Synthesis and Properties of Unsymmetrical Indamine Dyes Derived from 2,2′-Bis(dialkylamino)-4,5′-bithiazoles

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Unsymmetrical indamine dyes have been synthesized by the reaction of 2,2′-bis(dialkylamino)-4,5′-bithiazoles with 4-nitrosoanilines followed by heating with metal salts. The first UV/vis absorption bands of indamine dyes were observed at λ = 648–725 (ε = 3900–55000) nm in dichloromethane, being more bathochromic than those of the corresponding cyanine derivatives. The chromophoric system for these indamine dyes was described as a mixture of the π–π^* transition coming from the alternant chromophore inside the bithiazolyl moiety and the intramolecular charge-transfer transition from the anilino residue to the bithiazolyl moiety. Negative solvato- and halochromism have been observed for these indamine dyes.

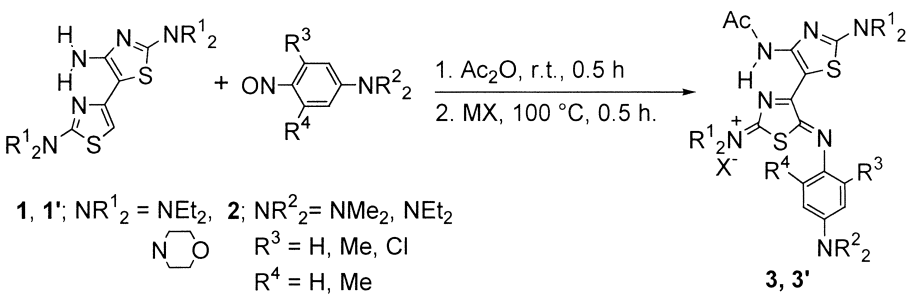
Indamine dyes are of importance due to their bathochromicity. Bindschedler's Green exhibits an intense absorption band at 725 nm in water, and the absorption maximum shifts to 400 nm upon the addition of acids.[1] Although symmetrical indamine dyes have been reported to have an alternant chromophoric system, no paper concerning the properties of unsymmetrical indamine dyes has been reported so far. In our previous paper, neutral azo dyes based on the 2,2′-bis(dialkylamino)-4,5′-bithiazoles chromophoric residue with strong electron-donating properties have been reported to show a negative solvatochromism.[2] Therefore, the synthesis and properties of the bithiazolyl-containing indamine dyes are also of interest. We report here on the synthesis, UV/vis absorption spectra, chromophoric characteristics, solvato- and halochromic behavior of unsymmetrical indamine dyes derived from 2,2′-bis(dialkylamino)-4,5′-bithiazoles.

Results and Discussion

Scheme 1 and Table 1 show the synthesis of indamine dyes, **3** and **3′**. These dyes were prepared by the reaction of 2,2′-bis(dialkylamino)-4,5′-bithiazoles **1** and **1′** with 4-nitrosoanilines **2** followed by heating with metal salts. The yields were dependent on the nature of the metal salt used, increasing in the order $Ni(BF_4)_2$, $NaBF_4 > Co(BF_4)_2 > Cu(BF_4)_2$. The yield of dye **3a** was also dependent on the salt used, increasing in the order $Ni(BF_4)_2$, $Ni(ClO_4)_2 > NiBr_2$. Since $Ni(BF_4)_2$ gave the best result, other dyes, **3b–e**, **3′a**, and **3′b**, were synthesized by using $Ni(BF_4)_2$.

The UV/vis absorption spectrum of dye **3a** is depicted in Fig. 1. The first and second absorption bands were observed at λ = 648 (ε = 38000 $dm^3\ mol^{-1}\ cm^{-1}$) and 506 (ε = 26000) nm in dichloromethane, respectively.

The observed UV/vis absorption spectra for dyes **3** and **3′** are summarized in Table 1. The bathochromic effect of the azomethine group in the indamine dye can be seen by comparing the first absorption bands of the morpholino derivatives **3′a** (λ_{max} = 670 nm, ε = 37000 in dichloromethane) and **3′b** (λ_{max} = 684 nm, ε = 55000) with those of the corresponding cyanine dyes: [4-(4-acetamido-2-morpholino-5-thiazolyl)-2-morpholino-5-thiazolyl]-[4-(dimethylamino)phenyl]methylium perchlorate (λ_{max} = 648 nm, ε = 49300 in dichloromethane) and [4-(4-acetamido-2-morpholino-5-thiazolyl)-2-morpholino-5-thiazolyl]-[4-(diethylamino)phenyl]methylium perchlorate (λ_{max} = 658 nm, ε = 49700), respectively.[3] The diethylamino derivative **3b** was more bathochromic than the corresponding dimethylamino derivative **3a**. Griffiths and Cox have



Scheme 1. Synthesis of indamine dyes **3** and **3′**.

