Synthesis of bisquaraine dyes. Novel homologues of 1,2-squaraines bearing symmetrical and unsymmetrical structures

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In order to investigate analogous structures of 1,2-squaraine dyes, bisquaraines **1** and **2** are newly prepared as their novel homologues. Symmetrical bisquaraine dye **1**, in which the same heterocyclic components are introduced at the 3 and 3′ positions of the bisquaryl skeleton, is obtained by reaction of 4,4′-bi(3-isopropoxycyclobut-3-ene-1,2-dione) **3** with a series of heterocyclic compounds **5**. The structure of one of the symmetrical dyes is confirmed by X-ray structural analysis, showing a largely extended π-conjugation system over the whole molecule. The synthesis of unsymmetrical dyes **2**, in which different aromatic components are introduced, is established by the reactions of **5** with 3′-monosubstituted bisquarates **6**. Each bisquaraine dye exhibits two absorption maxima separated by 56–75 nm, the lower-energy absorption of which is observed at 653–757 nm.

Introduction

Dye chemistry started at the end of 19th century, and has developed into various fields such as the evolution of synthesis, structural analysis, and computational chemistry of the delocalized π-electron systems. Recently, many dyes possessing useful functionalities have been synthesized and used for materials. In the optoelectronics field, several optical properties of organic dyes are required for applications: for example, the absorption maxima of dyes should correspond to the emitting wavelengths of the light sources, and the absorption coefficients are desired to be large enough for use with high efficiency. In terms of such technical requirements, squaraine (SQ) dyes have been attracting much interest because they exhibit large and intense light absorptions and their absorption bands are tunable by varying the constituent aromatic or heterocyclic components.

SQ dyes, in general, are classified into two types; 1,2- and 1,3-disubstituted derivatives of squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione). The 1,3-SQ dyes, which are often regarded as cyanine dyes as to their localized electronic structures, were first reported by Treibs and Jacob more than three decades ago,[1] and their various derivatives and related compounds have been reported because of interest in their unique structures and chromophoric properties.[2,3] On the other hand, the 1,2-SQ dyes possess a different electronic structure from the 1,3-SQs, that is, two cross-conjugated π-electron systems from the aromatic or heterocyclic donors to the carbonyl acceptors in the squarate afford merocyanine-type chromophoric systems.[2a] Thus, unique SQ chromophores promising variability of electro- and/or photochemical properties have been regarded as potential materials for optoelectronic applications such as xerographic devices,[4] solar cells,[5] optical recording media,[6,7] and so on. However, they possess a severe problem of limited synthetic methodology: SQ dyes are obtained by the condensation of squaric acid with two equivalents of nucleophilic aromatic or heterocyclic compounds,[8] but the traditional synthetic method offers only symmetrical SQ dyes, in which the same aromatic or heterocyclic components are attached to the cyclobutene ring. Recently, Law and Terpetschnig independently explored novel methods to obtain unsymmetrical 1,3-SQ dyes,[9,10] and these synthetic breakthroughs should extend the range of utility of SQ dyes. Another possibility for exploring new classes of SQ dyes lies in the modification of the central cyclobutene moiety. Here we report novel homologues of 1,2-SQ dyes, the bisquaraines, in which two heterocyclic components are attached to a bisquaryl skeleton. We successfully established selective methods to obtain the unsymmetrical dyes **2** as well as the symmetrical ones **1**.

Results and discussion

Synthesis of symmetrical bisquaraine dyes

The synthesis of the symmetrical bisquaraine dyes **1a–d** is shown in Scheme 1. 4,4′-Bi(cyclobut-3-ene-1,2-dione) (bisquaryl) was first reported by Liebeskind *et al.* and obtained using the palladium-catalyzed coupling reactions of cyclobut-3-ene-1,2-diones.[11] At first, we chose bisquaric acid **4** as a candidate for the starting material to obtain the bisquaraine dyes because a typical synthesis of SQ dyes starts with squaric acid. We examined the condensation of **4** and 2 equivalents of salts **5a–d** under conditions similar to the preparation of 1,3-SQ dyes [benzene–butan-1-ol 4 : 1 (v/v), a small amount of quinoline, reflux], which afforded too many products to be isolated by the usual procedures such as recrystallization and column chromatography. One can see that this is because there exist several tautomers of **4** which are produced by keto–enol tautomerism. Thus, diisopropyl bisquarate **3**, in which the tautomerism is prevented by exchanging two acidic protons with isopropyl groups, was employed as a precursor. The reaction of bisquarate **3** and **2** equivalents of **5a** in the presence of triethylamine in CH_2Cl_2 at rt afforded bisquaraine dye **1a** in 39% yield. The reaction proceeded under the mild conditions, and the resultant crude dye was purified as usual by silica gel column chromatography. By a similar procedure, the symmetrical bisquaraine dyes **1b–d** were obtained in 36–67% yield from **3** and 2 equivalents of **5b–d**, respectively. These results are summarized in Table 1. Although **1a** was characterized by ^{1}H NMR, **1b–d** could not be clearly identified by ^{1}H NMR due to their low solubility in the common solvents, but this was possible in CF_3COOD. In the ^{1}H NMR spectrum of **1a**, both indoline components are magnetically equivalent, indicating the highly symmetrical structure of the bisquaraine dye.

