Synthesis and Application of 2-Styryl-6,7-dichlorothiazolo[4,5-*b*]-quinoxaline Based Fluorescent Dyes: Part 3

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A new efficient synthesis of 2-styryl-6,7-dichlorothiazolo[4,5-*b*]quinoxaline based fluorescent dyes was achieved by the condensation of 2-methyl-6,7-dichlorothiazolo[4,5-*b*]quinoxaline with selected 4-*N*,*N*-dialkylaminoarylaldehydes and heteroarylaldehydes in the presence of piperidine. The coloristic, fluorophoric, and dyeing properties of these dyes were studied.

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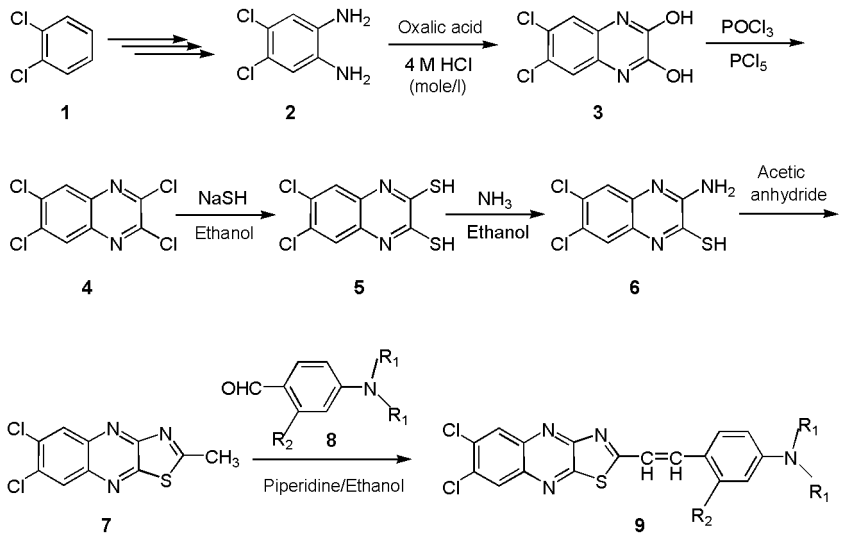
Introduction.

Fluorescent heterocyclic compounds were traditionally of interest in textile and polymer fields. Recently, these compounds have also gained much importance in the fields of molecular sensor [1], tunable dye lasers [2], and related hi-tech arenas, such as display [3]. Fluorophores also have an important role in search of new biologically active compounds and in the development of new diagnostic methods [4]. In the recent past, the fluorescence properties were used to determine the ion transport across the membrane [5]. Organic fluorescent compounds can be tailored to suppress some unwanted properties with the enhancement of desired character to fit for specific utility. While coumarins [6], triazoles [7], benzimidazols [8], napthalimides [9], pyrene [10], perylenes [11], *etc*. are well-established flurophores, there has been little investigation of heterofused quinoxaline systems as fluorescent styryl dyes. Styryl dyes with electron donor-acceptor moieties on either side of styryl bond are particularly attractive for their spectral sensitivity towards local host environment and optical and electronic properties.

Recently, the synthesis of novel dyes and fluorescence compounds containing thiazoles [12], thiophenes [13], pyridines [14], benzopyrans [15], and their application to the textiles have been reported. In earlier work from our laboratories, the versatility of quinoxalines has been demonstrated for the dyestuff area [16-19]. In addition, the thiazolo[4,5-*b*]quinoxaline [20] system was employed to develop new fluorescent dyes and their detailed photophysical properties are investigated [21]. The thiazolo-



		R_1	R_2
8a	**9a**	CH_3	H
8b	**9b**	C_2H_5	H
8c	**9c**	CH_3	OMe
8d	**9d**	C_2H_5	OMe
8e	**9e**	*n*-C_4H_9	OMe

quinoxaline system has also been used as a tool/probe for photophysical investigation [22,23]. A recent paper also discloses the importance of 6(7)-bromothiazolo[4,5-*b*]-quinoxalines nucleus for the synthesis of fluorescent styryl dyes [24]. These results have encouraged us to explore the utility of 2-methyl-6,7-dichlorothiazolo[4,5-*b*]quinoxaline **7** to produce daylight fluorescent dyes **9, 11**.