Table 1. Observed and Calculated UV/vis Absorption Spectra for Dyes **3** and **3′**

Dye	NR^1_2	NR^2_2	R^3	R^4	MX	Yields %	λ_{max}[a] nm	ε[a] $dm^3\ mol^{-1}\ cm^{-1}$	$\Delta\lambda$[b] nm	Dihedral angle Degree[c]	λ_{max}[d] nm	f[e]
3′a		NMe_2	H	H	$Ni(BF_4)_2$	23	512 670	27000 37000	7	—	—	—
3′b		NEt_2	H	H	$Ni(BF_4)_2$	27	513 684	32000 55000	21	—	—	—
3a	NEt_2	NMe_2	H	H	$Ni(BF_4)_2$	20	506 648	26000 38000	−15	0.1	452	0.88
					$NaBF_4$	18	—	—	—	—	—	—
					$Co(BF_4)_2$	14	—	—	—	—	—	—
					$Cu(BF_4)_2$	10	—	—	—	—	—	—
					$Ni(ClO_4)_2$	19	506 650	26000 38000	−13	—	—	—
					$NiBr_2$	10	506 648	24000 36000	−15	—	—	—
3b	NEt_2	NEt_2	H	H	$Ni(BF_4)_2$	52	509 663	29000 51000	0	0.1	460	0.88
3c	NEt_2	NEt_2	Me	H	$Ni(BF_4)_2$	76	517 684	23000 39000	21	9.5	471	0.86
3d	NEt_2	NEt_2	Cl	H	$Ni(BF_4)_2$	92	514 654	25000 38000	−9	0.6	455	0.88
3e	NEt_2	NEt_2	Me	Me	$Ni(BF_4)_2$	23	519 725	24000 3900	62	65.2	505	0.16

a) Measured in dichloromethane. b) $\Delta\lambda = \lambda_{max}$ (**3′a–b**, **3a–e**) $-\lambda_{max}$ (**3b**).
c) The PM3-optimized dihedral angle between bithiazolyl and anilino segments.
d) Calculated by INDO/S method. e) Oscillator strength.

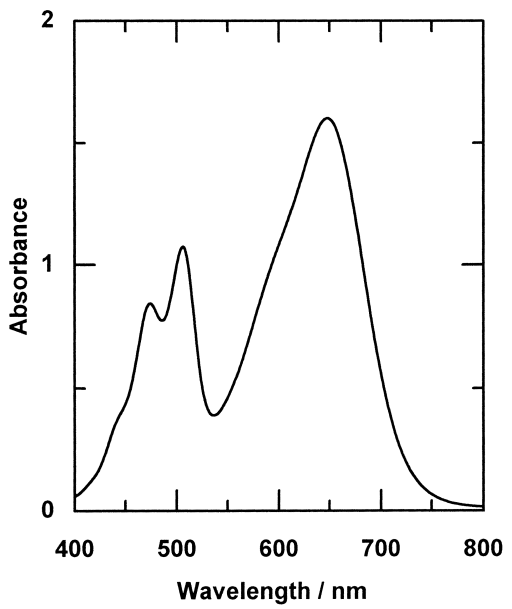


Fig. 1. UV/vis absorption spectrum of dye **3a** in dichloromethane.

reported that symmetrical indamine dyes have an alternant chromophoric system and that the electron-donating and -withdrawing groups attached to unstarred positions induced hypsochromic and bathochromic shifts in the first absorption band, respectively.[4]

The unsymmetrical indamine dye **3b** can also be indexed, as shown in Fig. 2. Among dyes **3b–d**, the bathochromicity was in the order of the dyes: **3c** ($\Delta\lambda$ = 21 nm) > **3b** ($\Delta\lambda$ = 0 nm) > **3d** ($\Delta\lambda$ = −9 nm). This result is not consistent with our dyes having the odd-alternant chromophoric system normally observed with indamine dyes.

