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Development of Molecular Photoswitch with Very Fast Photoresponse based on Asymmetrical Bis-Azospiropyran

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ABSTRACT

To study the effects of an extended bis-azo conjugated bridge with two different photochemical functions on a molecule in photochromic responses, a novel asymmetrical bifunctional bis-azo spiropyran photochromic dye was designed and synthesized. The obtained photoresponses were compared with symmetrical bifunctional bis-azo spiropyran analogues, and relative mono-azo and simple spiropyrans. Colorimetric behaviour, luminescence, and switching kinetics of all the dyes were studied. The largest molar absorption coefficient in merocyanine form, quickest response to light, and highest fluorescence quantum yield of the spiropyran form with a superior ratio of emission intensities of spiropyran to merocyanine form were achieved for the asymmetric bis-azospiropyran,. Solvatochromic effect was studied to observe the solvent effects on non-irradiation coloration of the photochromic dyes. Furthermore, The molecular energy levels for optimized geometries of the synthesized bis-azospiropyrans and their probable photochemical products were obtained at the B3LYP/6-31G(d) level of theory.

Keywords: Photochromic, Solvatochromic, Density functional theory, Azospiropyrans, Bi-dose response.

1. Introduction

The design and synthesis of novel photochromic molecules with high sensitivity and signal transduction capability are points of scientific interest and major activity in the field of color chemistry. A large variety of applications for photoresponsive molecules has been investigated in high-level technologies such as controlling the conformation and activity of biomolecules[1-3], sensors [4-10], data recording, optical storage, optical switching [11-14], displays, non-linear optics [15-18], and other photochemical and photophysical reactions [19, 20].

Molecular switches that exhibit reversible ring opening-closing behaviour have drawn much attention recently, owing to the well-separated absorption bands of the two isomers [21-26]. In these molecules, spiropyrans which have unique molecular binding abilities, and signal transduction functions are known as important classes [12, 13, 27]. Because, the stability and photosensitivity of spiropyrans are strongly dependent on the substituent, the design of novel structures of these photoswitches and the investigation of their optical behaviour are interesting [14, 15, 28].

In the investigation of spiropyrans, few bis-spiropyrans have been reported [15, 18-20]. The development of such spiropyrans has led to the development of bifunctional chromophores in one molecule as highly sensitive molecular switches. The two provided zwitterionic merocyanine units, which had a more sensible system, developed higher sensitivity and molar capacity than the mono-spiropyran [21]. Few studies have been conducted on bis-spiropyran systems and their unique properties [12, 15, 21, 29-31], and to the best of our knowledge, bis-azospiropyran systems have been introduced by authors only recently [32].

Therefore, in keeping with our earlier research on the synthesis and properties of symmetrical bis-azospiropyran dyes [32, 33], we developed in the current study an asymmetric azo spiropyran derivative on an extended conjugation push-pull system, in which two different spiropyrans are linked

by a bis-azo extended aromatic system to develop a very sensitive photochromic system with high-level color strength in merocyanine form. The colorimetric behaviour, luminescence, and switching kinetics as well as solvatochromic effects of all the synthesized photochemic compounds were also investigated. Moreover, in order to expose the particular photo properties of the target structure, six different derivatives of spiropyranes with relative structures were synthesized and studied as well. Besides, molecular level of energy for each photoreactive form of the synthesized bis-azospiropyrans was calculated using density functional theory method (DFT).

2. Experimental

2.1. Chemical and apparatus

Chemicals were purchased from Merck and used without further purification. Melting points were determined with a Büchi B-545 melting-point apparatus; uncorrected. UV/Vis Spectra were recorded with a Multispec-1501-Shimadzu UV/Vis spectrophotometer. Infrared spectra were recorded with a Perkin-Elmer-Spectrum-One-BX FT-IR spectrometer. Fluorescence spectra were obtained by a Perkin-Elmer-LS-55 spectrometer. ^{1}H-NMR Spectra were obtained with a Bruker-500-Avance Fourier-transform (FT) NMR instrument, at 500 MHz, in solvents that are indicated in parenthesis before the chemical shift values (δ relative to TMS and given in ppm). Mass spectrometry analyses were performed at the Finnigan-Mat-8430 mass spectrometer. Elemental analyses for C, H, and N were recorded with a Heraeus-CHN-O-Rapid analyzer. A 365 nm UV handheld lamp (8-watt cm^{-2}) were used as the excitation light sources for the photochromic ring-opening reactions.

2.2. Computation

Our theoretical results for the synthesized spiropyrans are based on first-principles density functional theory (DFT) calculations. Molecular geometries of the synthesized bis-azospiropyrans (**1**, **6a** and **6b**) and their probable photochemical products were optimized at the B3LYP/6-31G (d) level of theory

without applying any restrictions on the molecular symmetry. DFT calculations carried out using the GAMESS set [21]. Graphical representations of quantum chemical calculation outputs were prepared by MacMolPlt [34] and CHEMCRAFT [35] software.

2.4. Synthesis

2.4.1. Synthesis of azo salicylaldehydes

2.4.1.1. Mono-azosalicylaldehydes 2

A solution of $NaNO_2$ (0.8 g, 11.6 mmol) in 5 ml H_2O was added to a solution of salicylaldehyde (1.3 ml, 10.7 mmol) in 20 ml H_2O including NaOH (0.43 g) and the temperature was kept lower than 5 °C. The resulting solution was added dropwise to a solution of aniline (1 g, 10.7 mmol) and 3 ml HCl (36%) in 10 ml H_2O at 0 °C. The mixture was stirred for 1 h at room temperature; then the precipitate was filtered and washed out with distilled water. Compounds based on monoazo-salicylaldehyde **2** were crystallized in EtOH to afford pure compounds.

2-hydroxy-5-[(E)-phenyldiazenyl]benzaldehyde **2a.** Yellow powder (75%). M.p: 128-129°C. IR(KBr) υ= 3430(OH), 2975(CH=),1619 (C=O), 1342 cm^{-1} (C-N). ^{1}H-NMR ($CDCl_3$) δ =7.18 (d, 1H, *J*=8.83Hz, CH), 7.53 (t, 1H, *J* =7.32*Hz*, CH), 7.57 (t, 2H, *J*=7.32Hz, 2CH), 7.95 (d, 2H, *J*= 7.32Hz, 2CH), 8.23 (d, 1H, *J* = 8.83Hz, CH), 8.26 (s, 1H, CH), 10.08 (s, 1H, CHO), 11.37 (s, 1H, OH). Anal.calc. for $C_{13}H_{10}N_2O_2$ (226.235): C 69.02, H 4.45, N 12.38; found: C 68.99, H 4.47, N 12.42.

2.4.1.2. Synthesis of symmetrical bis-azo salicylaldehydes **3**

The diazotation of 1,4-diphenylenediamine performed according to the reported procedure in our previous work [32] as below:

A solution of $NaNO_2$ (1.6 g, 23.2 mmol) in H_2O (5 mL) was added to salicylaldehyde derivatives (21.8 mmol) in H_2O (10 mL) including NaOH (1.8 g) at 5 °C. The resulting solution was added

dropwise to a solution of 1,4-diaminobenzene (11.6 mmol) in HCl (10 mL, 1 %) at 0 °C. The mixture was stirred for 1 h at room temperature; then the precipitate was filtered and washed out with distilled water. The compounds 3 were crystallized in EtOH to afford pure compounds.

3,3'-[Benzene-1,4-diylidi(E)diazene-2,1-diyl]bis(6-hydroxybenzaldehyde) **3a.** Green powder (96%). Mp: 207-209 °C. IR (KBr) υ=3435 (OH), 2971 (CH=), 1621 (C=O), 1349 cm^{-1} (C-N). ^{1}H-NMR (DMSO-d_6) δ=6.95 (d, 2H, *J* =8.1Hz, 2CH), 7.41 (d, 2H, *J*= 8.1Hz, 2CH), 7.52 (s, 4H, 4CH), 7.65 (s, 1H, 2CH); 9.01 (s, 1H, 2CHO), 13.12 (s, 1H, 2OH). Anal. calc. for $C_{20}H_{14}N_4O_4$ (374.35): C 64.17, H 3.77, N 14.97; found: C 64.21, H 3.74, N 14.99.

3,3'-[benzene-1,4-diylidi(E)diazene-2,1-diyl]bis(4,4'-diethylamino-6-hydroxybenzaldehyde) **3b.** Reddish Yellow powder (95%). Mp: 190-192 °C. IR (KBr) υ= 3422 (OH); 2936 (CH=); 1619 (C=O); 1329 cm^{-1} (C-N). ^{1}H-NMR ($CDCl_3$) δ= 1.25 (t, 6H, *J*=7.2Hz, $2CH_3$), 3.46 (q, 4H, *J*=7.2Hz, $2CH_2$), 7.11 (s, 2H, 2CH), 7.67 (s, 4H, 4CH), 8.01 (s, 2H, 2CH), 8.46 (s, 2H, 2CHO), 13.12 (s, 2H, 2OH). Anal. Calc. for $C_{28}H_{32}N_6O_4$ (516.60): C 65.10, H 6.24, N 16.27. Found C 65.14, H 6.18; N 16.30.

