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ORIGINAL PAPER

Synthesis of novel diphenylamine-based fluorescent styryl colorants and study of their thermal, photophysical, and electrochemical properties

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Abstract Three novel "Y"-shaped acceptor–π-donor–π-acceptor-type compounds were synthesized from 4,4′-(hexylimino)bis(benzaldehyde) as a donor and 2-methylthiazolo[4,5-*b*]quinoxaline derivatives as strong electron acceptors condensed by classical Knoevenagel condensation. Their absorption, emission, and thermal properties and electrochemical stability were investigated. It was found that the strong electron acceptor–donor chromophoric system of these compounds showed high Stokes shift, excellent thermal stability, and electrochemical reversibility. The solvatochromic behavior of these colorants was studied by using various solvents such as toluene, chloroform, ethyl acetate, tetrahydrofuran, methanol, and *N*,*N*-dimethylformamide in increasing order of polarity. The dyes were characterized by means of elemental analysis, ^{1}H NMR, and mass spectrometry.

Keywords Dyes · Absorption spectra · Fluorescent colorants · Cyclic voltammetry · Knoevenagel condensation

Introduction

Electron transfer (ET) is one of the most fundamental phenomena in chemistry and biology [1]. Organic fluorescent heterocyclic chromophores have a wide range of applications in biochemistry and electronics such as molecular probes [2], organic light-emitting diodes [3], photovoltaic cells [4], and in traditional textile and polymer fields [5].

Electron donors like triphenylamine and diphenylamine with high electron mobility and thermal and photochemical stability are commonly used as hole-transporting materials or light-emitting materials for balanced charge injection. Recently triphenylamine derivatives have been widely investigated [6]. *N*-Alkyldiphenylamines have not been exploited much in the past, but attract increasing interest as they exhibit better solubility in common organic solvents, excellent thermal and electrochemical stability, electron-donating ability, and optoelectronic properties [7]. The rigidity and non-planar structure of *N*-alkyldiphenylamines offer a sterically well-hindered feature. The presence of two electron acceptor moieties increases the electron affinity of the compounds [8]. From the viewpoint of molecular design, structural features such as the long π conjugation style, the molecular planarity, and the length of the conjugated bridge play important roles in functional chromophores, which are highly promising for electronic applications like photonics materials [9, 10], holographic optical data storage [11], and organic photorefractive materials. It has been demonstrated that diarylamine- and triarylamine-based chromophores have extremely high electro-optic properties [12]. Exploitation of electron acceptor fused quinoxaline systems as fluorescent styryl dyes is of interest because of their strong fluorescence [13, 14] and their versatile applications [15, 16]. Quinoxalines are in general easy to prepare [17–19].

In this research work, our interest was to design and develop novel heterocycle-based chromophores with excellent photophysical and thermal properties. We report the synthesis and study of new chromophores based on 4,4′-(hexylimino)bis(benzaldehyde) (**11**). We have especially focused on the condensation and synthesis of two

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excellent molecular moieties, 2-methylthiazolo[4,5-*b*]-quinoxaline (**6**) and 4,4′-(hexylimino)bis(benzaldehyde) (**11**). Rangnekar et al. [20] reported the synthesis and study of quinoxaline-based styryl dyes for polyester applications. We have exploited that earlier work and now report the synthesis and study of novel quinoxaline-based styryl dyes for functional applications with improved photophysical properties.

Results and discussion

Most of organic dyes have limited applications because of some disadvantages such as lack of photophysical and thermal stability [21]. In order to overcome these problems, "Y"-shaped dyes were designed and synthesized. The linear long alkyl chain was introduced via the 4,4′-(hexylimino)bis(benzaldehyde) moiety to improve the solubility of the resulting fluorescent compounds in common organic solvents. The photophysical, thermal, and electrochemical properties of these dyes were studied (Table 1).