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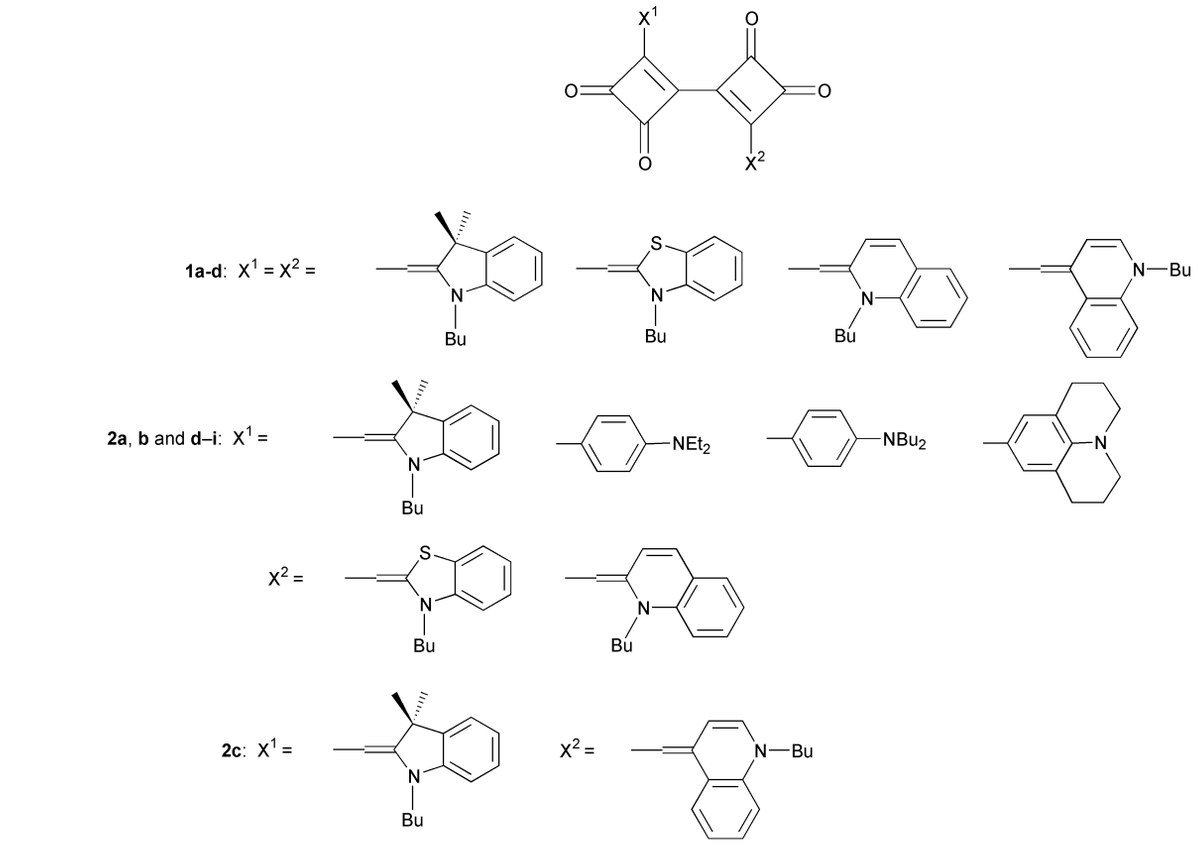
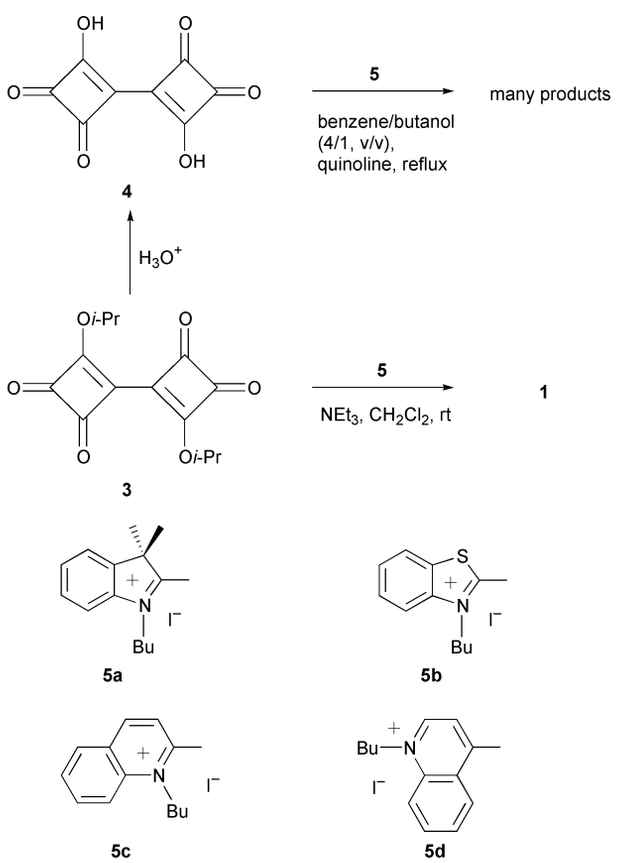




Scheme 1

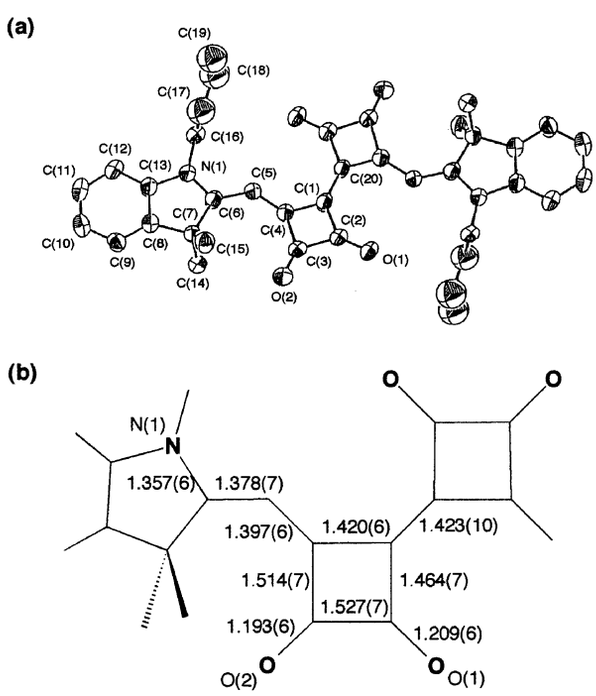
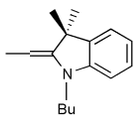
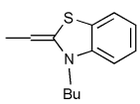
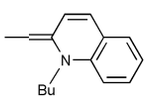
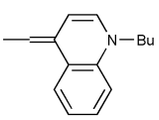
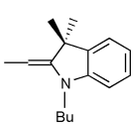
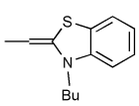
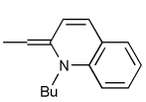
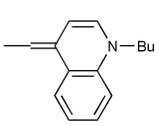
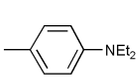
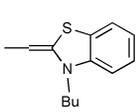
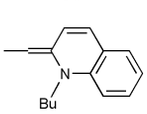
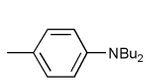
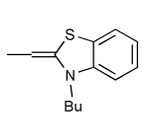
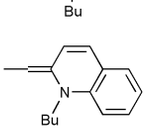
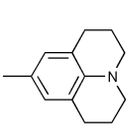
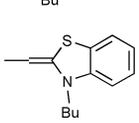
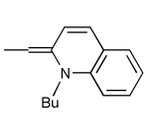


Fig. 1 (a) ORTEP drawing of the symmetrical bisquaraine dye **1a**. All hydrogen atoms are omitted for clarity. (b) Selected bond lengths of **1a**. Crystallographic numbering scheme is used.

The crystal structural analysis of the bisquaraine dye 1a

The structure of **1a** was confirmed by X-ray crystallography, and the ORTEP drawing of **1a** is shown in Fig. 1(a). The dye **1a** has C_2 rotational symmetry. The planarity of **1a** permits a large extension of the π-conjugation system from one indoline moiety to the other. As shown in Fig. 1(b), the bond lengths of N(1)–C(6), C(6)–C(5), C(5)–C(4), C(4)–C(1) and C(1)–C(20) are within the range 1.35–1.43 Å and exhibit a conjugated double-bond character. On the other hand, the bonds C(1)–C(2) and C(2)–C(3) are relatively longer and show a typical single-bond length, indicating that they are not likely to participate in the polymethine π-conjugation of the chromophore.

