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Towards Electrochromic Devices Having Visible Color Switching Using Electronic *Push–Push* and *Push–Pull* Cinnamaldehyde Derivatives

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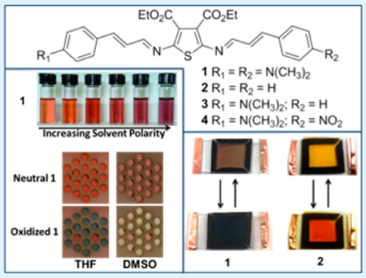
Ⓢ *Supporting Information*



ABSTRACT: A series of symmetric and unsymmetric conjugated azomethines derived from cinnamaldehyde and 2,5-diaminothiophene-3,4-dicarboxylic acid diethyl ester were prepared. The optical, electrochemical, and spectroelectrochemical properties of the electronic *push–pull* and *push–push* triads were investigated. Their properties could be tuned contingent on the cinnamaldehyde's electron withdrawing and donating substituents. The *push–push* symmetric derivative exhibited positive solvatochromism with the absorbance spanning some 31 nm, depending on the solvent polarity. Solvent dependent spectroelectrochemistry was also found for the symmetric *push–push* azomethine. The color of the neutral state and radical cation spanned 215 nm. The most pronounced color transition of the purple colored material was found in dimethyl sulfoxide (DMSO), where the color bleached with electrochemical oxidation. This was a result of the absorbance shifting into the near infrared (NIR) and not from decomposition of the azomethine. Electrochromic devices with the azomethines possessing desired reversible oxidation and color changes in the visible were fabricated and tested to demonstrate the applicability of these azomethine triads in devices.

KEYWORDS: *solvatochromism, spectroelectrochemistry, electrochromic device, azomethines, cinnamaldehyde*

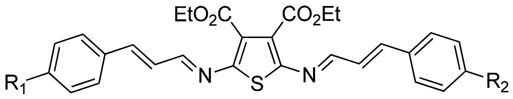
■ INTRODUCTION

Conjugated organic materials have received much attention in part owing to their optoelectronic properties that are well suited for many applications, including organic photovoltaics, field effect transistors, and light emitting diodes.[1−4] Apart from these, another important use of these conjugated materials is in electrochromic devices (ECDs), where they serve as the electrochromic layer. Such devices undergo detectable color changes with an applied potential between their neutral and charged states and they have been used in low-tech applications such as pricing display signs, curtainless windows, stealth technologies, switchable textiles, sun roofs, sunglasses, printed packages, and greeting cards.[5−8]

The palette of colors of electrochromic materials has often been satisfied with conjugated polymers having varying degrees of conjugations.[9] The ever-increasing consumer demand for devices with improved performance has required the design and preparation of new polymers having an extended color palette.[10] These needs have in part been satisfied with polymers containing π-donor–acceptor systems and vinylene linkages.[5] The challenges associated with conjugated polymer materials are they are often polydisperse and they require extensive purification for catalyst and oligomer removal.[1] The undesired by-products concomitant with the large molecular weight distribution impact the color purity.[11] They additionally make accurate structure–property studies difficult. Monodisperse and highly conjugated materials that can be easily prepared are therefore advantageous, especially for accurate structure–property studies.

Azomethine derivatives such as **1–4** (Chart 1) are ideal alternate materials for electrochromic use. This is because derivatives prepared from **5** (Scheme 1) are known to possess key electrochromic properties, including reversible oxidation, visible color transitions between their neutral and oxidized states, and resistance towards acid hydrolysis.[9,12] The azomethine bond is further advantageous because of its inherent electron withdrawing character. Strongly absorbing materials are possible when conjugating the azomethine with

Chart 1. Cinnamaldehyde Azomethine Derivatives Prepared and Studied



1 $R_1 = R_2 = N(CH_3)_2$
2 $R_1 = R_2 = H$
3 $R_1 = N(CH_3)_2$; $R_2 = H$
4 $R_1 = N(CH_3)_2$; $R_2 = NO_2$

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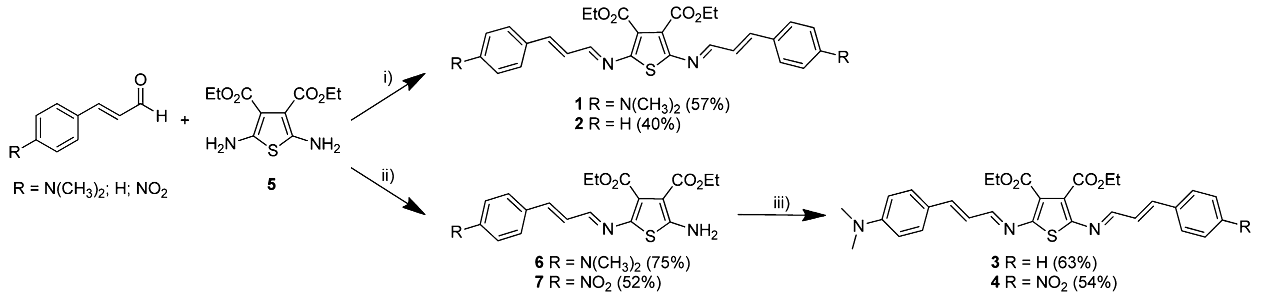
Scheme 1. Synthetic Scheme for the Preparation of Cinnamaldehyde Azomethine Derivatives[a]



[a](i) cat. TFA, IPA, excess aldehyde; (ii) cat. TFA, IPA, 1 equivalent aldehyde; (iii) DABCO, $TiCl_4$, reflux, 1 equivalent aldehyde.