2,3-Dimercaptoquinoxaline (**4**) was synthesized from benzene-1,2-diamine in three steps. The advantages of this method include good yields, short reaction times, and simple procedures and, in most cases, the product is precipitated from the reaction media. Partial ammonolysis of compound **4** using alcoholic ammonia yielded the crystalline compound **5**. An optimum condition for this temperature-sensitive reaction is 100–120 °C for 3 h, which gave 70% yield. Electron acceptors 2-methylthiazolo[4,5-*b*]quinoxaline (**6**) and 2,6-dimethylthiazolo[4,5-*b*]-quinoxaline (**7**) were synthesized by condensation reaction of 2,3-dichloroquinoxaline with sodium hydrogen sulfide, followed by subsequent reaction with ammonia and acetic anhydride (Scheme 1) [22, 23]. Key intermediate **11** was synthesized by N-hexylation of diphenylamine, followed by Vilsmeier–Haack formylation (Scheme 2) [24]. Chromophores **12a–12c** were synthesized by the classical Knoevenagel condensation of 4,4′-(hexylimino)bis(benzaldehyde) with electron acceptors **6** and **7** (Scheme 3). Chromophores **12a–12c** are soluble in common organic solvents such as chloroform, dichloromethane, 1,2-dichloroethane, acetonitrile, tetrahydrofuran (THF), and *N,N*-dimethylformamide (DMF) due to introduction of the long hexyl chain in the compounds. All intermediates and final compounds were characterized by ^{1}H NMR, ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis. The coupling constant ($J = 16.2$ Hz) of olefinic protons in purified chromophores **12a–12c** indicates that the reaction afforded the *trans* isomer [25]. There are chances of formation of isomeric compounds but these may get removed during recrystallization. No isomer was detected in the synthesis of colorant **12c** as proven by NMR spectra.

Table 1 Thermal and electrochemical properties of **12a–12c**

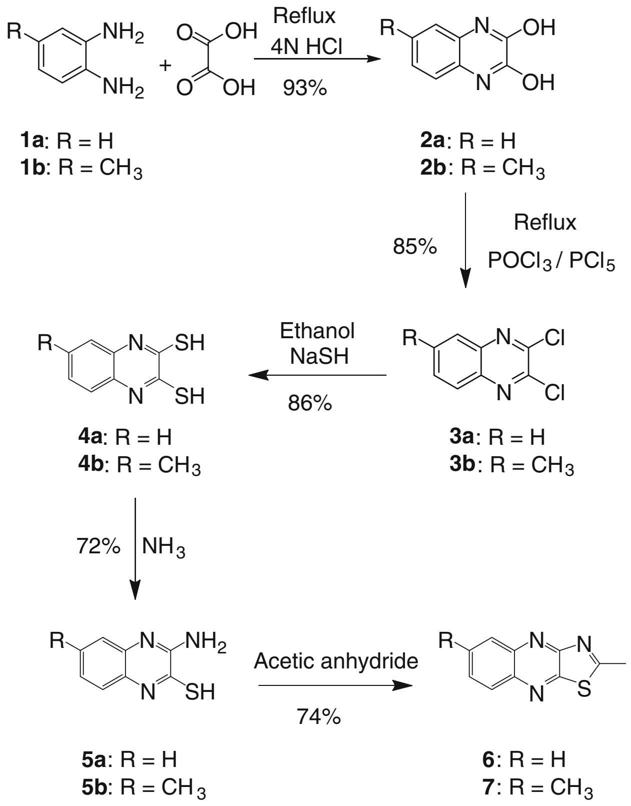
Compound	TGA[a] (°C)	DSC[b] (°C)	E_{ox} (V)	E_{red} (V)
12a	312	149	1.32	−1.04
12b	317	218	1.34	−1.08
12c	325	208		

[a] Thermogravimetric analysis (TGA), decomposition temperature of the respective compounds

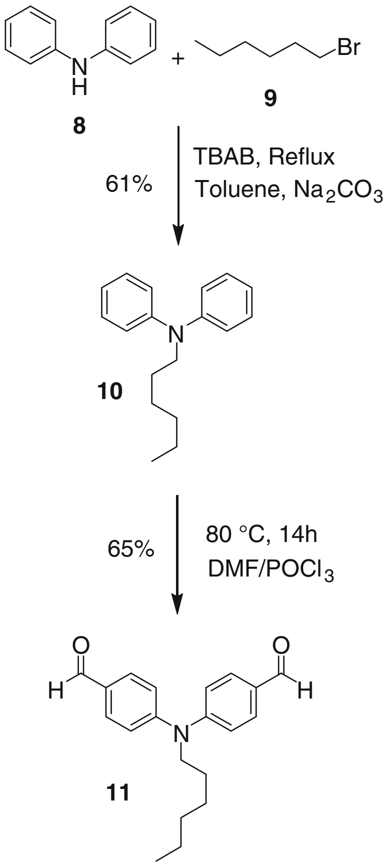
[b] Differential scanning calorimetry (DSC), transition temperature of the respective compounds