In the present paper, the chemistry of new fluorescent dyes is reported. A key goal of this work was to produce longer wavelength absorbing fluorescent dyes based on thiazolo[4,5-*b*]quinoxaline system and study the effect of chlorine substitution on the coloristic and fluorophoric properties of resultant styryl dyes **9a-e** and **11a-e**. We reported previously that halide substitution on quinoxaline ring of thiazolo[4,5-*b*]quinoxaline system results in bathochromic shift with no significant effect on fluorescent properties [24]. Taking advantage of this, the synthesis of longer wavelength absorbing dyes were achieved by introduction two chlorine atoms in quinoxalinyl ring of thiazolo[4,5-*b*]quinoxaline system.

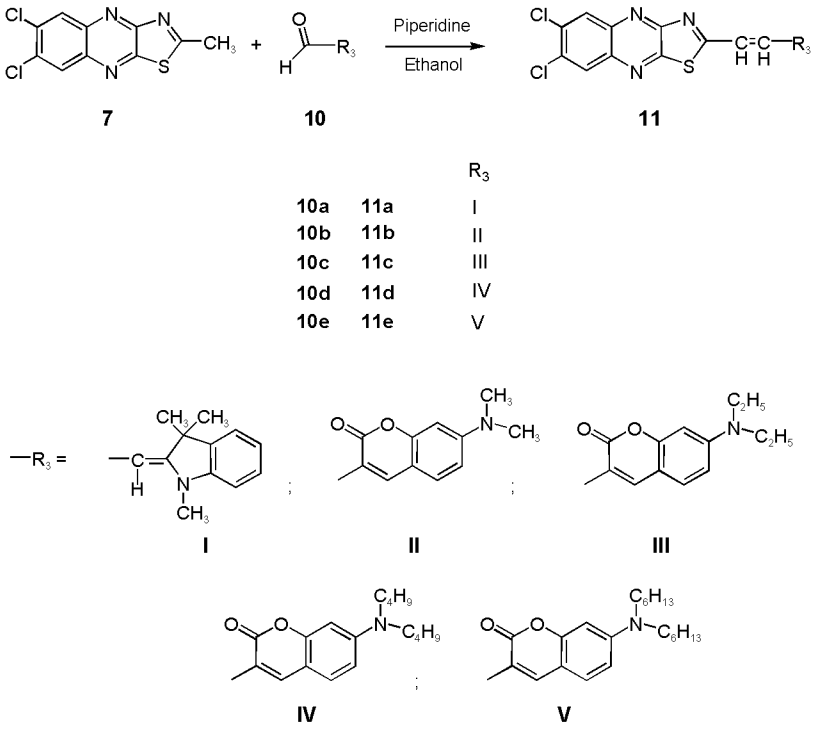
The key intermediate **7** was synthesized by the interaction of 2,3,6,7-tetrachloroquinoxalne **4** with sodium hydrosulfide followed by successive reactions involving alcoholic ammonia and refluxing acetic anhydride (Scheme 1). The synthesis involved the condensation of **7** with 4-*N*,*N*-dialkylaminosubstitutedaryl and heteroaryl-aldehydes in the presence of piperidine. The absorption and emission properties of these dyes were evaluated in various organic solvents and their dyeing properties were assessed on polyester fibers.

Results and Discussion.

Synthesis of Intermediates **7**.