electron rich moieties.[9] Similar spectral properties to conjugated polymers having high degrees of polymerization are possible with donor−acceptor azomethine triads, while also having the advantage of being monodisperse and easily purified.[13]

Azomethine derivatives were targeted as viable electroactive materials. Not only have cinnamaldehyde derivatives not been previously examined as functional electrochromic materials, but also they are believed to possess ideal properties for electrochromic use. They are expected to absorb in the visible with stark color transitions between their neutral and charged states, in part owing to their extended degrees of conjugation.[14] Moreover, color tuning of both the neutral and charged states are expected by incorporating electron donating and withdrawing groups in the cinnamaldehyde terminal positions.[9,15] The cinnamaldehyde derivatives **1−4** were therefore examined for their suitability as electrochromic materials. Their monodisperse nature further lends themselves to accurate structure−properties studies as a function of their electronic groups, in contrast to their polydisperse polymer counterparts. The synthesis and solvatochromic and optoelectronic properties of the cinnamaldehyde azomethine series having different terminal electronic groups are herein presented. These terminally electronic *push−pull* and *push−push* derivatives are of importance for better understanding more complex and conjugated polymers for ultimately designing and preparing new organic electronic materials.

■ EXPERIMENTAL SECTION

General Procedures. All reagents were obtained from commercial sources, and they were used as received unless otherwise stated. Anhydrous solvents were obtained from an activated alumina column solvent purification system. ^{1}H-NMR and ^{13}C-NMR were obtained on a 400 Mz NMR spectrometer using deuterated chloroform as the solvent. $CDCl_3$ was purified by repeatedly passing it over a plug of activated basic alumina.

Synthesis. 2,5-Diaminothiophene-3,4-dicarboxylic acid diethyl ester (**5**) was prepared according to known methods.[16]

*Diethyl 2,5-bis[(E)-[(E)-3-[4-(dimethylamino)phenyl]allylidene]amino]thiophene-3,4-dicarboxylate (**1**).* In a 50 mL two-neck round bottom flask equipped with a stir bar and a condenser, **5** (129 mg, 0.5 mmol) and 4-(dimethylamino)cinnamaldehyde (193 mg, 1.1 mmol) were dissolved in isopropanol (IPA; 20 mL) before adding a catalytic amount of trifluoroacetic acid (TFA). The mixture was refluxed in an oil bath overnight under nitrogen. The resulting dark purple solid (162 mg, 57%) was filtered and washed with copious amounts of IPA to remove any by-products and unreacted starting materials. The title compound was obtained sufficiently pure upon washing with IPA. ^{1}H-NMR ($CDCl_3$): δ = 8.15 (d, 2H, J = 8.8 Hz), 7.44 (d, 4H, J = 8.8 Hz), 7.10 (d, 2H, J = 15.6 Hz), 6.96 (dd, 2H, J = 15.6 Hz, J = 8.8 Hz), 6.68 (d, 4H, J = 8.8 Hz), 4.35 (q, 4H, J = 6.8 Hz), 3.04 (s, 12H), 1.39 (t, 6H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$): δ = 163.7, 161.9, 151.7, 150.6, 146.7, 129.8, 123.8, 123.5, 112.1, 61.3, 40.3, 14.3. HRMS(+) calculated for $[C_{32}H_{36}N_4O_4S + H]^+$: 573.2536, found: 573.2542.

*Diethyl 2,5-bis[(E)-[(E)-3-phenylallylidene]amino]thiophene-3,4-dicarboxylate (**2**).* In a 50 mL two-neck round bottom flask equipped with a stir bar and a reflux condenser, **5** (129 mg, 0.5 mmol) and *trans*-cinnamaldehyde (198 mg, 1.5 mmol) were dissolved in IPA (20 mL) before adding a catalytic amount of TFA. The mixture was refluxed in an oil bath for 3 days under nitrogen. The resulting bright orange solid was filtered and washed with copious amounts of IPA to afford the title compound (94 mg, 40 %). ^{1}H-NMR ($CDCl_3$): δ = 8.22 (d, 2H, J = 7.6 Hz), 7.55 (dd, 4H, J = 8.0 Hz, J = 1.6 Hz), 7.39 (m, 6H), 7.22−7.12 (m, 4H), 4.35 (q, 4H, J = 7.2 Hz), 1.37 (t, 6H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$): δ = 163.2, 161.4, 150.2, 145.9, 135.4, 130.2, 129.0, 128.0, 127.9, 127.0, 61.5, 14.2. HRMS(+) calculated for $[C_{28}H_{26}N_2O_4S + H]^+$: 487.1686, found: 487.1691.

*Diethyl 2-[(E)-[(E)-3-[4-(dimethylamino)phenyl]allylidene]amino]-5-[(E)-[(E)-3-phenylallylidene]amino]thiophene-3,4-dicarboxylate (**3**).* In a 50 mL two-neck round bottom flask equipped with a stir bar and a reflux condenser, *trans*-cinnamaldehyde (127 mg, 0.96 mmol) was dissolved in anhydrous toluene (25 mL). The solution was then cooled to 0°C followed by the addition of 1,4-diazabicyclo[2.2.2]octane (DABCO) (324 mg, 2.89 mmol) and 1 M titanium tetrachloride ($TiCl_4$, 1 mL, 1 mmol), followed by **6** (100 mg, 0.24 mmol). The mixture was refluxed for 3 h, and the solvent was removed in vacuo. The resulting solid (80 mg, 63%) was washed with copious amounts of IPA to afford the title compound. ^{1}H-NMR ($CDCl_3$): δ = 8.18 (m, 2H), 7.54 (d, 2H, J = 6.4 Hz), 7.38−7.45 (m, 5H), 7.14 (m, 3H), 6.98 (dd, 1H, J = 15.5 Hz, J = 9 Hz), 6.68 (d, 2H, J = 9.0 Hz), 4.36 (m, 4H), 3.05 (s, 6H), 1.36 (m, 6H). ^{13}C-NMR ($CDCl_3$): δ = 162.8, 160.6, 151.9, 147.5, 145.3, 135.7, 129.1, 128.3, 127.9, 123.6, 123.3, 112.1, 61.5, 61.4, 45.0, 40.3, 14.3. HRMS(+) calculated for $[C_{30}H_{31}N_3O_4S + H]^+$: 530.2108, found: 530.2108.

