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Synthesis, structure, and complexation properties with transition metal cations of a novel methine-bridged bisquarylium dye

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Abstract

A new class of squarylium homologue, namely, an electronically neutral methine-bridged bisquarylium dye, was synthesized by a reaction of 4-(4-*N*,*N*-dialkylaminophenyl)-3-hydroxy-3-cyclobutene-1,2-dione with an excess amount of triethyl orthoformate. The X-ray crystallographic analysis revealed that the bisquarylium dye consists of two anilino-substituted cyclobutene components which are bridged with each other by a methine carbon. It was also confirmed that it possesses a highly delocalized π-conjugation structure over the whole molecule. Its unique electronic structure yielded an intense light absorption in the near-infrared region. The complexation properties of the dye with various metal cations were investigated, and the complexation with transition metal cations such as Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+} and Cu^{2+} exclusively induced drastic absorption spectral changes with hypsochromic shifts (Δλ; 59–197 nm). © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Squarylium homologue; Methine-bridged bisquarylium dye; X-ray crystallographic analysis; Intramolecular hydrogen bonding; Delocalized π-conjugation system; Complexation-induced spectral change

1. Introduction

Squarylium (SQ) dyes are 1,3-disubstituted cyclobutene derivatives into which either aromatic or heterocyclic groups are introduced as electron-donating components, and are often classified into cyanine dyes because it is possible to draw a localized electronic structure of the π-conjugated chromophore consisting of a positively charged donor–acceptor system with polymethine carbons (Fig. 1) [1]. Such a unique electronic structure often affords a variety of interesting photochemical properties such as large light absorptions in visible or near-infrared (NIR) regions, intense fluorescence emissions, and photoconductivity. These properties are quite attractive in terms of potential applications in such fields as chemosensory systems [2–4], materials for displays, optical recording media, and solar cell and xerographic uses [5]. In spite of much growing attention, however, poor diversity of SQ structures has been preventing wider uses of SQ dyes in various fields because the traditional synthetic method yields only symmetrical SQ dyes [1]. In order to overcome this problem, developed synthetic

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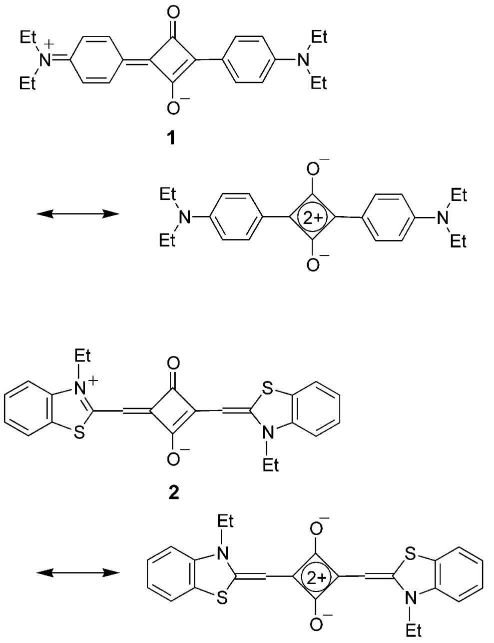


Fig. 1. Structures of typical SQ dyes showing commonly used electronic structures of their π-conjugation systems.

methods have been reported, where novel SQ dyes and their related compounds were demonstrated; unsymmetrical derivatives [6,7], polymers [8], and the other sophisticated derivatives [9,10]. We also have so far reported several SQ dyes and their homologues as shown in Fig. 2; unsymmetrical NIR SQ dyes **3** [11], cationic SQ homologues **4** [12], and bisquaraine dyes **5** [13]. Especially, to be emphasized is that the latter two dyes should greatly contribute to development of construction of novel SQ-based π-conjugation systems promising interesting photochemical and/or electrochemical properties. In the present paper, we show synthesis of a novel methine-bridged bisquarylium dye **6** and characterization of its structure by X-ray crystallographic structural analysis. In addition, in terms of potential application in a chemosensory system, absorption spectral changes upon complexation with various transition metal cations are discussed.