2.4.1.3. Synthesis of asymmetrical bis-azo salicylaldehyde **9**

First, a solution of $NaNO_2$ (1.14 g, 16.6 mmol) in H_2O (5 mL) was added to a solution of salicylaldehyde (16.6 mmol) in H_2O (10 mL) including NaOH (0.6 g, 15 mmol) at 5 °C. The resulting solution was added dropwise to the 1,4-phenylenediamine (2.6 g, 16.6 mmol) in HCl (60 mL, 1 %) at 0 °C. The mixture was stirred for 1h at room temperature; then the precipitate was filtered and washed out with distilled water, and dried at 50 °C in vacuum oven. At the second step, a solution of $NaNO_2$ (0.057 g, 0.82 mol) in H_2O (3 ml) was added dropwise to a solution of 4-(diethylamino)salicylaldehyde (0.16 g, 0.82 mmol) in H_2O (5 mL) including NaOH (0.06 g, 1.5 mmol) at 0-5 °C. Then the resulting solution was added to a solution of the obtained precipitate from the first

step (0.2 g, 0.82 mol) in HCl (11 mL, 1 %) at 0°C. The mixture was stirred for 1 h at room temperature; then the precipitate was filtered and washed out with distilled water. Compound **9** was crystallized in EtOH to afford pure substance.

4-(diethylamino)-5-((E)-(4-((E)-(3-formyl-4-hydroxyphenyl)diazenyl)phenyl)diazenyl)-2-hydroxybenzaldehyde **9**. Deep red powder (58%). Mp: 230 °C. IR (KBr) υ= 3421 (OH), 2974 (CH=), 1610 (C=O), 1333 cm^{-1} (C-N). ^{1}H-NMR ($CDCl_3$) δ = 1.26 (t,6H, J = 7.10Hz, $2CH_3$), 3.46 (q,4H, J =7.10Hz, 2 CH_2), 6.24-721 (m,9H, Ar H), 8.49 (s, 1H, CHO), 8.50 (s, 1H, CHO), 13.8 (s, 1H, OH), 13.9 (s, 1H, OH). Anal. calc. for $C_{24}H_{23}N_5O_4$ (445.479): C 64.71, H 5.20, N 15.72, Found: C 64.75, H 5.18, N 15.69.

2.4.2. Synthesis of Spiropyran compounds

The simple spiropyrans 4 were prepared by one step reaction of Fischer's base and salicyaldehyde derivatives according to known procedure[36]. Procedure to the synthesis of the other spiropyrans was as below:

*2.4.2.1. Synthesis of mono-azo spiropyran **5** and symmetrical bis-azo spiropyran **6***

2-Methylene-1,3,3-trimethylindoline (1 mmol for mono-spiropyran and 2 mmol for bis-spiropyran compounds) in 5 ml $CHCl_3$ was added dropwise to a refluxing solution of salicylaldehyde derivatives **2** or **3** (1 mmol) in 20 ml chloroform, in 20 minutes. The mixture was refluxed for 2 h, and then cooled to room temperature. Then the precipitate was filtered and washed out with distilled water, and crystallized in EtOH to afford the pure spiropyran compounds **5** or **6** accordingly.

(E)-1',3',3'-trimethyl-6-(phenyldiazenyl)spiro[chromene-2,2'-indoline] **5a.** Pink powder (87%). Mp: 180-182 °C. IR (KBr) υ= 2963 (CH=), 1654 (C(3)=C(4)), 1020 cm^{-1} (C(2)-O). ^{1}H NMR (DMSO-d_6) δ

= 1.25 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 2.80 (s, 3H, NCH_3), 4.29 (d, 1H, *J*=10.19 Hz, H-C(3)), 6.60-7.25 (m, 14H, 12ArH, and 2H-C(4)). Anal. calc. for $C_{25}H_{25}N_3O$ (383.494): C 78.30, H 6.57, N 10.96; found: C 78.34, H 6.53, N 10.92.

3,3'-[Benzene-1,4-diylidi(E)diazene-2,1-diyl]bis[1',3',3'- trimethylspiro(2H-1-benzopyran-2,2'-indoline)-6-yl] **6a**. White powder (89%). Mp: 203-205°C. IR (KBr) υ= 2966 (CH=), 1605 (C(3)=C(4)), 1311 (C(2)-N), 1021 cm^{-1} (C(2)-O). ^{1}H-NMR (DMSO-d_6) δ = 1.25 (s, 6H, $2CH_3$), 1.28 (s,6H, $2CH_3$), 2.80 (s, 6H, 2NCH), 4.20 (d, 2H, *J*=10.2Hz, 2H-C(3)), 6.60-7.26 (m, 20H, 18ArH, and 2H-C(4)). MS (EI) *m/z* (%): 685 (M+1, 1), 655 (M−2 Me, 1), 493 (15), 404 (2), 318 (88), 274 (25), 212 (100), 183 (18). Anal. calc. for $C_{44}H_{40}N_6O_2$ (684.84): C 77.17, H 5.89, N 12.27; found: C 77.20, H 5.85, N 12.30.

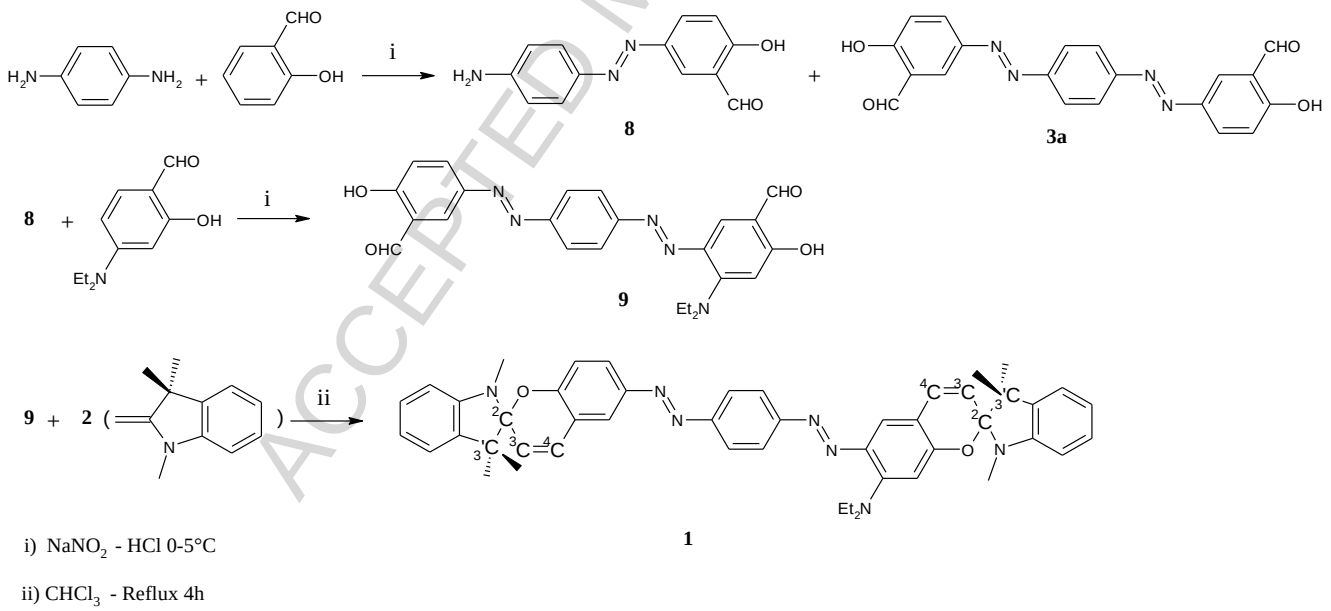
3,3'-[benzene-1,4-diylidi(E)diazene-2,1-diyl]bis[1',3',3'-trimethyl-6-diethylamino spiro(2H-1-benzopyran-2,2'-indoline)-6-yl] **6b**. Cream color powder (80%) Mp: 216-218 °C. IR (KBr) υ=2966(CH=), 1605 (C(3)=C(4)), 1313 (C(2)-N), 1020 cm^{-1} (C(2)-O). ^{1}H NMR ($CDCl_3$) δ= 1.13 (t, 6H, *J*=6.97 *Hz*, 2 CH_3) 1.38 (s,6H, 2 CH_3), 1.43 (s,6H, 2 CH_3), 2.92 (s, 6H, $2NCH_3$), 3.28 (q,4H, *J*=6.97Hz, 2 CH_2), 4.3 (d,2H, *J* =10.1 Hz,, 2H-C(3)); 6.37-7.28 (m, 16H, ArH and 2 H-C(4)). MS (EI) *m/z* (%): 828 (M+1, 1), 797 (M-2 CH_3, 1), 493 (16), 404 (2), 318 (79), 274 (28), 212 (100), 183 (20). Anal. Calc. for $C_{52}H_{58}N_8O_2$ (827.09): C 75.51, H 7.07, N 13.55; Found C 75.59, H 7.11, N 13.53.

