

Two Novel Push–Pull Series of Benzothiazole-Based Dyes: Synthesis and Characterization

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New dichromophoric cyanine dyes based on benzothiazol-2-amines as push–pull systems were synthesized in two series of disperse and cationic forms (see **4** in *Scheme 1* and **5** in *Scheme 2*, resp.). Their thermal stabilities, UV/VIS, fluorescence, and solvatochromic behavior, which are important parameters in push–pull systems, were also studied.

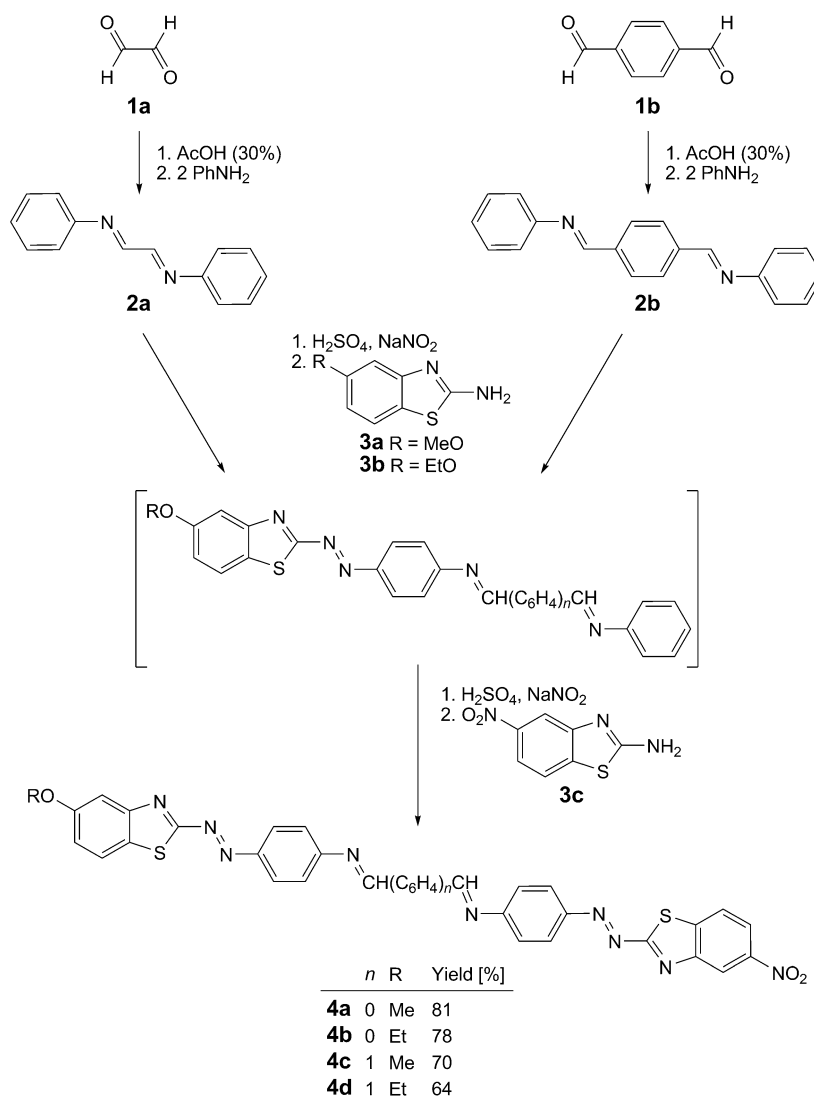
Introduction. – In continuation of our recent investigations on novel hemicyanine dyes [1] and considering the various applications of benzothiazol-2-amine-derived azo dyes, we decided to synthesize a series of dichromophoric cyanine dyes based on benzothiazol-2-amines as push–pull systems in disperse and cationic variations and study their thermal, UV/VIS, fluorescence, and solvatochromic behavior, important parameters in push–pull systems.