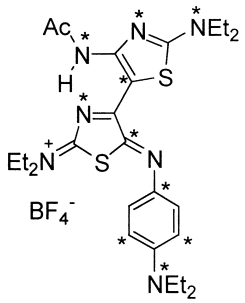


Fig. 2. Starring sequence in dye **3b**.

To explain this apparently anomalous substituent effect, semi-empirical MO calculations were carried out by the WinMOPAC ver. 2.0 package (Fujitsu, Chiba, Japan). Geometry optimizations were carried out using the PM3 method, and the absorption spectra were calculated with the INDO/S method. In the INDO/S calculation, the parameter of the sulfur atom (Es = 21.02, Ep = 10.97, Bsp = 13.5, G = 10.01)[5] was added for the calculations and 100 configurations were considered for the configuration interaction. The calculated λ_{max} values for the first absorption band showed a good linear correlation with the observed values, indicating that this calculation can analyze the chromophoric system of dye **3**. The first absorption

band was assigned to a HOMO–LUMO transition. The schematic representation of HOMO, LUMO and the difference in electron density between the ground and first excited states in dye **3b** are shown in Fig. 3. The first excitation was mainly described as the mixture of the π–π^* transition due to the alternant chromophore inside the bithiazolyl moiety and an intramolecular charge-transfer transition from the anilino to the bithiazolyl moieties. Namely, the anilino residue is not included in the alternant chromophoric system, but acts as an electron-donating group in the first excitation. The substituent effect on the *ortho*-position in the anilino residue can be explained by HOMO and LUMO's coefficients of 0.163 and 0.138, respectively. For example, a chlorine atom on the *ortho*-position stabilizes the HOMO more than the LUMO, thus increasing the energy gap between them.

The largest bathochromicity was observed in dye **3e**. A bulky group introduced into a naphthoquinone methide dye has been reported to cause a bathochromic shift.[6] In this case,

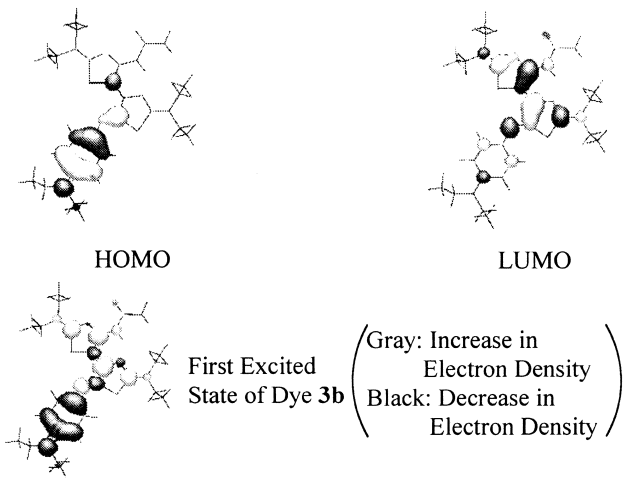


Fig. 3. Schematic representation of HOMO, LUMO and difference in electron density between ground and first excited states in dye **3b** calculated by INDO/S method for PM3-optimized geometry.

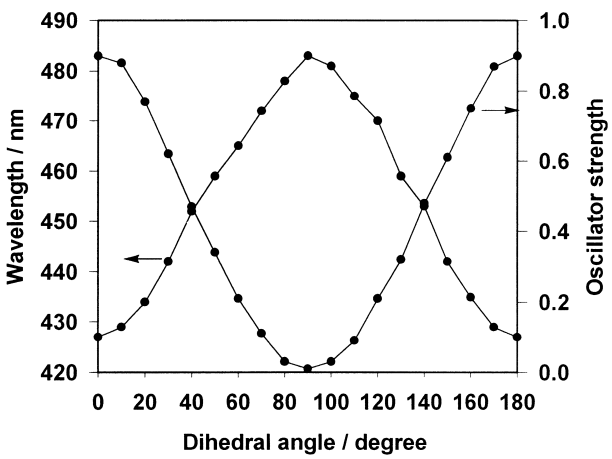


Fig. 4. Relationship between first absorption bands and oscillator strengths against dihedral angles for dye **3b**.

the configuration interaction calculations showed that bulky groups decrease the HOMO–LUMO energy gap. The dihedral angles (θ) between the bithiazolyl and anilino moieties in the optimized structures of dyes **3a–d** were calculated to be 0.1–9.5°. These results indicate that they are almost coplanar. The dihedral angle in dye **3e** was calculated to be 65.2°.