2,3-Dihydroxy-6,7-dichloroquinoxaline **3** was synthesized in good yield by condensation of corresponding 4,5-dichloro-1,2-benzendiamine **2**, prepared from **1**, with oxalic acid in refluxing 4 *M* hydrochloric acid [25] (Scheme 1). The compound **3** on chlorination gave a colorless crystalline 2,3,6,7-tetrachloroquinoxaline **4** [25], which on subsequent reaction with sodium hydrogen sulfide gave dark brown solid of 2,3-dimercapto-6,7-dichloroquinoxaline **5** [26] in quantitative yield. The advantages of this chemistry include good yields, short reaction times, and straightforward procedures. In most of the cases, the products precipitated from the reaction mixture in pure form.

Partial ammonolysis of compound **5,** using alcoholic ammonia, yielded bright yellow crystalline 2-amino-3-mercapto-6,7-dichloroquinoxaline **6**. Optimum conditions for this temperature sensitive reaction, 100-120° for 3 hours, gave 71% yield. The bright yellow compound **6** was purified by dissolving in aqueous sodium hydroxide solution followed by reprecipitation with acetic acid. It was further purified by recrystallization from ethanol. Refluxing compound **6** in acetic anhydride yielded brown colored mass of **7**. Following recrystallization from



aqueous methanol, the structure was elucidated by its elemental and spectral analysis. The ^{1}H nmr spectrum showed that the methyl protons of **7** are deshielded and observed at 2.80 ppm. In aromatic region two clear singlets were observed at 8.03 and 8.13 ppm for two protons of quinoxaline ring.

Reaction of **7** with Aryl and Heteroaryl Aldehydes.

The Knovenagel condensation reaction involving **7** with aldehydes, using piperidine as base catalyst, occurred smoothly, giving dyes **9a-e** and **11a-e** in excellent yields (Schemes 1 and 2). In most of the cases, dyes were precipitated out from the reaction mass, which made work up process simpler. The all styryl dyes were purified by recrystallization from ethanol.

Visible Absorption Spectra and Solvatochromism.

The visible absorption spectra of **9a-e** and **11a-e** were recorded in solvents of varying polarity (chloroform, ethyl acetate, acetone, methanol), to assess the solvatochromic properties of these dyes (Table 1). Absorption maxima were observed at 507-552 nm in chloroform. Examination of absorption spectra of this dialkylaminophenyl donor and dichlorothiazolo[4,5-*b*]quinoxalne acceptor system showed several features, as follows: 1) The electron donating groups in **9a-e** and **11a-e** generated bathochromic shifts according to the strength of their electron donation. 2) The dyes showed high molar extinction coefficients and the logarithms of extinction coefficients were in the range of 4.56-4.94. 3) The dyes showed modest positive solvatochromism. 4) In general, the dichlorosubstitution on quinoxalinyl ring (of styryl dyes **9a-e** and **11a-e**) results in bathochromic shifts as compared with unsubstituted and monosubstituted styryl dyes [20,24].

Table 1

Visible Spectral Data [a] (in nm) of **9a-e** and **11a-e**

Dye No.	Chloroform	Ethyl Acetate	Acetone	Methanol
	$CHCl_3$ (Log ε)			
9a	507 (4.61)	495	499	504
9b	520 (4.56)	506	520	524
9c	516 (4.77)	506	514	525
9d	525 (4.80)	517	524	536
9e	528 (4.69)	521	527	538
11a	552 (4.94)	549	553	564
11b	518 (4.66)	512	510	514
11c	522 (4.72)	511	513	518
11d	533 (4.56)	520	523	525
11e	532 (4.75)	520	524	525

[a] The concentrations of dyes were between 4-8μM.

Fluorescence Spectra.

Fluorescence spectra were recorded in chloroform and emission maxima are listed in Table 2. The compounds exhibited reddish orange to reddish pink fluorescence in most of the organic solvents. The fluorescence maxima of these dyes were in the range of 593-604 nm in chloroform. The fluorescence of styryl dyes **9a-e** and **11a-e** was strong in chloroform, dichloromethane and ethyl acetate and remarkably weak in other solvents like methanol and acetone (not shown). For example, compound **9b** in dichloromethane possesses 143 times greater fluorescence than in methanol. The dyes possess good fluorescence efficiencies and are in the range of 0.40-0.59 relative to the ketone red laser dye (Table 2). Fluorescence maxima varied with the polarity of the solvents employed. The fluorescence maxima of all dyes shifted from reddish orange in chloroform and in ethyl acetate, to pink in methanol and in acetone (Table 2). Stokes shifts were calculated in both wavenumbers (cm^{-1}) and wavelength (nm) (Table 2) and are highest in acetone, with compound **9a** showing highest Stokes shift and **11a** the lowest, in acetone.

