Benzothiazole-Based Bis-azo Cationic Fluorescent Dyes with Extended Conjugated Systems: Synthesis and Properties

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Abstract: Sixteen novel 2-aminobenzothiazole based dichromophoric cationic azo dyes were synthesized and their photophysical properties studied. The colors of the synthesized azo dyes were violet to blue with high molecular extinction coefficient ranged between 2.6 - 4.7× 10^4 ($M^{-1}.cm^{-1}$). All of the dyes showed unique fluorescence emission at a broad range of 409–494 nm. The absorption and emission spectral changes of selected dyes were also analyzed in solvents with different polarity. Furthermore, the antibacterial activities of the dyes were evaluated against gram positive and negative bacteria including S. *aureus*, *S. epidermidis*, *E. coli*, and *P. aeruginosa* and different concentrations of dyes showed an anti-gram positive bacterial activity.

Keywords: Benzothiazole, Azo Dyes, Fluorescence, Cationic dye, Antibacterial, Solvatochromism.

INTRODUCTION

2-aminobenzothiazole based diazonium dyes have found successful commercial utilization in production of cationic dyes [1-11]. In line with interest on benzothiazole cationic dyes for textiles dyeing [12], a diverse range of non-textile applications such as liquid crystal technology, reprography, nonlinear optics, and corrosion inhibitors have also been developed [13-24]. Recently, their biological activities such as antibacterial, antitumor, and antiviral activities have been reported as well [25-35].

Based on recently reported synthesis and application of dicationic dyes as bifunctional molecules [5, 22, 32, 36], and in keeping with our former investigations on novel bifunctional hemicyanine dyes [37-39], here we report synthesis of 2-aminobenzothiazoles-based dichromophoric cationic azo. In addition, several properties of the synthesized dyes such as electronic absorption and emission properties were studied, and their solvatochromic behavior were analyzed using Lippert-Mataga correlation and Reichardt–Dimroth's E_T(N) equation [40, 41]. Antibacterial activities of the synthesized dyes were also evaluated against gram positive bacteria including *Staphylococcus aureus*, and *Staphylococcus epidermidis*, and gram negative bacteria as *Escherichia coli and Pseudomonas aeruginosa*.

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RESULTS AND DISCUSSION

Glyoxal **1a** or Terephthalaldehyde **1b** was reacted with two equimolars of aniline to lead the corresponding Schiff base (or azomethine) **2a–b** in high yields (95 and 98%) (Scheme **1**). The symmetrical products **4a-h** were attained from the coupling of Schiff base **2a–b** with two equivalents of identical 6-substituted-2-azobenxothiazole **3a-d**, and asymmetrical products **4i-p** were obtained using two equivalents of different 6-substituted-2-azobenxothiazole **3a-d** (Scheme **1**). The structures of compounds **4a–p** were deduced from their mass spectroscopy and their IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopic and CHN analysis data and were in accordance with our previous report [38, 39].

Subsequently, novel cationic dyes (**5a-p**) were synthesized by quaternizaions of benzothiazole's amine groups of **4a-p** in very good yields (78-88%)**.** Mass spectroscopy, IR, ^{1}H-NMR spectroscopic and CHN analysis results confirmed the structures of the products **5a–p** that are showed in Scheme **1**.

Photophysical Properties

The photophysical properties of the synthesized cationic dyes **5a-p** were studied. The absorption spectral data are summarized in Table **1**, and fluorescence characteristics of the selected dyes are presented in Table **2**. The fluorescence quantum yields were calculated using integrated fluorescence peak area versus fraction of light absorbed at the excitation

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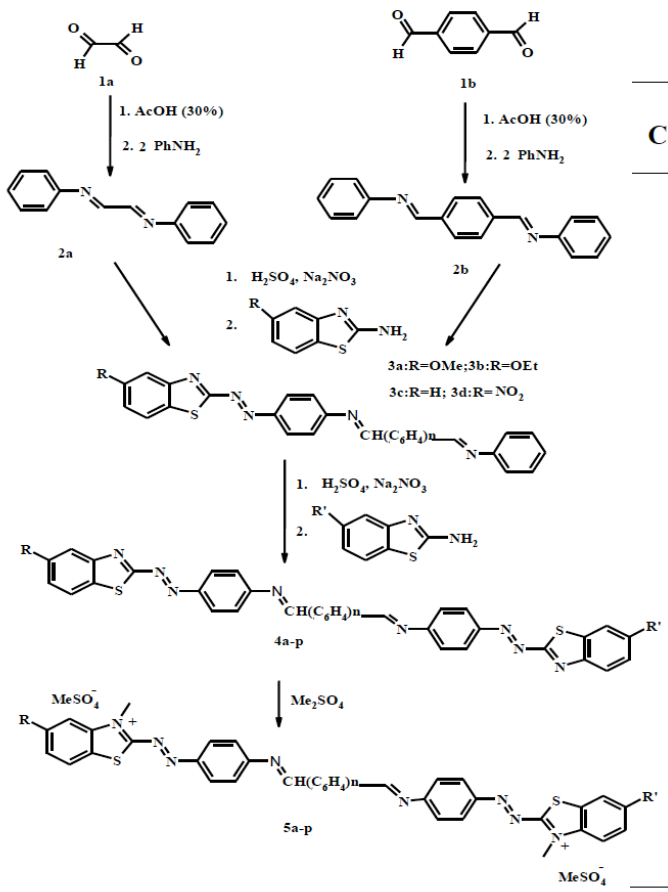

Compound	n	R	R′	Yield (%)
5a	0	OCH_3	OCH_3	85
5b	0	H	H	80
5c	0	OCH_2CH_3	OCH_2CH_3	85
5d	0	NO_2	NO_2	78
5e	1	OCH_3	OCH_3	88
5f	1	H	H	85
5g	1	OCH_2CH_3	OCH_2CH_3	85
5h	1	NO_2	NO_2	80
5i	1	OCH_3	H	82
5j	0	OCH_3	H	82
5k	0	OCH_3	OCH_2CH_3	85
5l	0	OCH_2CH_3	H	84
5m	0	NO_2	H	79
5n	1	OCH_3	OCH_2CH_3	85
5o	1	OCH_2CH_3	H	82
5p	1	NO_2	H	78

Scheme 1: Synthesis of dichromophoric benzothiazole-based cationic dyes **5a–p**.

wavelength, and were plotted for both of standards and cyanine dyes.

Absorption Spectra

In comparison with structures **4a-p** with orange-red, red and purple color (λ_{max}: 462-523 nm), cationic dyes **5a-p** revealed large bathochromic shifts ($\Delta\lambda_{max}$: 28-115 nm) and showed violet to blue colors (λ_{max}: 551-588 nm) with high molar absorption coefficients (ε: 2.1–4.4 × 10^4 $L.M^{-1}.cm^{-1}$) in ethanol (See Table **1**). Since, azo dyes are usually yellow, brown and red, so these violet and blue color azo dyes with great color strength can be very interesting achievement.