Results and Discussion. – The reaction of glyoxal (=ethanedial; **1a**) or terephthalaldehyde (=benzene-1,4-dicarboxaldehyde; **1b**) with 2 mol-equiv. of aniline (=benzenamine) under acidic conditions led within 1 h at 5° to the corresponding *Schiff* bases **2a** and **2b** in high yields (95 and 98%, resp.; *Scheme 1*). Coupling of the *Schiff* bases **2a** and **2b** with 1 mol-equiv. of diazotized **3a** or **3b** followed by 1 mol-equiv. of diazotized **3c** gave the unsymmetrically substituted diazo dyes **4a–4d** in good yields (64–81%). The structures of compounds **2a** and **2b** and **4a–4d** were deduced from their mass, IR, and ¹H- and ¹³C-NMR spectra and CHN analysis.

N-Methylation of the benzothiazole moieties of **4a–4d** with dimethyl sulfate gave **5a–5d** in good yields (62–80%), which represent a second cationic category of these novel dyes and are members of the important class of colorants with special applications [2–7] (*Scheme 2*). MS, IR, ¹H- and ¹³C-NMR data, and CHN analysis confirmed the structures of **5a–5d**.

Compounds **4a–4d** are purple to red dyes (λ_{max} 496–505 nm) with $2.0\text{--}2.7 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ molar absorption coefficients. Their corresponding cationic *N*-methyl forms **5a–5d** show 67–85 nm bathochromic shifts (indigo to deep blue colors, λ_{max} 572–584 nm) with a significant increase of the molar absorption coefficients ($2.9\text{--}3.7 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$; see *Table 1*).

Thermal Stabilities. To investigate the applicability of the synthesized dyes as push–pull systems in advanced technologies, such as nonlinear optical (NLO) devices,

Scheme 1. Synthesis of the Dichromophoric Benzothiazole-Based Dyes **4a–4d**

organic light-emitting diodes (OLEDs), and liquid crystals, their thermal stability was determined, which is an important requirement for their use in the mentioned technologies [8]. The thermal stabilities were evaluated by measuring the decomposition temperatures of **4a–4d** and **5a–5d** by means of thermal gravimetric analysis (TGA) (Fig. 1). Comparing the decomposition temperatures of **4a–4d** revealed that **4d** had the highest thermal stability. Thus, presence of an EtO group and a central 1,4-phenylene linker ($n = 1$) in the structure of **4d** efficiently enhanced its thermal stability. The thermal stabilities of the cationic dyes **5a–5d** were higher, and among them, **5c**,

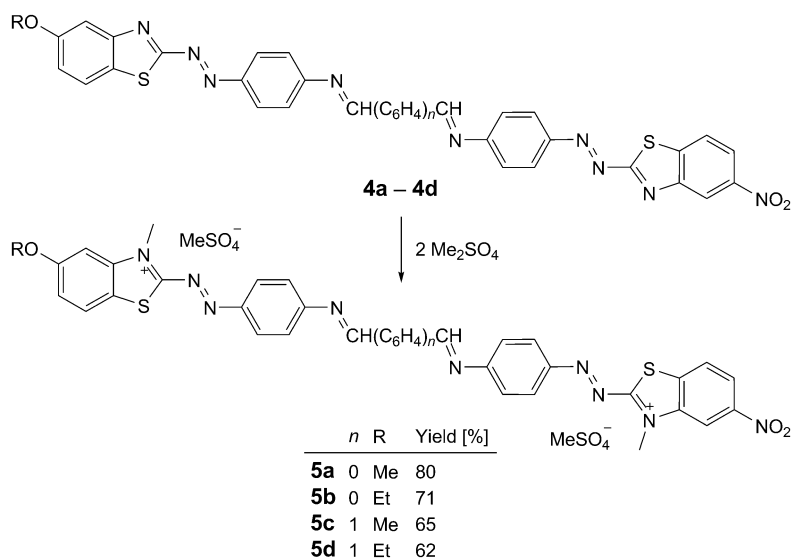
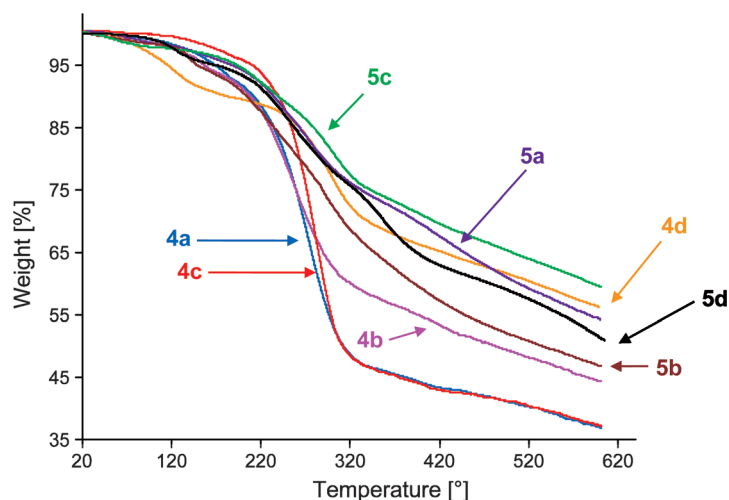
Scheme 2. N-Methylation of the Benzothiazole Moities of **4a–4d** to Produce the Cationic Dyes **5a–5d**