The relationship among the first absorption bands, the oscillator strengths and the dihedral angles in dye **3b** is shown in Fig. 4.

The most bathochromic shift was calculated at a dihedral angle of 90°.

The relationship between the HOMO, LUMO energy levels and the dihedral angles in dye **3b** is shown in Fig. 5. The closer is the dihedral angle between the bithiazolyl and anilino moieties to 90°, the higher is the energy level of HOMO, resulting in a bathochromic shift. Therefore, the bathochromicity of dye **3e** comes from a twisting between two segments due to the steric hindrance of the methyl groups at the *ortho*-positions in the anilino moiety. The decrease in the oscillator strength in dye **3e** can be also explained by a poor overlap of the wave functions between the donor and acceptor moieties.

The effect of solvents on the first absorption band of dye **3b** is shown in Fig. 6.

The relationship between the absorption maxima of dye **3b** and the polarity of all the solvents investigated was not clear. However, a reasonable correlation between the parameter of the solvent polarity (E_T) and negative solvatochromism was observed separately for aliphatic aprotic solvents, aromatic aprotic solvents and hydroxylic solvents.

The UV/vis absorption spectral changes of dye **3b** at different pH values using Britton-Robinson buffer solutions are depicted in Fig. 7. The dye **3b** possessed a good stability in the buffer solutions. No color change was observed in the range of pH values 7–11, showing λ_{max} at 606 nm. Then, the λ_{max} of dye **3b** shifted to 510 nm in the range of pH values 2–6. The isosbestic point was observed at λ = 551 nm, indicating the presence of a protic equilibrium. The electron-density at the diethylamino-nitrogen atom in the anilino moiety was calculat-

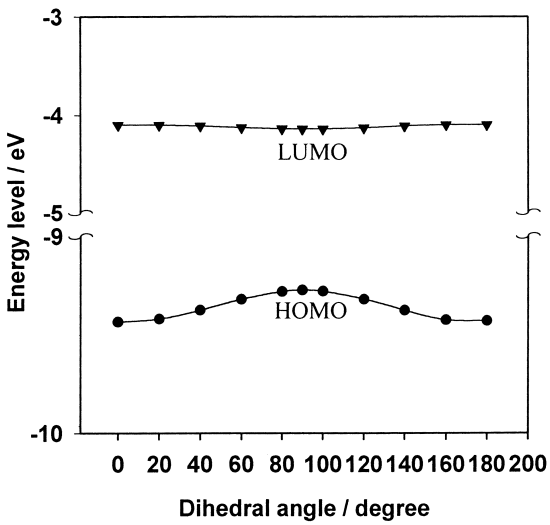


Fig. 5. Relationship between HOMO, LUMO energy levels and dihedral angles for dye **3b**.

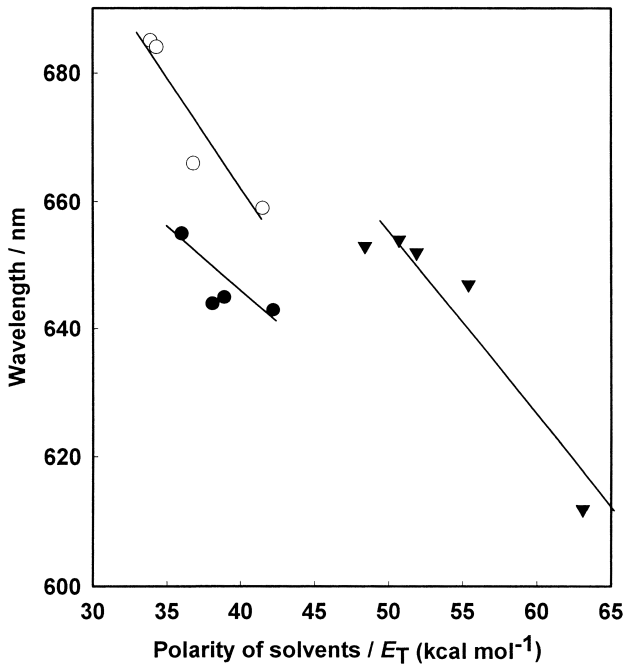


Fig. 6. Relationship between first absorption band of dye **3b** and polarity of solvents; ● aliphatic solvents; 1,4-dioxane (36.0 kcal mol^{-1}), ethyl acetate (38.1), triglyme (38.9), acetone (42.2), ○ aromatic solvents; toluene (33.9), benzene (34.3), chlorobenzene (36.8), benzonitrile (41.5), ▼ hydroxylic solvents; 2-propanol (48.4), 1-propanol (50.7), ethanol (51.9), methanol (55.4), water (63.1).