*Diethyl 2-[(E)-[(E)-3-[4-(dimethylamino)phenyl]allylidene]amino]-5-[(E)-[(E)-3-[4-nitrophenyl]allylidene]amino]thiophene-3,4-dicarboxylate (**4**).* In a 50 mL two-neck round bottom flask equipped with a stir bar and a reflux condenser, 4-nitrocinnamaldehyde (171 mg, 0.96 mmol) was dissolved in anhydrous toluene (25 mL). The solution was cooled to 0° C followed by the addition of DABCO (324 mg, 2.89 mmol), 1 M $TiCl_4$ (1 mL, 1 mmol), and then **6** (100 mg, 0.24 mmol). The mixture was refluxed for 3 h, and the solvent was removed in vacuo. The resulting solid was washed with copious amounts of IPA to afford the title compound (74 mg, 54%). The product had limited solubility in standard solvents, and extensive characterization was not possible. ^{1}H-NMR ($CDCl_3$): δ = 8.25 (d, 2H, J = 8.8 Hz), 8.18 (m, 2H), 7.66 (d, 2H, J = 8.8 Hz), 7.44 (d, 2H, J = 8.9 Hz), 7.13−7.24 (m, 2H), 6.99 (dd, 1H, J = 15.5 Hz, J = 9.1 Hz), 6.68 (d, 2H, J = 8.9 Hz), 4.37 (m, 4H), 3.05 (s, 6H), 1.36 (m, 6H). HRMS(+) calculated for $[C_{30}H_{30}N_4O_6S + H]^+$: 575.1959, found: 575.1962.

*Diethyl 2-amino-5-[(E)-[(E)-3-[4-(dimethylamino)phenyl]allylidene]amino]thiophene-3,4-dicarboxylate (**6**).* In a 50 mL single-neck round bottom flask equipped with a stir bar, **5** (200 mg, 0.77 mmol) and 4-(dimethylamino)cinnamaldehyde (135 mg, 0.77

mmol) were dissolved in IPA (20 mL) before adding a few drops of TFA. The mixture was stirred at room temperature overnight under nitrogen, and the resulting orange/red solid was filtered and washed with copious amounts of IPA to afford the pure title compound (239 mg, 75%). ^{1}H-NMR (CDCl$_3$): δ = 7.77 (d, 1H, J = 8.4 Hz), 7.38 (d, 2H, J = 8.8 Hz), 6.94 (d, 1H, J = 15.6 Hz), 6.84 (dd, 1H, J = 15.7 Hz, J = 8.6 Hz), 6.67 (d, 2H, J = 8.9 Hz), 6.23 (s, 2H), 4.38 (q, 2H, J = 7.2 Hz), 4.24 (q, 2H, J = 7.2 Hz), 1.39 (t, 3H, J = 7.2 Hz), 1.30 (t, 3H, J = 7.2 Hz). ^{13}C-NMR (CDCl$_3$): δ = 165.9, 164.7, 156.6, 151.3, 143.5, 136.2, 129.2, 124.1, 123.8, 112.2, 102.4, 61.7, 60.3, 40.4, 14.4. HRMS(+) calculated for [$C_{21}H_{25}N_3O_4S$ + H]$^+$: 416.1639, found: 416.1646.

*Diethyl 2-amino-5-[(E)-[(E)-3-(4-nitrophenyl)allylidene]amino]-thiophene-3,4-dicarboxylate (**7**).* In a 50 mL two-neck round bottom flask equipped with a stir bar and a condenser, **5** (129 mg, 0.5 mmol) and 4-nitrocinnamaldehyde (199 mg, 1.1 mmol) were dissolved in IPA (20 mL) before adding a catalytic amount of TFA. The mixture was refluxed in an oil bath overnight under nitrogen, and a red brown solid resulted. This was filtered and washed with copious amounts of IPA to afford the pure title compound (109 mg, 52%). ^{1}H-NMR (CDCl$_3$): δ = 8.22 (d, 2H, J = 8.8 Hz), 7.78 (d, 1H, J = 8.6 Hz), 7.60 (d, 2H, J = 8.8 Hz), 7.15 (dd, 1H, J = 16.0 Hz, J = 8.6 Hz), 7.01 (d, 1H, J = 16.0 Hz), 6.43 (s, 2H), 4.40 (q, 2H, , J = 7.1 Hz), 4.25 (q, 2H, J = 7.1 Hz), 1.41 (t, 3H, J = 7.1 Hz), 1.31 (t, 3H, J = 7.1 Hz). ^{13}C-NMR (CDCl$_3$): δ = 165.5, 164.5, 160.4, 153.1, 147.7, 142.3, 138.3, 134.2, 132.5, 131.2, 127.8, 124.4, 103.7, 61.9, 60.6, 14.4, 14.3. HRMS(+) calculated for [$C_{19}H_{19}N_3O_6S$ + H]$^+$: 418.1067, found: 418.1061.