2. Results and discussion

2.1. Synthesis of methine-bridged bisquarylium dye

The bisquarylium dye **6** resembles the cationic SQ homologue **4** in that two cyclobutene components are bridged by a methine carbon, but differs in that **6** lacks the cationic, heterocyclic component on the methine carbon to possess an electronically neutral structure. As shown in Scheme 1, we obtained this compound by the reaction of 1 equiv. of 4-(4-*N*,*N*-

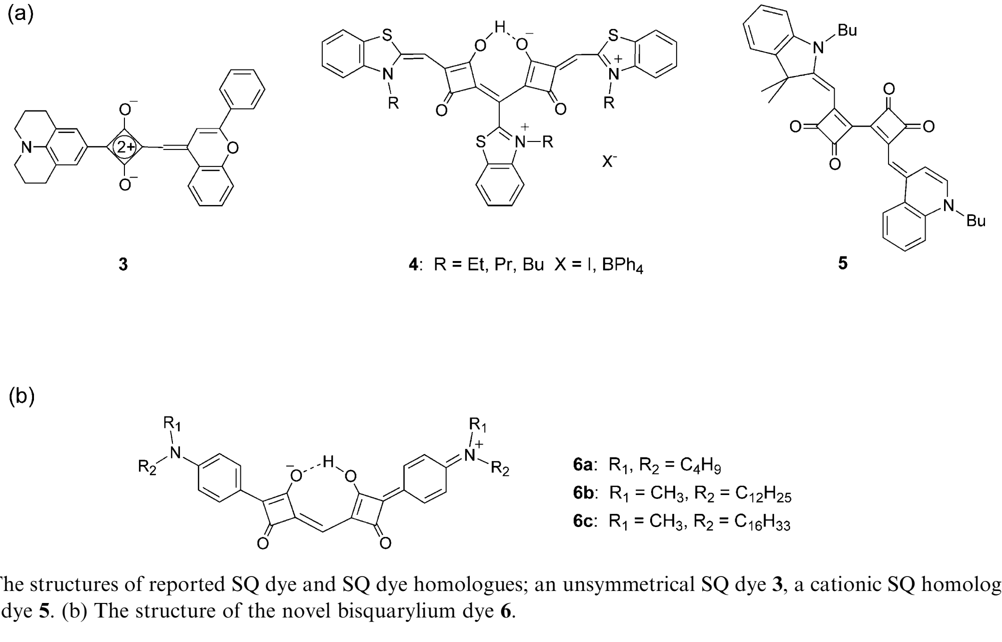
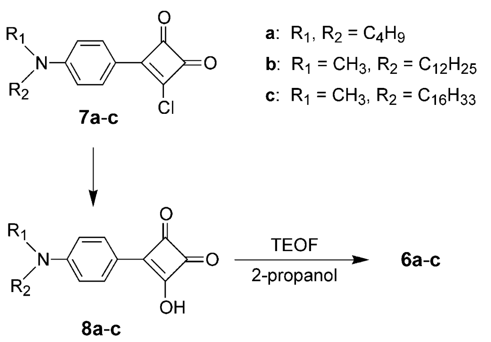


Fig. 2. (a) The structures of reported SQ dye and SQ dye homologues; an unsymmetrical SQ dye **3**, a cationic SQ homologue **4**, and a bisquaraine dye **5**. (b) The structure of the novel bisquarylium dye **6**.



Scheme 1.

dialkylaminophenyl)-3-hydroxy-3-cyclobutene-1,2-dione **8** with ca. 10 equiv. of triethyl orthoformate (TEOF) in 2-propanol, in 3–10% yield. The data in ^{1}H NMR, IR, and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra as well as elemental analysis afforded good agreement with the structure of **6**. The ^{1}H NMR spectrum of **6a** is shown in Fig. 3. The ratio of peak integrations between the singlet signal at 6.33 ppm (H^g), assigned to the central methine proton, and the triplet signal at 3.44 ppm (H^c), assigned to the N–CH_2 protons, was 1:8, showing two anilino-cyclobutene groups are symmetrically introduced to the methine carbon. In addition, the magnetic equivalence between the two anilino units indicates that **6a** possesses a highly symmetrical structure: π-electrons delocalizes over the whole molecule. The OH proton was observed at the far lower magnetic field (18.91 ppm), indicating that a hydrogen bond bridging the two cyclobutene rings is formed as observed in **4** [12]. Similar NMR spectral features were also observed in alkyl chain-modified derivatives **6b** and **6c**.

Although the detailed reaction mechanism has not been clarified at this point, the source of the methine carbon is expected to be TEOF because a reaction of **8** in the absence of TEOF did not proceeded at all. In general, TEOF is used as a cationic methylene synthon, i.e. a source of a carbocation, as seen in the synthesis of cyanine dyes [14]. Taking it into consideration that the cyclobutene derivative **8** behaves as an electrophile in the synthesis of SQ dyes [1], however, TEOF might be reduced to some carbanion synthon to react with **8**. The byproduct to be isolated and identified was the isopropyl ether of **8** produced by condensation with the solvent, 2-propanol. Although several reactions of **8** with other carbanion sources such as Grignard reagents, enolates, enamines, and Wittig reagents, any methine-bridged bisquaryliums were not produced.