In order to investigate photophysical properties the absorption and photoluminescence spectra of **12a–12c** in chloroform solution (1×10^{-4} M) were recorded. The absorption maxima and fluorescence were in the range of 447–516 nm and 570–610 nm, respectively. These dyes showed high molar extinction coefficients and their Stokes shifts were in the range of 74–163 nm (Tables 2, 3). The electron-donating groups in **12a–12c** generate the bathochromic shifts due to their long conjugation. Extended chromophores displayed dramatic enhancement in absorption and fluorescence properties and Stokes shift.

Absorption and emission maxima of chromophores **12a–12c** were compared with reported quinoxaline-based styryl dyes **12d** and **12e** [22] (Table 2). Absorption and



Scheme 1



Scheme 2

emission maxima of **12d** and **12e** are 515, 593 and 505, 586, respectively, which is not much different from **12a** to **12c**. Stokes shifts of chromophores **12a–12c** are higher than **12d** and **12e**. Two electron-withdrawing groups increase the hyperpolarizability in compounds **12a–12c**.

The compounds **12a–12c** exhibit absorption maxima at 459, 507, and 498 nm, respectively (Fig. 1). Emission maxima of **12a–12c** were observed at 570, 592, and 594 nm, respectively (Fig. 2). Absorption and emission maxima of **12b** and **12c** are significantly higher than those of chromophore **12a**, and the fluorescence intensity of **12c** is higher than that of **12a** and **12b**.

Solvatochromism [26] was studied by using various solvents such as toluene, chloroform, ethyl acetate, tetrahydrofuron, methanol, and *N*,*N*-dimethylformamide in increasing order of polarity. The data collected in Table 3 clearly indicate that absorption, emission maxima, and Stokes shift in DMF are higher than in toluene because of the higher solvatochromic effect of the polar solvent DMF. Chromophores **12b** and **12c** showed higher absorption maxima than **12a** because of the long extended conjugation. The higher Stokes shift of compound **12a** reveals that only one electron-withdrawing group is responsible for this change.

Thermal properties of dyes **12a–12c** were explored. Phase transitions of compounds **12a–12c** are displayed in Fig. 3. Heat stability of compounds **12a–12c** is shown in Fig. 4 and tabulated in Table 1.

Compounds **12a–12c** were subjected to thermogravimetric analysis to investigate their thermal stability. Stepwise isothermal ramping up to 600 °C at 10 °C/min was performed in a nitrogen atmosphere. The change in weight of the colorants was measured as a function of temperature. Thermogravimetric analysis of compound **12c** showed the highest decomposition temperature, 98% of the weight composition was stable up to 325 °C and underwent rapid thermal decomposition thereafter. Compound **12b** was 97% stable up to 317 °C and **12a** was 95% stable up to 312 °C. Phase transition of the chromophores **12a–12c** measured by differential scanning