Electrochemical Measurements. Electrochemical measurements were done with a BioLogic VSP electrochemical workstation. For solution electrochemistry, a 1 mM solution of the compound studied was prepared in dichloromethane (DCM) with 0.1 M tetrabutylammonium hexafluorophospahte (TBAPF$_6$) as the supporting electrolyte. A Pt button, Pt wire, and Ag/Ag$^+$ non-aqueous electrode were used as the working, counter, and reference electrodes, respectively. The reference electrode was prepared with a silver wire in dichloromethane with AgNO$_3$ (10 mM) and TBAPF$_6$ (0.1 M). Ferrocene was added at the end of the measurements as an internal reference.[17] The thin film electrochemistry of **1** was done by spray-coating films of the material onto indium tin oxide (ITO) coated glass slides that served as the working electrode. The circuit was completed by using a Pt wire and Ag/AgCl as counter and reference electrodes, respectively, in addition to 0.3 M NaCl electrolyte with 4:1 mixture of water/acetonitrile as the solvent.

Spectroscopic and Spectroelectrochemical Measurements. Absorbance spectra of the compounds were obtained on a Varian Cary 500 spectrophotometer. Solution spectroelectrochemistry of the compounds was done in 0.1 M TBAPF$_6$ solutions in DMSO, dichloromethane, or tetrahydrofuran by coupling the spectrophotometer and the electrochemical workstation. A special 1 mm optical path length spectroelectrochemical cell with a Pt mesh working, Pt wire counter, and Ag/Ag$^+$ non-aqueous reference electrodes was used. Alternatively, a gold honeycomb spectroelectrochemical cell from Pine Instruments with a built-in working and counter electrodes was also used along with an Ag/Ag$^+$ non-aqueous reference electrode. The advantage of the honeycomb electrode is enhanced color contrast of the electrochemically produced transient. The experimental setup is also more robust than the platinum mesh electrode. Both the mesh and honeycomb electrodes were used for solution spectroelectrochemistry. The spectroelectrochemistry of solid thin films of **1** was done on spray-coated films on ITO working electrodes with a Pt wire counter and Ag/AgCl reference electrodes. A 0.3 M NaCl solution was used as the supporting electrolyte in 4:1 water/acetonitrile.

Electrochromic Device Fabrication. Electrochromic devices of **1** and **2** were prepared according to previously reported and widely used methods.[12,18] Briefly, dichloromethane solutions of **1** or **2** (2 mg/mL) were spray coated onto three ITO glass slides having combined areas of 10 cm^2. The device was assembled by sandwiching a photocurable polymer gel electrolyte between two ITO slides, one coated with the compound studied and the other bare, using 1/2 in. thick double sided foam tape. The electrolyte gel consisted of propylene carbonate/polyethylene glycol diacrylate/tetrabutylammonium tetrafluoroborate in a 10:7:3 weight ratio with 0.5% of 2,2-dimethoxy-2-phenylacetophenone as the photoinitiator. The devices were cured in a UV-photoreactor with two 365 nm UV lamps for 2 min before testing them with the electrochemical workstation.

■ RESULTS AND DISCUSSION

Synthesis. Four symmetric and unsymmetric azomethine triads (**1**−**4**) consisting of either electron donating or withdrawing groups on the terminal phenyls (Chart 1 and Scheme 1) were prepared and examined. **1** and **2** were synthesized via TFA catalyzed condensation between the corresponding cinnamaldehydes and **5**. To ensure the double condensation with **5**, a stoichiometric excess of the cinnamaldehyde derivatives was used. While the syntheses of **1** and **2** were done in one-step, **3** and **4** were prepared in a two-step fashion. For both **3** and **4**, the first step was the synthesis of the mono-substituted amine **6**. This was carried out similarly to **1** but using exact stoichiometric amounts of the reagents. This was to ensure exclusive mono-substitution that was possible owing to the decreased reactivity of the amine of **6** with azomethine formation.[19] **3** and **4** were prepared from **6** using an excess of the corresponding cinnamaldehyde by refluxing with titanium tetrachloride (TiCl$_4$). This was required because of the amine's reduced reactivity. Monosubstituted amine **7** was formed by refluxing an excess of nitro-cinnamaldehyde with **5** in IPA with a catalytic amount of TFA. The nitro group further reduced the reactivity of the amine, preventing the double condensation. Refluxing an excess of nitro-cinnamaldehyde with **5** in the presence of TiCl$_4$ formed an insoluble red-brick solid that was assumed to be the symmetric dinitro-derivative. However, the insolubility of this material in common solvents prevented its characterization. In contrast, the other cinnamaldehyde derivatives were soluble in common organic solvents and they were characterized by ^{1}H NMR, ^{13}C NMR, and high resolution mass spectroscopy (see Supporting Information). Interestingly, the targeted products were easily isolated and purified by precipitating from IPA.

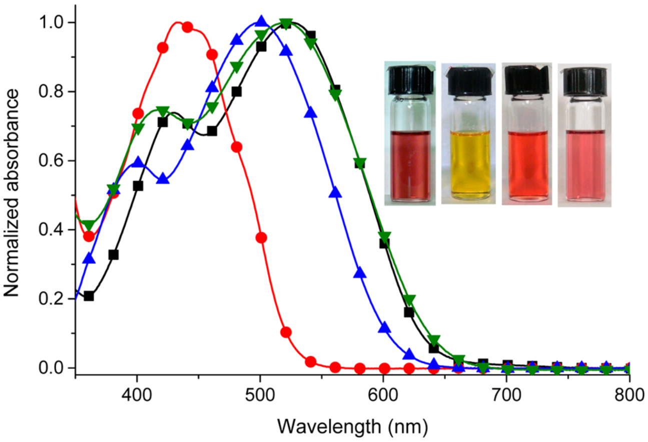


Figure 1. Normalized absorbance spectra of azomethines **1** (■), **2** (red ●), **3** (blue ▲), and **4** (green ▼) measured in dichloromethane. Inset: photographs of **1**−**4** in dichloromethane (left to right).