Table 1. Summarized Spectroscopic Data for the Push–Pull Systems in EtOH

	<i>n</i>	R	λ_{max} [nm]	ϵ [l M ⁻¹ cm ⁻¹]	Color
4a	0	Me	505	$2.4 \cdot 10^4$	purple
4b	0	Et	499	$2.7 \cdot 10^4$	red
4c	1	Me	496	$2.0 \cdot 10^4$	red
4d	1	Et	500	$2.6 \cdot 10^4$	purple
5a	0	Me	572	$3.7 \cdot 10^4$	indigo
5b	0	Et	581	$3.3 \cdot 10^4$	deep blue
5c	1	Me	581	$3.5 \cdot 10^4$	deep blue
5d	1	Et	584	$2.9 \cdot 10^4$	indigo

with an MeO group and a central 1,4-phenylene linker ($n = 1$) present in its structure, displayed the highest thermal stability.

Solvatochromic Effects. To study the solvatochromic effects, the maximum absorption wavelength in the UV/VIS spectra of **4a–4d** and **5a–5d** were measured in different solvents (Table 2). Thus, these dichromophore dyes revealed a negative solvatochromic effect (blue shift) in aprotic solvents and a positive solvatochromic effect (red shift) in protic solvents. The blue shift is caused by the decrease of the dichromophore's dipole moments an excitation and more stability of the ground-state than of the excited state in the more polar aprotic solvents; consequently, the energy difference between the ground and excited states will increase [9]. This means that the compounds are highly polar because they contain push–pull systems and linear properties. Although polar and protic solvents stabilize the excited state more than the ground state, the bathochromic shift or positive solvatochromic effect in these solvents is evident.

Fig. 1. Thermal gravimetric analysis (TGA) of the chromophores **4a–4d** and **5a–5d**Table 2. $\lambda_{\max}$ Values [nm] of the UV/VIS Spectra of Dyes **4** and **5** in Different Solvents

	4a	4b	4c	4d	5a	5b	5c	5d
THF	492	495	494	497	588	583	575	582
CHCl ₃	482	482	465	473	565	580	585	580
Me ₂ CO	479	482	477	479	572	573	581	581
EtOH	505	499	496	500	572	581	581	584
MeCN	481	482	484	491	570	562	579	581
DMSO	506	505	508	510	582	589	590	598

Fluorescence Emission. All dyes **4a–4d** showed fluorescence emission in a broad range at $2 \cdot 10^{-5}$ mol l⁻¹ concentration in *N,N*-dimethylformamide (DMF) at 293 K (Fig. 2). The dyes were excited at 325–350 nm, and the fluorescence peaks emerged at 400–500 nm, **4a** showing the highest and **4d** the lowest emission. Similarly, the fluorescence emission spectra of the cationic dyes **5a–5d** were measured with an excitation at 288–345 nm (Fig. 3).