*2.4.2.2. Synthesis of asymmetrical bis-azo Spiropyran compound **1***

2-Methylene-1,3,3-trimethylindoline (0.35 ml, 2 mmol) in 5 ml $CHCl_3$ was added dropwise to a refluxing solution of salicylaldehyde derivatives **9** (0.44 g, 1 mmol) in 20 ml chloroform, in 20 minutes. The mixture was refluxed for 2 h, and then cooled to room temperature. Then the precipitate was filtered and washed out with distilled water, and crystallized in EtOH to afford the pure spiropyran

compound **1**.

N,*N*-diethyl-1',3',3'-trimethyl-6-((E)(4-((E)-(1',3',3'-trimethylspiro[chromene-2,2'-indoline]-6-yl)diazenyl)phenyl) diazenyl) spiro [chromene-2,2'-indolin]-7-amine **1**. Cream-colored powder (44%). Mp: 185-186 °C. IR (KBr) υ= 2967(CH=), 1612(C(3)=C(4)), 1310 cm^{-1} (C(2)-N),1021(C(2)-O). ^{1}H-NMR ($CDCl_3$) δ= 1.00 (t,3H, *J*=6.9*Hz*, CH_3), 1.23 (s,3H, CH_3), 1.25 (s,3H, CH_3), 1.55 (s,3H, CH_3), 1.56 (s,3H, CH_3), 2.79 (s,3H, NCH_3), 3.00 (s, 3H, NCH_3), 3.21 (q, 2H, *J*=6.9*Hz*, CH_2), 4.10 (d,1H, *J*=9.98*Hz*, H-C(3)), 4.23 (d,1H, *J*=10.18*Hz*, H-C(3)), 6.15-7.17 (m,19H, 17Ar H, and 2H-C(4)). MS (EI) *m/z* (%): 756 (M^+, 1), 727 (M-2CH_3, 1), 493 (10), 348 (100), 19 (31), 158 (81). Anal. Calc. for $C_{48}H_{49}N_7O_2$ (755.967): C 76.26, H 6.5307, N 12.97; Found C 76.22, H 6.56, N 13.01.



Scheme 1. Synthesis of asymmetric bis-azospiropyran photochromic dye **1**

3. Results and Discussion

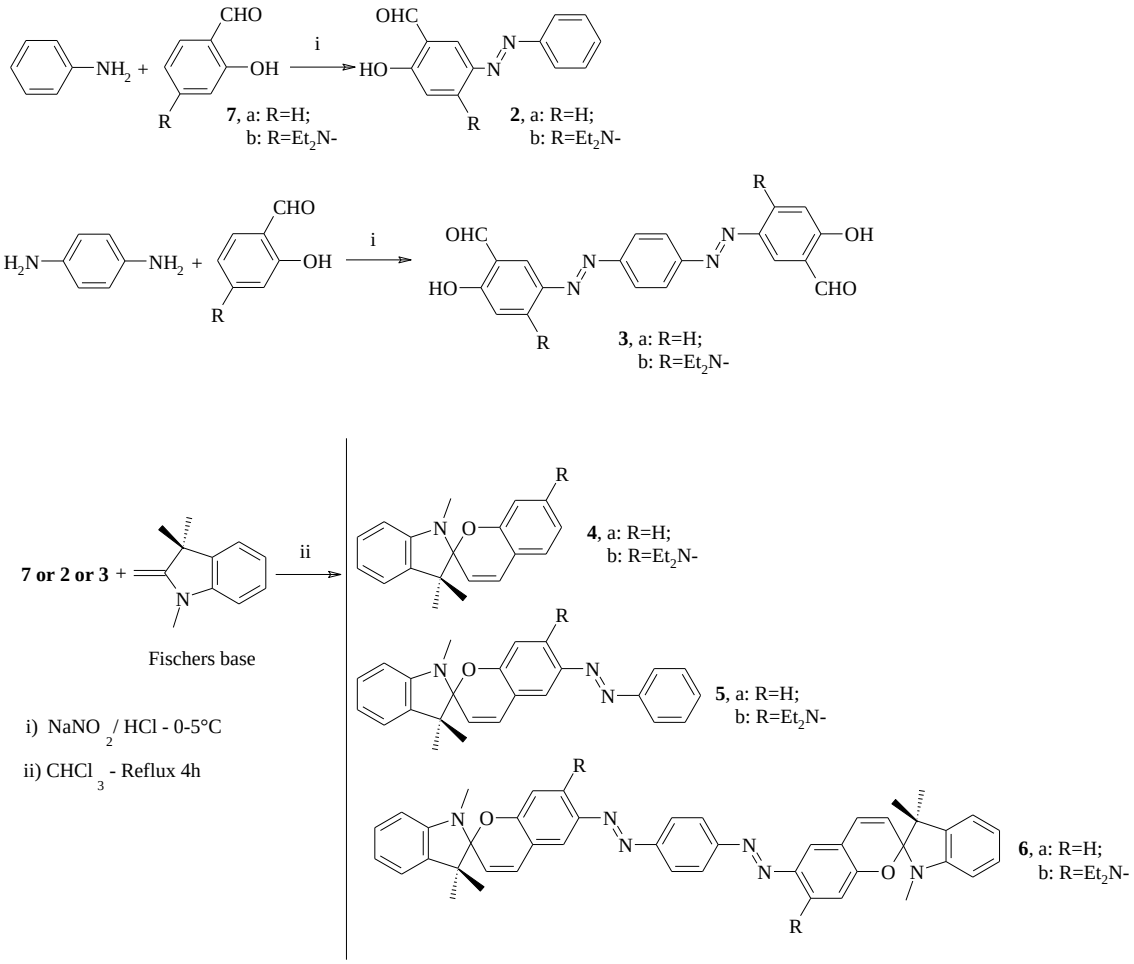
Synthesis of asymmetrical substituted of bis-azospiropyran **1** as a target dyad molecule was designed

in order to study the effect of a highly conjugated bis-azo bridge between two different spiropyrans with and without an electron donor group (Et_2N-) as a push-pull arrangement (Scheme 1).

To study the effects of electron-donating group (Et_2N-) and a conjugated azo bridge, simple spiropyrans **4**, mono-azo spiropyrans **5**, and symmetrical bis-azospiropyranes **6**, all with and without Et_2N- substitution were synthesized (Scheme 2). Their optical properties were compared with asymmetric bis-azospiropyran **1** as an electron conjugated push-pull system. Photoresponses, color intensities in merocyanine (Mc) forms, emission intensities in spiropyran (Sp) forms and their photokinetic conversion of Sp into Mc forms were studied.

In the synthesis procedure, spiropyrans **4** were prepared according to the references.[26] Azospiropyrans **5** were obtained by the coupling reaction of salicylaldehyde derivatives **2** with Fischer's base, i.e. 1,3,3-trimethyl-2-methyleneindoline in good yields (≥80%) (Scheme 2), and 6-hydroxybenzaldehyde derivatives **2** were obtained from the diazotization of *aniline* with the subsequent coupling with salicylaldehydes **7** in high yields (≥95%).

Accordingly, bis-azospiropyrans **6** were obtained in good yields (≥80%) by the coupling reaction of bissalicylaldehyde derivatives **3** with Fischer's base (Scheme 2), and bis(6-hydroxybenzaldehyde) derivatives **3** in high yields (≥95%) were obtained from the bis-diazotization of *p*-phenylenediamine with subsequent coupling with salicylaldehydes **7**.



Scheme 2. Synthesis of spiropyran derivatives **3-5**

Asymmetrical bis-azospiropyran **1** was synthesized by the reaction of asymmetrical bis-azo precursor **9** with Fischer's base in 2:1 mole ratios; the precursor **9** was prepared in two steps. First, the mono-azo product **8** was obtained from the product of the diazotization and coupling of 1,4-phenylenediamine with salicylaldehyde **7a** in 1:1 mole ratios as a major product (70%) and the doubly coupled product **3a** as the minor product (30%), according to TLC. Then, the precursor **9** was achieved from the diazotization and coupling of mono-azo product **8** with *N*,*N*-diethyl salicylaldehyde **7b** in 1:1 mole ratios. The structures of products were identified from their MS, FT-IR, and ^{1}H-NMR spectroscopic data and CHN analysis.