As it presented in Table **1**, molar absorption coefficients of the derivatives with n=1 are usually higher than those for the same structure with n=0, and it might be resulted from development of a full conjugation structure in such cationic dyes.

In the symmetric structures with n=0, the least molar absorption coefficient was 2.6 × 10^4 $L.M^{-1}.cm^{-1}$ for **5c** (R=R'=OEt) and the highest molar absorption coefficient was 3.6 × 10^4 $L.M^{-1}.cm^{-1}$ for **5d** (R=R'=NO_2). In the symmetric structures with n=1, the least molar absorption coefficient was 2.6 × 10^4 $L.M^{-1}.cm^{-1}$ for **5g** (R=R'=OEt) and the highest molar absorption coefficient was 4.6 × 10^4 $L.M^{-1}.cm^{-1}$for **5h** (R=R'=NO_2) as well.

Fluorescence Properties

Each of dyes **5a-p** was excited at a unique wavelength within range of 272-315 nm and showed fluorescence emission at a corresponding wavelength within range of 380–494 nm (Figure **1**). Stokes shift (ν_A-ν_F), the important characteristic for fluorescent compounds,[42] has been evaluated for the selected bischromophoric dyes.

The Stokes shift (cm^{-1}) indicates difference in properties and structure of a fluorophore between ground (S_0) and first excited (S_1) states, and could be calculated by Eq. (1).

$$(\nu_A-\nu_F) = (1/\lambda_A - 1/\lambda_F) \times 10^7 \quad (1)$$

The Stokes shifts values of the studied dyes were found among 7936-11480 cm^{-1} (Table **2**). The

Table 1: Summarized Absorption Spectral Data for the 5a-p Compounds Comparison with 4a-p

5	n	R	R'	λ_{max} [a]	ε [b]× 10^{-4}	Color	4	λ_{max} [a]	ε [b]× 10^{-4}	Color	$\Delta\lambda_{max}$
5a	0	OMe	OMe	588	3.1	Blue	**4a**	494	3.8	Red	94
5b	0	H	H	571	2.9	Blue	**4b**	477	2.6	Orange-red	94
5c	0	OEt	OEt	576	2.6	Blue	**4c**	496	2.3	Red	80
5d	0	NO_2	NO_2	554	3.6	Violet	**4d**	521	2.5	Purple	33
5e	1	OMe	OMe	573	3.2	Blue	**4e**	499	4.3	Red	74
5f	1	H	H	571	4.2	Blue	**4f**	485	3.5	Red	86
5g	1	OEt	OEt	578	2.6	Blue	**4g**	497	2.7	Red	81
5h	1	NO_2	NO_2	551	4.6	Violet	**4h**	523	2.7	Purple	28
5i	1	OMe	H	580	4.6	Blue	**4i**	493	4.4	Red	87
5j	0	OMe	H	578	4.1	Blue	**4j**	465	3.3	Orange	113
5k	0	OMe	OEt	584	3.1	Blue	**4k**	493	2.7	Red	91
5l	0	OEt	H	577	3.4	Blue	**4l**	462	2.6	Orange	115
5m	0	NO_2	H	565	3.4	Indigo Blue	**4m**	474	2.1	Orange-red	91
5n	1	OMe	OEt	584	3.4	Blue	**4n**	494	3.5	Red	54
5o	1	OEt	H	579	3.6	Blue	**4o**	468	2.7	Orange	85
5p	1	NO_2	H	563	4.7	Indigo Blue	**4p**	482	2.9	Red	81

All data are obtained in ethanol. λ_{max}: maximum absorption wavelength (nm); ε: corresponding molar absorption coefficient ($L.M^{-1}.cm^{-1}$).

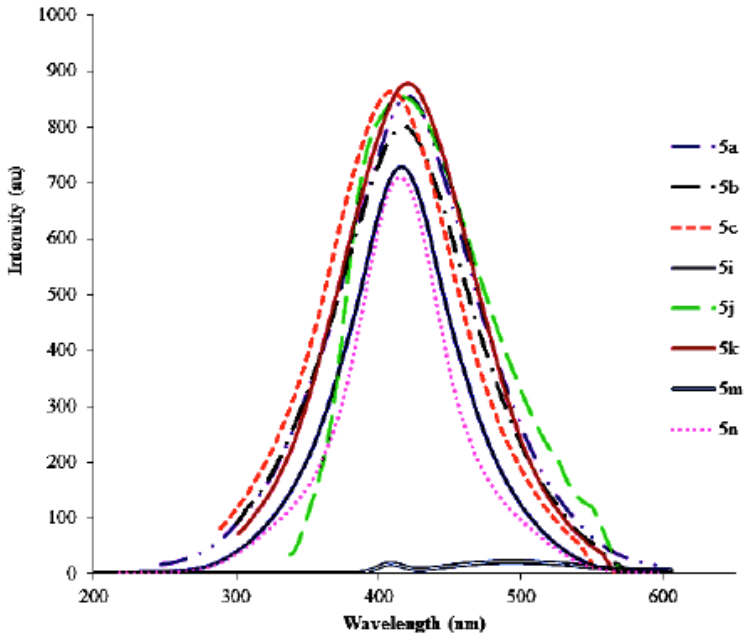

Figure 1: The fluorescence emission of the eight selected dyes in acetonitrile.

fluorescence quantum yield (Φ_F), the ratio of the absorbed to the emitted photons during the process of fluorescence, of the selected cationic dyes in acetonitrile (1×10^{-4} mol.l^{-1}) at 293 K were calculated using Eq. (2), and 1,1,4,4-tetraphenyl-1,3- butadiene (Φ_{ref}=0.7) was used as a reference.

$$\Phi_F = \Phi_{ref}\left(\frac{S_{sample}}{S_{ref}}\right)\left(\frac{A_{ref}}{A_{sample}}\right)\left(\frac{n^2_{sample}}{n^2_{ref}}\right) \quad (2)$$

A_{sample}, S_{sample}, n_{sample} and A_{ref}, S_{ref}, n_{ref} are absorbance at the excitation wavelength, the integrated

Table 2: Fluorescence Emission Characteristics of the Selected Bichromophoric Dyes in Acetonitrile at Room Temperature

Compound	n	R	R'	λ_{ex} (nm)	λ_{em} (nm)	ν_A-ν_F (cm^{-1})	Intensity (au)	Φ_F	E_F
5a	0	OMe	OMe	315	420	7936	855	0.13	0.097
5b	0	H	H	272	417	12783	801	0.17	0.11
5c	0	OEt	OEt	300	409	8883	862	0.14	0.10
5i	1	OMe	H	350	416	4532	728	0.09	0.075
5j	0	OMe	H	282	417	11480	853	0.18	0.12
5k	0	OMe	OEt	315	420	7936	878	0.12	0.09
5m	0	NO_2	H	404	494	4509	21.5	0.02	0.016
5n	1	OMe	OEt	350	422	4874	689	0.08	0.066

emission band area and the refractive index of the sample and reference, respectively.