Two important characteristics for fluorescent compounds, the *Stokes* shift ($\tilde{\nu}_A - \tilde{\nu}_F$) and the oscillator strength (f) were studied for the selected dichromophoric dyes. The *Stokes* shift is a parameter which indicates the difference in the properties and structure of the fluorophores between the ground-state S_0 and the first excited state S_1 . The *Stokes* shifts (cm⁻¹) for **4a–4d** and **5a–5d** were calculated by Eqn. 1, which gave values between 5529 and 8680 cm⁻¹ (Table 3).

$$(\tilde{\nu}_A - \tilde{\nu}_F) = (1/\lambda_A - 1/\lambda_F) \cdot 10^7 \quad (1)$$

The oscillator strength (f) shows the effective number of electrons whose transition from the ground to the excited state gives the absorption area in the electron spectrum. The oscillator strengths for **4a–4d** and **5a–5d** were calculated with Eqn. 2 where $\Delta\tilde{\nu}_{1/2}$

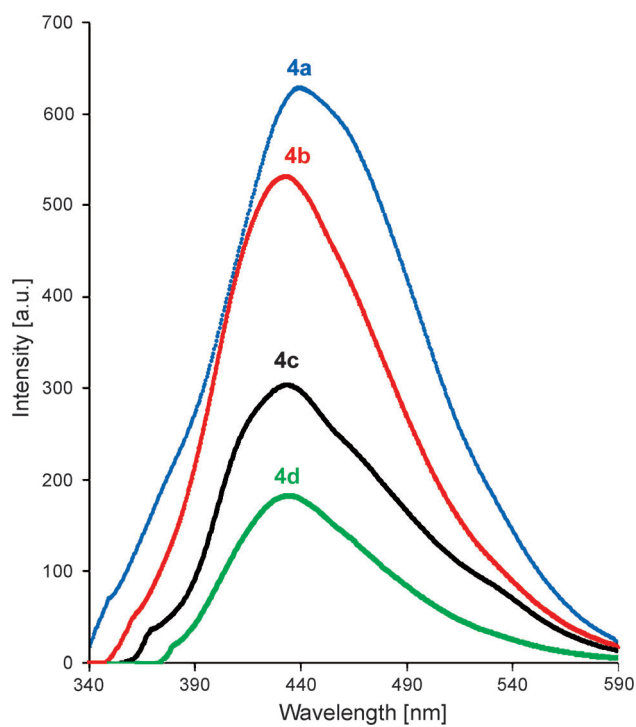


Fig. 2. Fluorescence emission spectra of **4a–4d** in DMF

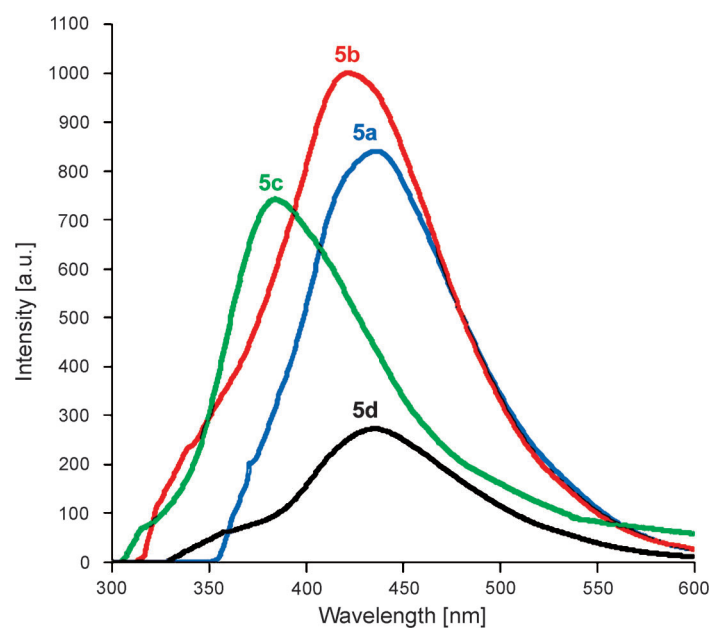


Fig. 3. Fluorescence emission spectra of **5a–5d** in DMF

Table 3. Absorption and Fluorescence Characteristics of the Dichromophoric Dyes **4** and **5** in DMF at 293 K ($c = 2 \cdot 10^{-5}$ mol l⁻¹)