The absorption frequencies in FT-IR spectra of **1** revealed that the peak at 2967 cm^{-1} was due to C-H (aromatic); the peak at 1612 cm^{-1} was related to C(3)=C(4) stretch (Scheme 1); the stretching vibration of the C(2)-N was observed at 1310 cm^{-1}; and the C(2)-O stretching frequencies occurred at 1021 cm^{-1}. The ^{1}H-NMR spectra for **1** clearly showed four singlet signals at 1.23 and 1.25 ppm (6H) and 1.55 and 1.56 ppm (6H) for four CH_3 at 2 C(3)-$(CH_3)_2$ protons (Scheme 1). The close proximity of two CH_3 of indoline moieties (C(3)-$(CH_3)_2$) to the olefinic proton or an oxygen moiety of the pyranyl group made them magnetically non-equivalent [8]. Two singlet signals appeared in 2.79 and 3.00 ppm (6H) for two N-CH_3 protons of **1**, which are chemically and magnetically non-equivalent. The olefinic protons of **1** revealed four doubles, two of them at 4.10 and 4.23 ppm for two H-C(3) with large coupling constants (*J*=9.98-10.18 Hz), and the other two for olefinic protons 2 H-C(4) in the aromatic regions. The former doublet for olefinic protons with large coupling is very characteristic of a spiropyran system. Fig. 1 shows the absorption spectrum of 10^{-5} M dyad **1**, **6b** and **5b** and 10^{-4} M **4b**, **4a**, **5a** and **6a.** It shows the maximum absorptions of the photochromic compounds in dark (OFF) and in their photostationary states in dichloromethane (DCM) after exposure to UV light. All the photochromic compounds were bleached in DMF at 125-130 °C.

Fig. 2 shows the color strengths of 10^{-5} M photochromic compounds **1** and **4-6** in dichloromethane (DCM) after 0, 10, and 30 minutes exposure to UV light at the ambient temperature. The asymmetric photochemically bifunctional compound **1** revealed the fastest speed and best color strength photo response. The addition of a diethyl amine group to the pyran moieties of spiropyrans **4** and **5** as an electron-donating substitution increased the rapidness and strength of photoresponses of photochromic molecules. Although **6b** with a high electron density is colored (yellow) in Sp form, it revealed a different shade in Mc form due to the combination of the colors yellow (λ_{max} 420 nm, ε 4.7×10^{4} $M^{-1}.cm^{-1}$) and red (λ_{max} 555 nm, ε 2.7×10^{4} $M^{-1}.cm^{-1}$).

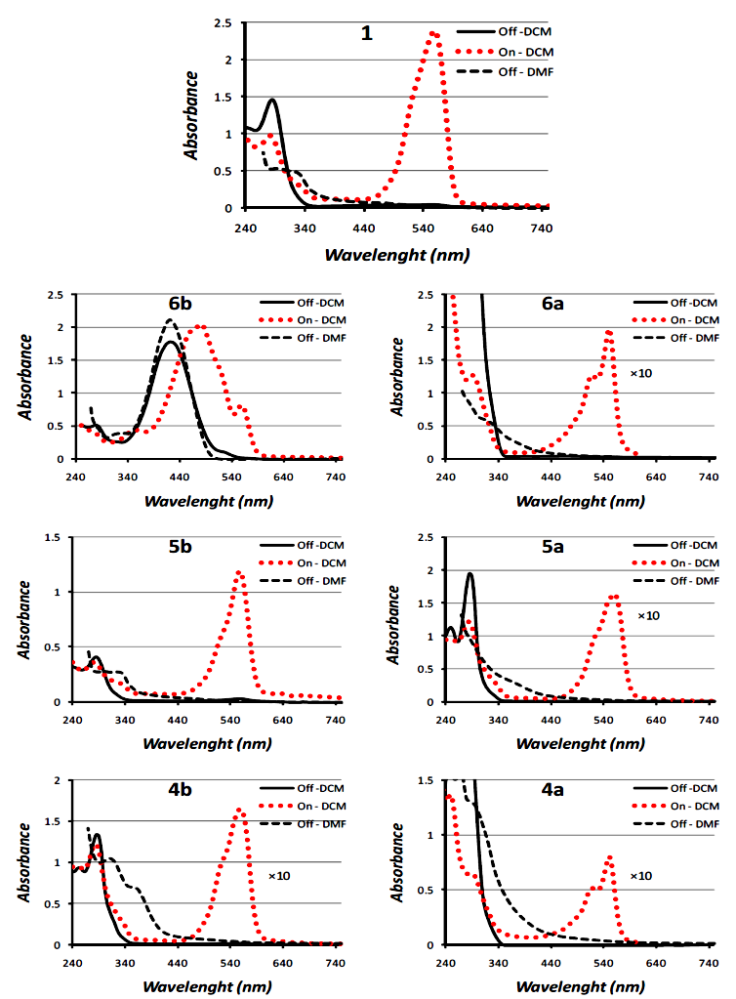


Fig. 1. UV-Vis spectra of the photochromic molecules before and after exposure to 366 nm UV light and the Mc forms are reversible to Sp forms at 125-130˚ in DMF (Concentrations of **1**, **6b** and **5b** is 10^{-5} M and **4b**, **6a**, **5a** and **4a** is 10^{-4} M to adjust the maximum absorbance of color form.)

As shown in Fig. 1-3, absorption intensity and subsequently the color strength of photochromic molecules were in the order of **1**>>**6**>**5**>**4**. The color strength of merocyanine forms of mono azospiropyrans **5** were more than that of the corresponding spiropyrans **4**.

As mentioned, a large molar absorption coefficient of as much 9.7×10^{4} $M^{-1}\cdot cm^{-1}$ formed in merocyanine state of **1**. That is considerably high, even for a commercial non photochromic dye. The superior strength of the color produced in Mc form of the asymmetric bis-azospiropyran **1** was

astonishingly higher than that of the symmetric bis-azospiropyrans **6** (2.7 and 3.8 × 10^4 $M^{-1}\cdot cm^{-1}$ for **6b** and **6a** respectively). Moreover, their absorption coefficient was much more than the corresponding known spiropyran **4** and mono-azospiropyran **5** chromophores (ε = 3.1 × 10^3 $M^{-1}\cdot cm^{-1}$ and 1.3 × 10^4 $M^{-1}\cdot cm^{-1}$, respectively) (Fig. 3). Such a high absorption coefficient indicates high sensitivity to the irradiation and thus such a distinguished response. Practically, we have developed a novel photoswitch with improved light sensitivity and resolution between Sp (OFF) and Mc (ON) forms.

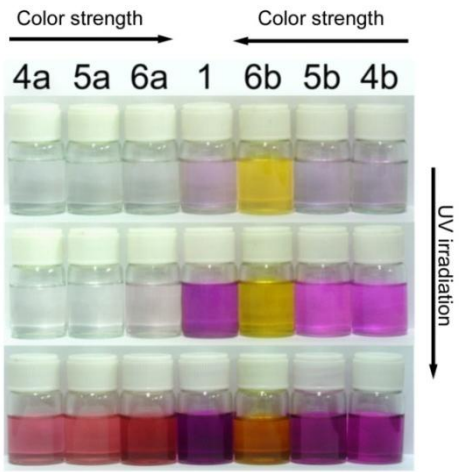
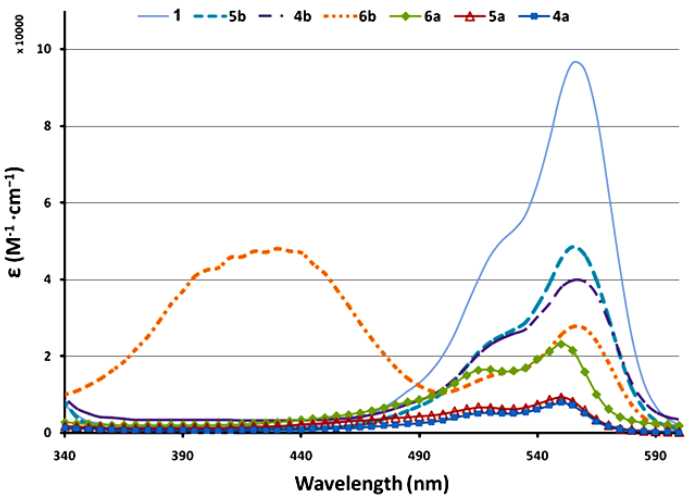


Fig. 2. Time and strength of photoresponses of 10^{-5} M photochromic molecules **1** and **4-6** in DCM after 0, 10, and 30 minutes exposure to UV light at ambient temperature.

