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Properties of unsymmetrical squarylium dyes containing strongly electron-donating 4′-amino-2,2′-bis(diethylamino)-4,5′-bithiazole residue

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Abstract

Novel unsymmetrical squarylium dyes containing the strongly electron-donating 4′-amino-2,2′-bis(diethylamino)-4,5′-bithiazole moiety were fluorescent and showed emission maxima around 640 nm. They have both alternant and intramolecular charge-transfer chromophoric systems.

Keywords: Squarylium dyes; Fluorescence spectra; MO calculations; Chromophoric system

1. Introduction

Squarylium (SQ) dyes are unique compounds due to their absorption and fluorescence bands in the near-infrared region [1–4]. They have been used as sensitizers and charge-generation materials. Symmetrical SQ dyes have been reported to show an alternant or a donor–acceptor–donor chromophoric system [5,6]. However, less is known about the properties of unsymmetrical SQ dyes [7,8]. We report here the synthesis, UV–vis absorption and fluorescence spectra, chromophoric character, and solubility of unsymmetrical SQ dyes derived from 4′-amino-2,2′-bis(diethylamino)-4,5′-bithiazole.

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2. Results and discussion

Scheme 1 shows the synthesis of SQ dyes **1**,**2**,**3**, and **5**. The symmetrical derivatives **1**,**2**, and **3** were prepared in moderate yields by the condensation of dibutyl squarate with two molar amounts of an arylamine. The SQ dyes **2** and **3** are known compounds and were synthesized as reference materials. The unsymmetrical derivatives **5** were prepared by a stepwise reaction of the appropriate 1-aryl-2-hydroxycyclobutene-3,4-dione **4** with 4′-amino-2,2′-bis(diethylamino)-4,5′-bithiazole.

The UV-vis absorption spectra of **1**, **3**, and **5a** are shown in Fig. 1. The properties of SQ dyes **1**, **2, 3**, and **5** are indicated in Table 1. The symmetrical reference compound **3** shows an intense (molar absorption coefficient (ϵ) = 140,000 dm^3 mol cm^{-1}) and sharp (half band width ($\nu_{1/2}$) = 32 nm) absorption band (λ_{max}) at 657 nm. In marked contrast, the dye **1** shows broad absorption bands

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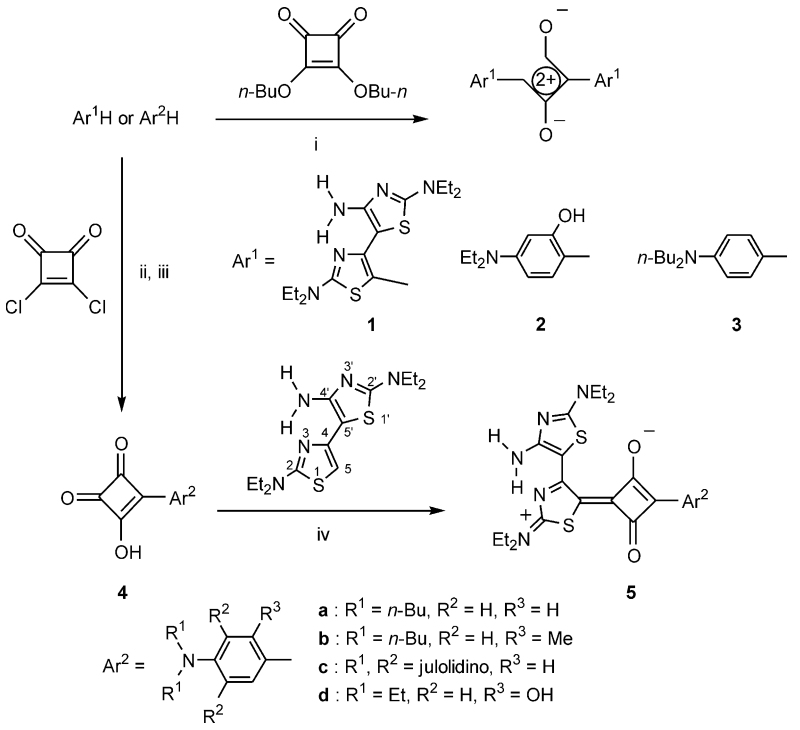

Scheme 1. Reaction conditions: (i) *n*-BuOH: toluene, reflux, 3 h; (ii) CH_2Cl_2, r.t., 24 h; (iii) $AcOH/H_2O$; (iv) *n*-BuOH: benzene, reflux, 8 h.