	λ_{ex} [nm]	λ_{em} [nm]	ϵ_{max} [l M ⁻¹ cm ⁻¹]	$\tilde{\nu}_{\text{A}} - \tilde{\nu}_{\text{F}}$ [cm ⁻¹]	Intensity [a.u.]	f
4a	325	439	$2.4 \cdot 10^4$	7990	628	0.400
4b	335	433	$2.7 \cdot 10^4$	6756	531.6	0.299
4c	340	431	$2.0 \cdot 10^4$	6209	302.7	0.198
4d	350	434	$2.6 \cdot 10^4$	5529	182.6	0.158
5a	345	435	$3.7 \cdot 10^4$	5997	840	0.399
5b	315	421	$3.3 \cdot 10^4$	7993	999	0.405
5c	288	384	$3.5 \cdot 10^4$	8680	741.4	0.362
5d	330	435	$2.9 \cdot 10^4$	7314	272.9	0.369

is the half-band width of the absorption band [cm⁻¹] at ϵ_{max} [10]. The f values 0.158–0.400 were thus obtained for **4a**–**4d** and 0.362–0.405 for **5a**–**5d** (Table 3).

$$f = 4.32 \cdot 10^{-9} \cdot \Delta\tilde{\nu}_{1/2} \cdot \epsilon_{\text{max}} \quad (2)$$

Conclusion. – A series of novel dichromophoric cyanine dyes based on benzothiazol-2-amines as push–pull systems in two series of disperse and cationic forms, **4** and **5**, respectively, were synthesized and their thermal stabilities studied up to 200–220°. The disperse dyes **4** in EtOH revealed absorptions at 496–505 nm in red and purple with 2.0 – $2.71 \cdot 10^4$ l M⁻¹ cm⁻¹ molar extinction coefficients. The corresponding cationic dyes **5** showed 67–85 nm bathochromic shifts (indigo to deep blue colors, λ_{max} 572–584 nm) with a significant increase in the molar absorption coefficients (2.9 – $3.7 \cdot 10^4$ l M⁻¹ cm⁻¹). These dyes were excited at 288–350 nm whereupon they showed fluorescence emission in the broad range of 400–500 nm. Moreover, these dyes revealed negative solvatochromic effects in aprotic solvents and positive solvatochromic effects in protic solvents.

Experimental Part

General. Chemicals were purchased from Merck and used without further purification. M.p.: Büchi B-545 melting-point apparatus; uncorrected. UV/VIS Spectra: Multispec-1501-Shimadzu UV/VIS spectrophotometer. IR Spectra: Perkin-Elmer-Spectrum-One-BX FT-IR spectrometer; in KBr; $\tilde{\nu}$ in cm⁻¹. Fluorescence spectra: Perkin-Elmer-LS-55 spectrometer. ¹H- and ¹³C-NMR Spectra: Bruker-500-Avance Fourier-transform (FT) NMR instrument, at 500 and 125.7 MHz, resp., in dimethyl sulfoxide ((D₆)DMSO) and CDCl₃; δ in ppm rel. to SiMe₄, J in Hz. MS: Finnigan-Mat-8430 mass spectrometer; ionization potential 20 eV, electrospray ionization (ESI), pos. mode; in m/z (rel. %). Elemental analyses for C, H, and N: Heraeus-CHN-O-Rapid analyzer.

1. *Compounds 2a and 2b: General Procedure.* Aniline (0.02 mol) was added dropwise to a stirred soln. of glyoxal (**1a**; 0.01 mol) or terephthalaldehyde (**1b**; 0.01 mol) in 30% aq. AcOH soln. (20 ml) at 5°. The mixture was stirred for 1 h and filtered. Compounds **2a** and **2b** were crystallized from H₂O to get the pure forms.