Prompt response to light is another important parameter for photoresponsive dyes. Hence, absorbance variations at wavelengths of maximum absorption for the dyes **4a**, **5a**, **6a** at 550 nm and for **1** at 555nm under irradiation at 365 nm were studied and their photokinetic curves are presented in Fig. 4. The response rates are in this order: asymmetric bis-azospiropyran **1**>>symmetric bis-azospiropyran **6a**> azospiropyran **5a** > spiropyran **4a**.

Photoreversibility as an inherent property of spiropyrans is revealed in Fig. 5 for the product **1** as well. In this regard, 10^{-3} M of photochromic molecule **1** in DCM was exposed to 365 nm UV and then Vis light in 5 minute intervals.

This highly sensitive light-driven molecular switch is particularly valuable for designing of instruments with high resolution light sensing, and it could be used in optical storages [37, 38].



Subs	λ_{max} (nm)	ε_{PSS} [a] ($M^{-1}.cm^{-1}$)
1	555	9.7×10^4
6b	420	4.7×10^4
	555	2.7×10^4
5b	555	4.8×10^4
4b	555	4.0×10^4
6a	550	3.8×10^4
5a	550	1.3×10^4
4a	550	3.1×10^3

[a] ε_{pss}: ε at photo-stationary state

Fig. 3. UV-Vis spectra (right) and Spectroscopic data (Left) of the photochromic compounds in photostationary states Mc forms.

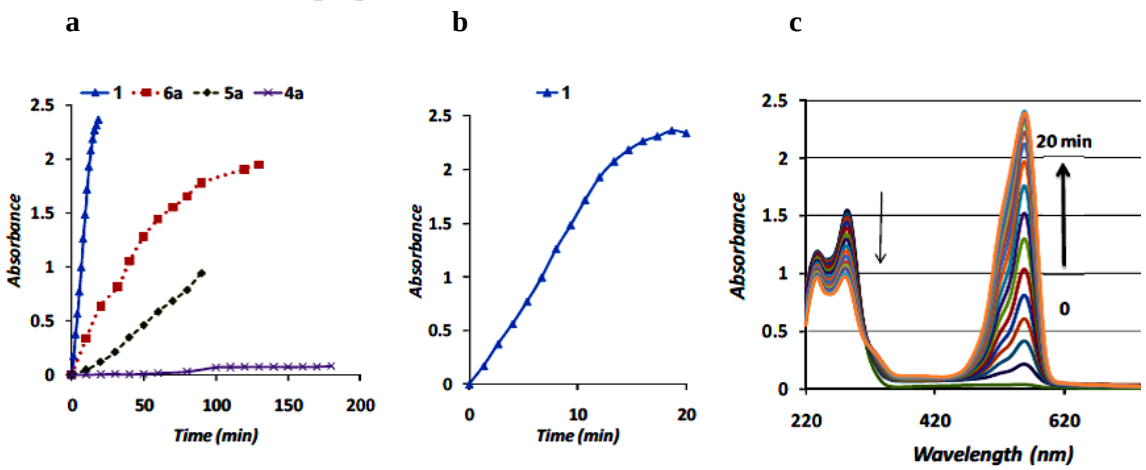


Fig. 4. Time-evolution of the maximum absorbance of 10^{-5} M photochromic materials (**4a**, **5a**, **6a** at 550nm and at 555nm) under irradiation at 365 nm (a), zoom out of the curve for **1** (b) in DCM, and UV-Vis absorption spectra of **1** during 20 min UV irradiation (c).

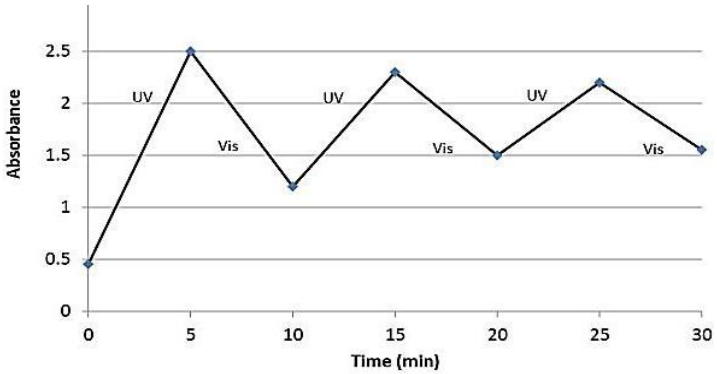


Fig. 5. Photoreversibility of 10^{-3} M photochromic molecule **1** at 555 nm under irradiation at 365 nm UV and Vis light in DCM.

The other possibility for photochemical process is the well-known cis-trans isomerization of azo-bonds that leads to decrease of color intensity [39-43]. As we reported earlier [44], cis-trans isomerization of bis-azo precursor (**3a)** was leaded to reduction of color intensity. Therefore, such isomerization of azobenzene moieties should elicit a negligible decreasing impact on the resulted immensely increased color intensities due to mero forms spiropyrans.

In addition, this novel bisazospiropyran revealed a high fluorescence quantum yield value in Sp form with the maximum difference ratio in emission intensity in Sp to Mc forms (F_{SP}/F_{MC}) rather than on the other structures (Table 1). These results indicate they are potentially suitable for photoswitch applications with high sensitivity and resolution using fluorescence emission.

3.1. Fluorescence properties of the synthesized photoresponsive products

All the synthesized photoresponsive dyes, **4a-b**, **5a-b**, **6a-b**, and **1**, revealed fluorescence emission in their colorless forms; their emission intensities diminished when exposed to UV irradiation. The Stokes shift[45] was studied for all the dyes and the values were calculated for open and closed forms, which yielded between 1752-9960 cm^{-1} for Sp forms and 3329-11711 cm^{-1} for Mc forms (Table 1).

The fluorescence quantum yields [45, 46] of spiropyrans were calculated using anthracene ($Ø_{ref}$=0.27) as a reference. For Sp forms, the fluorescence quantum yields were obtained between 0.33-0.45, thus, the minimum fluorescence quantum yield was observed in **5a** and the maximum belonged to **1** (0.45).

Ratio of emission intensity of Sp to Mc form (F_{SP}/F_{MC}) is another interesting parameter, indicating signal to noise ratio in this issue. Therefore, higher F_{SP}/F_{MC} ratio makes the molecules potentially more suitable for photoswitch application using fluorescence emission. This parameter was obtained for all the synthesized photochromic molecules and the asymmetric bis-azospiropyran **1** revealed the highest ratio of F_{SP}/F_{MC} (Table 1). Bis-azospiropyrans **1** and **6** declared higher F_{SP}/F_{MC} ratios than mono-azo **5** and simple **4** spiropyrans.

The novel asymmetric bis-azospiropyran structure **1** revealed a high ratio of F_{SP}/F_{MC} fluorescent which make it potentially applicable in many molecular actuators including optical memory devices, holographic gratings, and drug delivery vesicles [38, 47].

3.2. Exposure–response modelling to study the bifunctional photochromic activity of **1**

Dose–response relationships are well-known methods to study biological processes [48-51]. Herein, we have applied that to study the bifunctional photochromic activity of **1** by describing "absorbance of the UV irradiated molecules" as response and "time of exposure" as dose. To the best of our knowledge, application of this model for photochromic molecules is for the first time. Subsequently, to define whether the two spiropyrans moieties of the bifunctional dyes will open or not, bi-dose response (Eq. 1) and dose-response (Eq. 2) fitted on absorbance (558 nm)-time curve of photochromic molecule **1** (10^{-5} M in DCM) by employing Levenberg-Marquardt as an iteration algorithm (Fig. 6).

$$A = A_0 + (A_1 - A_0)\left[\left(\frac{p}{1+10^{(logT1-t).h1}}\right) + \left(\frac{1-p}{1+10^{(logT2-t).h2}}\right)\right] \qquad (1)$$

$$A = A_0 + \left(\frac{A_1 - A_0}{1 + 10^{(logT - t).h}}\right) \qquad (2)$$

Wherein, A_0 is the absorbance at time = 0, A_1 is the absorbance at stationary state. P is proportion of response spans known as proportion of SP-MC to MC-MC photochromic products of **1**. Logarithms of T, T_1 and T_2 are centres of related spans in time logarithmic axis and h, h_1 and h_2 are hill slopes at T, T_1 and T_2 respectively.