2.2. A solid state structure of the dye 6a

The precise molecular structure of **6a** was confirmed by X-ray crystallographic analysis. A suitable

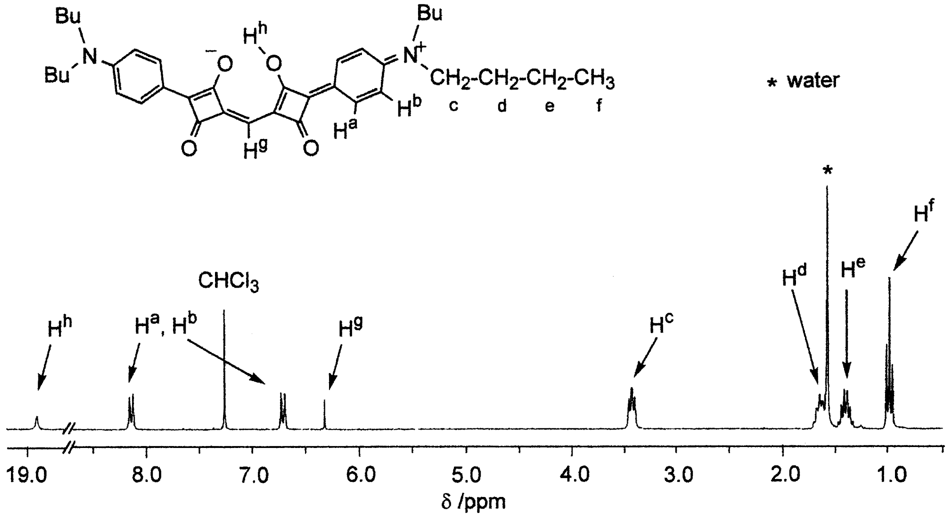


Fig. 3. 270 MHz ^{1}H NMR spectrum of **6a** in $CDCl_3$.

single crystal for the analysis was obtained by recrystallization from a benzene–hexane mixture. The overall structure and the selected bond lengths are shown in Fig. 4 and Table 1, respectively. The molecule of the dye **6a** possesses a pseudo C_{2v} symmetrical structure in the crystal packing. The least-squares planes of two anilinocyclobutene moieties omitting the alkyl chaines (plane 1 consisting of O1, O2, N1, and C1–C11 and plane 2 consisting of O3, O4, N2, and C12–C21) deviate from each other by 6.55°, whereas the mean deviations of the constituent atoms from the planes 1 and 2 are 0.00645 and 0.00220 nm, respectively, and those from the bisquarylium skeleton consisting the plane 1 and 2 is 0.00950 nm. Thus, **6a** adopts high planarity of the π-conjugation system. The bond distances of all C–C, C–O and C–N bonds except for C2–C5, C4–C5, C12–C15 and C14–C15 shows double bond or conjugated double bond characters, indicating a highly delocalized π-conjugation system over the whole molecule. The X-ray analysis shows that the OH proton (H40) lies in the middle of the two oxygen atoms, O1 and O3, within van der Waals radii from both oxygen atoms (O1–H40, 0.129(6) nm; O3–H40, 0.115(5) nm; O1–O3, 0.2433(4) nm, O1–H40–O3, 170(6)°), revealing the formation of a hydrogen bond to bridge the cyclobutene rings as observed in the ^{1}H NMR spectrum. Thus, one can see that two cyclobutene moieties are tightly fixed by the non-covalent intramolecular interaction so that the high planarity of the choromophore is maintained.

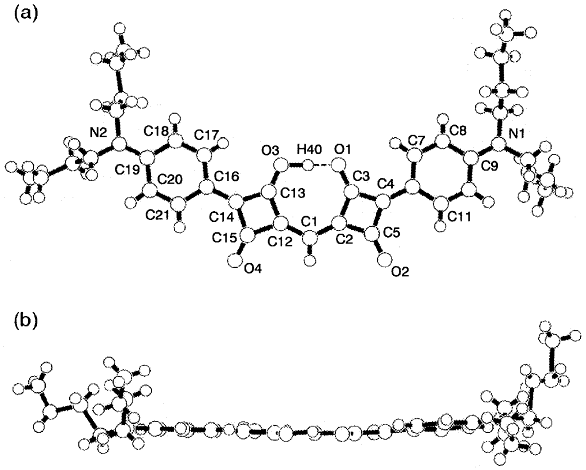


Fig. 4. A molecular structure of the dye **6a** (CHARON drawing); (a) the top view and (b) the side view.