N,N'-Diphenylethane-1,2-diimine (=N,N'-Ethane-1,2-diylidenebis[benzenamine]; **2a**). Yield 95%. Cream-colored powder. M.p. 103–105°. IR (KBr): 2935 (CH=), 1608 (C=N), 1529 (C=C). ¹H-NMR (CDCl₃): 6.65 (*s*, 2 CH=N); 6.73 (*d*, $J = 7.8$, 4 CH); 6.84 (*t*, $J = 7.8$, 2 CH); 7.2 (*dd*, $J = 7.8$, 4 CH). ¹³C-NMR (CDCl₃): 158.9; 152.1; 129.8; 125.8; 121.4 (14 C). Anal. calc. for C₁₄H₁₂N₂ (208.26): C 80.74, H 5.81, N 13.45; found: C 80.80, H 5.72, N 13.44.

1,1'-(1,4-Phenylene)bis[N-phenylmethanimine] (= N,N'-(1,4-Phenylenedimethylidene)bis[benzenamine]; **2b**). Yield 97%. Cream-colored powder. M.p. 155–157°. IR (KBr): 2922 (CH=), 1614 (C=N), 1541 (C=C). ¹H-NMR (CDCl₃): 7.29 (d, *J* = 7.2, 4 CH); 7.30 (t, *J* = 7.2, 2 CH); 7.45 (dd, *J* = 7.2, 4 CH); 8.05 (s, 4 CH); 8.54 (s, 2 CH). ¹³C-NMR (CDCl₃): 159.9; 152.2; 130.2; 129.7; 129.6; 126.8; 121.4 (20 C). Anal. calc. for C₂₀H₁₆N₂ (284.35): C 84.48, H 5.67, N 9.85; found: C 84.56, H 5.59, N 9.91.

2. *Preparation of Compounds 4a–4d: General Procedure.* A soln. of benzothiazol-2-amine derivative **3a** or **3b** (10 mmol) in 50% H₂SO₄ soln. (12.5 ml) was cooled in an ice-water bath, and an aq. NaNO₂ soln. (10 mmol in 2.5 ml H₂O) was added within 15 min at 0°. The resulting yellow-to-orange soln. was stirred at 0° for 1 h. Then, a suspension of **2a** or **2b** (10 mmol) in 1% HCl soln. (20 ml) was added dropwise to the diazonium salt at 0–5°. The cooling bath was removed, and the mixture was stirred at r.t. for 1 h.

The second diazonium salt was prepared separately by dissolution of 5-nitrobenzothiazol-2-amine (**3c**; 10 mmol) in 50% H₂SO₄ soln. (12.5 ml). The mixture was cooled in an ice-water bath, and an aq. NaNO₂ soln. (10 mmol in 2.5 ml H₂O) was added within 15 min at 0°. The resulting yellow-to-orange soln. was stirred at 0° for 1 h.

Then, the mixture of the first soln. (obtained from **3a** or **3b**) was added to this second diazonium salt (from **3c**) at 0–5° and stirred at r.t. for 1 h and then neutralized by adding 10% NH₃ soln. The precipitated dye was isolated by filtration, washed with excess H₂O, and crystallized in EtOH to afford pure **4**.

4-[(1*E*)-2-(5-Methoxybenzothiazol-2-yl)diazeryl]-N-[(1*E*,2*E*)-2-{4-[(1*E*)-2-(5-nitrobenzothiazol-2-yl)diazeryl]phenyl}imino]ethylidene]benzenamine (**4a**). Yield 81%. Purple powder. M.p. 160–162°. IR (KBr): 2929 (CH=), 1633 (C=N), 1598 (C=C), 1278 (C–N). ¹H-NMR (CDCl₃): 3.81 (s, MeO); 6.72 (s, 2 CH=N); 6.91–8.00 (*m*, 14 arom. H). ESI-MS: 604 (3, *M*⁺), 310 (9), 295 (12), 180 (61), 165 (75), 106 (12), 92 (100). Anal. calc. for C₂₉H₁₉N₉O₃S₂ (605.65): C 57.51, H 3.16, N 20.81; found: C 57.57, H 3.11, N 20.86.