As it shown in Table **2**, the fluorescence quantum yield values of some selected dyes were 0.02-0.18. The structures with NO_2 group showed very low fluorescence quantum yield.

The energy yields of fluorescence E_F, as conversion of energy to light efficiency [38, 39], for selected cationic dyes were also calculated by Eq. (3) and the results were reported in Table **2**. The energy yields of fluorescence in this series were 0.016-0.12.

$$E_F = \Phi_F \frac{\lambda_A}{\lambda_F} \quad (3)$$

Solvathochromic Effects

Solvatochromism refers to an ability of a chemical compound to change the color due to change in solvent polarity and solvatochromic dye molecules have recently attracted much attention owing to their application as probes for the determination of solvent polarity [14, 42-45].

Solvatochromism lies at the basis of interaction between solvent and molecules' functional groups such as dipole moment change upon excitation from ground to excited state; therefore solvent-dependent spectral changes of solvatochromic dyes provide a precise sensor of changes in the surrounding environment [14, 42-45]. Solvatochromic behavior of cationic dyes **5** with symmetrical (**5a-h)** and asymmetrical **(5i-p)** structures were studied in different common solvents varying in polarity. The obtained results were compared with the spectroscopic behavior of their corresponded nonquaternized structures **4.** Some solvent parameters as ε: dielectric constant; α: hydrogen bonding acceptor ability polarity scale; β: hydrogen bonding donor ability polarity scale; π*: dipolarity/polarizability polarity scales for seven common used solvents are presented in Table **3** [39, 46].

Table 3: Solvents Dielectric Constant (ε); Hydrogen Bonding Acceptor Ability Polarity Scale (α); Hydrogen Bonding Donor Ability Polarity Scale (β); and Dipolarity/Polarizability Polarity Scale (π*) [39, 46]

Solvent	ε	α	β	π*
$CHCl_3$	4.81	0.44	0.00	0.76
THF	7.58	0.00	0.55	0.55
Acetone	21.01	0.08	0.48	0.62
EtOH	24.30	0.86	0.75	0.54
MeOH	33.70	0.98	0.66	0.60
CH_3CN	35.94	0.19	0.40	0.66
DMSO	47.24	0.00	0.76	1.00

Maximum absorption wavelengths of the cationic dyes **5** in two series of *n*=0 and *n*=1 in seven common solvents have been studied and the results are shown Table **4**. The most solvatochromic shift for the first series, *n*=0, was 30 nm for **5b** (R=R'=H). Hence, different solvents, such as chloroform, ethyl acetate, acetonitrile, and dimethylformamide, can be distinguished based on the maximum absorption wavelength of **5b** and it can be used as indicator of the aforementioned solvents. Likewise, for the second series of these dyes, *n*=1, the most solvatochromic shift was 36 nm for **5n** (Table **4**).

Correlation of Stokes Shifts with Solvent Polarity

The fluorescence emission of most dyes was highly sensitive to polarity of different organic solvents. The

Table 4: The Maximum Absorption Wavelengths, λ_{max} (nm), of 5 in the Different Solvents at Ambient Temperature

Solvent	n=0								n=1							
	5a	5b	5c	5d	5j	5k	5l	5m	5e	5f	5g	5h	5i	5n	50	5p
$CHCl_3$	581	579	577	555	570	575	569	563	576	576	575	578	571	587	576	561
THF	594	589	582	559	574	578	570	562	584	584	582	585	575	594	576	560
Acetone	584	591	580	560	576	579	575	566	580	580	578	582	576	558	580	564
EtOH	588	571	576	554	578	584	577	565	573	573	571	578	580	584	579	563
MeOH	588	566	576	554	573	578	574	564	578	578	575	575	575	582	578	561
CH_3CN	584	588	576	558	575	578	573	564	576	576	576	577	575	583	577	562
DMSO	592	596	579	557	579	583	580	568	587	587	585	584	579	589	583	584

fluorescence and Stokes shifts were showed a linear correlation, with the orientation polarizability (Δf) and empirical polarity parameter $E_T(30)$ [42-45].

Lippert-Mataga Equation

Generally, Lippert-Mataga equation (4 and 5) describe how the stokes shift changes as a function of solvent properties [42-45].

$$\Delta\upsilon = \frac{2\Delta f}{4\pi s_o hca^s}(\mu_e - \mu_g)^2 + C \quad (4)$$

$$\Delta f = \frac{s-1}{2s+1} - \frac{n^2-1}{2n^2+1} \quad (5)$$

Where ε_0 denotes the permittivity of the vacuum, Δ*v* explain the Stokes shift , μ_e and μ_g are the dipole in the ground-state and in the excited-state geometry, respectively, h, c, a and Δ*f are* the Planck's constant, velocity of light in vacuum, Onsager cavity radius, and orientation polarizability, respectively. The Lippert-Mataga correlations of the Stokes shifts of some derivatives of compounds **4** and **5** are illustrated in Figures **2** and **3**. Poor linearity was found for all the studied compounds. The non-ionic structures of dyes **4** revealed positive slope i.e. positive solvatochromic effects to Δ*f* in the applied solvents as tetrahydrofuran, ethyl acetate, acetone, *N*,*N*-dimethylformamide, dimethyl sulfoxide, acetonitrile, dichloromethane, chloroform, ethanol, and methanol, but the cationic dyes **5** showed negative slope i.e. negative solvatochromic effects to Δ*f*. Since, Stokes shift is caused by the effect of solvent on stability of exited state, current findings suggest that polar solvents more stabilize the dipole moment of the molecules in the ground state than the excited state, and it leads to blue shift or negative solvatochromic effect. Poor linear correlations were also observed for **5**, suggesting that solute–solvent interactions in the excited states of the dyes are stronger than dipole–dipole interaction.

The Lippert–Mataga equation accounts for the general solvent effect and does not account for specific solvent–fluorophore interactions, hence the non-linearity of the aforementioned correlations might be resulted from a specific solvent effect, presumably intermolecular hydrogen bonding between the solute and the solvent molecules [20].