Absorbance and Solvatochromic Properties. The normalized absorbance spectra of the cinnamaldehyde azomethine derivatives in dichloromethane are shown in Figure 1. It is clear from these spectra that **1**, **3**, and **4** have two strong absorbances in the visible region. **2** was found to have a large

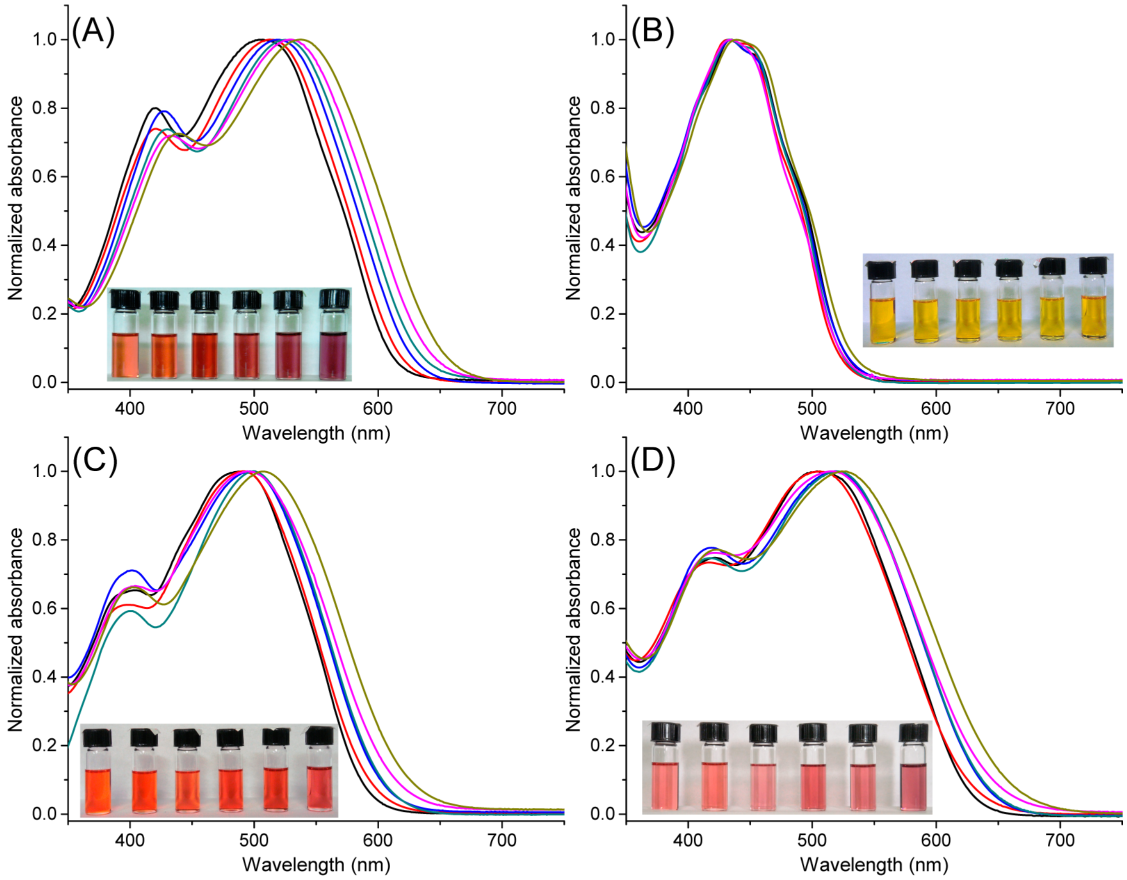


Figure 2. Absorbance spectra of **1** (A), **2** (B), **3** (C), and **4** (D) in toluene (black –), THF (red –), CHCl$_3$ (blue –), DCM (green –), DMF (pink –), and DMSO (olive green –). The inset in each plot shows a photograph of the corresponding azomethine in toluene, THF, CHCl$_3$, CH$_2$Cl$_2$, DMF, and DMSO, respectively, from left to right.

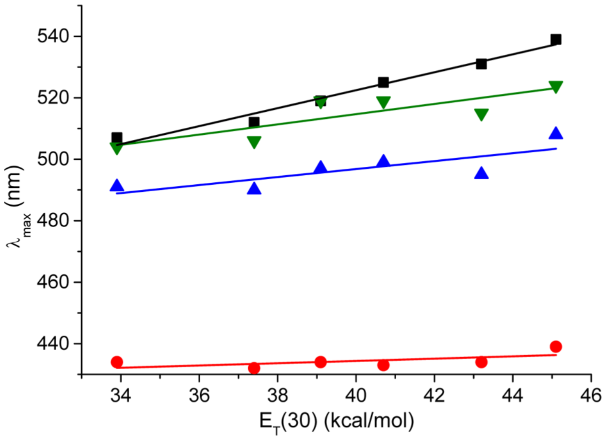


Figure 3. Absorbance of **1** (■), **2** (red ●), **3** (blue ▲), and **4** (green ▼) as a function of $E_T(30)$ in toluene, THF, CHCl$_3$, CH$_2$Cl$_2$, DMF, and DMSO.