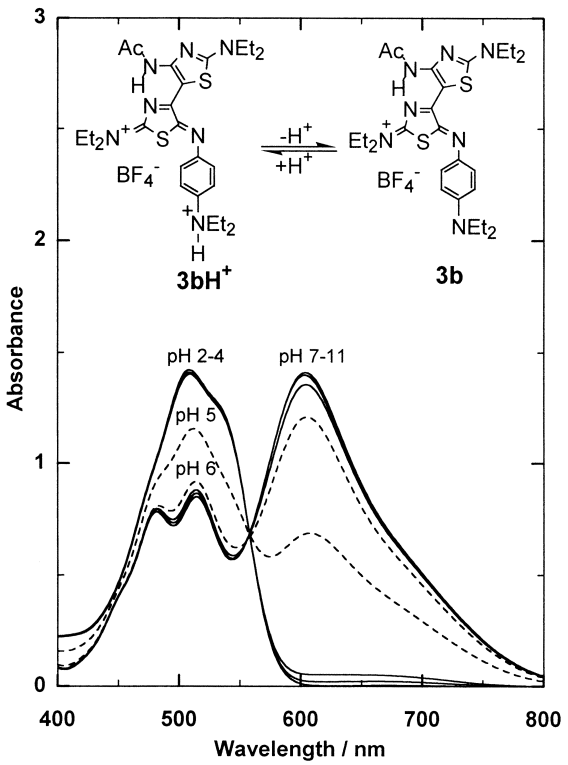


Fig. 7. UV/vis absorption spectral changes of dye **3b** at different pH values.

ed to be higher than those of other nitrogen atoms by a PM3 method, resulting in the formation of dye **3bH**$^+$ by the protonation of dye **3b**.

Conclusion

We have synthesized unsymmetrical indamine dyes derived from 2,2′-bis(dialkylamino)-4,5′-bithiazoles. Their first and second UV/vis absorption bands were observed at λ = 648–725 (ε = 3900–55000) and 506–519 (ε = 23000–32000) nm in dichloromethane, respectively. The substituent effect and INDO/S calculation showed that these indamine dyes had both alternant and intramolecular charge-transfer chromophoric systems. A large bathochromic shift was observed, caused by the large steric hindrance of two methyl groups at the *ortho*-positions in the anilino moiety. These new indamine dyes showed negative solvatochromism, and also negative halochromism upon the addition of acids.

Experimental

Apparatus. The melting points were measured with a Yanagimoto micro-melting-point apparatus. NMR spectra were recorded in $CDCl_3$ on JEOL α 400 and Varian Inova 400 spectrometers using tetramethylsilane as an internal standard. Mass spectra were taken on a Shimadzu QP-1000 spectrometer. UV/vis absorption spectra were measured with Shimadzu UV-160A and Hitachi U-3500 spectrometers.

Materials. *N*,*N*-dimethyl-4-nitrosoaniline (**2a**) and *N*,*N*-diethyl-4-nitrosoaniline (**2b**) were purchased from Tokyo Kasei Co., Ltd. 4′-Amino-2,2′-bis(diethylamino)-4,5′-bithiazole (**1**),[3] 4′-amino-2,2′-dimorpholino-4,5′-bithiazole (**1′**),[3] 3-methyl-4-nitroso-*N*,*N*-diethylaniline (**2c**),[4] 3-chloro-4-nitroso-*N*,*N*-diethylaniline (**2d**)[4] and 3,5-dimethyl-4-nitroso-*N*,*N*-diethylaniline (**2e**)[4] were prepared according to the literature.