Dyeing Properties.

Dyes **9a-e** and **11a-e** were applied to polyester fibers as fluorescent disperse dyes. The dyes produced the color range from reddish orange to pink. The dyeing properties such as pick up, light fastness and sublimation fastness

Table 2

Fluorescence Spectral Data of **9a-e** and **11a-e** in (λ_{max} in nm)

Dye No.	$CHCl_3$	(ϕ) [a]	CH_2Cl_2	AcOEt	CH_3OH	CH_3COCH_3	Stokes shifts in acetone Wavenumber (cm^{-1})	Wavelength(nm)
9a	594	(0.51)	602	607	657	656	4796	157
9b	600	(0.46)	616	610	654	657	4010	137
9c	597	(0.59)	609	603	648	650	4070	136
9d	602	(0.43)	617	602	647	651	3722	127
9e	603	(0.40)	620	604	649	656	3731	129
11a	604	(0.44)	612	604	628	648	2651	95
11b	594	(0.45)	610	602	650	656	4363	146
11c	593	(0.48)	610	606	653	664	4432	151
11d	599	(0.47)	614	608	668	669	4172	146
11e	599	(0.51)	617	609	655	674	4247	150

[a] The quantum efficiency of dyes in choloroform were calculated relative to Keton Red laser dye in same solvent.

were evaluated on polyester fabric and summarized in Table 3.

These novel dyes possessed excellent sublimation fastness. Typical of fluorescent dyes the light fastness of all dyes was poor.

Table 3

Dyeing Properties of **9a-e** and **11a-e**

Dye No.	Color on polyester fiber	Light fastness	Sublimation Fastness
9a	Brilliant orange	1	4
9b	Luminescent red	1	4
9c	Brilliant red	1	5
9d	Bright reddish pink	1	5
9e	Bright reddish pink	1	4
11a	Pink	1	5
11b	Dark scarlet	1	5
11c	Fluorescent scarlet	1	5
11d	Dark reddish pink	1	5
11e	Pink	1	5

EXPERIMENTAL

All melting points are uncorrected and expressed in °C. The ^{1}H nmr spectra were recorded on either a Verian-300 MHz or a Hitachi-60MHz instrument, using tetramethylsilane as internal standard. Chemical shifts are given in δ (ppm). Mass spectra were recorded on a Varian Mat-311 instrument (70 eV). Absorption and fluorescence emission spectra were recorded on a Beckmann model-25 spectrophotometer and a SPEX 1681fluorolog T-Format fluoremeter, respectively. For fluorescence measurements, the excitation wavelength was wavelength of maximum absorption. Evaluation of 1.0% dye shades on polyester fabric (1.0% o.w.f.) was carried out according to standard fastness testing procedures [27]. The B02: 1978 test was used to assess the light fastness, and sublimation fastness was evaluated using P01: 1978 test, with polyester as an adjacent fabric at 180° ± 2°C [27].

Aldehydes **8a-b** were obtained from Aldrich chemicals and **8c, 10a** were procured from M/S Jalan Dyes & chemicals, Boisar, Maharashtra, India. Coumarin aldehydes **10b-10e** was synthesized from corresponding 7-(*N*,*N*-dialkylamino)coumarins *via* a Vilsmeier reaction [28].

2-Methyl-6,7-dichlorothiazolo[4,5-*b*]quinoxaline (**7**).