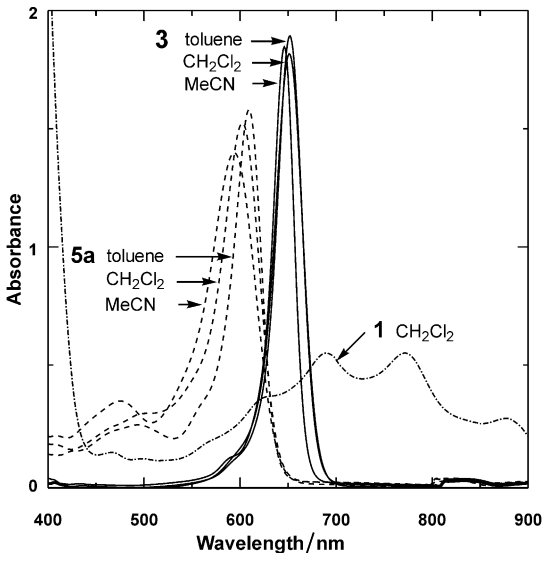

Fig. 1. UV-vis absorption spectra of **1**, **3**, and **5a**.

in the range of 600–900 nm. To analyze the chromophoric system of the SQ dyes, semi-empirical MO calculations were carried out [9]. Geometry optimization was obtained using the AM1 method, and the absorption spectra were calculated by the INDO/S method. In these calculations, the sulfur parameters (Es = 21.02, Ep = 10.97, Bsp = 13.5, G = 10.01) were used [10–12]. One hundred configurations were considered for the configuration interaction. Interestingly, one bithiazolyl moiety in **1** and **5** was calculated to be coplanar to the central cyclobutene ring. The conjugation of the bithiazolyl residue with the cyclobutene ring may be more favored than that of the phenyl moiety in the unsymmetrical derivatives **5**. AM1 geometry optimization calculations for **1** showed that one of the bithiazolyl to cyclobutene linkages had double bond character and the other had single bond character. Three isomers **1a**, **1b**, and **1c** were obtained, arising from rotation

Table 1
Properties of squarylium dyes **1**, **2**, **3**, and **5**

Dye	λ_{max} (nm)	(ε)[a]	λ_{ex}[a] (nm)	λ_{em}[a] (nm)	RFI[a,b]	SS[c]	Solubility[d] (mmol dm^{-3})
	879 (5000)						
1	775 (10000)		–[e]	–[e]	–[e]	–[e]	0.01, –[f]
	689 (9500)						
2	648 (387000)		652	662	216	10	0.11
3	657 (140000)		664	674	100	10	0.16, 0.03[g]
5a	603 (110000)		602	636	18	34	0.50
			607[h]	643[h]	16[h]	36[h]	
			601[i]	633[i]	18[i]	32[i]	
5b	614 (100000)		616	647	12	31	0.81, 0.20[g]
5c	624 (110000)		624	655	27	31	0.47
5d	616 (120000)		617	640	18	23	0.23

[a] Measured in dichloromethane at 25 °C.
[b] Relative fluorescence intensity (substrate: 1×10^{-5} mol dm^{-3})
[c] Stokes shift.
[d] Measured in ethyl acetate at 25 °C.
[e] No fluorescence.
[f] Insoluble in hexane at 25 °C.
[g] Measured in hexane at 25 °C.
[h] Measured in toluene at 25 °C.
[i] Measured in acetonitrile at 25 °C.