Table 1
Selected bondlengths (nm) in the crystal structure of **6a**

Atom–atom	Distance	Atom–atom	Distance
O1–C3	0.1280(4)	C6–C11	0.1408(5)
O1–H40	0.129(6)	C7–C8	0.1351(6)
O2–C5	0.1215(5)	C8–C9	0.1407(6)
O3–C13	0.1269(5)	C9–C10	0.1392(6)
O3–H40	0.115(5)	C10–C11	0.1359(6)
O4–C15	0.1209(5)	C12–C13	0.1445(6)
N1–C9	0.1368(6)	C12–C15	0.1494(6)
N2–C19	0.1336(5)	C13–C14	0.1430(6)
C1–C2	0.1374(5)	C14–C15	0.1489(6)
C1–C12	0.1384(6)	C14–C16	0.1408(6)
C2–C3	0.1439(5)	C16–C17	0.1388(6)
C2–C5	0.1487(6)	C16–C21	0.1405(6)
C3–C4	0.1413(5)	C17–C18	0.1367(6)
C4–C5	0.1468(6)	C18–C19	0.1403(6)
C4–C6	0.1418(6)	C19–C20	0.1410(6)
C6–C7	0.1381(6)	C20–C21	0.1356(6)

2.3. *Light absorbing properties of the dye **6***

The structural feature of the largely extended π-conjugation system of **6** reflected upon its light absorbing properties. That is, as shown in Fig. 5, the dye **6a** exhibited a large electronic absorption in the NIR region (λ_{max}; 828 nm in $CHCl_3$) and modest one in the visible region (400–550 nm). The dyes **6b** and **6c** also exhibited their λ_{max} at the

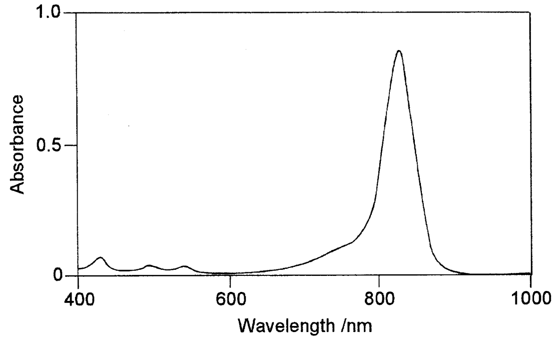


Fig. 5. The electronic absorption spectrum of **6a** (3.1×10^{-6} M) in $CHCl_3$ at 298 K.

similar wavelength (λ_{max}; 815 nm in $CHCl_3$ for both **6b** and **6c**).

Although failure to obtain another series of neutral methine-bridged bisquarylium dyes prevents us from referring in detail to the electronic structures, a comparison between the cationic **4** and the neutral **6** allows us to give some comment on the effect of the substituent branching at the central methine carbon. The typical anilinosquarylium dye **1** shows its λ_{max} at a shorter wavelength (634 nm in CH_2Cl_2) [15] than the benzothiazolinosquarylium **2** (667 nm in $CHCl_3$) [16], whereas the λ_{max} of **6** was observed at the longer wavelength than that of **4** (796 nm in $CHCl_3$). Thus, this comparison suggests that replacing a cationic heterocyclic component branching at the methine carbon in **4** by a neutral hydrogen atom gives rise to a bathochromic shift in the methine-bridged bisquarylium system.

*2.4. Complexation properties of the dye **6** with various transition metal cations*

One of interesting properties of methine-bridged bisquarylium dyes is complexation with various transition metal cations in a 1:1 manner, as demonstrated by Das and his coworkers using the dye **4** (R = Et, X = I) [4]. Since drastic absorption spectral changes are induced upon complexation, these dyes are potentially applicable to chemical indicators for metal cations. Thus, in the present system, the complexation-induced absorption spectral changes of **6** were studied using a series of transition metal cations as well as alkali and alkaline earth metal cations.