A mixture of **5** (2 g) [26] and alcoholic ammonia (20 ml saturated at 20°) was heated in an autoclave at 100-120° for 3 hours. The reaction mixture was evaporated and the residue was dissolved in 5% aqueous solution of sodium hydroxide (50ml) at 50-60°. The mixture was filtered and the filtrate was neutralized with acetic acid to produce a bright yellow precipitate. The precipitate was isolated by filtration, washed with water, dried and recrystallized from hot ethanol to yield 1.67 g (68%) of **6** as yellow crystals.

Anal. Calcd. for $C_8H_5Cl_2N_3S$: C, 39.04; H, 2.05; N, 17.07. Found: C, 39.16; H, 2.12; N, 16.98.

Compound **6** (2 g) was stirred in refluxing acetic anhydride (120 ml) for 4 hours. The excess anhydride was removed by vacuum distillation, and the residue obtained was diluted with 5% aqueous solution of sodium bicarbonate (50 ml) and left overnight. The dark brown precipitate was collected by filtration, washed with water, dried and recrystallized from 30% aqueous methanol to yield 1.57 g (71%) of **7** as pale orange yellow crystals, mp 139-140°; ^{1}H nmr (60 MHz, deuteriochloroform): δ 2.80 (s, 3H, CH_3), 8.03 (s, 1H, aromatic), 8.13 (s, 1H, aromatic); ms: m/z 270 (M^+), 269 (M^+ - 1), 255 (M^+ - CH_3).

Anal. Calcd. for $C_{10}H_5Cl_2N_3S$: C, 44.46; H, 1.87; N, 15.55. Found: C, 44.29; H, 1.94; N, 15.68.

2-[2-(4-*N*,*N*-Dimethylaminophenyl)ethenyl]-6,7-dichlorothiazolo[4,5-*b*]quinoxaline (9a).

A mixture of **7** (2.70 g, 0.01 mole) and **8a** (1.49 g, 0.01 mole) in absolute ethanol (10 ml) and piperidine (2-3 drops) was stirred at reflux for 8 hours. The precipitate was filtered, washed with ethanol, dried and recrystallized from ethanol to yield 3.35 g (83%) of **9a** as red crystalline solid, mp >300°; ^{1}H nmr (300 MHz, deuteriochloroform): δ 3.21 (s, 6H, $N(CH_3)_2$), 6.65 (d, 2H, aromatic, *J* = 8.8Hz), 7.13 (d, 1H, olefinic CH, *J* = 15.3 Hz), 7.51 (d, 2H, aromatic, *J* = 8.8 Hz), 7.72 (d, 1H, olefinic CH, *J* = 15.7 Hz), 8.18 (s, 1H, aromatic), 8.24 (s, 1H, aromatic); ms: m/z 401 (M^+), 400 (M^+ - 1).

Anal. Calcd. for $C_{19}H_{14}Cl_2N_4S$: C, 56.87; H, 3.52; N, 13.96. Found: C, 56.69; H, 3.61; N, 13.81.

2-[2-(4-*N*,*N*-Diethylaminophenyl)ethenyl]-6,7-dichlorothiazolo[4,5-*b*]quinoxaline (**9b**).

The procedure described above for **9a** were employed, except that **8b** was used in place of **8a**. Crude **9b** was recrystallized from ethanol to yield 3.46 g (80%) of **9b** as dark red crystalline solid, mp 247-250°; ^{1}H nmr (300 MHz, deuteriochloroform): δ 1.32 (t, 6H, $N(C_2H_5)_2$, *J* = 7.3 Hz), 3.43 (q, 4H, $N(C_2H_5)_2$, *J* = 7.3 Hz), 6.66 (d, 2H, aromatic, *J* = 8.8 Hz), 7.17 (d, 1H, olefinic CH, *J* = 15.4 Hz), 7.50 (d, 2H, aromatic, *J* = 8.8 Hz), 7.73 (d, 1H, olefinic CH, *J* = 15.7 Hz), 8.18 (s, 1H, aromatic), 8.26 (s, 1H, aromatic); ms: m/z 429 (M^+), 428 (M^+ - 1).