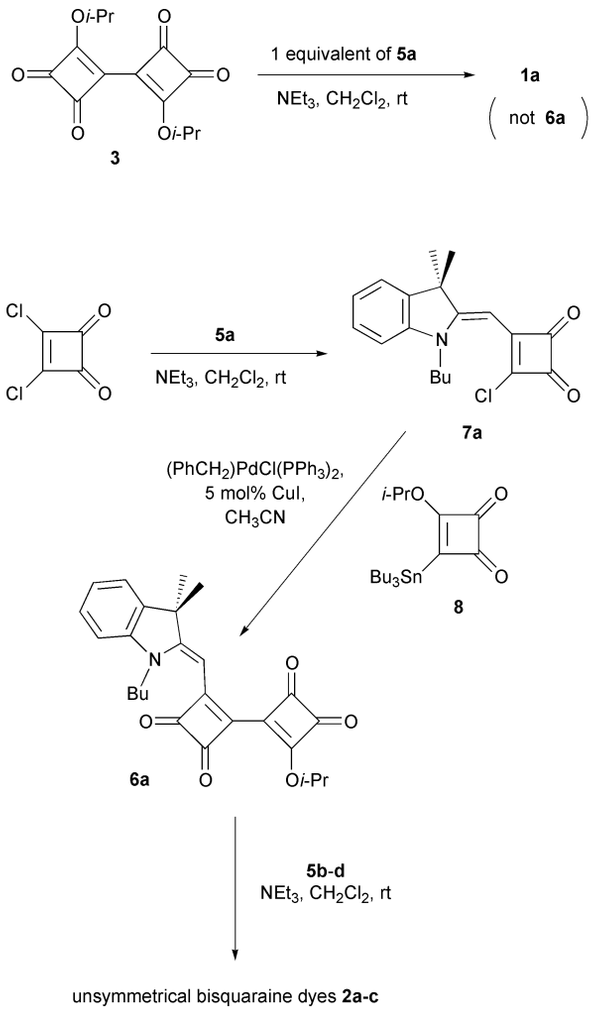
Table 1 Preparation, absorption maxima and extinction coefficients of the bisquaraine dyes **1** and **2**

	X^1	X^2	Yield (%)	λ_{max} [a]/nm	logε [a]
1a			39	657 601 ≈550	4.87 4.73 [b]
1b			67	653 595 ≈550	4.92 4.73 [b]
1c			41	692 628 ≈600	5.04 4.79 [b]
1d			36	757 682 ≈620	5.14 4.76 [b]
2a			70	653 598 ≈585	5.01 4.85 [b]
2b			50	672 613 ≈600	5.02 4.82 [b]
2c			50	705 641 ≈550	5.10 4.82 [b]
2d			38	640 600	4.71 4.68
2e			70	648 620	4.73 4.72
2f			33	642 604	4.70 4.67
2g			30	649 620	4.73 4.72
2h			35	656 620	4.70 4.61
2i			30	673 630	4.73 4.67

[a] In $CHCl_3$ at 298 K within visible–near-IR region. [b] Shoulder.

Synthesis of unsymmetrical bisquaraine dyes

Monosubstituted bisquarates should offer the opportunity for stepwise introduction of different heterocyclic moieties into the bisquaryl skeleton. In order to explore a reliable synthesis for unsymmetrical bisquaraine dyes, we examined the synthesis of the monosubstituted bisquarate intermediate **6a**, as shown in Scheme 2. We examined the condensation of bisquarate **3** with 1 equivalent of **5a** to obtain the monosubstituted bisquarate **6a**, but, contrary to our expectation, the symmetrical bisquaraine dye **1a** was exclusively formed. This is most likely because the intermediate **6a** is not less reactive than bisquarate **3**. Therefore, another route to prepare the monosubstituted bisquarate was examined. The reaction of indolium **5a** with 1 equivalent of



Scheme 2

3,4-dichlorocyclobut-3-ene-1,2-dione afforded 3-(*N*-butyl-3,3-dimethylindolin-2-ylidenemethyl)-4-chlorocyclobut-3-ene-1,2-dione **7a** in 47% yield. The palladium-catalyzed cross-coupling reaction of **7a** with the (tributyl)stannylcyclobutene-1,2-dione **8** afforded the intermediate **6a** in 10% yield.

The reaction of **6a** with **5b–d** afforded the unsymmetrical bisquaraine dyes **2a–c** in 50–70% yield, respectively, under reaction conditions similar to those for the synthesis of the symmetrical bisquaraine dyes (NEt_3, CH_2Cl_2, rt). The same reaction steps beginning with dialkylanilines and 3,4-dichlorocyclobut-3-ene-1,2-dione to yield the monosubstituted squaraates **6b–d** were also successful, and the subsequent reactions of **5b** and **5c** with **6b–d** afforded the unsymmetrical squaraines **2d–i** in 30–70% yield, respectively. The results are summarized in Table 1. The structure of each dye was confirmed by ^{1}H NMR, IR, UV–vis, and FAB-MS spectroscopy as well as elemental analysis. As a typical example, the ^{1}H NMR spectrum of **2c** is shown in Fig. 2. The signal of each proton was assigned by ^{1}H decoupling, ^{1}H–^{1}H COSY and NOE techniques. The spectrum clearly shows that **2c** possesses two different heterocyclic components, the indoline and quinoline rings. One may possibly expect formation of a mixture of **1a** and **1d** in this reaction, but the results of the FAB-MS spectrum and elemental analysis also support the unsymmetrical structure **2c**. Although the structure of compound **2c** has not yet been confirmed by X-ray crystallographic analysis, the NOE correlations (shown by arrows in Fig. 2) indicate that both *exo*-double bonds attached to the indoline and quinoline rings adopt the *E* configuration, as seen in the X-ray structure of **1a**. The possibility of a mixture of two symmetrical squaraine dyes can also be excluded based on the following experimental evidence: the dye **2a** possesses a different R_f-value on silica gel thin-layer chromatography [CH_2Cl_2–MeOH 40 : 1 (v/v)] from those of the dyes **1a** and **1b** (0.17, 0.63 and 0.27 for **2a**, **1a** and **1b**, respectively), and the presence of only one spot on the TLC plate for **2a** indicated that the isolated dye **2a** was a single product. For the other unsymmetrical dyes, similar results were obtained in the TLC study.