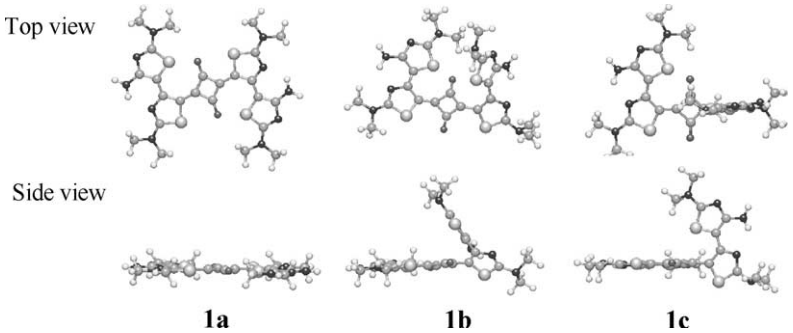

Fig. 2. AM1-optimized structures for **1**, with calculated heats of formation 235.4 (**1a**), 221.4 (**1b**), and 222.1 kcal mol^{-1} (**1c**). The INDO/S calculation gave a band at 761 nm (oscillator strength = 1.591) for **1a**; 862 nm (0.012) and 526 nm (0.469) for **1b**; 496 nm (0.074) and 468 nm (0.378) for **1c**.

about the single bond as shown in Fig. 2. AM1 geometry optimization gave planar structures for the compounds **2**, **3**, **5a**,**5c**, and **5d**. For the compound **5b**, a dihedral angle of 13.0 degrees between the phenyl and the cyclobutene rings was obtained, caused by the steric effect of the *o*-methyl group in the phenyl ring. Since the bithiazolyl moieties in **1** can rotate freely in solution, the broad absorption bands around 600–900 nm with small molar coefficients are observed. Assuming that isomers **1a** and **1b** show the UV-vis absorption band at 775 and 879 nm, respectively, a good linear relationship between the calculated and observed absorption bands was obtained, as shown in Fig. 3. A schematic representation of the differences in electron density between the ground and excited states in dyes **3** and **5a** is shown in Fig. 4. The first excitation of **5a** can be described as a mixture of a π–π* transition within the bithiazolyl moiety and an intramolecular charge-transfer transition from the dialkylaminophenyl to bithiazolyl moieties. This is completely different

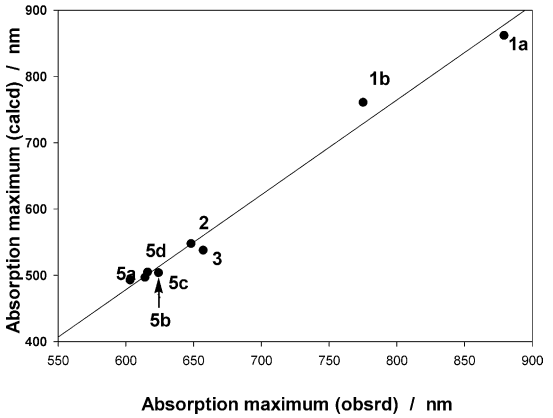

Fig. 3. Relationship between observed and calculated absorption maxima.

from the known alternant chromophoric system of symmetrical SQ dye **3**. Dyes **5b** and **5d** having electron-donating methyl and hydroxyl groups in the substituted phenyl moiety respectively, were more bathochromic than **5a**. Solvent effects on the absorption bands (of dyes **3** and **5a**) are also shown in Fig. 1. No significant solvent effect was observed for the symmetrical derivative **3**, whereas, the unsmmetrical dye **5a** showed a clear negative solvatochromism. The diplole moments of dye **3** in both ground and excited states were calculated to be 0.0 debye, whereas those of dye **5a** were calculated to be 10.36 and 3.61 debye, respectively. These results support the contribution of intramolecular charge-transfer chromophoric system in the unsymmetrical SQ dyes **5**.