Scheme 3

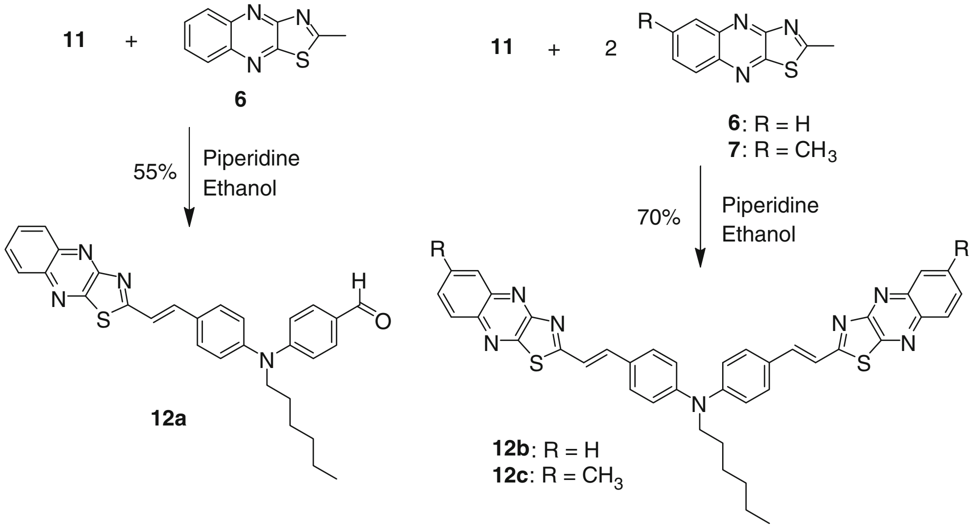
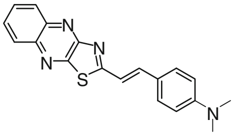
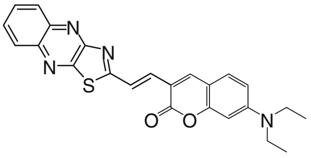


Table 2 Comparison of the spectral properties of the dyes **12a–12c** with those of **12d–12e** in chloroform

	λ_{max} (nm)	λ_{em} (nm)	Stokes shift	ε (dm^3 mol^{-1} cm^{-1})
12a	459	570	111	50,000
12b	507	592	85	68,261
12c	498	594	96	77,440
12d	515	593	78	–
12e	505	586	81	–



12d



12e

calorimetry showed sharp transitions. Compounds **12c** (217 °C) and **12b** (208 °C) showed higher phase transition temperatures than **12a** (149 °C). These data indicate that all of these chromophores have good thermal stability and are therefore applicable for polymers requiring higher extrusion temperature ranges.

The electrochemical properties of the compounds were studied and showed reversible redox potential. Cyclic voltammetry (CV) experiments were performed in dichloromethane solutions containing Bu_4NPF_6 as the supporting electrolyte. Voltammograms of $\sim 10^{-4}$ M solutions of chromophores **12a–12c** were recorded and E_{ox} and E_{red} for each compound were determined from each data set and tabulated in Table 1. Cyclic voltammetric traces recorded for **12a** and **12b** are shown in Figs. 5 and 6.

The dyes show a strong fluorescence at long UV. Photographs of dyes in daylight and under long UV (365 nm) are presented in Fig. 7.

Conclusion

We have successfully designed and synthesized novel "Y"-shaped organic chromophores by using 4,4′-(hexylimino)bis(benzaldehyde) (**11**) as electron donor center and 2-methyl- (**6**) and 2,6-dimethylthiazolo[4,5-*b*]quinoxaline (**7**) as electron-withdrawing groups. Compounds **12a–12c** exhibited high thermal stability and excellent electrochemical reversibility. These compounds showed solvatochromism in different solvents. The dyes **12a–12c** displayed excellent photoluminescent properties and high molar extinction coefficient and Stokes shift.

Experimental

Materials and equipments

All solvents and chemicals were procured from sd fine chemicals (India) and were used without further purification. The reactions were monitored by TLC using 0.25 mm E-Merck silica gel 60 F_{254} precoated plates, which were visualized with UV light. Melting points were measured on a standard melting point apparatus from Sunder Industrial Products, Mumbai. UV–Vis absorption spectra were recorded on a Spectronic GENEYSIS 2 spectrophotometer instrument from dye solutions ($\sim 10^{-4}$ M) in chloroform. The fluorescence maxima were recorded on a Jasco FP-1520 fluorimeter from dye solutions in chloroform. The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 and