UV–vis absorption and fluorescence emission properties of bisquaraine dyes

Typical absorption spectra of the bisquaraine dyes **1a**, **1d**, and **2c** are shown in Fig. 3, and the UV–vis spectral data of all the dyes are summarized in Table 1. Characteristic is that all these bisquaraine dyes have two broad absorption bands at longer wavelengths, although typical squaraine dyes possess single, sharp absorption maxima.[12] For these three compounds the two absorption maxima wavelengths differ by 56 to 75 nm, and the intensity ratios of the longer-wavelength absorption to the second one are 1.4–2.4. Taking into consideration that the PPP (Pariser–Parr–Pople) MO calculations for **1a**, **1d**, and **2c** yielded single lowest-energy transitions at 633, 727, and

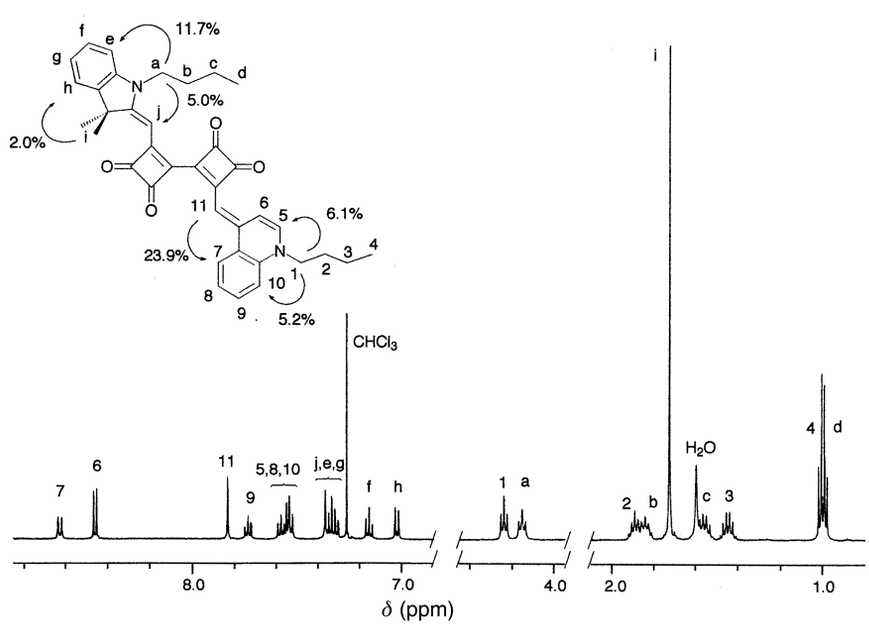


Fig. 2 ^{1}H NMR spectrum (500 MHz) and NOE correlations of the unsymmetrical bisquaraine dye **2c** in $CDCl_3$ at 298 K.

Table 2 Fluorescence properties of the bisquaraine dyes **1** and **2**[a]

Compound	F_{ex}/nm[b]	F_{em}/nm[c]	Lifetime/ns
1a	653.2, ≈600 (sh)	685.6	2.9
1b	651.6, ≈590 (sh)	680.8	1.1
1c	690.4, 624.8	712.0, ≈800 (sh)	2.3
1d	758.8	777.2	[d]
2a	652.0, 600.0	681.6, ≈770 (sh)	1.1
2b	670.4, 618.0	696.4, ≈770 (sh)	[d]
2c	712.4, 692.0, 650.0	726.4, ≈800 (sh)	[d]
2d	650.4, ≈610 (sh)	686.0	[d]
2e	651.2, ≈610 (sh)	698.4	[d]
2f	650.4, ≈610 (sh)	693.6	1.1
2g	649.6, ≈630 (sh)	686.0	[d]
2h	689.2, ≈640 (sh)	713.2	[d]
2i	685.2, ≈660 (sh)	721.6	[d]

[a] 2.0 μM $CHCl_3$ solution at 15 °C. [b] F_{ex} is the maximum wavelength in the excitation spectrum monitored at the emission maximum (F_{em}). [c] F_{em} is the fluorescence maximum in the emission spectrum excited at λ_{max}. [d] Not measured due to low intensity.

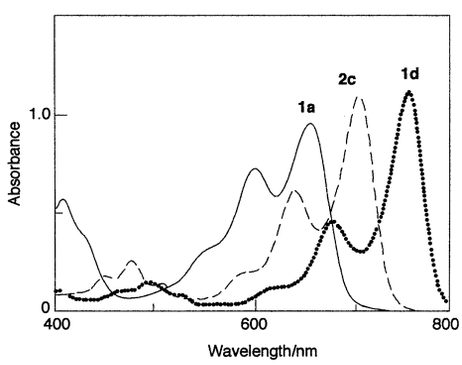


Fig. 3 UV–vis absorption spectra of **1a**, **1d** and **2c** in $CHCl_3$ at 298 K.

680 nm (f = 2.711, 2.490, and 2.504), respectively, these peak splittings are likely to be based on the vibrational structures. The absorption maxima of the symmetrical and unsymmetrical dyes are observed in the range 640–757 nm, with extinction coefficients of $\approx 10^5$ L cm^{-1} mol^{-1}: the absorption maxima of the dyes depend on the aromatic and heterocyclic moieties. It is noteworthy that the longest-wavelength absorption of the unsymmetrical dye is at an average wavelength of the two corresponding symmetrical dyes. For example, the absorption-maximum wavelength of **2b** shows a half-value of the sum of the wavelengths of **1a** and **1c**. The same tendency was found in the calculated values of λ_{max} obtained by the PPP MO method.

The emission maxima (F_{em}), excitation maxima (F_{ex}), and fluorescence lifetimes of **1** and **2** in the fluorescence spectra are summarized in Table 2. The fluorescence emissions observed at the F_{em} by excitation at the λ_{max} of **1** and **2** exhibited much larger intensities than those observed by excitation at the shorter wavelength of the absorption bands of **1** and **2**. The fluorescence lifetimes in solution (*ca.* 1–3 ns) were similar to that of a typical squarylium dye.[13] Proximity between the λ_{max} and the F_{ex} as well as the single-component fluorescence lifetime also suggests that the split lowest-energy absorptions are due to vibrational modes of the electronic structures.

Conclusions

We demonstrate here the first synthesis of novel bisquaraine dyes which can be regarded as homologues of 1,2-SQ dyes. Diisopropyl bisquarate **3** easily reacted with two equivalents of heterocyclic compounds **5** to afford the symmetrical bisquaraine dyes **1a**–**d**. The structure was confirmed by X-ray crystallographic analysis for **1a**, the planarity of which showed a large extension of π-conjugation from one heterocyclic component to the other. The selective synthesis of the unsymmetrical dyes was also achieved by using the monosubstituted intermediate **6**. Thus, a wide range of combinations of aromatic and heterocyclic components at the 3 and 3′ positions were made possible, leading to tuning of the absorption maxima over *ca.* 100 nm (653–757 nm). The results obtained here have great implications in the search for novel structures of squaraine dyes and related compounds and, furthermore, should open the way to new families of polymethine dyes.

Experimental

General

^{1}H NMR spectra were recorded on JEOL GX-270 (270 MHz) or JEOL A-500 (500 MHz) FT-NMR spectrometers, and chemical shifts are reported in ppm downfield from the TMS signal (δ 0) as internal standard. ^{1}H Decoupling, ^{1}H–^{1}H COSY and NOE spectra were taken at 500 MHz. 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 matrix. IR spectra were recorded on a Horiba FT-200 spectrometer using KBr pellets. UV–vis absorption spectra were recorded on a Shimadzu UV-3100 spectrometer. Fluorescence spectra were recorded on a Shimadzu RF-5000 spectrofluorophotometer. Fluorescence-lifetime analyses were carried out with a Horiba NAES 550 nanosecond fluorometer. Elemental analyses were carried out with a Yanaco CHN-CORDER MT-3 recorder.