Reichardt–Dimroth's E_T(N)

Reichardt–Dimroth equation (Eq. 6) is another useful scale to correlate the solvent induced Stokes shift (cm^{-1}) with the molar electronic transition energies, i.e. the $E_T(30)$ values [40, 41].

$$E_T(30)\ (kcal.mol^{-1}) = hc\ N_A\ \tilde{\nu}_{max} = 28591/\lambda_{max} \quad (6)$$

where *h*, *c*, and N_A are Planck's constant, speed of light, and Avogadro's constant, respectively, $\tilde{\nu}_{max}$ is the wavenumber (cm^{-1}), and λ_{max} is the wavelength (nm) corresponding to the highest absorption band in the visible/near-IR region. The normalized E_T^N scale could be defined as Eq. 7.

$$E_T^N = \frac{E_T(solvent) - E_T(SiMe_4)}{E_T(water) - E_T(SiMe_4)} = \frac{E_T(solvent) - 30.7}{32.4} \quad (7)$$

A representative correlation for **4c**, **4e**, **5c** and **5e** and is depicted in Figure **3**.

Nevertheless, no reasonable linear correlations were obtained with plotting the Stokes shift values against the Dimroth-Reichardt solvent parameters, as well. In general, increasing of solvent polarity was leaded to a red shift of fluorescence maxima for dyes **4c**, **4e**, **5c** and **5e**. The findings implicate that the interactions between solvent and dyes are more

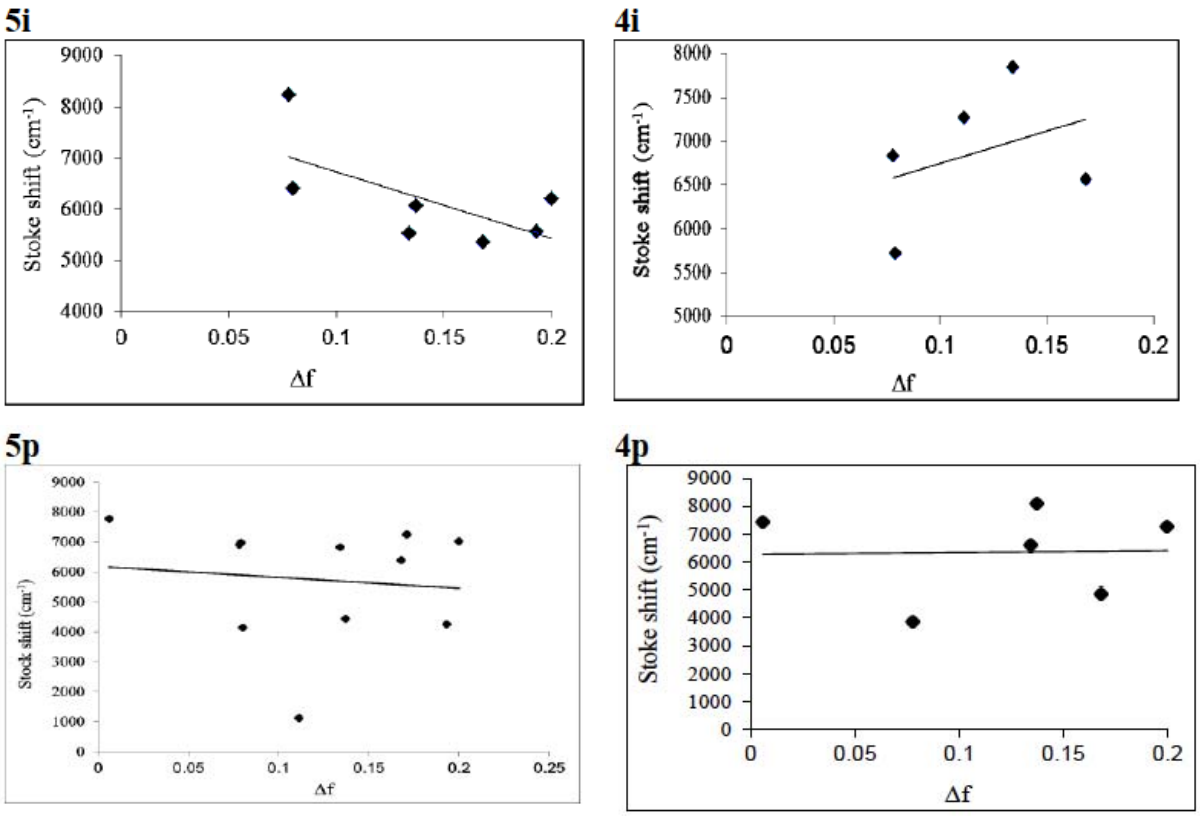

Figure 2: Lippert–Mataga plot showing Stokes shift as a function of solvent orientation polarizibility (Δ*f*) for **5i** and **5p** and **4i** and **4p**.

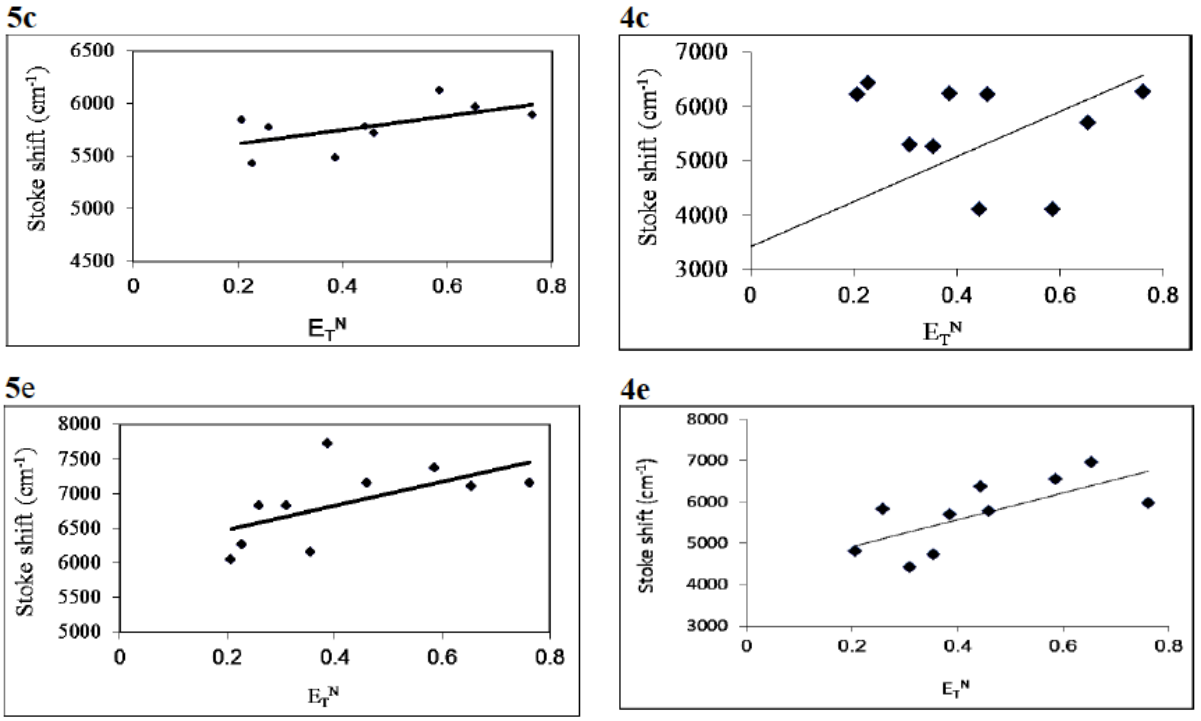

Figure 3: Relationship between the Stokes shift values (Δ*v*, Stokes shift, cm^{-1}) and $E_T(N)$ for **4c**, **4e**, **5c**, and **5e** in tetrahydrofuran, ethyl acetate, acetone, *N*,*N*-dimethylformamide, dimethyl sulfoxide, acetonitrile; dichloromethane, chloroform, ethanol, Methanol. Excitation wavelength: 385 nm.