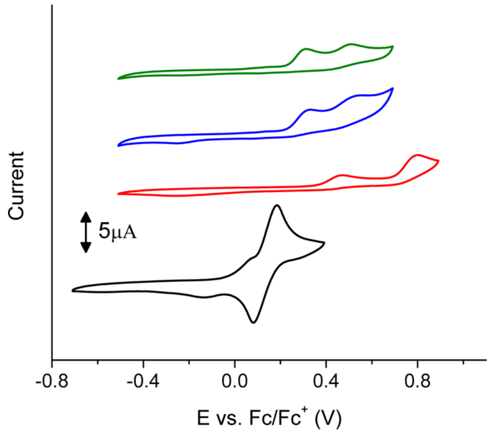


Figure 4. Anodic cyclic voltammograms of 1 mM dichloromethane solutions of **1** (black –), **2** (red –), **3** (blue –), and **4** (green –) measured in 0.1 M TBAPF$_6$ electrolyte at 100 mV/s.

separation between the two absorbance peaks, whose second absorbance was centered at 334 nm. From Figure 1, it is apparent that the electron donating *N,N*-dimethylamino group induces a significant red-shift in the absorbance. This can be clearly seen by comparing the spectra of **1**, which has two *N,N*-dimethyl groups, and **3**, having only one *N,N*-dimethylamino group. The weak high energy absorbance of **4** is blue-shifted differently in comparison to **1** due to the electron withdrawing nitro group. The collective absorbance data demonstrate that spectral differences are possible with the terminal electronic groups of the conjugated azomethines. More importantly, the cinnamaldehyde derivatives strongly absorb in the visible, being a key property for electrochromic materials for display applications.

The excited state of highly π-conjugated systems is known to be sensitive to solvent effects.[20,21] The spectroscopic properties of the azomethines were therefore expected to be solvent dependent, in part owing to their extended degrees of

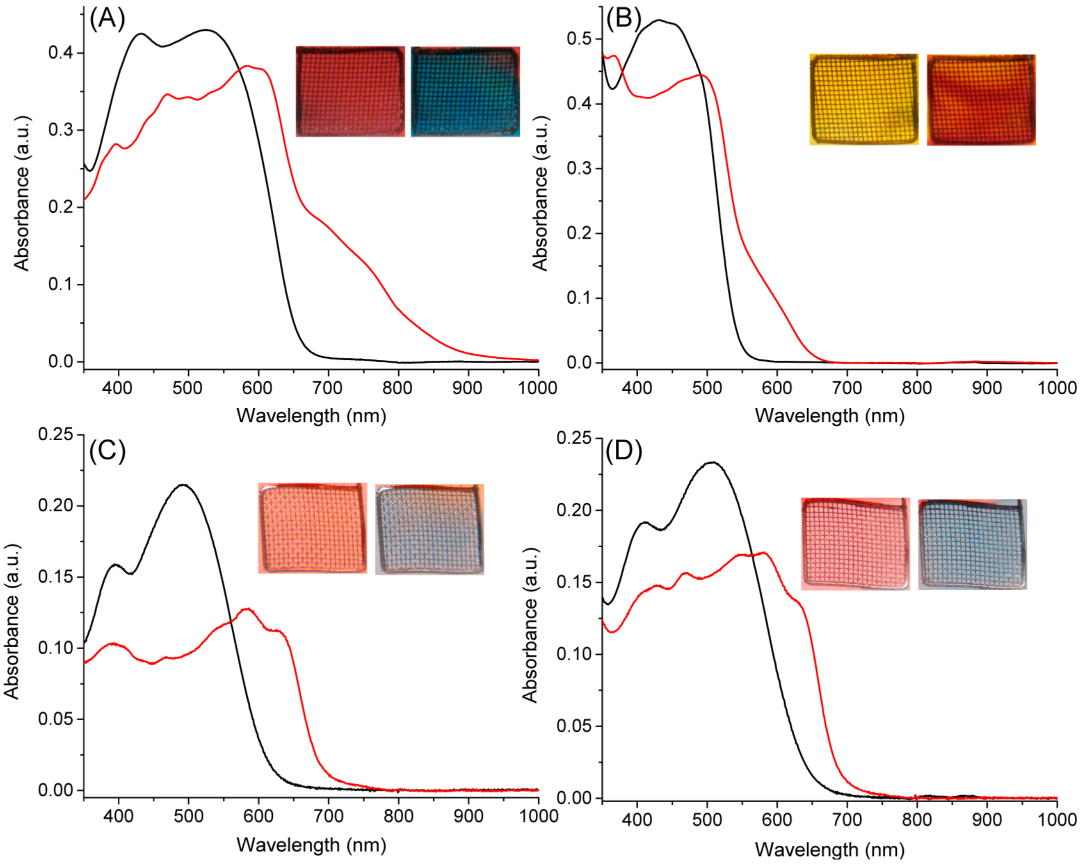


Figure 5. Spectroelectrochemistry of the neutral (black —) and oxidized (red —) states of **1** (A), **2** (B), **3** (C), and **4** (D) measured in 0.1 M $TBAPF_6$ in dichloromethane. Insets: photographs of the Pt mesh electrode of the corresponding azomethine in the neutral (left) and oxidized (right) states. The oxidized states were produced by applying a potential 100 mV greater than the oxidation potential of the corresponding compounds in Figure 4.