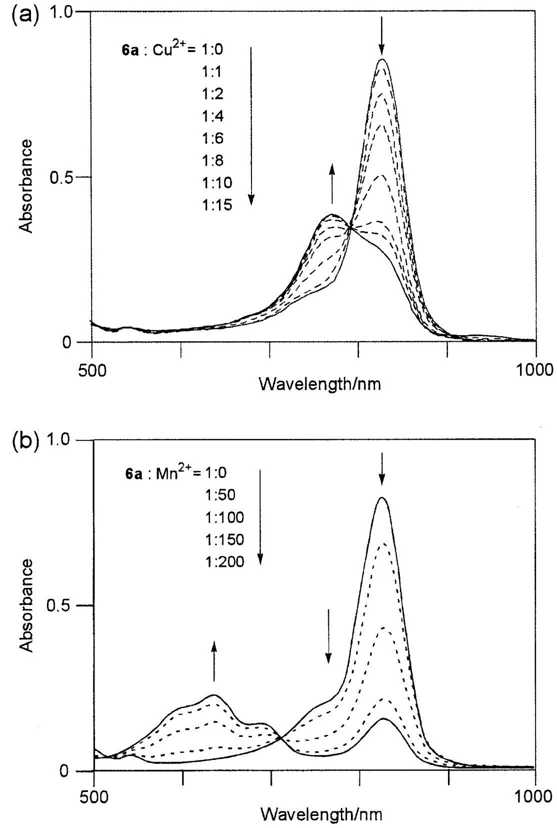


Fig. 6. Absorption spectral changes of acetone solution of **6a** upon addition of varying concentrations of (a) $Cu(ClO_4)_2$ and (b) $Mn(ClO_4)_2$ at 298 K.

Table 2
Absorption maxima of **6a**–metal cation complexes in acetone at 298 K

Cation	Cr^{3+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Cu^{2+}	Li^{+}	Na^{+}	K^{+}	Mg^{2+}	Ca^{2+}
λ_{max}/ nm	634	633	764	634	771	830	830	830	830	830
$\delta\lambda_{max}{}^{a}$/ nm	196	197	66	196	59	–[b]	–[b]	–[b]	–[b]	–[b]

[a] Hypsochromic shift at λ_{max} of **6a**.

[b] No absorption spectral changes were observed.

In Fig. 6a and b are shown electronic absorption spectral changes of **6a** in acetone upon successive additions of increasing amounts of Cu^{2+} and Mn^{2+} ions, respectively. For Cu^{2+}, the increase of the concentration of the cation induced the reduction of the absorbance at 830 nm, and instead, a new absorption band emerged at 771 nm. An isosbestic point at 794 nm indicates the **6**·Cu^{2+} complex is formed in a similar manner to **4**-metal cation complexes; chelation by two oxygens in the cyclobutene rings [4]. Absorption spectral changes of **6a** were also observed upon addition of varying concentrations of Mn^{2+} with appearance of a new absorption maximum at 633 nm. In Table 2 are summarized absorption maxima generating upon complexation with various metal cations. Any alkali or alkaline earth metal cations did not induce absorption spectral changes, whereas the spectral changes were sensitive to transition metal cations. The profiles of the spectral changes induced by the complexation with metal cations are classified into two types; the one showing λ_{max} at ca. 770 nm and the other at ca. 630 nm. The MALDI-TOF mass analysis afforded suggestive information for stoichiometry of the **6a**–metal cation complexes. The parent peak was observed at *m/z* 644 for the complex of **6a** with Cu^{2+}, corresponding to $[\mathbf{6a}\text{–}H^{+}]\cdot M^{2+}$. On the other hand, the formation of $[\mathbf{6a}]_2\cdot M^{n+}$ or $[\mathbf{6a}\text{–}H^{+}]_2\cdot M^{n+}$ complexes were indicated for Cr^{3+}, Mn^{2+}, and Co^{2+} (*m/z* 1217, 1218, and 1222, respectively). For Fe^{2+}, the molar ratio analysis based on the absorption spectral changes revealed that the 1:1 complex was predominantly formed in the **6a**–Fe^{2+} system. Taking it into consideration that the 1:2 complexes (Cr^{3+}, Mn^{2+}, and Co^{2+}) exhibited larger hypsochromic shifts of λ_{max} than the 1:1 complexes (Cu^{2+} and Fe^{2+}), the stoichiometry of the complexes would have close relation to the absorption spectral changes. Thus, it is possible to draw the complexation manners as shown in Fig. 7. It is agreeable to see that the complexation-induced hypsochromic shift of λ_{max} originates from electron-withdrawing properties of metal cations affecting the intramolecular charge transfer as well as reduction of the planarity of the π-conjugation system upon complexation with cations possessing larger ion radii than H^{+}.