Materials and solvents

4,4′-Bi(3-hydroxycyclobut-3-ene-1,2-dione) **4** (bisquaric acid) and 4,4′-bi(3-isopropoxycyclobut-3-ene-1,2-dione) **3** (diisopropyl bisquarate) were synthesized according to Liebeskind's procedure cited in ref. 11. Deuterated chloroform and trifluoroacetic acid were purchased from Aldrich. Chloroform used for UV–vis spectral analyses was of spectroscopic grade.

4,4′-Bi[3-(1-butyl-3,3-dimethylindolin-2-ylidenemethyl)cyclobut-3-ene-1,2-dione] 1a

To a dispersed solution of 1-butyl-2,3,3-trimethylindolium iodide **5a** (0.689 g, 2.01 mmol) in CH_2Cl_2 (20 mL) was added NEt_3 (0.28 mL), followed by dropwise addition of a solution of bi(3-isopropoxycyclobut-3-ene-1,2-dione) **3** (0.278 g, 1.00 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred for 2 h at rt, and then the solvent was removed on a rotary evaporator. The residue was purified by silica gel chromatography (CH_2Cl_2 as eluent), and further purification by recrystallization from CH_2Cl_2–hexane afforded crystals of **1a** (0.231 g, 0.393 mmol, 39%), mp 278 °C (decomp.); ^{1}H NMR (270 MHz; $CDCl_3$) δ 0.99 (t, J = 7.3 Hz, 6 H), 1.47–1.69 (m, 4 H), 1.72 (s, 12 H), 1.78–1.86 (m, 4 H), 4.17 (t, J = 7.3 Hz, 4 H), 7.05 (d, J = 7.3 Hz, 2 H), 7.18 (d, J = 7.3 Hz, 2 H), 7.30–7.37 (m, 6 H); IR (KBr) ν 1726, 1722, 1697 cm^{-1}; FAB MS *m/z* 589 ($[M + H]^+$) (Calc. for $C_{38}H_{40}N_2O_4 \cdot 0.5H_2O$: C, 76.36; H, 6.91; N, 4.69. Found: C, 75.88; H, 6.79; N, 4.47%).

4,4′-Bi[3-(3-butyl-2,3-dihydrobenzothiazol-2-ylidenemethyl)-cyclobut-3-ene-1,2-dione] 1b

To a dispersed solution of 3-butyl-2-methylbenzothiazolium iodide **5b** (0.670 g, 2.01 mmol) in CH_2Cl_2 (20 mL) was added NEt_3 (0.28 mL), followed by dropwise addition of a solution of diester **3** (0.278 g, 1.00 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred for 2 h at rt, and a precipitate with metallic luster was produced, which was separated by filtration, washed with water, and dried *in vacuo* over silica gel to afford crystals of **1b** (0.382 g, 0.671 mmol, 67%), mp 314 °C (decomp.); ^{1}H NMR (270 MHz; CF_3COOD) δ 1.01–1.09 (m, 6 H), 1.58–1.66 (m, 4 H), 1.90–2.20 (m, 4 H), 4.61 (t, J = 7.6 Hz, 2 H), 4.91 (t, J = 7.9

Hz, 2 H), 7.60–7.76 (m, 4 H), 7.81–7.97 (m, 3 H), 8.06–8.13 (m, 3 H); IR (KBr) ν 1712, 1693 cm^{-1}; FAB MS *m/z* 569 ($[M + H]^+$) (Calc. for $C_{32}H_{28}N_2O_4S_2$: C, 67.58; H, 4.96; N, 4.92. Found: C, 67.75; H, 4.93; N, 4.80%).

Symmetrical bisquaraine dyes **1c** and **1d** were prepared by the same procedure outlined above for **1b**, using the salts **5c** and **5d**.

4,4′-Bi[3-(1-butyl-1,2-dihydroquinolin-2-ylidenemethyl)-cyclobut-3-ene-1,2-dione] 1c. 41% yield; mp 308 °C (decomp.); ^{1}H NMR (270 MHz; CF_3COOD) δ 1.09–1.16 (m, 6 H), 1.65–1.79 (m, 4 H), 2.05–2.25 (m, 4 H), 4.84 (m, 4 H), 5.15 (m, 2 H), 7.75–7.80 (m, 1 H), 8.01–8.07 (m, 6 H), 8.25–8.38 (m, 2 H), 8.48–8.92 (m, 3 H); IR (KBr) ν 1710, 1697 cm^{-1}; FAB MS *m/z* 557 ($[M + H]^+$) (Calc. for $C_{36}H_{32}N_2O_4$: C, 77.68; H, 5.79; N, 5.03. Found: C, 77.39; H, 5.79; N, 4.79%).

4,4′-Bi[3-(1-butyl-1,4-dihydroquinolin-4-ylidenemethyl)-cyclobut-3-ene-1,2-dione] 1d. 36% Yield; mp 305 °C (decomp.); ^{1}H NMR (270 MHz; CF_3COOD) δ 1.07–1.14 (m, 6 H), 1.65–1.80 (m, 4 H), 2.05–2.25 (m, 4 H), 4.82 (m, 4 H), 5.14 (m, 2 H), 7.73–7.79 (m, 1 H), 7.98–8.07 (m, 6 H), 8.24–8.37 (m, 2 H), 8.44–8.91 (m, 3 H); IR (KBr) ν 1708, 1693 cm^{-1}; FAB MS *m/z* 557 ($[M + H]^+$) (Calc. for $C_{36}H_{32}N_2O_4$: C, 77.68; H, 5.79; N, 5.03. Found: C, 77.60; H, 5.73; N, 4.88%).

3-(1-Butyl-3,3-dimethylindolin-2-ylidenemethyl)-4-chlorocyclobut-3-ene-1,2-dione 7a

To a mixture of **5a** (3.91 g, 11.4 mmol) and 3,4-dichlorocyclobut-3-ene-1,2-dione[14] (1.71 g, 11.3 mmol) in benzene (40 mL) was added dropwise 1.6 mL of NEt_3, and the mixture was stirred for 2 h at rt. Then, 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 CH_2Cl_2–hexane to afford crystals of **7a** (1.75 g, 5.31 mmol, 47%), mp 102.3–103.1 °C; ^{1}H NMR (270 MHz; $CDCl_3$) δ 1.03 (t, J = 7.3 Hz, 3 H), 1.41–1.59 (m, 2 H), 1.66 (s, 6 H), 1.70–1.82 (m, 2 H), 3.95 (t, J = 7.3 Hz, 2 H), 5.56 (s, 1 H), 7.05 (d, J = 7.3 Hz, 1 H), 7.18 (t, J = 7.3 Hz, 1 H), 7.31–7.36 (m, 2 H); IR (KBr) ν 1767, 1727 cm^{-1}; EI MS *m/z* 331 (M^+ + 2, 10%), 329 (M^+, 29), 273 (M^+ − 2CO, 72), 258 ($[M - 2CO - CH_3]^+$, 72) (Calc. for $C_{19}H_{20}ClNO_2$: C, 69.19; H, 6.11; N, 4.25. Found: C, 68.81; H, 6.14; N, 4.25%).