Table 5: The *In Vitro* Antibacterial Activities of the Selected Bichromophoric Dyes

		Zone of inhibition[1] (mm)			
		Gram-positive bacteria		Gram-negative bacteria	
Dye	**Conc. (µg/disc)**	***S. aureus* ATCC 25923**	***S. epidermidis* ATCC 12228**	***E. coli* ATCC 25922**	***P. Aeruginosa* ATCC 27853**
5g	60	15.0	11	0.0	0.0
	30	13.0	8.0	0.0	0.0
	15	8.0	0.0	0.0	0.0
5i	60	11.0	0.0	0.0	0.0
	30	12.0	0.0	0.0	0.0
	15	9.0	0.0	0.0	0.0
5m	60	9.0	7.0	0.0	0.0
	30	8.0	0.0	0.0	0.0
	15	0.0	0.0	0.0	0.0
Positive control		40 (Penicillin)	35 (Penicillin)	12 (Ampicillin)	12 (Ciprofloxacin)

[1]Distilled water has been used as negative control.

complex than those which considered in the Reichardt–Dimroth equation or Lippert–Mataga equation.

Antibacterial Effects

Antibacterial effects of the synthesized cationic dyes were assessed against gram positive bacteria *S. epidermidis and S. aureus* and *gram negative* bacteria *E. coli*, and *P. aeruginosa via* the diffusion plate method.[43] Paper disks (r =2.5 mm) containing a serial dilutions of the dyes, i.e. 1:1 to 1:128, was placed on a plate (9 cm diameter) containing a solid bacterial growth medium (nutrient agar) which was heavily seeded with suspension of the selected bacterial strains. After 24 hours incubation at 37°C, the inhibitory power of the dyes were measured based on the diameter of inhibition zone around the discs. Ampicillin and Ciprofloxacin were used as reference antibiotics to evaluate the relative potency of the given compounds under the same conditions. The results revealed that **5g**, **5i** and **5m** have mild antibacterial property against gram positive bacteria (Table **5**).

CONCLUSIONS

Sixteen 2-aminobenzothiazoles based dichromophoric cationic azo dyes were synthesized and produced violet to blue color (λ_{max}: 551-588 nm) with high molecular extinction coefficient (2.6 - 4.7× 10^4 $L.M^{-1}.cm^{-1}$). All of dyes showed strong fluorescence with quantum yield of 0.02-0.18. Their unique excitation and emission wavelength were found at a broad range of 272-404 nm and 409–494 nm, respectively. The effects of solvents, with different polarity, were studied and negative slope, and negative solvatochromic effects to Δ*f*, were found for cationic dyes **5**. Furthermore, mild antibacterial effects were observed against gram positive bacteria *S. aureus*, and *S. epidermidis* in different concentration of dyes.

EXPERIMENTAL SECTION

General

All Chemicals were purchased from *Merck* and used without further purification. Melting points were measured using a Buchi melting-point B-545 apparatus. ^{1}H-NMR spectra was measured at 500 MHz, by a Bruker 500-Avance Fourier transform (FT)–NMR instrument with dimethyl sulfoxide (DMSO-d_6) and $CDCl_3$ as solvent. All chemical shifts (*δ)* are quoted in ppm and coupling constant (*J)* in Hz. The abbreviations used for the multiplicity of the NMR signals are: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, etc. FT-IR spectra were obtained with a Perkin-Elmer Spectrum One BX FTIR spectrometer. The UV/VIS spectra were recorded using a UV/VIS spectrophotometer, Multispec-1501 Shimadzu. Fluorescence spectra were taken on Fluorescence Spectrometer Perkin Elmer LS 55. Mass spectra were recorded on a Finnigan-Mat 8430 mass spectrometer operating at an ionization potential of 20 eV.

General Procedure for the Preparation of Compounds 2a–b

Aniline (0.02 mol) was added drop wise to a stirred solution of glyoxal 1a (0.01 mol) or terephthalaldehyde 1b in acetic acid 30% (20 ml) at 5 °C. The reaction mixture was stirred for 1 hour, filtered, and crystallized in water to afford the pure title compounds.

General Procedure for the Preparation of Compounds 5a–p

The synthetic pathway and properties of bis-azo dyes 4a-p, as disperse dyes, was achieved according to our previous reported [39, 46]. Then to a magnetically stirred suspension of 4a-p (10 mmol) and $NaHCO_3$ (1.7 gr, 20 mmol) in water (4 ml), dimethyl sulfate (4.4 ml, 36 mmol) was added dropwise at 30 ^{0}C. The reaction mixture was stirred at 60 ^{0}C for 2 h. The reaction was monitored by TLC (chloroform: methanol, 8:1). Afterward, the pH was adjusted to 4 by addition of HCl solution (1 M). The precipitated dye was filtered and recrystallized three times in water to afford the pure title compounds.

(5a) Mono(5-methoxy-3-methyl-2-((E)-(4- ((E)-((E)-2-((4-((E)-(3--methyl-5-methoxybenzo[d]thiazol-3-ium-2-yl)diazenyl)phenyl)imino)ethylidene)amino) phenyl)diazenyl)benzo[d]thiazol-3-ium mono(methyl sulfate)

Blue powder, yield (85%), m.p. >360 °C. IR (KBr) (ν_{max},cm^{-1}): 2932 (CH=), 1628 (C=N), 1512 (C=C), 1294 (C-N); ^{1}H-NMR (500 MHz, DMSO-d_6): δ_H 3.86 (s, 6H, 2OCH_3), 4.13 (s, 6H, 2NCH_3), 7.01 (d, 2H, $^3J_{HH}$ 8.15 Hz, 2CH), 7.20 (d, 4H,$^3J_{HH}$ 7.83 Hz, 4CH), 7.32 (d, 4H,$^3J_{HH}$ 7.83 Hz, 4CH), 7.45 (d, 2H, $^3J_{HH}$ 8.14 Hz, 2CH), 7.75 (d, 2H,$^3J_{HH}$ 8.14 Hz, 2CH), 8.08 (s, 2H, 2CH). MS *m/z* (%): 619 (M^+, 1), 605 (14), 310 (34), 281 (14), 165 (12), 133 (100).