Table 3 Spectral properties of the dyes **12a–12c** in different solvents

Dye no.	Toluene				Chloroform				Ethyl acetate			
	λ_{max} (nm)	λ_{em} (nm)	Stokes shift	ε (dm^3 mol^{-1} cm^{-1})	λ_{max} (nm)	λ_{em} (nm)	Stokes shift	ε (dm^3 mol^{-1} cm^{-1})	λ_{max} (nm)	λ_{em} (nm)	Stokes shift	ε (dm^3 mol^{-1} cm^{-1})
12a	450	576	126	24,108	459	570	111	50,000	447	610	163	35,424
12b	489	606	117	39,875	507	592	85	68,261	516	592	76	47,310
12c	510	584	74	42,240	498	594	96	77,440	486	580	94	47,168
Dye no.	THF				Methanol				DMF			
	λ_{max} (nm)	λ_{em} (nm)	Stokes shift	ε (dm^3 mol^{-1} cm^{-1})	λ_{max} (nm)	λ_{em} (nm)	Stokes shift	ε (dm^3 mol^{-1} cm^{-1})	λ_{max} (nm)	λ_{em} (nm)	Stokes shift	ε (dm^3 mol^{-1} cm^{-1})
12a	462	594	132	34,440	456	604	148	34,064	459	602	143	36,424
12b	498	596	98	50,689	510	622	112	51,703	513	610	97	48,710
12c	516	594	78	57,024	504	610	106	41,606	510	608	98	47,268