4-[(1*E*)-2-(5-Ethoxybenzothiazol-2-yl)diazeryl]-N-[(1*E*,2*E*)-2-{4-[(1*E*)-2-(5-nitrobenzothiazol-2-yl)diazeryl]phenyl}imino]ethylidene]benzenamine (**4b**). Yield 78%. Red powder. M.p. 145–147°. IR (KBr): 2979 (CH=), 1614 (C=N), 1509 (C=C), 1256 (C–N). ¹H-NMR (CDCl₃): 1.49 (t, *J* = 6.8, Me); 4.14 (*q*, *J* = 6.8, CH₂O); 6.81 (s, 2 CH=N); 6.96–8.22 (*m*, 14 arom. H). ESI-MS: 618 (4, *M*⁺), 310 (5), 309 (10), 194 (68), 165 (71), 120 (15), 92 (100). Anal. calc. for C₃₀H₂₁N₉O₃S₂ (619.68): C 58.15, H 3.42, N 20.34; found: C 58.14, H 3.42, N 20.39.

4-[(1*E*)-2-(5-Methoxybenzothiazol-2-yl)diazeryl]-N-[(1*E*)-4-[(1*E*)-{4-[(1*E*)-2-(5-nitrobenzothiazol-2-yl)diazeryl]phenyl}imino]methyl]phenyl]methylenebenzenamine (**4c**). Yield 70%. Red powder. M.p. 197–199°. IR (KBr): 2928 (CH=), 1634 (C=N), 1525 (C=C), 1294 (C–N). ¹H-NMR (CDCl₃): 3.87 (s, MeO); 7.21 (s, 4 CH); 7.48–8.23 (*m*, 14 arom. H); 8.49 (s, 2 CH). ESI-MS: 680 (3, *M*⁺), 348 (11), 333 (9), 348 (12), 241 (74), 180 (66), 106 (18), 92 (100). Anal. calc. for C₃₅H₂₃N₉O₃S₂ (681.75): C 61.66, H 3.40, N 18.49; found: C 61.64, H 3.33, N 18.52.

4-[(1*E*)-2-(5-Ethoxybenzothiazol-2-yl)diazeryl]-N-[(1*E*)-4-[(1*E*)-{4-[(1*E*)-2-(5-nitrobenzothiazol-2-yl)diazeryl]phenyl}imino]methyl]phenyl]methylenebenzenamine (**4d**). Yield 64%. Red powder. M.p. 226–228°. IR (KBr): 2970 (CH=), 1614 (C=N), 1522 (C=C), 1282 (C–N). ¹H-NMR (CDCl₃): 1.52 (t, *J* = 6.8, Me); 4.17 (*q*, *J* = 6.82, CH₂O); 7.23 (s, 4 CH); 7.34–8.28 (*m*, 14 arom. H); 8.50 (s, 2 CH). ESI-MS: 694 (2, *M*⁺), 348 (11), 347 (7), 241 (69), 194 (64), 120 (16), 92 (100). Anal. calc. for C₃₆H₂₅N₉O₃S₂ (695.77): C 62.14, H 3.62, N 18.12; found: C 62.14, H 3.64, N 18.17.

3. *Compounds 5a–5d: General Procedure.* To a magnetically stirred suspension of **4** (10 mmol) and NaHCO₃ (1.7 g, 20 mmol) in H₂O (4 ml), dimethyl sulfate (4.4 ml, 0.036 mol) was added dropwise at 30°. The mixture was stirred at 60° for 2 h (TLC (CHCl₃/MeOH 8 : 1) monitoring). Then, the pH was adjusted to 4 by addition of 1M HCl. The precipitated dye was filtered and crystallized in H₂O to afford pure **5**.