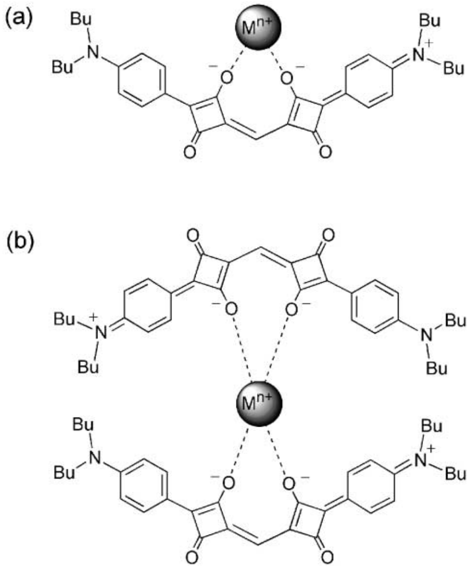


Fig 7. Possible stuructures of (a) the 1:1 complex and (b) the 1:2 complex formed by complexation of **6a** with transition metal cations.

3. Conclusions

In the present study, we demonstrated the synthesis of the novel SQ dye homologue, i.e., methine-bridged bisquarylium dye **6**, by the reaction of 4-(4-*N*,*N*-dialkylaminophenyl)-3-hydroxy-3-cyclobutene-1,2-dione **(8)** with an excess amount of triethyl orthoformate. The structure of the dye **6** was clearly confirmed by the X-ray crystallographic analysis, and characteristic is that the molecular structure shows high planarity of the π-conjugation system, which is maintained by the intramolecular hydrogen bonding formed between the two cyclobutene moieties. The dye **6** exhibited an intense light absorption in the NIR region ($\varepsilon = 2.51\text{–}3.92\times10^{5}$ mol^{-1} dm^{3} cm^{-1} at 815–828 nm in $CHCl_3$), and the complexation with a series of transition metal cations induced hypochromic shifts of λ_{max} of **6** by 59–197 nm. Thus, the methine-bridged bisquarylium dye **6** should be potentially applicable as the molecular sensory material for transition metal cations.

4. Experimental

4.1. General remarks

^{1}H and ^{13}C NMR spectra were obtained on a Jeol JNM-GX 270 FT–NMR spectrometer, and the chemical shifts are reported in ppm downfield from an internal TMS reference. Electronic absorption spectra were obtained on a Shimadzu UV-3100 spectrometer. IR spectra were recorded on a Horiba FT-200 spectrometer using KBr pellets. FAB and MALDI–TOF mass spectra were obtained on a Finnigan Mat TSQ-70 and Kratos Kompact MALDI 2 mass spectrometers, respectively. Elemental analyses were recorded on a Yanaco CHN-CORDER MT3 recorder. Solvents used for electronic absorption spectra were of spectroscopic grade. The procedure of the preparation of the compounds **7a** and **8a** were reported previously [11].

4.2. Sample preparation

4.2.1. Preparation of 3-chloro-4-[4-(N-dodecyl-N-methylamino)phenyl]-1,2-dioxo-3-cyclobutene **7b**

A mixture of *N*-dodecyl-*N*-methylaniline (2.76 g, 10.0 mmol) and 3,4-dichloro-3-cyclobutene-1,2-dione [17] (2.26 g, 15.0 mmol) in CH_2Cl_2 (15 ml) was stirred for 25 h under nitrogen atmosphere at ambient temperature. Then, the reaction mixture was washed with water, and the organic layer was dried with K_2CO_3, followed by removal of the solvent on a rotary evaporator. The residue was purified by silica gel column chromatography (CH_2Cl_2/hexane, 1/1 as eluent) to afford 1.81 g of **7b** (4.64 mmol, 46%): mp 184–185 °C (dec); ^{1}H NMR ($CDCl_3$) δ 0.88 (*t*, $J = 6.6$ Hz, 3H), 1.26 (*m*, 20H), 3.10 (*s*, 3H), 3.44 (*t*, $J = 7.5$ Hz, 2H), 6.74 (*d*, $J = 9.2$ Hz, 2H), 8.13 (*d*, $J = 9.2$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.20, 21.14, 22.76, 26.73, 26.96, 27.02, 29.39, 29.46, 29.61, 29.67, 31.96, 38.98, 52.95, 112.00, 131.50, 153.31, 185.92, 189.87, 195.65; FAB–MS (relative intensity) *m/z* 390 (60, $[M+H]^+$), 360 (74, $[M–CHO]^+$); IR (KBr) 2919, 2850, 1797, 1761 cm^{-1}. This compound was used for preparation of **8b** without further purification.