3-[4-(Diethylamino)phenyl]-4-chlorocyclobut-3-ene-1,2-dione 7b

To a CH_2Cl_2 (20 mL) solution of 3,4-dichlorocyclobut-3-ene-1,2-dione[14] (1.51 g, 10 mmol) was added dropwise a CH_2Cl_2 solution (10 mL) of *N,N*-diethylaniline, and the mixture was stirred at rt for 3 h. Then, the solvent was removed and the residue was purified by column chromatography (CH_2Cl_2 as eluent) to give **7b** as the yellow solid in 73% yield, mp 152 °C (decomp.); ^{1}H NMR ($CDCl_3$) δ 1.24 (t, J = 7.3 Hz, 6 H), 3.48 (q, J = 7.3 Hz, 4 H), 6.72 (d, J = 9.2 Hz, 2 H), 8.11 (d, J = 9.2 Hz, 2 H); IR (KBr) ν 1738, 1733 cm^{-1} (C=O); EI MS *m/z* 265 (M^+ + 2, 7%), 263 (M^+, 22), 209 (M^+ + 2 − 2CO, 11), 207 (M^+ − 2CO, 38), 194 (M^+ + 2 − 2CO − CH_3, 35), 192 (M^+ − 2CO − CH_3, 100) (Calc. for $C_{14}H_{14}ClNO_2$: C, 63.78; H, 5.35; N, 5.31. Found: C, 63.42; H, 5.43; N, 5.47%).

3-[4-(Dibutylamino)phenyl]-4-chlorocyclobut-3-ene-1,2-dione 7c

This compound was synthesized in a similar manner to **7b** in 22% yield, mp 80–81 °C; ^{1}H NMR($CDCl_3$) δ 0.98 (t, J = 7.3 Hz, 6 H), 1.39 (sextet, J = 7.3 Hz, 4 H), 1.63 (quint, J = 7.3 Hz, 4 H), 3.40 (t, J = 7.3 Hz, 4 H), 6.76 (d, J = 9.2 Hz, 2 H), 8.13 (d, J = 9.2 Hz, 2 H); IR (KBr) ν 1795 (C=O), 1759 cm^{-1} (C=O); FAB-MS *m/z* 321 (M^+ + 2, 26%), 319 (M^+, 100), 265 ($[M - 2CO]^+$ + 2, 37), 263 ($[M - 2CO]^+$, 81) (Calc. for $C_{18}H_{22}ClNO_2$: C, 67.60; H, 6.93; N, 4.38. Found: C, 67.79; H, 7.00; N, 4.45%).

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

This compound was synthesized in a similar manner to **7b** in 35% yield, mp 209 °C (decomp.); ^{1}H NMR ($CDCl_3$) δ 1.99 (quint, J = 5.9 Hz, 2 H), 2.78 (t, J = 5.9 Hz, 4 H), 3.37 (t, J = 5.9 Hz, 4 H), 7.70 (s, 2 H); IR (KBr) ν 1774, 1749 cm^{-1} (C=O); EI MS (*m/z*) 289 (M^+ + 2, 5%), 287 (M^+, 16), 233 (M^+ + 2 − 2CO, 34), 231 (M^+ − 2CO, 100); this compound was used for the following reaction without further purification.

3-(1-Butyl-3,3-dimethylindolin-2-ylidenemethyl)-3′-isopropoxy-4,4′-bis(cyclobut-3-ene-1,2-dione) 6a

To a mixture of **7a** (1.69 g, 5.12 mmol) and 3-isopropoxy-4-(tributylstannyl)cyclobut-3-ene-1,2-dione **8** (2.20 g, 5.14 mmol) in acetonitrile (30 mL) was added $(PhCH_2)PdCl(PPh_3)_2$ (0.194 g, 5 mol% for **7a**) and CuI (0.049 g, 5 mol% for **7a**), and the mixture was stirred for 4 h at 50 °C under nitrogen atmosphere. After cooling, the reaction mixture was washed with hexane, and the solvent was removed on a rotary evaporator. The residue was dissolved in CH_2Cl_2 (20 mL), and a small amount of activated carbon powder was added. The mixture was heated at reflux for 1 h and filtered through Celite powder. The filtrate was evaporated, and the residue was purified by silica gel column chromatography (CH_2Cl_2 as eluent), followed by recrystallization from CH_2Cl_2–hexane to afford crystals of **6a** (0.232 g, 0.536 mmol, 10%), mp 153–154 °C; ^{1}H NMR (270 MHz; $CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 3 H), 1.37–1.60 (m, 8 H), 1.62 (s, 6 H), 1.69–1.78 (m, 2 H), 4.70 (t, J = 7.3 Hz, 2 H), 5.58 (t, J = 6.1 Hz, 1 H), 6.95 (s, 1 H), 7.01 (d, J = 7.9 Hz, 1 H), 7.16 (m, 1 H), 7.26–7.32 (m, 2 H); IR (KBr) ν 1788, 1743, 1736, 1728 cm^{-1}; EI MS *m/z* 433 (M^+, 1.4%), 334 (M^+ − 2CO − C_3H_7, 100) (Calc. for $C_{26}H_{27}NO_5$: C, 72.04; H, 6.28; N, 3.23. Found: C, 72.23; H, 6.41; N, 3.29%).

3-[4-(Diethylamino)phenyl]-3′-isopropoxy-4,4′-bis(cyclobut-3-ene-1,2-dione) 6b

3-[4-(Diethylamino)phenyl]-4-chlorocyclobut-3-ene-1,2-dione **7b** (1.69 g, 5.12 mmol), 3-isopropoxy-4-(tributylstannyl)cyclobut-3-ene-1,2-dione (2.20 g, 5.14 mmol), $(Ph_3P)_2Pd(CH_2Ph)Cl$ (0.194 g, 5 mol%) and CuI (0.049 g, 5 mol%) were dissolved in 30 mL of acetonitrile under nitrogen atmosphere. After being refluxed for 4 h, the reaction mixture was cooled to room temperature and poured into hexane to remove tributylstannyl chloride. The hexane layer, immiscible with acetonitrile, was removed and the acetonitrile layer was evaporated. The residue was dissolved in CH_2Cl_2, treated with activated carbon, and the solution was refluxed. The suspension was filtered through Celite and the filtrate was evaporated. The residue was recrystallized from CH_2Cl_2–hexane to give the purple solid **6b** (0.23 g, 98%), mp 137 °C (decomp.); MS (*m/z*) 367 (M^+, 14%), 213 (100).

Compounds **6c** and **6d** were prepared in similar manner and used in the next step without further purification.

3-[4-(Dibutylamino)phenyl]-3′-isopropoxy-4,4′-bis(cyclobut-3-ene-1,2-dione) 6c. Yield 80%; mp 75–80 °C; MS (*m/z*) 423 (M^+, 11%), 367 ($[M - C_4H_9]^+$, 8), 324 ($[M - C_4H_9 - C_3H_7]^+$, 14).

3-(2,3,6,7-Tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-yl)-3′-isopropoxy-4,4′-bis(cyclobut-3-ene-1,2-dione) 6d. Yield 85%; mp 149–151 °C; MS (*m/z*) 391 (M^+, 1.6%), 213 (100).