Anal. Calcd. for $C_{21}H_{18}Cl_2N_4S$: C, 58.74; H, 4.23; N, 13.04. Found: C, 58.85; H, 4.14; N, 13.13.

2-[2-(4-*N*,*N*-Dimethylamino-2-methoxyphenyl)ethenyl]-6,7-dichlorothiazolo[4,5-*b*]quinoxaline (**9c**).

The procedure described above for **9a** were employed, except that **8c** was used in place of **8a**. Crude **9c** was recrystallized from ethanol to yield 3.68 g (85%) of **9c** as black red crystalline solid, mp >300°; ^{1}H nmr (300 MHz, deuteriochloroform): δ 3.12 (s, 6H, $N(CH_3)_2$), 3.90 (s, 3H, OCH_3), 6.11 (d, 1H, aromatic, *J* = 2.2 Hz), 6.30 (dd, 1H, aromatic, *J* =8.8, 2.2 Hz), 7.25 (d, 1H, olefinic CH, *J* = 15.4 Hz), 7.52 (d, 1H, aromatic, *J* = 8.8 Hz), 7.84 (d, 1H, olefinic CH, *J* = 15.6 Hz), 8.18 (s, 1H, aromatic), 8.25 (s, 1H, aromatic); ms: m/z 431 (M^+), 430 (M^+ - 1).

Anal. Calcd. for $C_{20}H_{16}Cl_2N_4OS$: C, 55.69; H, 3.74; N, 12.98. Found: C, 55.81; H, 3.85; N, 12.85.

2-[2-(4-*N*,*N*-Diethylamino-2-methoxyphenyl)ethenyl]-6,7-dichlorothiazolo[4,5-*b*]quinoxaline (**9d**).

The procedure described above for **9a** were employed, except that **8d** was used in place of **8a**. Crude **9d** was recrystallized from ethanol to yield 3.41 g (74%) of **9d** as dark red crystalline solid, mp 205-208°; ^{1}H nmr (300 MHz, deuteriochloroform): δ 1.34 (t, 6H, $N(C_2H_5)_2$, *J* =7.3 Hz), 3.45 (q, 4H, $N(C_2H_5)_2$, *J* =7.3 Hz), 3.92 (s, 3H, OCH_3), 6.14 (d, 1H, aromatic, *J* = 2.2 Hz), 6.32 (dd, 1H, aromatic, *J* =8.7, 2.2 Hz), 7.27 (d, 1H, olefinic CH, *J* = 15.7

Hz), 7.50 (d, 1H, aromatic, *J* = 8.7 Hz), 7.91 (d, 1H, olefinic CH, *J* = 15.6 Hz), 8.16 (s, 1H, aromatic), 8.26 (s, 1H, aromatic); ms: m/z 459 (M^+), 458 (M^+ - 1).

Anal. Calcd. for $C_{22}H_{20}Cl_2N_4OS$: C, 57.52; H, 4.39; N, 12.19. Found: C, 57.67; H, 4.56; N, 12.38.

2-[2-(4-*N*,*N*-Di-*n*-butylamino-2-methoxyphenyl)ethenyl]-6,7-dichlorothiazolo[4,5-*b*]quinoxaline (**9e**).

The procedure described above for **9a** were employed, except that **8e** was used in place of **8a**. Crude **9e** was recrystallized from ethanol to yield 3.66 g (71%) of **9e** as red solid, mp 161-163°; ^{1}H nmr (300 MHz, deuteriochloroform): δ 0.99 (t, 6H, $N(C_4H_9)_2$, *J* = 7.3 Hz), 1.25-1.45 (m, 4H, $N(C_4H_9)_2$), 1.58-1.68 (m, 4H, $N(C_4H_9)_2$), 3.35 (t, 4H, $N(C_4H_9)_2$, *J* = 7.3 Hz), 3.93 (s, 3H, OCH_3), 6.09 (d, 1H, aromatic, *J* = 2.2 Hz), 6.31 (dd, 1H, aromatic, *J* = 8.79 2.2Hz), 7.36 (d, 1H, olefinic CH, *J* = 15.7 Hz), 7.49 (d, 1H, aromatic, *J* = 8.8 Hz), 8.11 (d, 1H, olefinic CH, *J* = 15.8 Hz), 8.17 (s, 1H, aromatic), 8.24 (s, 1H, aromatic); ms: m/z 515 (M^+), 514 (M^+ - 1).