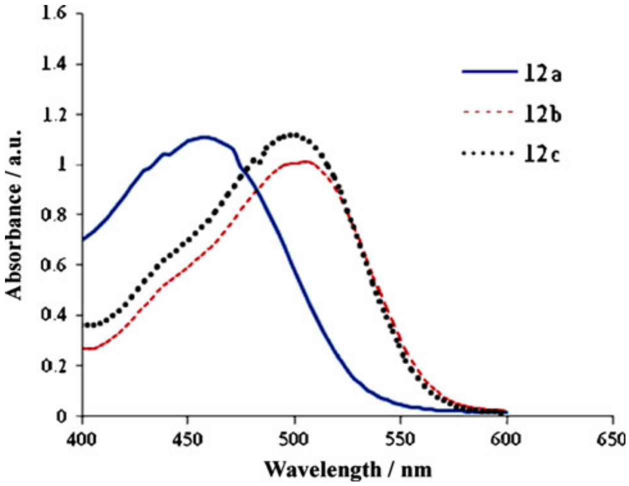


Fig. 1 UV–Vis spectra of **12a–12c** (10^{-4} M) in chloroform

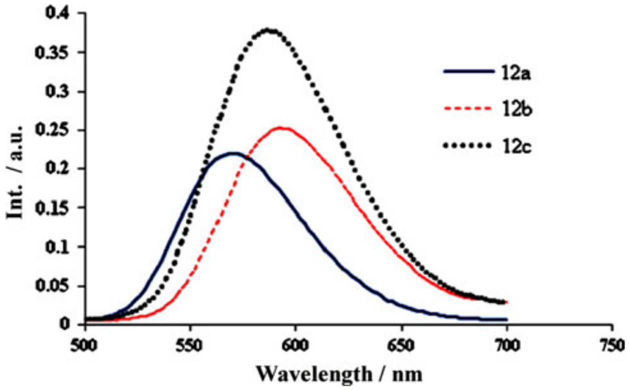


Fig. 2 Fluorescence spectra of **12a–12c** (10^{-4} M) in chloroform

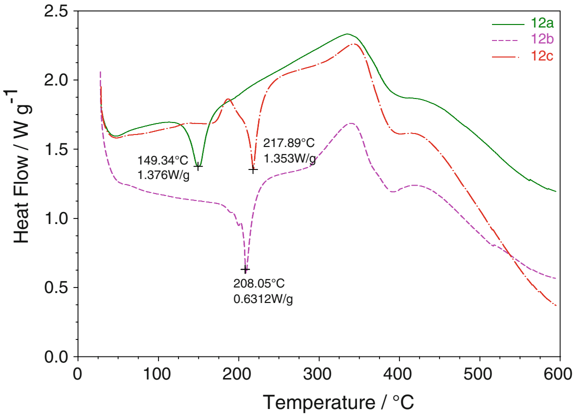


Fig. 3 Differential scanning calorimetry of compounds **12a–12c**

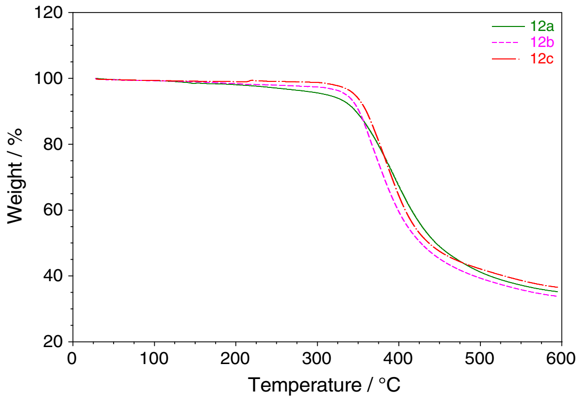


Fig. 4 Thermogravimetric analysis of the dyes **12a–12c**

100 MHz, respectively, on a Varian Mercury Plus spectrometer. Chemical shifts are expressed in δ (ppm) using TMS as an internal standard. Mass spectral data were obtained with a Micromass Q-Tof (YA105) spectrometer. Elemental analysis was done on a Harieus rapid analyzer. Thermogravimetric analysis was carried out on an SDT Q600 v8.2 Build 100 model of TA instruments. Cyclic voltammetric analyses were recorded on a μ Autolab type-III 663 VAstand Ω Metrohm.

4-[N-Hexyl-N-[4-[(E)-2-(thiazolo[4,5-b]quinoxalin-2-yl)ethenyl]phenyl]amino]benzaldehyde
(**12a**, $C_{30}H_{28}N_4OS$)

A mixture of 1 g **11** (3.1 mmol), 0.63 g **6** (3.1 mmol), and piperidine (2–3 drops) in 15 cm^3 absolute ethanol was stirred at reflux for 6 h. The precipitated solid was filtered, washed with ethanol, dried, and purified by column chromatography (toluene, 100–200 mesh silica gel) to obtain orange crystals, yield 0.9 g (55%); m.p.: 146–148 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.89$ (t, 3H), 1.32 (m, 4H), 1.58 (m, 2H), 1.72 (m, 2H), 3.83 (t, 2H), 7.01 (d, $J = 9.47$ Hz, 2H), 7.25 (d, $J = 8.9$ Hz, 2H), 7.47 (d, $J = 16.2$ Hz, 2H, olefinic), 7.66 (d, $J = 8.16$ Hz, 2H), 7.74 (d, $J = 8.8$ Hz, 2H), 7.82 (dd, $J = 8.8$ Hz, 2H), 7.82 (dd, $J = 2.4$ Hz, 1H), 8.14 (dd, $J = 2.1$ Hz, 1H), 9.83 (s, 1H, aldehyde) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.1$, 22.7, 26.8, 27.6, 31.6, 52.7, 77.5, 76.9, 117.4, 121.3, 124.5, 128.3, 129.8, 129.9, 129.9, 130.1, 130.4, 131.8, 140.9, 141.8, 148.6, 152.5, 153.9, 158.1, 174.1, 190.5 ppm; TOF–MS (ES+): $m/z = 493.2$ (M + 1).

N-Hexyl-4-[(E)-2-(thiazolo[4,5-b]quinoxalin-2-yl)-ethenyl]-N-[4-[(E)-2-(thiazolo[4,5-b]quinoxalin-2-yl)-ethenyl]phenyl]benzenamine (**12b**, $C_{40}H_{33}N_7S_2$)

A mixture of 1 g **11** (3.1 mmol), 1.20 g **6** (6.2 mmol), and piperidine (3–4 drops) in 25 cm^3 absolute ethanol was stirred at reflux for 6 h. The precipitated solid was filtered, washed with ethanol, dried, and purified by column chromatography (toluene, 100–200 mesh silica gel). Yield 1.52 g (70%) red crystals; m.p.: 204–206 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.90$ (t, $J = 7.2$ Hz, 3H), 1.32 (m, 4H), 1.58 (m, 2H), 1.73 (m, 2H), 3.84 (t, 2H), 7.14 (d, $J = 8.86$ Hz, 4H), 7.40 (d, $J = 16.2$ Hz, 2H, olefinic), 7.84