No fluorescence was observed for dye **1**, probably due to the rotation between bithiazolyl and cyclobutene moieties. However, the dyes **5** were fluorescent. The emission maxima (λ_{em}) of **5** were more hypsochromic than those of **2** and **3**, due to hypsochromicity of the absorption λ_{max} of **5**. The Stokes shifts of dyes **5** were slightly larger than those of **2** and **3**. The relative fluorescence intensities (RFI) of **5** were smaller than those of **2** and **3**.

The SQ dyes **1**, **3**, and **5b** were more soluble in ethyl acetate than in hexane. The unsymmetrical SQ dyes **5** were more soluble than the symmetrical derivatives **1**, **2**, and **3**. The solubility of the unsymmetrical SQ dyes **5** was influence by the nature of substituents at the *o*-position in the phenyl ring; thus: Me > H > OH. This suggests

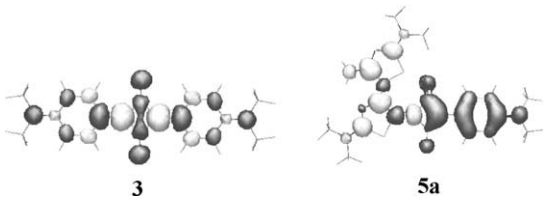

Fig. 4. Schematic representation of the changes in electron density between ground and first excited states of dyes **3** and **5a** (as the tris(dimethylamino) derivative) calculated by the INDO/S method for an AM1-optimized geometry. Gray and black colours indicate an increase and a decrease in electron density, respectively.

that a bulky substituent near the central cyclobutene ring helps increase the solubility, and that intramolecular hydrogen bonding decreases the solubility.

3. Experimental

3.1. Instruments

Melting points were measured with a Yanagimoto MP-S2 micro-melting-point apparatus. NMR spectra were recorded on a Varian Inova 400 spectrometer. Mass spectra were taken on a Shimadzu QP-1000 spectrometer. UV-vis absorption spectra were measured with a Hitachi U-3500 spectrometer.

3.2. Materials

3,4-Dihydroxy-3-cyclobutene-1,2-dione, *N,N*-dibutylaniline, 3-diethylaminophenol, and *m*-toluidine were purchased from Tokyo Kasei Co., Ltd. 2,3,6,7-Tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline was purchased from Sigma-Aldrich Co., Ltd. 2,4-Bis(4 - diethylamino - 2 - hydroxyphenyl)cyclobutanediylium-1,3-diolate (**2**) [13], 2,4-bis[4-(dibutylamino)phenyl]cyclobutenediylium-1,3-diolate (**3**) [13], 4-amino-2-diethylamino-5-(2-diethylamino-4-thiazolyl)thiazole [14], 4-[4-(dibutylamino)phenyl]-3-hydroxycyclobut-3-ene-1,2-dione (**4a**) [15], 4-(4-dibutylamino-2-methylphenyl)-3-hydroxycyclobut-3-ene-1,2-dione (**4b**) [15], 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 (**4c**) [15], and 4-(4-diethyl-

amino-2-hydroxyphenyl)-3-hydroxycyclobut-3-ene-1,2-dione (**4d**) [15] were prepared as described in the literature.

3.3. Synthesis of 2,4-bis{4-[4-amino-2-(diethylamino)thiazol-5-yl]-2-(diethylamino)thiazol-5-yl}-cyclobutenenediylium-1,3-diolate (*1*)