Anal. Calcd. for $C_{26}H_{28}Cl_2N_4OS$: C, 60.58; H, 5.47; N, 10.87. Found: C, 60.74; H, 5.59; N, 10.72.

2-[3-(1,3-Dihydro-1,3,3-trimethyl-2*H*-indol-2-ylidene)-1-propenyl]-6,7-dichlorothiazolo[4,5-*b*]quinoxaline (**11a**).

The procedure described above for **9a** were employed, except that **10a** was used in place of **8a**. Crude **11a** was recrystallized from ethanol to yield 3.67 g (81%) of **11a** as dark red crystals solid, mp 295-298°; ^{1}H nmr (300 MHz, deuteriochloroform): δ 1.70 (s, 6H, $2CH_3$), 3.32 (s, 3H, N-CH_3), 5.68 (d, 1H, olefinic CH, *J* = 12.8 Hz), 6.54 (d, 1H, olefinic CH, *J* = 13.9 Hz), 6.84 (d, 1H, olefinic CH, *J* = 8.1 Hz), 7.04 (t, 1H, aromatic, *J* = 7.0 Hz), 7.25-7.30 (m, 2H, aromatic), 8.13 (s, 1H, aromatic), 8.20 (s, 1H, aromatic), 8.28 (t, 1H, aromatic, *J* = 9.8 Hz); ms: m/z 453 (M^+).

Anal. Calcd. for $C_{23}H_{18}Cl_2N_4S$: C, 60.93; H, 4.00; N, 12.35. Found: C, 60.80; H, 4.12; N, 12.47.

2-[2-(7-*N*,*N*-Dimethylamino-3-coumarinyl)ethenyl]-6,7-dichlorothiazolo[4,5-*b*]quinoxaline (**11b**).

The procedure described above for **9a** were employed, except that **10b** was used in place of **8a**. Crude **11b** was recrystallized from ethanol to yield 3.24 g (69%) of **11b** as blackish red crystalline solid, mp 288-290°; ^{1}H nmr (300 MHz, deuteriochloroform): δ 3.11 (s, 6H, $N(CH_3)_2$), 6.42 (d, 1H, aromatic, *J* = 1.6 Hz), 6.66 (dd, 1H, aromatic, *J* = 8.8, 1.6 Hz), 7.37 (d, 1H, aromatic, *J* = 8.7 Hz), 7.80 (s, 1H, aromatic), 7.93 (d, 1H, olefinic CH, *J* = 15.5 Hz), 8.04 (d, 1H, olefinic CH, *J* = 15.7 Hz), 8.22 (s, 1H, aromatic), 8.30 (s, 1H, aromatic); ms: m/z 469 (M^+).

Anal. Calcd. for $C_{22}H_{14}Cl_2N_4O_2S$: C, 56.30; H, 3.01; N, 11.93. Found: C, 56.44; H, 3.15; N, 11.79.

2-[2-(7-*N*,*N*-Diethylamino-3-coumarinyl)ethenyl]-6,7-dichlorothiazolo[4,5-*b*]quinoxaline (**11c**).