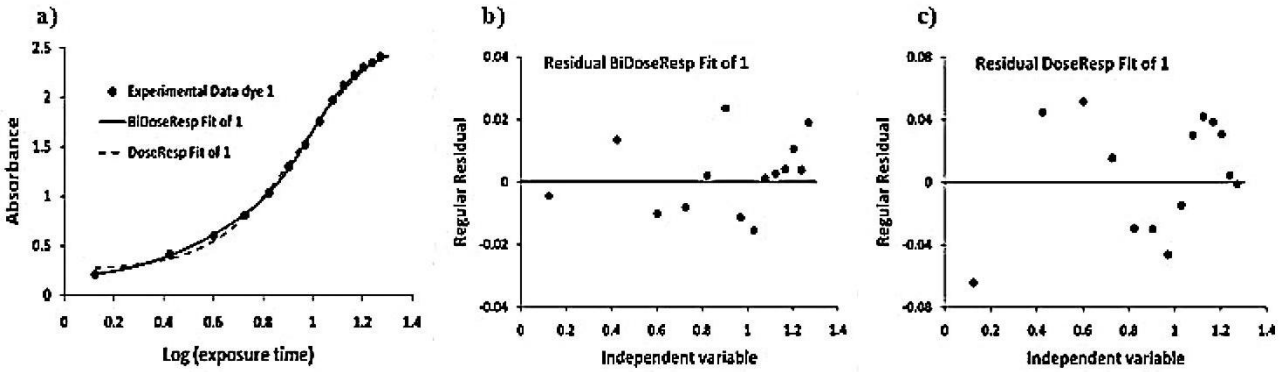
Consequently, by successfully fitted the obtained experimental data to a bi-dose exposure–response relationship model, we observed that both photochromic moieties in the dye **1** are photoactive. Contrary to the dyes **6a** and **6b** which failed in bi-dose response fitting, and cannot find direction to change parameters to reduce Chi-sqr.

This algorithm could help us to show the reason of higher color ability of molecule **1** than **6a** and **6b** owing to produce Mc forms of both spiro moieties in photochromic bifunctional molecule **1** during UV light exposure.

Table 1 Excitation and fluorescence characteristics of the produced photochromic dyes in DCM at 293 K (C= 1×10^{-5} mol.l^{-1}).

Spectroscopic properties		**1**	**6b**	**5b**	**4b**	**6a**	**5a**	**4a**
SP	λ_{ex} (nm)	395	343	323	335	345	318	330
	λ_{em} (nm)	459	524	383	411	348	381	380
	$\Delta\lambda$(nm)	64	181	60	76	3	63	50
	ν_A-ν_B (cm^{-1})	3530	10070	4850	5519	250	5199	3987
	Intensity	1510	1491	582	480	845	755	518
	φ	0.45	0.39	0.36	0.37	0.38	0.33	0.36
MC	λ_A (nm)	361	343	344	330	345	345	344
	λ_F (nm)	440	513	437	430	432	438	427
	$\Delta\lambda$ (nm)	79	170	93	100	87	93	83
	ν_A-ν_B (cm^{-1})	4974	9661	6186	4047	5842	6154	5651
	Intensity	359	418	500	440	337	593	295
	φ	0.19	0.26	0.02	0.33	0.016	0.02	0.23
F_{SP}/F_{MC} [a]		4.2	3.6	1.2	1.1	2.5	1.3	1.8

[a] Fluorescence Intensity of colorless spiropyran form (F_{SP}), and merocyanine form (F_{MC}) in stationary state.



d)

Model	A_0	A_1	P	$LogT_1$, LogT	$LogT_2$	h_1	h_2	Adj. R-Square	Residual Sum of Squares	Reduced Chi-Sqr	Regular Residual Pattern
BiDoseResp	0.13	2.52	0.45	0.67	1.00	2.05	4.55	0.99942	0.00279	0.00034	Succeeded
DoseResp	0.25	2.75	-	0.95	-	2.49	-	0.99648	0.02346	0.00213	Failed

Fig. 6. (a) Bi-dose response fitted to absorbance (558 nm)-logarithmic time data for photochromic molecule 1 (10^{-5} M in DCM), (b,c) the related residuals of related fitted curved for both bi-dose and dose responses of 1; and (d) the obtained fit statistics and parameters

3.3. Solvatochromic effects

Photoresponsive materials with light controlled polarizability has been of significant interest in many applications such as microfluidic devices, photocontrol of liquid motion, and self-cleaning surfaces. Hence, it seems essential to find an appropriate controllable medium by spectroscopic evaluation of media related impacts on the photoresponsive materials [52-55] .

Herein, the spectroscopic results of spontaneous and photochemical colorations of the synthesized dyes **1** and **6b** were studied in different solvents at room temperature. The solvents used in this study were categorized in three classes of polar-aprotic, polar-protic and polar-halogenated, regarding to

their dipole moments and polarity parameters (E_T) according to Fig. 7.

The symmetric bis-azo spiropyran **6b** in polar-aprotic solvents not only was not revealed coloration spontaneously in dark, but also photochemically even after one hour exposing to 365 nm UV light. Polar-protic solvents may stabilize Mc form of the photochromic dye **6b** and led the Sp-Mc equilibrium to Mc formation, thus the coloration was observed in dark. Moreover, the dye **6b** was diluted five-fold in methanol for spectroscopic study due to more Mc formation and high color strength. As expected, water could not dissolve the dyes. According to the results, polar-halogenate solvents as chloroform and dichloromethane (DCM) could stabilize the Mc form of **6b**, and coloration was observed in dark.

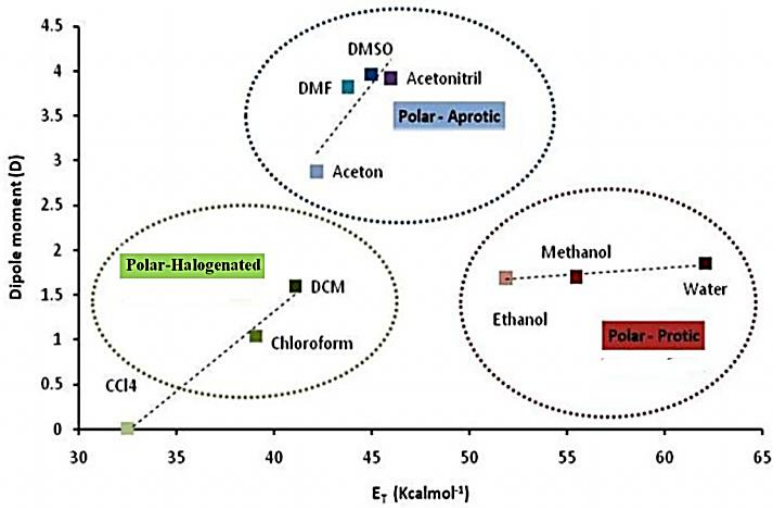


Fig. 7. The solvents categorized regarding to their dipole moments versus polarity parameters (E_T).

The same solvatochromic study was achieved for asymmetrical bifunctional bis-azo spiropyran **1** (Table 2). In this case, only polar-protic solvents led Mc-Sp equilibrium to Mc form and caused coloration. Aprotic-polar and also polar-halogenated solvents could not drive the dye to Mc form in

dark. That means the polarity of the push-pull molecule **1** in Sp form is more than the symmetry derivatives; so, only polar and protic solvents could push it to mero form in dark.

Table 2 The spectroscopic results of spontaneous coloration (in dark) of the synthesized photochromic dye **1** and **6b** in different solvents at 293 K.

Solvents	6b					1				
	C (M)	λ_{max} [a] (nm)	A_0 [b]	A_1 [c]	Time (min)	C (M)	λ_{max} (nm)	A_0	A_1	Time (min)
Acetone	10^{-4}	-	0	0	60	10^{-5}	-	0	0	60
THF	10^{-4}	-	0	0	60	10^{-5}	-	0	0	60
EtOAc	10^{-4}	-	0	0	60	10^{-5}	-	0	0	60
Acetonitrile	10^{-4}	-	0	0	60	10^{-5}	-	0	0	60
DMF	10^{-4}	-	0	0	60	10^{-5}	-	0	0	60
Dioxane	10^{-4}	-	0	0	60	10^{-5}	-	0	0	60
1-Butanol	10^{-4}	552	0.28	1.5	60	10^{-5}	550	0.03	0.38	60
Methanol	5×10^{-5}	548	0.56	1.38	70	10^{-5}	550	0.54	1.31	10
Ethanol	10^{-4}	548	0.14	0.65	60	10^{-5}	548	0	0.53	30
DCM	10^{-4}	558	0.01	1.05	60	10^{-5}	-	0	0	60
Chloroform	10^{-4}	562	0	1.08	60	10^{-5}	-	0	0	60

λ_{max} [a]: wavelength of maximum absorbance for coloration; [b] A_0: Visible light absorbance at time = 0; [c] A_1: Visible light absorbance at stationary state.