5-Methoxy-3-methyl-2-[(1*E*)-2-{4-[(1*E*,2*E*)-2-{4-[(1*E*)-2-(3-methyl-5-nitrobenzothiazol-3-ium-2-yl)diazeryl]phenyl}imino]ethylidene]amino]phenyl]diazeryl]benzothiazol-3-ium Bis(methyl Sulfate) (**5a**). Yield 80%. Indigo powder. M.p. 267–269°. IR (KBr): 2941 (CH=), 1645 (C=N), 1588 (C=C), 1297 (C–N). ¹H-NMR ((D₆)DMSO): 3.85 (s, MeO); 4.12 (s, 2 MeN); 6.83 (d, *J* = 8.1, 2 CH); 7.00–8.70 (*m*, 14 arom. H). ESI-MS: 634 (1, *M*⁺), 620 (8), 325 (12), 310 (8), 165 (18), 133 (100). Anal. calc. for C₃₃H₃₁N₉O₁₁S₄ (857.91): C 46.20, H 3.64, N 14.69; found: C 46.18, H 3.59, N 14.77.

5-Ethoxy-3-methyl-2-((1E)-2-(4-(((1E,2E)-2-((4-[(1E)-2-(3-methyl-5-nitrobenzothiazol-3-ium-2-yl)diazenyl]phenyl)imino)ethylidene)amino)phenyl)diazenyl)benzothiazol-3-ium Bis(methyl Sulfate) (**5b**): Yield 71%. Blue powder. M.p. 195–197°. IR (KBr): 2971 (CH=), 1613 (C=N) 1558 (C=C) 1287 (C–N). ¹H-NMR ((D₆)DMSO): 1.53 (t, J = 6.6, Me); 4.10 (q, J = 6.6, CH₂O); 4.15 (s, 2 MeN); 6.95 (d, J = 8.3, 2 CH); 7.11–8.43 (m, 14 arom. H). ESI-MS: 648 (3, M⁺), 635 (7), 325 (6), 324 (13), 165 (19), 133 (100). Anal. calc. for C₃₄H₃₃N₉O₁₁S₄ (871.94): C 46.83, H 3.81, N 14.46; found: C 46.87, H 3.83, N 14.42.

5-Methoxy-3-methyl-2-((1E)-2-(4-(((1E)-4-((1E)-4-[(1E)-2-(3-methyl-5-nitrobenzothiazol-3-ium-2-yl)diazenyl]phenyl)imino)methyl]phenyl)methylene)amino)phenyl)diazenyl)benzothiazol-3-ium Bis(methyl Sulfate) (**5c**): Yield 65%. Blue powder. M.p. 208–210°. IR (KBr): 2935 (CH=), 1622 (C=N), 1514 (C=C), 1278 (C–N). ¹H-NMR ((D₆)DMSO): 3.93 (s, MeO); 4.16 (s, 2 MeN); 7.16 (s, 4 CH); 7.44–8.28 (m, 14 arom. H); 8.52 (s, 2 CH). ESI-MS: 710 (3, M⁺), 696 (5), 363 (11), 348 (17), 241 (38), 133 (100). Anal. calc. for C₃₉H₃₅N₉O₁₁S₄ (934.01): C 50.15, H 3.78, N 13.50; found: C 50.12, H 3.79, N 13.47.

5-Ethoxy-3-methyl-2-((1E)-2-(4-(((1E)-4-((1E)-4-[(1E)-2-(3-methyl-5-nitrobenzothiazol-3-ium-2-yl)diazenyl]phenyl)imino)methyl]phenyl)methylene)amino)phenyl)diazenyl)benzothiazol-3-ium Bis(methyl Sulfate) (**5d**): Yield 62%. Indigo powder. M.p. 237–239°. IR (KBr): 2956 (CH=), 15612 (C=N), 1528 (C=C), 1294 (C–N). ¹H-NMR ((D₆)DMSO): 1.49 (t, J = 6.7, Me), 4.12 (q, J = 6.7, CH₂O), 4.08 (s, 2 MeN); 7.21 (s, 4 CH); 7.42–8.46 (m, 14 arom. H); 8.59 (s, 2 CH). ESI-MS: 724 (2, M⁺), 710 (6), 343 (9), 342 (11), 241 (25), 133 (100). Anal. calc. for C₄₀H₃₇N₉O₁₁S₄ (948.04): C 50.68, H 3.93, N 13.30; found: C 50.71, H 3.87, N 13.35.

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