A butanol–benzene mixed solution (4:1, 30 cm^{-3}) of 4′-amino-2,2′-bis(diethylamino)-4,5′-bithiazole (0.32 g, 1 mmol) and 3,4-dibutoxy-3-cyclobutene-1,2-dione (0.12 g, 0.5 mmol) was refluxed for 3 h. After cooling, the solvent was removed *in vacuo* and the residue was purified by column chromatography (SiO_2, CH_2Cl_2) and recrystallized from ethanol. Yield 27%; mp 248 °C (decomposition); ^1H NMR ($CDCl_3$) δ 1.18 (t, $J=7.5$ Hz, 12H), 1.20 (t, $J=7.5$ Hz, 12H), 3.33–3.42 (m, 16H); EIMS (70 eV) m/z (rel intensity) 729 (M^+; 59) and 714 (100). Anal. found: C, 51.01; H, 6.21; N, 19.48%. Calcd for $C_{32}H_{44}N_{10}O_2S_2$: C, 52.72; H, 6.08; N, 19.21%.

3.4. Synthesis of unsymmetrical squarylium dyes *5*

A butanol-benzene mixed solution (4:1, 50 cm^{-3}) of 4′-amino-2,2′-bis(diethylamino)-4,5′-bithiazole (0.39 g, 1.2 mmol), 1-aryl-2-hydroxycyclobutene-3,4-diones **4** (1 mmol), and quinoline (0.19 g, 1.5 mmol) was refluxed for 8 h. After cooling, the solvent was removed *in vacuo*. The resulting solid was purified by column chromatography (SiO_2, CH_2Cl_2:AcOEt = 3:1) and recrystallized from ethanol.

3.4.1. 2-{4-[4-Amino-2-(diethylamino)thiazol-5-yl]-2-(diethylamino)thiazol-5-yl}-4-[4-(dibutylamino)phenyl]cyclobutenediylium-1,3-diolate (*5a*)

Yield 13%; mp 141–142 °C ; ^1H NMR ($CDCl_3$) δ 0.96 (t, $J=7.2$ Hz, 6H), 1.20–1.33 (m, 12H), 1.35 (sextet, $J=7.2$ Hz, 4H), 1.92 (quintet, $J=7.2$ Hz, 4H), 3.34 (t, $J=7.2$ Hz, 4H), 3.42–3.83 (m, 8H), 6.64 (d, $J=9.2$ Hz, 2H), 8.16 (d, $J=9.2$ Hz, 2H); IR (KBr) 1566 cm^{-1}; EIMS (70 eV) m/z (rel intensity) 608 (M^+; 41) and 607 (100). Anal. found: C, 62.88; H, 7.00; N, 14.05%. Calcd for $C_{32}H_{44}N_6O_2S_2$: C, 63.12; H, 7.28; N, 13.80%.

3.4.2. 2-[4-(4-Amino-2-(diethylamino)thiazol-5-yl]-2-(diethylamino)thiazol-5-yl]-4-(4-dibutylamino-2-methylphenyl)cyclobutenediylium-1,3-diolate (*5b*)

Yield 10%; mp 69–70 °C ; ^1H NMR ($CDCl_3$) δ 0.96 (t, $J=7.4$ Hz, 6H), 1.20–1.32 (m, 12H), 1.35 (sextet, $J=7.4$ Hz, 4H), 1.92 (quintet, $J=7.4$ Hz, 4H), 2.82 (s, 3H), 3.33 (t, $J=7.4$ Hz, 4H), 3.39–3.83 (m, 8H), 6.44 (s, 1H), 6.47 (d, $J=9.1$ Hz, 1H), 8.59 (d, $J=9.1$ Hz, 1H); EIMS (70 eV) m/z (rel intensity) 622 (M^+; 68) and 607 (100). Anal. found: C, 63.28; H, 7.25; N, 13.56%. Calcd for $C_{33}H_{46}N_6O_2S_2$: C, 63.63; H, 7.44; N, 13.49%.