(5b) Mono(3-methyl-2-((E)-(4- ((E)-((E)-2-((4-((E)-(3--methyl-benzo[d]thiazol-3-ium-2-yl)diazenyl)phenyl) imino)ethylidene)amino)phenyl)diazenyl)benzo[d]thiazol-3-ium mono(methyl sulfate)

Blue powder, yield (80%), m.p. 256-258 °C. IR (KBr) (ν_{max},cm^{-1}): 2939 (CH=), 1614 (C=N), 1587 (C=C), 1271 (C-N). ^{1}H-NMR (500 MHz, DMSO-d_6): δ_H 4.15 (s, 6H, 2NCH_3), 6.89 (d, 2H,$^3J_{HH}$ 8.09 Hz, 2CH), 7.07 (d, 4H,$^3J_{HH}$ 7.58 Hz, 4CH), 7.35 (d, 4H,$^3J_{HH}$ 7.58 Hz, 4CH), 7.58 (t, 2H, $^3J_{HH}$ 8.30 Hz, 2CH), 7.64 (t,2H, $^3J_{HH}$ 8.30 Hz, 2CH), 7.95 (d, 2H,$^3J_{HH}$ 8.30 Hz, 2CH), 8.10 (d, 2H,$^3J_{HH}$ 8.30 Hz, 2CH); MS *m/z* (%): 559 (M^+, 2), 545 (10), 280 (18), 252 (15), 165 (10), 133 (100).

(5c) Mono(5-ethoxy-3-methyl-2-((E)-(4- ((E)-((E)-2-((4-((E)-(3--methyl-5-ethoxybenzo[d]thiazol-3-ium-2-yl)diazenyl)phenyl)imino)ethylidene)amino)phenyl) diazenyl)benzo[d]thiazol-3-ium mono(methyl sulfate)

Blue powder, yield (85%), m.p. 227-229 °C. IR (KBr) (ν_{max},cm^{-1}): 2929 (CH=), 1603 (C=N), 1573 (C=C), 1261 (C-N).^{1}H-NMR (500 MHz, DMSO-d_6): δ_H 1.29 (t, 6H, $^3J_{HH}$ 6.86 Hz, 2CH_3), 4.12 (q, 4H,$^3J_{HH}$ 6.86 Hz, 2 OCH_2), 4.15 (s, 6H, 2NCH_3), 6.87 (d, 2H,$^3J_{HH}$ 8.18 Hz, 2CH), 7.08 (d, 4H,$^3J_{HH}$ 7.24 Hz, 4CH), 7.38 (d, 4H,$^3J_{HH}$ 7.24 Hz, 4CH), 7.86 (d, 2H,$^3J_{HH}$ 8.38 Hz, 2CH), 7.98 (d, 2H,$^3J_{HH}$ 8.38 Hz, 2CH), 8.07 (s, 2H, 2CH). MS *m/z* (%): 647 (M^+, 1), 633 (7), 324 (31), 296(15), 165 (12), 133 (100).

(5d) Mono(5-nitro-3-methyl-2-((E)-(4- ((E)-((E)-2-((4-((E)-(3--methyl-5-nitrobenzo[d]thiazol-3-ium-2-yl) diazenyl)phenyl)imino)ethylidene)amino)phenyl)diazenyl)benzo[d]thiazol-3-ium mono(methyl sulfate)

Indigo Blue powder, yield (78%), m.p. 2247-249 °C. IR (KBr) (ν_{max},cm^{-1}): 2928 (CH=), 1632 (C=N), 1519 (C=C), 1292 (C-N); ^{1}H-NMR (500 MHz, DMSO-d_6): δ_H 6.82 (d, 2H,$^3J_{HH}$ 8.22 Hz, 2CH), 7.12 (d, 4H,$^3J_{HH}$ 7.72 Hz, 4CH), 7.44 (d, 4H,$^3J_{HH}$ 7.42 Hz, 4CH), 8.12 (d, 2H,$^3J_{HH}$ 8.05 Hz, 2CH), 8.25 (d, 2H,$^3J_{HH}$ 8.05 Hz, 2CH), 8.41 (s, 2H, 2 CH). MS *m/z* (%): 649 (M^+, 3), 635 (9), 325 (26), 297 (12), 165 (14), 133 (100).

(5e) Mono(5-methoxy-3-methyl-2-((E)-(4- ((E)-(4-((E)-((4-((E)-(3--methyl-5-mthoxybenzo[d]thiazol-3-ium-2-yl)diazenyl)phenyl)imino)methyl)benzylidene) amino)phenyl)diazenyl)benzo[d]thiazol-3-ium mono(methyl sulfate)

Blue powder, yield (88%), m.p. 315-317 °C. IR (KBr) (ν_{max},cm^{-1}): 2961(CH=), 1632 (C=N), 1574 (C=C), 1288 (C-N); ^{1}H-NMR (500 MHz, DMSO-d_6): δ_H 3.98 (s, 6H, 2OCH_3), 4.11 (s, 6H, 2NCH_3), 7.03 (s, 4H, 4CH), 7.36 (d, 4H,$^3J_{HH}$ 7.57 Hz, 4CH), 7.55 (d, 4H,$^3J_{HH}$ 7.57 Hz, 4CH), 7.99 (d, 2H,$^3J_{HH}$ 8.12 Hz, 2CH), 8.11 (d, 2H,$^3J_{HH}$ 8.12 Hz, 2CH), 8.28 (s, 2H, 2CH), 8.50 (s, 2H, 2CH). MS *m/z* (%): 695 (M^+, 2), 681 (5), 348 (12), 241 (42), 106 (17), 133 (100).

(5f) Mono(3-methyl-2-((E)-(4- ((E)-(4-((E)-((4-((E)-(3--methyl-benzo[d]thiazol-3-ium-2-yl)diazenyl)phenyl) imino)methyl)benzylidene)amino)phenyl)diazenyl)benzo[d]thiazol-3-ium mono(methyl sulfate)

Blue powder, yield (85%), m.p. 291-293 °C. IR (KBr) (ν_{max},cm^{-1}): 2958 (CH=), 1605 (C=N), 1568 (C=C), 1284 (C-N); ^{1}H-NMR (500 MHz, DMSO-d_6): δ_H 4.13 (s, 6H, 2NCH_3), 7.15 (s, 4H, 4CH), 7.53 (d, 4H,$^3J_{HH}$ 7.49 Hz, 4CH), 7.83 (d, 4H,$^3J_{HH}$ 7.49 Hz, 4CH), 7.97 (t, 2H,$^3J_{HH}$ 8.52 Hz, 2CH), 8.02 (t, 2H,$^3J_{HH}$ 8.52 Hz, 2CH),

8.09 (d, 2H, $^3J_{HH}$ 8.52 Hz, 2CH), 8.23 (d, 2H, $^3J_{HH}$ 8.52 Hz, 2CH), 8.49 (s, 2H, 2CH). MS *m/z* (%): 635 (M^+, 3), 621 (10), 318 (18), 241 (16), 133 (100).