4.2.2. Preparation of 3-chloro-4-[4-(N-hexadecyl-N-methylamino)phenyl]-3- cyclobutene-1,2-dione **7c**

This compound was synthesized from *N*-hexadecyl-*N*-methylaniline by a similar method to preparation of **7b**: yield 38%; mp 86–87 °C (dec); ^{1}H NMR ($CDCl_3$) δ 0.88 (*t*, $J = 6.6$ Hz, 3H), 1.25 (*m*, 28H), 3.10 (*s*, 3H), 3.44 (*t*, $J = 7.5$ Hz, 2H), 6.74 (*d*, $J = 9.2$ Hz, 2H), 8.13 (*d*, $J = 9.2$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.18, 22.73, 26.95, 26.99, 29.38, 29.44, 29.59, 29.66, 29.69, 29.71, 29.72, 31.94, 38.36, 52.82, 111.82, 114.30, 131.44, 153.38, 185.78, 189.78, 195.61; FAB–MS (relative intensity) *m/z* 446 (100, $[M+H]^+$), 389 (42, $[M–2CO]^+$); IR (KBr) 2951, 2920, 2850, 1797, 1761 cm^{-1}. This compound was used for preparation of **8c** without further purification.

4.2.3. Preparation of 3-hydroxy-4-[4-(N-dodecyl-N-methylamino)phenyl]-3-cyclobutene-1,2-dione **8b**

To 5.5 ml of $AcOH/H_2O$ (4/1, v/v) was added **7b** (1.42 g, 3.64 mmol), and the mixture was heated at reflux for 4.5 h. After cooling, the reaction mixture was filtered, and the precipitate was washed with ether. The solid was sufficiently dried in vacuo to afford 1.15 g of **8b** (3.10 mmol, 85%): mp 212–213 °C (dec); ^{1}H NMR (DMSO-d_6) δ 0.83 (*t*, $J = 6.6$ Hz, 3H), 1.21 (*m*, 20H), 2.97 (*s*, 3H), 3.38 (*t*, $J = 7.6$ Hz, 2H), 6.83 (br, 2H), 7.82 (*br*, 2H); FAB–MS (relative intensity) *m/z* 371 (83, M^+), 315 (37, $[M-2CO]^+$); IR (KBr) 2926, 2852, 1764, 1749, 1704 cm^{-1}; Anal. calcd for $C_{23}H_{33}NO_3$: C, 74.36; H 8.95; N, 3.77%. Found: C, 74.18; H 9.21; N, 3.65%.

4.2.4. Preparation of 3-hydroxy-4-[4-(N-methyl-N-dodecylamino)phenyl]-3-cyclobutene-1,2-dione **8c**

This compound was synthesized from **7c** by a similar method to the preparation of **8b**: yield 95%; mp 202–203 °C (dec); ^{1}H NMR (DMSO-d_6) δ 0.83 (*t*, $J = 6.6$ Hz, 3H), 1.21 (*m*, 28H), 2.98 (*s*, 3H), 3.39 (*t*, $J = 7.1$ Hz, 2H), 6.85 (*d*, $J = 8.5$ Hz, 2H), 7.84 (*d*, $J = 8.5$ Hz, 2H); FAB–MS (relative intensity) *m/z* 428 (100, $[M+H]^+$), 371 (45, $[M–2CO]^+$); IR (KBr) 2918, 2852, 1767, 1751, 1704 cm^{-1}; Anal. calcd for $C_{27}H_{41}NO_3$: C, 75.84; H 9.66; N, 3.28%. Found: C, 75.74; H 9.98; N, 3.13%.

4.2.5. Preparation of the dye **6a**: general procedure for preparation of the dye **6**

To a suspension of the compound **8a** (2.25 g, 7.47 mmol) in 2-propanol (40 ml) was added triethyl orthoformate (10 ml), and the mixture was heated at reflux for 30 h. After cooling, the solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography, first eluted with CH_2Cl_2 to remove byproducts and then with $CHCl_3$ to isolate **6a**. Further purification by recrystallization from hexane-benzene afforded a crystal of **6a** with metallic luster (230 mg, 0.395 mmol, 10%): mp 182.2–182.5 °C (dec); ^{1}H NMR ($CDCl_3$) δ 0.99 (*t*, $J = 7.3$ Hz, 12H), 1.30–1.47 (*m*, 8H), 1.49–1.71 (*m*, 8H), 3.44 (*t*, $J = 7.3$ Hz, 8H), 6.33 (*s*, 1H), 6.72 (*d*, $J = 9.2$ Hz, 4H), 8.13 (*d*, $J = 9.2$ Hz, 4H), 18.91 (*s*, 1H); TOF–MS *m/z* 582 (M^+); IR (KBr) 1754, 1627, 1604, 1583 cm^{-1}; Vis–NIR ($CHCl_3$) λ_{max} (ε) 828 nm (2.77×10^5 mol^{-1} dm^3 cm^{-1}); Anal. calcd for $C_{37}H_{46}N_2O_4$: C, 76.26; H 7.96; N, 4.81%. Found: C, 75.87; H 8.00; N, 4.70%.

