **108**, 66058e); (*d*) GP 3 631 843/1988 (*Chem. Abstr.*, 1988, **109**, 75205y); (*e*) N. Kuramoto, K. Natsukawa and K. Asao, *Dyes Pigments*, 1989, **11**, 21.

6 K.-Y. Law and F. C. Bailey, *J. Org. Chem.*, 1992, **57**, 3278.

7 E. Terpetschnig and J. R. Lakowicz, *Dyes Pigments*, 1993, **21**, 227.

8 R. C. DeSelms, C. J. Fox and R. C. Riordan, *Tetrahedron Lett.*, 1970, **10**, 781.

9 M. Matsuoka, *Absorption Spectra of Dyes for Diode Lasers*, Bunshin, Tokyo, 1990, pp. 51–59.

10 S. Yagi, K. Maeda and H. Nakazumi, *J. Mater. Chem.*, 1999, **9**, 2991.

11 R. Witzinger and H. Tobel, *Helv. Chim. Acta*, 1957, **40**, 1305.

12 K.-Y. Law, F. C. Bailey and L. J. Bluett, *Can. J. Chem.*, 1986, **64**, 1607.

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