(5g) Mono(5-ethoxy-3-methyl-2-((E)-(4- ((E)-(4-((E)-((4-((E)-(3--methyl-5-ethoxybenzo[d]thiazol-3-ium-2-yl)diazenyl)phenyl)imino)methyl)benzylidene) amino)phenyl)diazenyl)benzo[d]thiazol-3-ium mono (methyl sulfate)

Blue powder, yield (85%), m.p. 278-280 °C. IR (KBr) (ν_{max},cm^{-1}): 2932 (CH=), 1651 (C=N), 1587 (C=C) 1274 (C-N); ^{1}H-NMR (500 MHz, DMSO-d_6): δ_H 1.48 (t, 6H, $^3J_{HH}$ 6.82 Hz, $2CH_3$), 4.11 (q, 4H, $^3J_{HH}$ 6.82 Hz, $2OCH_2$), 4.15 (s, 6H, $2NCH_3$), 7.12 (s, 4H, 4CH), 7.32 (d, 4H, $^3J_{HH}$ 7.59 Hz, 4CH), 7.57 (d, 4H, $^3J_{HH}$ 7.59 Hz, 4CH), 7.96 (d, 2H, $^3J_{HH}$ 8.24 Hz, 2CH), 8.07 (d, 2H, $^3J_{HH}$ 8.24 Hz, 2CH), 8.17 (s, 4H, 4CH), 8.31 (s, 2H, 2CH), 8.61 (s, 2H, 2CH). MS *m/z* (%): 723 (M^+, 2), 709 (7), 362 (10), 241 (32), 133 (100).

(5h) Mono(5-nitro-3-methyl-2-((E)-(4- ((E)-(4-((E)-((4-((E)-(3--methyl-5-nitrobenzo[d]thiazol-3-ium-2-yl) diazenyl)phenyl)imino)methyl)benzylidene)amino) phenyl)diazenyl)benzo[d]thiazol-3-ium mono(methyl sulfate)

Indigo Blue powder, yield (80%), m.p. 264-266 °C. IR (KBr) (ν_{max},cm^{-1}): 2936 (CH=), 1641 (C=N), 1592 (C=C), 1283 (C-N); ^{1}H-NMR (500 MHz, DMSO-d_6): δ_H 4.10 (s, 6H, $2NCH_3$), 7.05 (s, 4H, 4CH), 7.28 (d, 4H, $^3J_{HH}$ 7.73 Hz, 4CH), 7.78 (d, 4H, $^3J_{HH}$ 7.73 Hz, 4CH), 8.22 (d, 2H, $^3J_{HH}$ 8.35 Hz, 2CH), 8.34 (d, 2H, $^3J_{HH}$ 8.35 Hz, 2CH), 8.52 (s, 2H, 2CH), 8.59 (s, 2H, 2CH). MS *m/z* (%): 725 (M^+, 3), 711 (7), 363 (19), 241 (32), 133 (100).

(5i) Mono(5-methoxy-3-methyl-2-((E)-(4- ((E)-(4-((E)-((4-((E)-(3--methyl-benzo[d]thiazol-3-ium-2-yl) diazenyl)phenyl)imino)methyl)benzylidene)amino) phenyl)diazenyl)benzo[d]thiazol-3-ium mono(methyl sulfate)

Blue powder, yield (82%), m.p. 315-317 °C. IR (KBr) (ν_{max},cm^{-1}): 2979 (CH=), 1617 (C=N), 1574 (C=C), 1283 (C-N); ^{1}H-NMR (500 MHz, DMSO-d_6): δ_H 3.96 (s, 3H, OCH_3), 4.12 (s, 6H, $2NCH_3$), 7.06 (s, 4H, 4CH), 7.38-8.38 (m, 15H, Ar), 8.52 (s, 2H, 2CH). MS *m/z* (%): 665 (M^+, 2), 651 (4), 348 (11), 318 (14), 241 (27), 133 (100).

(5j) Mono(5-methoxy-3-methyl-2-((E)-(4- ((E)-((E)-2-((4-((E)-(3--methyl-benzo[d]thiazol-3-ium-2-yl) diazenyl)phenyl)imino)ethylidene)amino)phenyl)dia zenyl)benzo[d]thiazol-3-ium mono(methyl sulfate)

Blue powder, yield (95%), m.p. 293-295 °C. IR (KBr) (ν_{max},cm^{-1}): 2933 (CH=), 1609(C=N), 1585 (C=C), 1277 (C-N); ^{1}H-NMR (500 MHz, DMSO-d_6): δ_H 3.85 (s, 3H, OCH_3), 4.17 (s, 6H, $2NCH_3$), 6.89 (d, 2H, $^3J_{HH}$ 8.85 Hz, 2CH), 7.01-8.13 (m, Ar, 15H). MS *m/z* (%): 589 (M^+, 2), 310 (15), 280 (9), 165 (14), 133 (100).

(5k) Mono(5-ethoxy-3-methyl-2-((E)-(4- ((E)-((E)-2-((4-((E)-(3--methyl-5-methoxybenzo[d]thiazol-3-ium-2-yl)diazenyl)phenyl)imino)ethylidene)amino) phenyl)diazenyl)benzo[d]thiazol-3-ium mono(methyl sulfate)

Blue powder, yield (85%), m.p. >360 °C. IR (KBr) (ν_{max},cm^{-1}): 2928 (CH=), 1623 (C=N), 1536 (C=C), 1292 (C-N); ^{1}H-NMR (500 MHz, DMSO-d_6): δ_H 1.51 (t, 3H, $^3J_{HH}$ 6.71 Hz, CH_3), 3.93 (s, 3H, OCH_3), 4.11 (q, 2H, $^3J_{HH}$ 6.71 Hz, OCH_2), 4.16 (s, 6H, $2NCH_3$), 6.91 (d, 2H, $^3J_{HH}$ 8.36 Hz, 2CH), 6.98-8.24 (m, 14H, Ar). MS *m/z* (%): 633 (M^+, 3), 619 (5), 324 (10), 310 (15), 165 (22), 133 (100).