*4.2.6. Preparation of the dye**6b***

This compound was prepared by the reaction of **8b** (0.185 g, 0.498 mmol) with triethyl orthoformate (0.7 ml) in 2-propanol (3 ml). On purification by silica gel column chromatography, byproducts were eluted with CH_2Cl_2, and then, **6b** was obtained using CH_2Cl_2/EtOH (20/1, v/v) as eluent: yield 9%; mp 167.0–167.3 °C (dec); ^1H NMR ($CDCl_3$) δ 0.88 (*t*, $J=6.8$ Hz, 6H), 1.16–1.42 (*m*, 36H), 1.65 (*m*, 4H), 3.15 (*s*, 6H), 3.48 (*t*, $J=7.3$ Hz, 4H), 6.35 (*s*, 1H), 6.75 (*d*, $J=9.2$ Hz, 4H), 8.15 (*d*, $J=9.2$ Hz, 4H), 18.92 (*s*, 1H); TOF–MS *m/z* 723 (M^+); IR (KBr) 1753, 1637, 1602, 1585 cm^{-1}; Vis–NIR ($CHCl_3$) λ_{max} (ε) 815 nm (3.92×10^5 mol^{-1} dm^3 cm^{-1}); Anal. calcd for $C_{47}H_{66}N_2O_4+0.5H_2O$: C, 77.11; H 9.23; N, 3.83%. Found: C, 77.04; H 9.56; N, 3.54%.

*4.2.7. Preparation of the dye **6c***

This compound was prepared by the reaction of **8c** (0.213 g, 0.498 mmol) with triethyl orthoformate (0.7 ml) in 2-propanol (3 ml). Upon purification by silica gel column chromatography, byproducts were eluted with CH_2Cl_2, and then, **6c** was obtained using CH_2Cl_2/EtOH (20/1, v/v) as eluent: yield 3%; mp 160.1–160.9 °C (dec); ^1H NMR ($CDCl_3$) δ 0.87 (*t*, $J=6.8$ Hz, 6H), 1.26 (*m*, 52H), 1.64 (*m*, 4H), 3.14 (*s*, 6H), 3.45 (*t*, $J=6.9$ Hz, 4H), 6.36 (*s*, 1H), 6.74 (*d*, $J=9.2$ Hz, 4H), 8.14 (*d*, $J=9.2$ Hz, 4H), 18.92 (*s*, 1H); TOF–MS *m/z* 834 (M^+); IR (KBr) 1755, 1638, 1600, 1583 cm^{-1}; Vis–NIR ($CHCl_3$) λ_{max} (ε) 815 nm (2.51×10^5 mol^{-1} dm^3 cm^{-1}); Anal. calcd for $C_{55}H_{82}N_2O_4+0.5H_2O$: C, 78.24; H 9.91; N, 3.32%. Found: C, 78.26; H 10.11; N, 3.04%.

*4.3. X-ray crystallographic analysis of **6a***

A single crystal of **6a** suitable for the X-ray structural analysis was obtained by slow solvent diffusion of a benzene solution of **6a** into hexane. All data were collected on a Rigaku AFC-5R diffractmeter using graphite-monochromated Mo^{α}_{K} radiation. The intensity data were collected in the range of $5<2\theta<50°$ using a ω–2θ scan technique. The structure was solved by a direct method and refined by a full matrix least-squares procedure. All the reflections were used for the structure refinement. For the refinement, the TEXSAN program was used, and all non-hydrogen atoms were refined using anisotropic thermal parameters.

Crystal data: formula, $C_{37}H_{46}N_2O_4$; formula weight, 582.78; crystal system, P_{-1}; space group, triclinic; cell constants, $a=1.2292(3)$ nm, $b=1.3568(2)$ nm, $c=1.1344(1)$ nm, $\alpha=97.18(1)$, $\beta=97.73(1)$, $\gamma=113.15(1)$; V, 1.6907(5) nm^3; D_{calcd}, 1.145 g cm^{-3}; $Z=2$; crystal dimension, $0.30\times0.25\times0.15$; Refrections, 2255; residuals; $R=0.096$, $R_W=0.169$.

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