Synthesis of indamine dyes 3 and 3′. A mixture of 4′-amino-2,2′-bis(dialkylamino)-4,5′-bithiazole **1** or **1′** (0.5 mmol) and 4-nitrosoanilines **2** (0.5 mmol) in acetic anhydride (20 mL) was stirred at room temperature for 0.5 h. To the mixture was added an acetic anhydride solution (1 mL) of nickel(II) tetrafluoroborate (0.25 mmol) and then heated at 100 °C for 0.5 h. After cooling, to the reaction mixture was added ethyl acetate (100 mL). The resulting precipitate was collected by filtration and recrystallized from a chloroform-hexane mixed solution. The physical and spectral data of the products are shown below.

{4-(4-Acetamido-2-diethylamino-5-thiazolyl)-2,5-dihydro-5-[4-(dimethylamino)phenyl]imino-2-thiazolylidene}diethylammonium Tetrafluoroborate (3a). Yield 20%; mp 255–257 °C; ^{1}H NMR ($CDCl_3$) δ 1.40 (t, J = 6.9 Hz, 3H), 1.45 (t, J = 6.9 Hz, 3H), 1.47 (t, J = 6.9 Hz, 3H), 1.48 (t, J = 6.9 Hz, 3H), 2.65 (s, 3H), 3.14 (s, 6H), 3.75 (q, J = 6.9 Hz, 2H), 3.77 (q, J = 6.9 Hz, 2H), 3.94 (q, J = 6.9 Hz, 2H), 3.95 (q, J = 6.9 Hz, 2H), 6.84 (d, J = 9.3 Hz, 2H), 7.48 (d, J = 9.3 Hz, 2H), 11.92 (s, 1H); EIMS (70 eV) *m*/*z* (rel intensity) 500 ($M^+ - BF_4$; 79), 458 (100), 360 (17). Anal. Found: C, 48.92; H, 5.82; N, 16.61%. Calcd for $C_{24}H_{34}BF_4N_7OS_2$: C, 49.06; H, 5.83; N, 16.69%.

{4-(4-Acetamido-2-diethylamino-5-thiazolyl)-5-[4-(diethylamino)phenyl]imino-2,5-dihydro-2-thiazolylidene}diethylammonium Tetrafluoroborate (3b). Yield 52%; mp 278–279 °C; ^{1}H NMR ($CDCl_3$) δ 1.26 (t, J = 7.1 Hz, 6H), 1.39 (t, J = 7.2 Hz, 3H), 1.45 (t, J = 7.2 Hz, 3H), 1.47 (t, J = 7.2 Hz, 3H), 1.48 (t, J = 7.2 Hz, 3H), 2.65 (s, 3H), 3.49 (q, J = 7.1 Hz, 4H), 3.74 (q, J = 7.2 Hz, 2H), 3.76 (q, J = 7.2 Hz, 2H), 3.93 (q, J = 7.2 Hz, 2H),

3.95 (q, J = 7.2 Hz, 2H), 6.83 (d, J = 9.0 Hz, 2H), 7.47 (d, J = 9.0 Hz, 2H), 11.92 (s, 1H); EIMS (70 eV) *m/z* (rel intensity) 528 (M^+-BF_4 ; 75), 499 (46), 486 (100), 456 (45). Anal. Found: C, 50.35; H, 6.09; N, 15.67%. Calcd for $C_{26}H_{38}BF_4N_7OS_2$: C, 50.73; H, 6.22; N, 15.93%.

[4-(4-Acetamido-2-diethylamino-5-thiazolyl)-5-(4-diethylamino-2-methylphenyl)imino-2,5-dihydro-2-thiazolylidene]diethylammonium Tetrafluoroborate (3c). Yield 76%; mp 242–243 °C; ^{1}H NMR ($CDCl_3$) δ 1.25 (t, J = 7.1 Hz, 6H), 1.38–1.49 (m, 12H), 2.54 (s, 3H), 2.65 (s, 3H), 3.47 (q, J = 7.1 Hz, 4H), 3.67–3.78 (m, 4H), 3.93–3.99 (m, 4H), 6.64 (s, 1H), 6.69 (d, J = 9.3 Hz, 1H), 7.34 (d, J = 9.3 Hz, 1H), 11.97 (s, 1H); EIMS (70 eV) *m/z* (rel intensity) 542 (M^+-BF_4 ; 100), 527 (16), 511 (30), 500 (54). Anal. Found: C, 51.51; H, 6.23; N, 15.18%. Calcd for $C_{27}H_{40}BF_4N_7OS_2$: C, 51.51; H, 6.40; N, 15.57%.