3.4.3. 2-{4-[4-Amino-2-(diethylamino)thiazol-5-yl]-2-(diethylamino)thiazol-5-yl}-4-(2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-9-yl)cyclobutenediylium-1,3-diolate (*5c*)

Yield 23%; mp 208 °C (decomposition); ^1H NMR ($CDCl_3$) δ 1.25–1.33 (m, 12H), 1.94 (quintet, $J=6.2$ Hz, 4H), 2.75 (t, $J=6.2$ Hz, 4H), 3.29 (t, $J=6.2$ Hz, 4H), 3.51–3.87 (m, 8H), 7.80 (s, 2H); EIMS (70 eV) m/z (rel intensity) 576 (M^+; 72), 575 (100), and 561 (53). Anal. Found: C, 62.58; H, 6.17; N, 14.01%. Calcd for $C_{30}H_{36}N_6O_2S_2$: C, 62.47; H, 6.29; N, 14.57%.

3.4.4. 2-{4-[4-Amino-2-(diethylamino)thiazol-5-yl]-2-(diethylamino)thiazol-5-yl}-4-(4-diethylamino-2-hydroxyphenyl)cyclobutenediylium-1,3-diolate (*5d*)

Yield 11%; mp 185–187 °C; ^1H NMR ($CDCl_3$) δ 1.21–1.33 (m, 12H), 1.24 (t, $J=7.2$ Hz, 6H), 3.37 (q, $J=7.2$ Hz, 4H), 3.40–3.78 (m, 8H), 6.52 (d, $J=8.6$ Hz, 1H), 6.56 (s, 1H), 8.10 (d, $J=8.6$ Hz, 1H); EIMS (70 eV) m/z (rel intensity) 568 (M^+; 100) and 553 (49). Anal. found: C, 59.01; H, 6.12; N, 14.58%. Calcd for $C_{28}H_{36}N_6O_3S_2$: C, 59.13; H, 6.38; N, 14.78%.

4. Conclusions

Novel SQ dyes containing the strongly electron-donating 4′-amino-2,2′-bis(diethylamino)-4,5′-bithiazole residue were synthesized. The symmetrical bis(bithiazolyl) SQ dye showed broad absorption bands in the range of 600–900 nm,

whereas, the unsymmetrical derivatives showed intense and sharp absorption bands around 610 nm. The unsymmetrical SQ dyes were fluorescent compounds. MO theory indicated these unsymmetrical SQ dyes have mixed alternant and intramolecuar charge-transfer chromophoric systems. The solubility of the unsymmetrical SQ dyes was generally higher than that of corresponding symmetrical derivatives.

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References

[1] Griffiths J, Mama J. Dyes Pigm 2000;44:9.
[2] Nakazumi H, Natsukawa K, Nakai K, Isagawa K. Angew Chem, Int Ed Engl 1994;33:1001.
[3] Fabian J, Nakazumi H, Matsuoka M. Chem Rev 1992; 92:1197.
[4] Law KY. J Phys Chem 1987;91:5184.
[5] Yasui S, Matsuoka M, Kitao T. Dyes Pigm 1998; 10:13.
[6] Bigelow RW, Freund HJ. J Chem Phys 1986;107:159.
[7] Yagi S, Hyodo Y, Matsumoto S, Takahashi N, Kono H, Nakazumi H. J Chem Soc Perkin Trans 2000;1:599.
[8] Law KY, Bailey FC. J Org Chem 1992;57:3278.
[9] WinMOPAC ver. 2.0 package (Fujitsu, Chiba, Japan).
[10] Uchiyama S, Santa T, Imai K. J Chem Soc Perkin Trans 1999;2:2525.
[11] Sandman DJ, Ceaser GP, Fisher APIII, Schramm E, Titus DD, Baker AD. Chem Mater 1989;1:421.
[12] Bauman H, CNDUV99 Quantum Chemistry Program Exchange #333 Available from: http://qape.chem.indiana.edu/catalog.html.
[13] Keil D, Hartmann H. Liebigs Ann Chem 1995:979.
[14] Flaig R, Hartmann H. J Heterocycl Chem 1997; 34:1291.
[15] Deselm RC, Fox CJ, Riordan RC. Tetrahedron Lett 1970; 10:781.