3-(3-Butyl-2,3-dihydrobenzothiazol-2-ylidenemethyl)-3′-(1-butyl-3,3-dimethylindolin-2-ylidenemethyl)-4,4′-bis(cyclobut-3-ene-1,2-dione) 2a

To a dispersed solution of **5b** (0.067 g, 0.20 mmol) in CH_2Cl_2 (4 mL) was added 0.1 mL of NEt_3, and then a solution of **6a**

(0.087 g, 0.20 mmol) in CH_2Cl_2 (4 mL) was added dropwise. The mixture was stirred for 2 h at rt. 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 CH_2Cl_2–hexane to afford crystals of **2a** (0.082 g, 0.14 mmol, 70%), mp 292 °C (decomp.); ^{1}H NMR (270 MHz; $CDCl_3$) δ 0.99 (t, J = 7.3 Hz, 3 H), 1.03 (t, J = 7.3 Hz, 3 H), 1.50–1.63 (m, 4 H), 1.71 (s, 6 H), 1.81–1.94 (m, 4 H), 4.14 (t, J = 7.3 Hz, 2 H), 4.29 (t, J = 7.3 Hz, 2 H), 7.03 (d, J = 7.3 Hz, 1 H), 7.16 (d, J = 7.3 Hz, 1 H), 7.26–7.36 (m, 6 H), 7.46 (t, J = 7.3 Hz, 1 H), 7.64 (d, J = 7.3 Hz, 1 H); IR (KBr) ν 1726, 1722, 1697 cm^{-1}; FAB MS m/z 579 ([M + H]$^+$) (Calc. for $C_{35}H_{34}N_2O_4S$: C, 72.64; H, 5.92; N, 4.84. Found: C, 72.90; H, 5.92; N, 4.94%).

Unsymmetrical bisquaraine dyes **2b**–**i** were prepared by the general procedure outlined for **2a**.

3-(1-Butyl-3,3-dimethylindolin-2-ylidenemethyl)-3′-(1-butyl-1,2-dihydroquinolin-2-ylidenemethyl)-4,4′-bis(cyclobut-3-ene-1,2-dione) 2b

Yield 50%; mp 283 °C (decomp.); ^{1}H NMR (270 MHz; $CDCl_3$) δ 0.99 (t, J = 7.3 Hz, 3 H), 1.10 (t, J = 7.3 Hz, 3 H), 1.48–1.66 (m, 4 H), 1.71 (s, 6 H), 1.76–1.95 (m, 4 H), 4.15 (t, J = 7.3 Hz, 2 H), 4.46 (t, J = 7.3 Hz, 2 H), 7.03 (d, J = 7.3 Hz, 1 H), 7.16 (d, J = 7.3 Hz, 1 H), 7.26–7.42 (m, 5 H), 7.57–7.75 (m, 4 H), 8.90 (d, J = 9.8 Hz, 1 H); IR (KBr) ν 1724, 1718, 1699 cm^{-1}; FAB MS m/z 573 ([M + H]$^+$) (Calc. for $C_{37}H_{36}N_2O_4$: C, 77.60; H, 6.34; N, 4.89. Found: C, 77.84; H, 6.39; N, 4.98%).

3-(1-Butyl-3,3-dimethylindolin-2-ylidenemethyl)-3′-(1-butyl-1,4-dihydroquinolin-4-ylidenemethyl)-4,4′-bi(cyclobut-3-ene-1,2-dione) 2c

Yield 50%; mp 274 °C; ^{1}H NMR (270 MHz; $CDCl_3$) δ 0.99 (t, J = 7.3 Hz, 3 H), 1.01 (t, J = 7.3 Hz, 3 H), 1.41–1.60 (m, 4 H), 1.72 (s, 6 H), 1.82–1.92 (m, 4 H), 4.15 (t, J = 7.3 Hz, 2 H), 4.24 (t, J = 7.3 Hz, 2 H), 7.02 (d, J = 7.3 Hz, 1 H), 7.15 (d, J = 7.3 Hz, 1 H), 7.29–7.37 (m, 3 H), 7.52–7.61 (m, 3 H), 7.74 (m, 1 H), 7.85 (s, 1 H), 8.47 (d, J = 7.3 Hz, 1 H), 8.64 (dd, J = 1.2 and 8.6 Hz, 1 H); IR (KBr) ν 1724, 1697 cm^{-1}; FAB MS m/z 573 ([M + H]$^+$) (Calc. for $C_{37}H_{36}N_2O_4$: C, 77.60; H, 6.34; N, 4.89. Found: C, 77.34; H, 6.31; N, 4.89%).

3-[4-(Diethylamino)phenyl]-3′-(3-butyl-2,3-dihydrobenzothiazol-2-ylidenemethyl)-4,4′-bis(cyclobut-3-ene-1,2-dione) 2d. Yield 38%; mp 252 °C (decomp.); ^{1}H NMR ($CDCl_3$) δ 1.04 (t, J = 7.3 Hz, 3 H), 1.45–1.64 (m, 2 H), 1.25 (t, J = 7.3 Hz, 6 H), 1.92 (quint, J = 7.3 Hz, 2 H), 3.50 (q, J = 7.3 Hz, 4 H), 4.31 (t, J = 7.9 Hz, 2 H), 6.78 (t, J = 9.2 Hz, 2 H), 7.26–7.38 (m, 3 H), 7.49 (t, J = 7.9 Hz, 1 H), 7.68 (d, J = 7.9 Hz, 1 H), 8.46 (d, J = 9.2 Hz, 2 H); IR (KBr) ν 1738, 1733 cm^{-1} (C=O); FAB MS (m/z), 513 (M$^+$ + H, 100%), 512 (M$^+$, 69) (Calc. for $C_{30}H_{28}N_2O_4S$: C, 70.29; H, 5.51; N, 5.46. Found: C, 69.99; H, 5.49; N, 5.30%).

3-[4-(Diethylamino)phenyl]-3′-(1-butyl-1,2-dihydroquinolin-2-ylidenemethyl)-4,4′-bis(cyclobut-3-ene-1,2-dione) 2e. Yield 70%; mp 248 °C (decomp.); ^{1}H NMR ($CDCl_3$) δ 1.10 (t, J = 7.3 Hz, 3 H), 1.25 (t, J = 7.3 Hz, 6 H), 1.70–1.99 (m, 4 H), 3.49 (q, J = 7.3 Hz, 4 H), 4.48 (t, J = 7.9 Hz, 2 H), 6.77 (d, J = 9.2 Hz, 2 H), 7.09 (s, vinyl H, 1 H), 7.47 (t, J = 6.7 Hz, 1 H), 7.61–7.71 (m, 3 H), 7.82 (d, J = 9.2 Hz, 1 H), 8.40 (d, J = 9.2 Hz, 2 H), 8.91 (d, J = 9.2 Hz, 1 H); IR (KBr) ν 1738, 1732 cm^{-1} (C=O); FAB MS (m/z) 507 (M$^+$ + H, 100%), 506 (M$^+$, 52) (Calc. for $C_{32}H_{30}N_2O_4$: C, 75.86; H, 5.97; N, 5.53. Found: C, 74.94; H, 5.71; N, 5.43%).