Table 1. CIE Color Coordinates Calculated under Different Conditions with D65 Illuminant and 2° Observer Angle for the Azomethine Triads

		neutral state			oxidized state		
compound	solvent	*L**	*a**	*b**	*L**	*a**	*b**
1[a]	dichloromethane	72.6	19.2	6.7	71.5	3.0	−3.5
2[a]	dichloromethane	92.7	1.1	51.7	84.6	16.1	22.5
3[a]	dichloromethane	91.4	13.8	9.6	91.5	0.9	−3.0
4[a]	dichloromethane	83.9	14.5	5.3	83.9	2.9	−1.3
1[b]	THF	60.9	47.3	19.2	62.9	4.3	−9.8
1[b]	DMSO	82.4	24.1	9.1	97.7	−3.0	−0.2
1[c]	electrochromic device	61.3	3.8	18.0	48.1	−1.0	−15.8
2[c]	electrochromic device	80.0	−5.4	67.6	70.0	37.6	46.0

[a] Spectroelectrochemistry with a Pt mesh working electrode with 0.1 M $TBAPF_6$ supporting electrolyte. [b] Spectroelectrochemistry with a gold honeycomb electrode with 0.1 M $TBAPF_6$ supporting electrolyte. [c] Azomethine used as the electrochromic layer in window-type electrochromic devices.

conjugation. This would be confirmed by bathochromic shifts in the absorbance with polar solvents. The collective electron withdrawing character of the azomethine bonds conjugated with the terminal electronic groups were further expected to enhance the absorbance shifts in polar solvents because of solvent induced perturbations of both the ground and excited states. While aprotic solvents are beneficial for providing a wide polarity range for solvatochromic studies, hydrocarbons and other apolar solvents could not be used for studying **1**−**4**. This was because of their limited solubility in these solvents. The solvatochromism was therefore examined in more detail using toluene, tetrahydrofuran (THF), chloroform ($CHCl_3$), dichloromethane (DCM), *N*,*N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). The solvent effect on the azomethine absorbance maxima was done using the well-established Reichardt-Dimroth's $E_T(30)$ solvent index.[20−22] The $E_T(30)$ parameter was chosen because it takes into account both general polarity and specific solvent−solute interactions, such as hydrogen bonding effects. The latter is of particular importance given that both the nitro and amine groups are known to hydrogen bond with polar protic solvents.[23] A better correlation with the change in absorbance maxima with polar solvents was obtained with the $E_T(30)$ parameter than with the dielectric constant and polarity indices (see Supporting

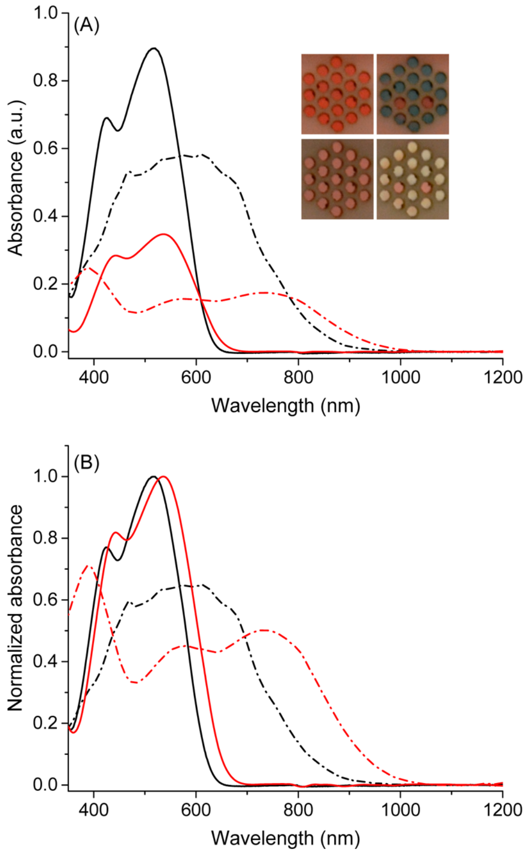


Figure 6. (A) Spectroelectrochemistry of the neutral (solid lines) and oxidized states (broken lines) of **1** in THF (black –) and DMSO (red –) using a honeycomb electrode. Inset: photographs of the honeycomb electrode in THF (top pair) and DMSO (bottom pair) in the neutral (left) and oxidized (right) states. (B) Normalized spectroelectrochemical absorbance spectra from (A). The oxidized states were obtained by applying a potential of 550 mV vs. a silver wire electrode.

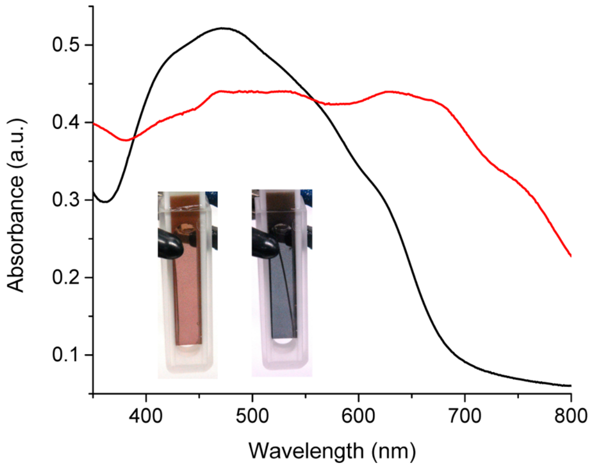


Figure 7. Solid state spectroelectrochemistry of spray-coated thin films of **1** on ITO coated glass in a 4:1 water/acetonitrile mixture with 0.3 M NaCl; neutral (black –) and oxidized (red –) states. Inset: photographs of spray-coated films on ITO in the neutral (left) and oxidized (right) states.

Information). The resulting solvatochromic effect is seen in Figure 2. The solvent dependent color changes can also be visually seen in the inset photographs.