3.4. Density functional theory study of the synthesized bis-azospiropyrans

To obtain the molecular energy levels for each photoreactive form, molecular structure of the synthesized bis-azospiropyrans (**1**, **6a** and **6b**) were studied by quantum molecular calculation with density functional theory method (DFT) at the B3LYP/6-31G (d) level of theory without applying any restrictions on the molecular symmetry. The results summarized in Fig. 8 and Table 3. To compare the obtained energy levels, the related Sp-Sp forms as a more stable isomer were chosen. As shown in Fig. 8, the energies of Sp-Mc isomers are higher than Sp-Sp forms. In photoreactive molecule **1** with two different spiro moieties, diethyl amino substituted Mc form is only 1 $kJ.Mol^{-1}$ less stable than the unsubstituted moiety, however they both are less stable than the same isomers in the symmetric molecules **6a** and **6b**. The interesting point is that the difference energy between Sp-Mc (and Mc-Sp) with Mc-Mc form in structure **1** is less than the symmetric structures (**6a** and **6b**), and it shows that going to Mc-Mc form in this structure is easier than that in **6a** and **6b**. These findings are in accordance with experimental results that revealed more color ability (higher ε) in photostationary state of photochromic molecule **1** than **6a** and **6b**. They also support exposure–response modelling results which revealed bifunctional activity of asymmetric bis-azospyropyran dye **1** rather than monofunctional activity of the symmetric bis-azospyropyrans.

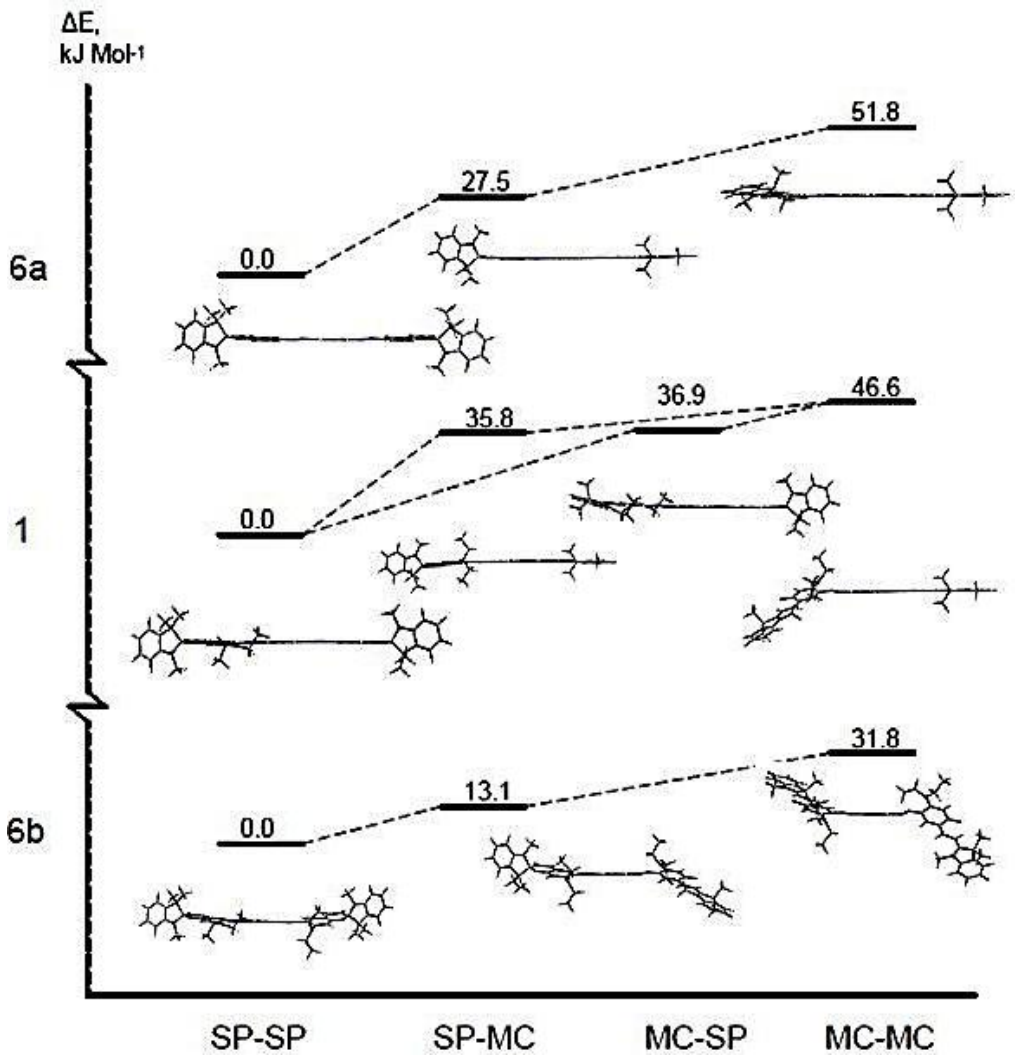
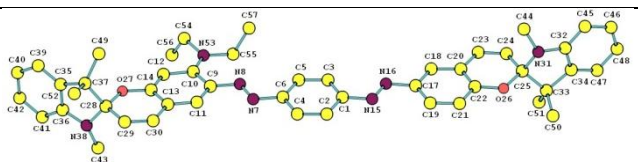


Fig. 8. Molecular energy level for each photoreactive forms of the synthesized bis-azospiropyrans (**1**, **6a** and **6b**)

Table 3 The obtained molecular level of energy, and C-O bond lengths for each photoreactive form of the synthesized bis-azospiropyrans (**1**, **6a** and **6b**).



Dye	Form	Bond Length (A) C25-O26	Bond Length (A) C28-O27	E (kJ/mol)	ΔE (kJ/mol)
6a	Sp-Sp	1.48	1.44	-5722660	0.0
	Sp-Mc	-	1.44	-5722632	27.5
	Mc-Mc	-	-	-5722608	51.8
6b	Sp-Sp	1.44	1.48	-6838954	0.0
	Sp-Mc	-	1.44	-6838941	13.1
	Mc-Mc	-	-	-6838922	31.8
1	Sp-Sp	1.44	1.48	-6280823	0.0
	Sp-Mc	-	1.44	-6280788	35.8
	Mc-Sp	1.44	-	-6280787	36.9
	Mc-Mc	-	-	-6280777	46.6

The obtained molecular energy levels, which schematically declare in Fig. 8, are presented in Table 3. Also, the reactive C-O bond lengths in Sp forms of **1**, **6a** and **6b** revealed that one of the C-O bond lengths are longer than the second one.

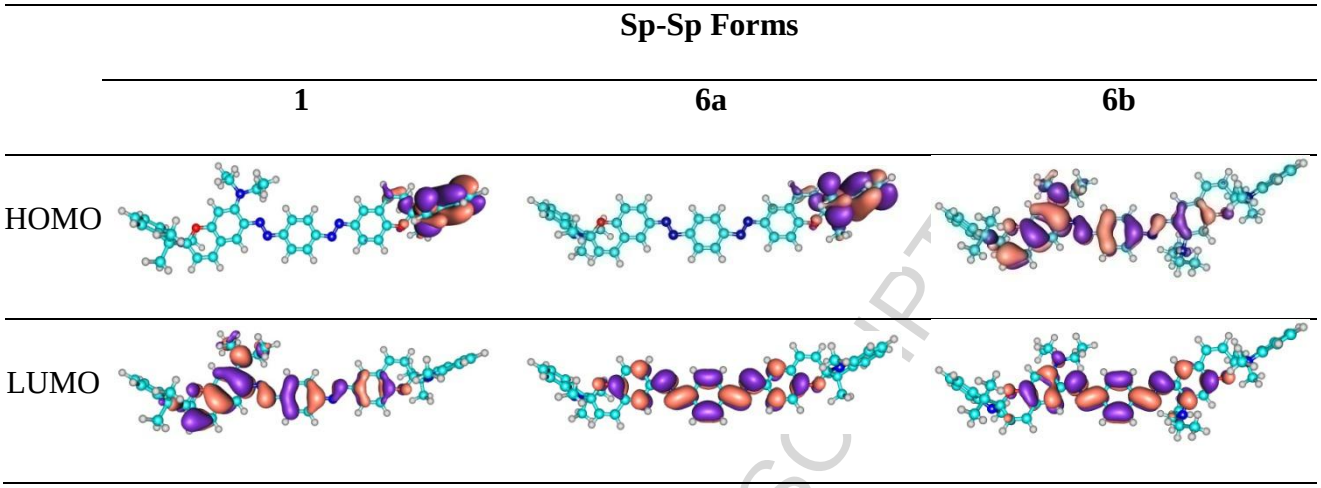


Fig. 9. Molecular orbitals for Sp-Sp forms of the synthesized bis-azospiropyrans (**1**, **6a** and **6b**)

Moreover, HOMO and LUMO of Sp-Sp forms for the optimized structures of bis-azospiropyrans are revealed in Fig. 9. Consistent with the frontier orbital theory [56], in the reactant molecules, the chemistry of conjugated π systems is mainly influenced by the HOMO and LUMO π orbitals. *Here*, the extended conjugation in HOMO π orbitals of the electron rich structure (**6b**) in Sp-Sp form could confirm the yellow color of this derivative than two other colorless Sp-Sp forms.