3-[4-(Dibutylamino)phenyl]-3′-(3-butyl-2,3-dihydrobenzothiazol-2-ylidenemethyl)-4,4′-bis(cyclobut-3-ene-1,2-dione) 2f. Yield 33%; mp 257 °C (decomp.); ^{1}H NMR ($CDCl_3$) δ 1.86–0.06 (m, 9 H), 1.25–1.67 (m, 10 H), 1.91 (quint, J = 7.9 Hz, 2 H), 3.40 (q, J = 7.9 Hz, 4 H), 4.31 (t, J = 7.9 Hz, 2 H), 6.75 (d, J = 9.2 Hz, 2 H), 7.26–7.38 (m, 3 H), 7.49 (t, J = 7.9 Hz, 1 H), 7.68 (d, J = 7.3 Hz, 1 H), 8.45 (d, J = 9.2 Hz, 2 H); IR (KBr) ν 1726, 1710 cm^{-1} (C=O); FAB MS (m/z) 569 (M$^+$ + H, 100%), 568 (M$^+$, 97) (Calc. for $C_{34}H_{36}N_2O_4S$ + 0.2H_2O: C, 71.35; H, 6.41; N, 4.89. Found: C, 71.28; H, 6.43; N, 4.83%).

3-[4-(Dibutylamino)phenyl]-3′-(1-butyl-1,2-dihydroquinolin-2-ylidenemethyl)-4,4′-bis(cyclobut-3-ene-1,2-dione) 2g. Yield 30%; mp 250 °C (decomp.); ^{1}H NMR ($CDCl_3$) δ 0.98 (t, J = 7.3 Hz, 3 H), 1.11 (t, J = 7.3 Hz, 6 H), 1.21–1.76 (m, 12 H), 3.36 (q, J = 7.3 Hz, 4 H), 4.47 (t, J = 7.3 Hz, 2 H), 6.75 (d, J = 9.2 Hz, 2 H), 7.09 (s, vinyl H, 1 H), 7.47 (t, J = 7.3 Hz, 1 H), 7.61–7.74 (m, 3 H), 7.82 (d, J = 9.8 Hz, 1 H), 8.39 (d, J = 9.2 Hz, 2 H), 8.91 (d, J = 9.8 Hz, 1 H); IR (KBr) ν 1733, 1714 cm^{-1} (C=O); FAB MS (m/z) 563 (M$^+$ + H, 100%), 562 (M$^+$, 74) (Calc. for $C_{36}H_{38}N_2O_4$ + 0.75H_2O: C, 75.04; H, 6.91; N, 4.86. Found: C, 75.10; H, 6.77; N, 4.69%).

3-(2,3,6,7-Tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-yl)-3′-(3-butyl-2,3-dihydrobenzothiazol-2-ylidenemethyl)-4,4′-bis-(cyclobut-3-ene-1,2-dione) 2h. Yield 35%; ^{1}H NMR ($CDCl_3$) δ 1.06 (t, J = 7.3 Hz, 3 H), 1.52–2.23 (m, 8 H), 2.81 (quint, J = 6.2 Hz, 4 H), 3.36 (t, J = 6.7 Hz, 4 H), 4.30 (t, J = 7.3 Hz, 2 H), 7.26–7.38 (m, 2 H), 7.45 (m, 2 H), 7.66 (d, J = 7.9 Hz, 1 H), 8.07 (s, 2 H); IR (KBr) ν 1709, 1687 cm^{-1} (C=O); FAB MS (m/z) 537 (M$^+$ + H, 28%), 536 (M$^+$, 30) (Calc. for $C_{32}H_{28}N_2O_4S$: C, 71.62; H, 5.25; N, 5.22. Found: C, 71.45; H, 5.30; N, 5.04%).

3-(2,3,6,7-Tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-yl)-3′-(1-butyl-1,2-dihydroquinolin-2-ylidenemethyl)-4,4′-bis(cyclobut-3-ene-1,2-dione) 2i. Yield 30%; mp 320 °C (decomp.); ^{1}H NMR ($CDCl_3$) δ 1.10 (t, J = 7.3 Hz, 3 H), 1.52–1.88 (m, 2 H), 1.92–2.20 (m, 6 H), 2.81 (quint, J = 6.1 Hz, 4 H), 3.37 (t, J = 6.1 Hz, 4 H), 4.47 (t, J = 7.9 Hz, 2 H), 7.10 (s, vinyl H, 1 H), 7.39–7.70 (m, 4 H), 7.79 (d, J = 9.7 Hz, 2 H), 8.01 (s, 2 H), 8.91 (d, J = 9.7 Hz, 1 H); IR (KBr) ν 1730, 1713 cm^{-1} (C=O); FAB MS (m/z) 532 (M$^+$ + H, 26%), 531 (M$^+$, 43) (Calc. for $C_{34}H_{30}N_2O_4$ + 0.2H_2O: C, 76.44; H, 5.74; N, 5.24%. Found: C, 76.38; H, 5.63; N, 5.28%).

X-Ray crystallographic analysis of 1a

A single crystal of **1a** suitable for X-ray crystallography was obtained by recrystallization from a CH_2Cl_2 solution of **1a** in hexane by slow solvent diffusion. All reflection data were collected on a Rigaku AFC5-R diffractometer using graphite-monochromated Mo-Kα radiation. Intensity data were collected in the range of $3 < 2\theta < 55°$ using an ω–2θ scan technique. The structure was solved by a direct method and refined by a full matrix least-square procedure. The reflections with $I > 4\sigma(I)$ were used for the structure refinement. All non-hydrogen atoms, except C(9), were refined with anisotropic thermal parameters. All hydrogen atoms were placed at the calculated positions, and subsequently included in the structure refinement. For the refinement, the TEXSAN program was used. Tables of the atomic coordinates, isotropic thermal parameters, full lists of bond lengths and angles, and least-squares planes have been deposited in supplementary Tables.

Crystal data: $C_{38}H_{40}N_2O_4$, M 588.74, triclinic, space group P-1, cell constants: a = 10.933(3), b = 17.941(5), c = 8.474(2) Å, α = 92.31(3)°, β = 102.96(3)°, γ = 81.59(2)°, V = 1602.3(7) Å^3, Z = 2, D_{calc} = 1.220 g cm^{-3}, unique reflections 4263, final R = 0.083, R_w = 0.089. †

† CCDC reference number 163768. See http://www.rsc.org/suppdata/p1/b1/b104059f/ for crystallographic files in .cif or other electronic format.

PPP MO calculations

The PPP MO method was used with a valuable *b* approximation described in a previous paper.[15] The standard ionization potential and one-centre electron-repulsion integral for carbon and oxygen atoms were used. For nitrogen atoms, I_p = 23.0 eV and γ_{rr} = 17.44 eV were used. The simplest possible geometries and planar structures were assumed for the molecules studied in the PPP MO calculations.

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