{4-(4-Acetamido-2-diethylamino-5-thiazolyl)-5-[2-chloro-4-(diethylamino)phenyl]imino-2,5-dihydro-2-thiazolylidene}diethylammonium Tetrafluoroborate (3d). Yield 92%, mp 246–248 °C; ^{1}H NMR ($CDCl_3$) δ 1.25 (t, J = 7.3 Hz, 6H), 1.38–1.45 (m, 12H), 2.65 (s, 3H), 3.44–3.49 (m, 4H), 3.68 (q, J = 7.3 Hz, 2H), 3.80 (q, J = 7.3 Hz, 2H), 3.92–3.99 (m, 4H), 6.81 (d, J = 9.8 Hz, 1H), 6.83 (s, 1H), 7.49 (d, J = 9.8 Hz, 1H), 11.96 (s, 1H); EIMS (70 eV) *m/z* (rel intensity) 564 (M^+-BF_4 + 2 ; 42), 562 (M^+-BF_4 ; 78), 520 (100), 117 (66), 88 (77). Anal. Found: C, 47.87; H, 5.69; N, 14.95%. Calcd for $C_{26}H_{37}BClF_4N_7OS_2$: C, 48.04; H, 5.74; N, 15.08%.

[4-(4-Acetamido-2-diethylamino-5-thiazolyl)-5-(4-diethylamino-2,6-dimethylphenyl)imino-2,5-dihydro-2-thiazolylidene]diethylammonium Tetrafluoroborate (3e). Yield 23%, mp 97–98 °C; ^{1}H NMR ($CDCl_3$) δ 1.20 (t, J = 7.0 Hz, 6H), 1.30–1.76 (m, 12H), 2.13 (s, 6H), 2.67 (s, 3H), 3.32–3.76 (m, 8H), 3.98 (q, J = 7.0 Hz, 4H), 6.95 (s, 2H), 11.88 (s, 1H); EIMS (70 eV) *m/z* (rel intensity) 556 (M^+-BF_4 ; 100), 528 (60), 514 (73). Anal. Found: C, 51.93; H, 6.25; N, 14.14%. Calcd for $C_{28}H_{42}BF_4N_7OS_2$: C, 52.25; H, 6.58; N, 15.23%.

1-{4-(4-Acetamido-2-morpholino-5-thiazolyl)-2,5-dihydro-5-[4-(dimethylamino)phenyl]imino-2-thiazolylidene}morpholinium Tetrafluoroborate (3′a). Yield 23%, mp 248–250 °C; ^{1}H NMR ($CDCl_3$) δ 2.64 (s, 3H), 3.13 (s, 6H), 3.87–3.90 (m, 8H), 3.95–4.12 (m, 8H), 6.82 (d, J = 9.3 Hz, 2H), 7.52 (d, J = 9.3 Hz, 2H), 11.72 (s, 1H) ; EIMS (70 eV) *m/z* (rel intensity) 528 (M^+-BF_4 ; 54), 511 (27), 486 (100)). Anal. Found: C, 45.86; H, 4.77; N, 15.50%. Calcd for $C_{24}H_{30}BF_4N_7O_3S_2$: C, 46.83; H, 4.91; N, 15.93%.

1-{4-(4-Acetamido-2-morpholino-5-thiazolyl)-5-[4-(diethylamino)phenyl]imino-2,5-dihydro-2-thiazolylidene}morpholinium Tetrafluoroborate (3′b). Yield 27%, mp 239–241 °C; ^{1}H NMR ($CDCl_3$) δ 1.25 (t, J = 7.1 Hz, 6H), 2.62 (s, 3H), 3.48 (q, J = 7.1 Hz, 4H), 3.81–3.92 (m, 8H), 3.93–4.07 (m, 8H), 6.83 (d, J = 9.3 Hz, 2H), 7.52 (d, J = 9.3 Hz, 2H), 11.64 (s, 1H); EIMS (70 eV) *m/z* (rel intensity) 556 (M^+-BF_4 ; 31), 525 (100), 514 (32), 486 (54). Anal. Found: C, 48.41; H, 5.25; N, 15.13%. Calcd for $C_{26}H_{34}BF_4N_7O_3S_2$: C, 48.53; H, 5.33; N, 15.24%.

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