Further detailed studies on the exact quantitative analysis of the dynamic behaviour of such asymmetric bis-azospiropyn dyes are going to deliberate mathematically and will be reported afterward.

4. Conclusions

Large molar absorption coefficient in the Mc form as 9.7×10^4 $M^{-1}\cdot cm^{-1}$ was obtained for asymmetric bis-azospiropyran **1**. Whilst molar absorption coefficient about 3.0×10^4 $M^{-1}\cdot cm^{-1}$ was obtained for symmetric bis-azospiropyrans, and 1.3×10^4 $M^{-1}\cdot cm^{-1}$ and 3.1×10^3 $M^{-1}\cdot cm^{-1}$ for the corresponding mono-azospiropyran and spiropyran chromophores respectively, which indicate the strength of

produced color in the Mc form of the developed molecular photoswitch. Also, the asymmetric bis-azospiropyran exposed quickest response to light in the synthesized photochromic molecules. In addition, this novel bis-azospiropyran revealed high fluorescence quantum yield (0.45) in the spiro form and higher ratio of emission intensity of spiro to Mc form (F_{SP}/F_{MC}) than the other structures, which make it potentially suitable for photoswitch applications with high sensitivity and resolution using fluorescence emission. Practically, it implies that we have novel photoswitch with improved light sensitivity and superior discrimination between Sp (OFF) and Mc (ON) forms.

Density functional theory (DFT) calculation revealed that the difference energy between Sp-Mc (and Mc-Sp) with Mc-Mc form in structure **1** is less than other derivatives (**6a** and **6b**), and it shows that going to Mc-Mc form in this structure is easier than that in **6a** and **6b**. This is in accordance with experimental results that revealed more color ability (higher ε) in the steady state form of photochromic molecule **1** than **6a** and **6b**, and also exposure–response modelling results which showed the bifunctional activity of photochromic dye **1** rather than monofunctional activity of photochromic dyes **6a** and **6b**.

Acknowledgements

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Captions of Schemes and Figures:

Scheme 1. Synthesis of asymmetric bis-azospiropyran photochromic dye **1**.

Scheme 2. Synthesis of spiropyran derivatives **3-5**.

Fig. 1. UV-Vis spectra of the photochromic molecules before and after exposure to 366 nm UV light and the Mc forms are reversible to Sp forms at 125-130˚ in DMF (Concentrations of **1**, **6b** and **5b** is 10^{-5} M and **4b**, **6a**, **5a** and **4a** is 10^{-4} M to adjust the maximum absorbance of color form).

Fig. 2. Time and strength of photoresponses of 10^{-5} M photochromic molecules **1** and **4-6** in DCM after 0, 10, and 30 minutes exposure to UV light at ambient temperature.

Fig. 3. UV-Vis spectra (right) and Spectroscopic data (Left) of the photochromic compounds in photostationary states Mc forms.

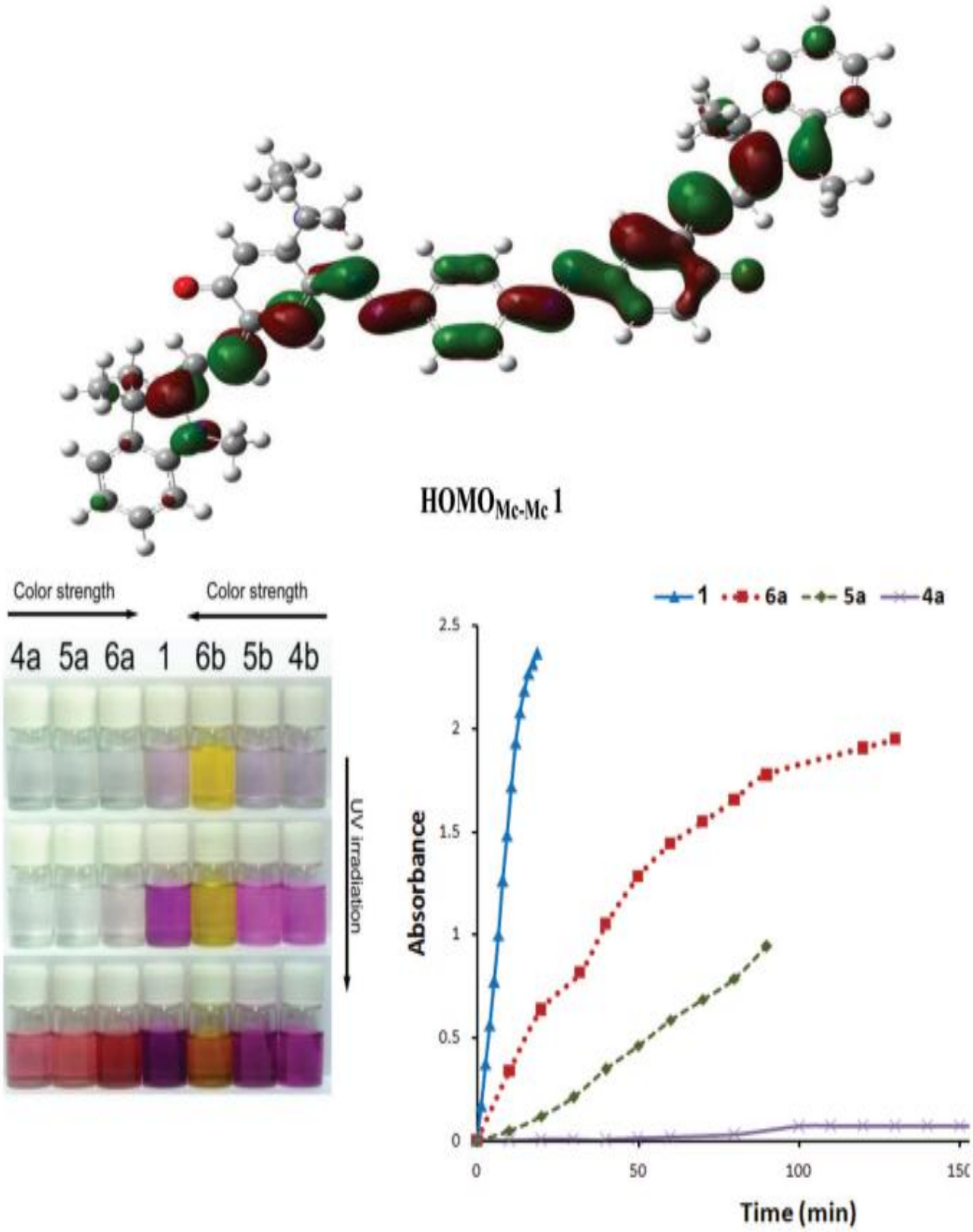
Fig. 4. Time-evolution of the maximum absorbance of 10^{-5} M photochromic materials (**4a**, **5a**, **6a** at 550nm and at 555nm) under irradiation at 365 nm (a), zoom out of the curve for **1** (b) in DCM, and UV-Vis absorption spectra of **1** during 20 min UV irradiation (c).

Fig. 5. Photoreversibility of 10^{-3} M photochromic molecule **1** at 555 nm under irradiation at 365 nm UV and Vis light in DCM.

Fig. 6. (a) Bi-dose response fitted to absorbance (558 nm)-logarithmic time data for photochromic molecule **1** (10^{-5} M in DCM), (b, c) the related residuals of related fitted curved for both bi-dose and dose responses of **1**; and (d) the obtained fit statistics and parameters.

Fig. 7. The solvents categorized regarding to their dipole moments versus polarity parameters (E_T).

Fig. 9. Molecular orbitals for Sp-Sp forms of the synthesized bis-azospiropyrans (**1**, **6a** and **6b**).



Graphical abstract

The following points are some highlights showing originality of the manuscript and how it fits with the scope of *Journal of Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy:*

- Synthesis of novel asymmetrical bifunctional bis-azo spiropyran photochromic dye is reported
- The largest molar absorption coefficient in mero form, quickest response to light, and highest fluorescence quantum yield of the spiro form with a superior ratio of emission intensities of spiro to mero form were achieved for the synthesized asymmetric bis-azospiropyran comparing to the six relative synthesized photochroms.
- Practically, it implies that we have novel photoswitch with improved light sensitivity and superior discrimination power between spiro (OFF) and mero (ON) forms.