(5l) Mono(5-ethoxy-3-methyl-2-((E)-(4- ((E)-((E)-2-((4-((E)-(3--methyl-benzo[d]thiazol-3-ium-2-yl)diazenyl) phenyl)imino)ethylidene)amino)phenyl)diazenyl)be nzo[d]thiazol-3-ium mono(methyl sulfate)

Blue powder, yield (84%), m.p. 305-307 °C. IR (KBr) (ν_{max},cm^{-1}): 2938 (CH=), 1624 (C=N), 1529 (C=C), 1295 (C-N). ^{1}H-NMR (500 MHz, DMSO-d_6): δ_H 1.53 (t, 3H, $^3J_{HH}$ 6.94 Hz, CH_3), 4.11 (q, 2H, $^3J_{HH}$ 6.94 Hz, OCH_2), 4.14 (s, 6H, 2 NCH_3), 6.91 (d, 2H, $^3J_{HH}$ 8.47 Hz, 2CH), 7.04-8.28 (m, 15H , Ar). MS *m/z* (%): 603 (M^+, 1), 589 (10); 324 (14), 280 (22), 165 (26), 133 (100).

(5m) Mono(5-nitro-3-methyl-2-((E)-(4- ((E)-((E)-2-((4-((E)-(3--methyl-benzo[d]thiazol-3-ium-2-yl)diazenyl) phenyl)imino)ethylidene)amino)phenyl)diazenyl)be nzo[d]thiazol-3-ium mono(methyl sulfate)

Indigo Blue powder, yield (79%), m.p. 229-231 °C. IR (KBr) (ν_{max},cm^{-1}): 2934 (CH=), 1619 (C=N), 1574 (C=C), 1289 (C-N); ^{1}H-NMR (500 MHz, DMSO-d_6): δ_H 4.18 (s, 6H, $2NCH_3$), 6.94 (d, 2H, $^3J_{HH}$ 8.75 Hz, 2CH), 7.12 (d, 2H, $^3J_{HH}$ 6.64 Hz, 2CH), 7.37 (d, 2H, $^3J_{HH}$ 6.64 Hz, 2CH), 7.52 (d, 2H, $^3J_{HH}$ 6.64 Hz, 2CH), 7.71 (d, 2H, $^3J_{HH}$ 6.64 Hz, 2CH), 7.82 (t, 1H, $^3J_{HH}$ 8.32 Hz, CH), 8.01(t, 1H, $^3J_{HH}$ 8.32 Hz, CH), 8.08 (d, 1H, $^3J_{HH}$ 8.32 Hz, CH), 8.14 (d, 1H, $^3J_{HH}$ 8.32 Hz, CH), 8.26 (d, 1H, $^3J_{HH}$ 8.32 Hz, CH); 8.34 (d, 1H, $^3J_{HH}$ 8.32 Hz, CH); 8.61 (s, 1H, CH). MS *m/z* (%): 604 (M^+, 1), 590 (12), 325 (11), 280 (16), 165 (24), 133 (100).

(5n) Mono(5-ethoxy-3-methyl-2-((E)-(4- ((E)-(4-((E)-((4-((E)-(3--methyl-5-methoxybenzo[d]thiazol-3-ium-2-yl)diazenyl)phenyl)imino)methyl)benzylidene) amino)phenyl)diazenyl)benzo[d]thiazol-3-ium mono(methyl sulfate)

Blue powder, yield (85%), m.p>360 °C. IR (KBr) (ν_{max},cm^{-1}): 2954 (CH=), 1641 (C=N), 1585 (C=C),

1274 (C-N); ^{1}H-NMR (500 MHz, DMSO-d_6): δ_H 1.50 (t, 3H, $^3J_{HH}$ 6.74 Hz, CH_3), 3.99 (s, 3H, OCH_3), 4.11 (q, 2H, $^3J_{HH}$ 6.74 Hz, OCH_2), 4.16 (s, 6H, $2NCH_3$), 7.11 (s, 4H, 4CH), 7.35-8.37 (m, 14H, Ar), 8.54 (s, 2H, 2CH). MS *m/z* (%): 709 (M^+, 1), 695 (4), 342 (13), 348 (14), 241 (41), 133 (100).

(5o) Mono(5-ethoxy-3-methyl-2-((E)-(4- ((E)-(4-((E)-((4-((E)-(3--methyl-benzo[d]thiazol-3-ium-2-yl) diazenyl)phenyl)imino)methyl)benzylidene)amino) phenyl)diazenyl)benzo[d]thiazol-3-ium mono(methyl sulfate)

Blue powder, yield (82%), m.p. 272-274 °C. IR (KBr) (ν_{max},cm^{-1}): 2978 (CH=), 1623 (C=N), 1518 (C=C), 1289 (C-N); ^{1}H-NMR (500 MHz, DMSO-d_6): δ_H 1.48 (t, 3H, $^3J_{HH}$ 6.84 Hz, CH_3), 4.10 (q, 2H, $^3J_{HH}$ 6.84 Hz, OCH_2), 4.14 (s, 6H, $2NCH_3$), 6.99 (s, 4H, 4CH), 7.29-8.31 (m, 15H, Ar), 8.55 (s, 2H, 2CH). MS *m/z* (%): 679 (M^+, 3), 665 (6), 342 (16), 318 (6), 241 (34), 133 (100).

(5p) Mono(5-nitro-3-methyl-2-((E)-(4-((E)-(4-((E)-((4-((E)-(3--methyl-benzo[d]thiazol-3-ium-2-yl)diazenyl) phenyl)imino)methyl)benzylidene)amino)phenyl)dia zenyl)benzo[d]thiazol-3-ium mono(methyl sulfate)

Indigo Blue powder, yield (78%), m.p. 245-247 °C. IR (KBr) (ν_{max},cm^{-1}): 2948 (CH=), 1626 (C=N), 1516 (C=C), 1294 (C-N); ^{1}H-NMR (500 MHz, DMSO-d_6): δ_H 4.13 (s, 6H, $2NCH_3$), 7.14 (s, 4H, 4CH), 7.49 (d, $^3J_{HH}$ 7.54 Hz, 2CH), 7.62 (d, 2H, $^3J_{HH}$ 7.54 Hz, 2CH), 7.75 (d, 2H, $^3J_{HH}$ 7.54 Hz, 2CH), 7.79 (d, 2H, $^3J_{HH}$ 7.54 Hz, 2CH), 7.86 (t, 1H, $^3J_{HH}$ 8.28 Hz, CH), 7.95 (t, 1H, $^3J_{HH}$ 8.28 Hz, CH), 8.02 (d, 1H, $^3J_{HH}$ 8.28 Hz, CH), 8.10 (d, 1H, $^3J_{HH}$ 8.28 Hz, CH), 8.32 (d, 1H, $^3J_{HH}$ 8.28 Hz, CH), 8.42 (d, 1H, $^3J_{HH}$ 8.28 Hz, CH), 8.49 (s, 1H, CH), 8.63 (s, 2H, 2CH). MS *m/z* (%): 680 (M^+, 2), 666 (4), 343 (16), 318 (14), 241 (22), 133 (100).

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