The procedure described above for **9a** were employed, except that **10c** was used in place of **8a**. Crude **11c** was recrystallized from ethanol to yield 3.58 g (72%) of **11c** as blackish red solid, mp 276-278°; ^{1}H nmr (300 MHz, deuteriochloroform): δ 1.21 (t, 6H, $N(C_2H_5)_2$, *J* = 7.0 Hz), 3.43 (q, 4H, $N(C_2H_5)_2$), 6.44 (d, 1H, aromatic, *J* = 1.6 Hz), 6.67 (dd, 1H, aromatic, *J* = 8.7, 1.6 Hz), 7.35 (d, 1H, aromatic, *J* = 8.8 Hz), 7.78 (s, 1H, aromatic), 7.91 (d, 1H, olefinic CH, *J* = 15.6 Hz), 8.02 (d, 1H, olefinic CH, *J* = 15.7 Hz), 8.19 (s, 1H, aromatic), 8.28 (s, 1H, aromatic); ms: m/z 497 (M^+).

Anal. Calcd. for $C_{24}H_{18}Cl_2N_4O_2S$: C, 57.95; H, 3.65; N, 11.26. Found: C, 58.09; H, 3.44; N, 11.49.

2-[2-(7-*N*,*N*-Di-*n*-butylamino-3-coumarinyl)ethenyl]-6,7-dichlorothiazolo[4,5-*b*]quinoxaline (**11d**).

The procedure described above for **9a** were employed, except that **10d** was used in place of **8a**. Crude **11d** was recrystallized from ethanol to yield 4.20 g (76%) of **11d** as dark solid, mp 220-225°; ^{1}H nmr (300 MHz, deuteriochloroform): δ 0.99 (t, 6H, $N(C_4H_9)_2$, *J* =7.3 Hz), 1.38 (m, 4H, $N(C_4H_9)_2$), 1.56 (m, 4H, $N(C_4H_9)_2$), 3.38 (t, 4H, $N(C_4H_9)_2$, *J* = 7.7 Hz), 6.48 (d, 1H, aromatic, *J* =1.5 Hz), 6.62 (dd, 1H, aromatic, *J* = 8.8, 1.6 Hz), 7.37 (d, 1H, aromatic, *J* = 8.8 Hz), 7.84 (s, 1H, aromatic), 7.91 (d, 1H, olefinic CH, *J* = 15.4 Hz), 8.01 (d, 1H, olefinic CH, *J* = 15.7 Hz), 8.23 (s, 1H, aromatic), 8.31 (s, 1H, aromatic); ms: m/z 553 (M^+).

Anal. Calcd. for $C_{28}H_{26}Cl_2N_4O_2S$: C, 60.76; H, 4.73; N, 10.11. Found: C, 60.52; H, 4.56; N, 10.21.

2-[2-(7-*N*,*N*-Di-*n*-hexylamino-3-coumarinyl)ethenyl]-6,7-dichlorothiazolo[4,5-*b*]quinoxaline (**11e**).

The procedure described above for **9a** were employed, except that **10e** was used in place of **8a**. Crude **11e** was recrystallized from ethanol to yield 4.75 g (78%) of **11e** as dark solid, mp 230-232°; ^{1}H nmr (300 MHz, deuteriochloroform): δ 0.92 (t, 6H, $N(C_6H_{13})_2$, *J* =7.3 Hz), 1.35 (m, 8H, $N(C_6H_{13})_2$), 1.58 (m, 8H, $N(C_6H_{13})_2$), 3.35 (t, 4H, $N(C_6H_{13})_2$, *J* = 7.7 Hz), 6.45 (d, 1H, aromatic, *J* =1.8 Hz), 6.59 (dd, 1H, aromatic, *J* = 8.8, 1.6 Hz), 7.34 (d, 1H, aromatic, *J* = 8.8 Hz), 7.80 (s, 1H, aromatic), 7.87 (d, 1H, olefinic CH, *J* = 15.4 Hz), 7.98 (d, 1H, olefinic CH, *J* = 15.8 Hz), 8.21 (s, 1H, aromatic), 8.28 (s, 1H, aromatic) ms: m/z 609 (M^+).

Anal. Calcd. for $C_{32}H_{34}Cl_2N_4O_2S$: C, 63.05; H, 5.62; N, 9.18. Found: C, 63.23; H, 5.45; N, 9.23.

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