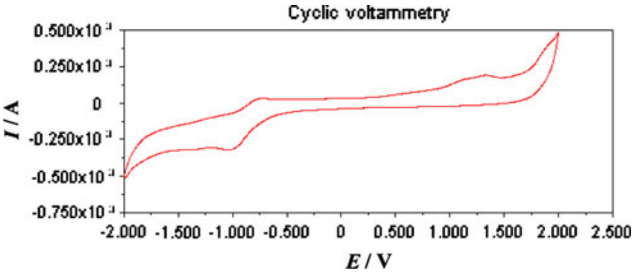


Fig. 5 Cyclic voltammogram of **12a** recorded in dichloromethane using tetrabutylammonium hexafluorophosphate as supporting electrolyte

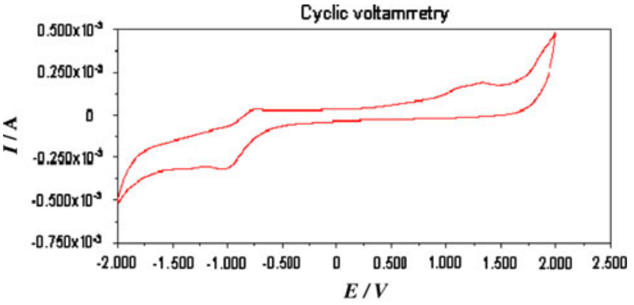


Fig. 6 Cyclic voltammogram of **12b** recorded in dichloromethane using tetrabutylammonium hexafluorophosphate as supporting electrolyte

Fig. 7 Photographs of dyes **12a–12c** (*left* to *right*) in daylight (*left*) and long UV (365 nm) (*right*)

(d, 2H, olefinic), 7.60–7.63 (d, $J = 8.5$ Hz, 4H), 7.79–7.81 (m, $J = 3.0$ Hz, 4H), 8.15 (dd, $J = 1.53$ Hz, 2H), 8.25 (dd, $J = 2.13$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.2$, 22.8, 26.9, 27.7, 31.7, 52.6, 120.2, 121.3, 128.3, 129.6, 129.8, 129.9, 130.1, 140.8, 141.8, 142.3, 149.4, 154.1, 158.3, 174.4 ppm; TOF–MS (ES+): $m/z = 676.44$ (M + 1).

N-Hexyl-4-[(E)-2-(6-methylthiazolo[4,5-b]quinoxalin-2-yl)ethenyl]-N-[4-[(E)-2-(6-methylthiazolo[4,5-b]-quinoxalin-2-yl)ethenyl]phenyl]benzenamine (**12c**, $C_{42}H_{37}N_7S_2$)

A mixture of 1 g **11** (3.1 mmol), 1.33 g **7** (6.2 mmol), and piperidine (3–4 drops) in 25 cm^3 absolute ethanol was stirred at reflux for 6 h. The precipitated solid was filtered, washed with ethanol, dried, and purified by column chromatography (toluene, 100–200 mesh silica gel). Yield 1.26 g (60%) red crystals; m.p.: 208–210 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.89$ (t, $J = 7.02$ Hz, 3H), 1.32–1.36 (m, 4H), 1.59 (m, 2H), 1.73 (m, 2H), 2.64 (s, 6H), 3.83 (t, 2H), 7.12 (d, $J = 7.94$ Hz, 4H), 7.36 (d, $J = 14.65$ Hz, 2H, olefinic), 7.82 (d, 2H, olefinic), 7.61–7.64 (d, $J = 7.02$ Hz, 4H), 7.78 (d, $J = 7.9$ Hz, 2H), 8.02 (d, $J = 7.02$ Hz, 2H), 8.12 (d, $J = 2.2$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.2$, 22.1, 22.8, 26.8, 27.7, 31.7, 52.6, 120.2, 121.2, 127.1, 127.7, 128.3, 128.6, 129.4, 130.0, 132.1, 139.4, 140.2, 140.3, 140.4, 140.9, 141.8, 141.9, 149.2, 152.9, 157.8, 158.3, 173.5, 173.9 ppm; TOF–MS (ES+): $m/z = 704.37$ (M + 1).

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