Among the azomethines investigated, **4** was expected to show the strongest solvatochromism because of the electronic *push–pull* effect of the complementary terminal nitro and *N*,*N*-dimethylamino groups. Surprisingly, **1** showed the strongest positive solvatochromic effect. This is based on the pronounced linear correlation of bathochromic shift with increasing $E_T(30)$ (Figure 3). Cursory review of the plot parameters revealed that **1** had the best linear fit (adjusted R^2 = 0.968) and steepest slope (2.92), while **2** exhibited the least linear (adjusted R^2 = 0.227) and smallest slope (0.371). The steep slope confirms that **1** is more sensitive to solvent polarity. This is coherent with the excited state being more polar than the ground state. The pronounced red-shift in polar solvents is consistent with similar electronic *push–push* azomethines.[24] This is in contrast to **2** whose absorbance was essentially solvent independent. Therefore, the *N*,*N*-dimethylamino electron donating groups of **1** cause the largest shifts in absorbance and best linear fit with increasing $E_T(30)$ among the triads examined. These trends demonstrate the importance of the *N*,*N*-dimethylamino group for intramolecular charge transfer.[25] The pronounced solvatochromism of **1** implies that the charge transfer takes place between the electron donating *N*,*N*-dimethylamines on the adjacent electronic withdrawing azomethines to which they are conjugated. No solvatochromism was observed with **2** because of the absence of any electronic groups in the terminal positions. Meanwhile, a less than expected solvatochromic behavior was observed with **4**. This is possibly due to the two electron withdrawing azomethines that weaken the collective *push–pull* effect of the *N*,*N*-dimethylamino and nitro terminal groups.

Electrochemistry and Spectroelectrochemistry. The electrochemistry of the azomethines in solution was investigated in 0.1 M TBAPF$_6$ in dichloromethane. The resulting anodic cyclic voltammograms are shown in Figure 4. All the compounds showed two oxidation peaks. Among the four azomethines, only **1** showed a reversible oxidation, whereas the oxidation of the other azomethines was irreversible. The oxidation potential was contingent on the electron donating groups.[26] This is evident in Figure 4 where **1** has the least positive oxidation potential owing to the two electron donating *N*,*N*-dimethyl amines. As expected, the most positive oxidation potential was observed for **2**. From the cyclic voltammetry data, it can be concluded that the electron withdrawing nitro group has little effect on the oxidation potential.[26]

Spectroelectrochemistry of the azomethines was done to evaluate the spectral changes between their neutral and oxidized states. This is of importance for assessing their suitability as electrochromic materials. For this, the azomethines were dissolved in 0.1 M TBAPF$_6$ solutions in dichloromethane and the spectroelectrochemical studies were done using a Pt mesh working electrode. Alternatively, a gold honeycomb electrode setup along with an Ag/Ag$^+$ non-aqueous reference electrode was also used for the solution spectroelectrochemistry of **1** in solvents of different polarity. The spectroelectrochemistry of the azomethines was first measured in dichloromethane owing in part to their solubility of this solvent. As seen in Figure 5, the colors of **1**, **3**, and **4** changed from shades of crimson/purple in the neutral state to various shades of blue upon oxidation, whereas the color of **2** changed from yellow in the neutral state to red/orange in the oxidized state. The true colors of the neutral and oxidized states are quantified from the CIE coordinates in Table 1. The visually detectably color changes between the neutral and oxidized

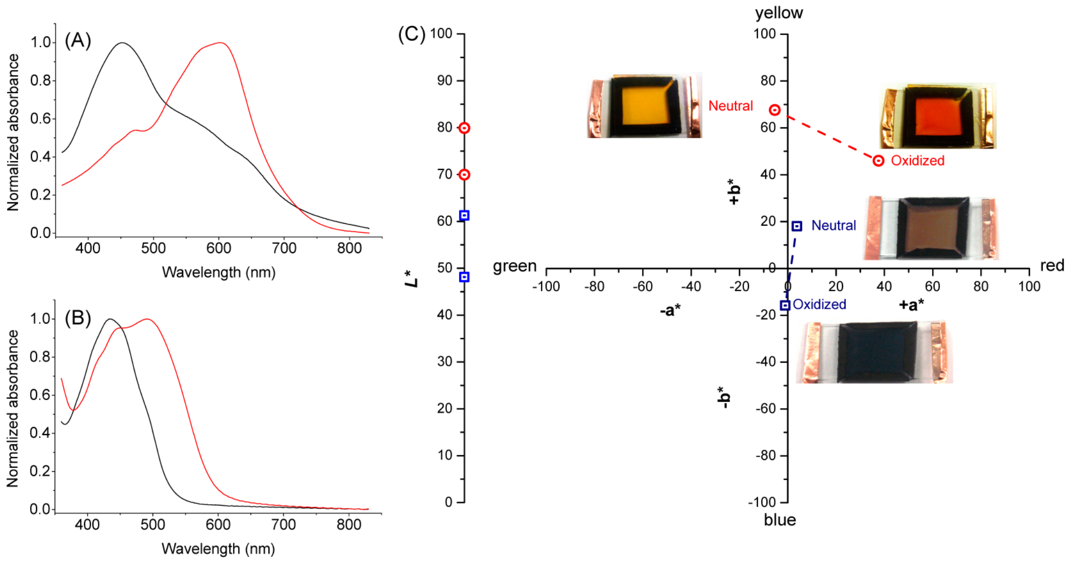


Figure 8. Absorbance spectra of electrochromic devices made from **1** (A) and **2** (B). (C) CIE L^* a^*b^* color coordinates of the electrochromic devices of **1** (blue □) and **2** (red ○).

states suggest the triads are viable electrochromic materials in plastic devices for display applications.

Given the solvatochromic and electrochromic behavior of **1**, its solvent dependent electrochromism was investigated. THF and DMSO were used to examine the solvato-electrochromic behavior given the large difference in their $E_T(30)$ values. Figure 6 shows the spectroelectrochemistry of **1** in these two solvents using a honeycomb electrode. It should be noted that the weak absorbance spectrum of **1** in DMSO is due to its limited solubility in this solvent as compared to THF. The absorbance spectra were therefore normalized (Figure 6B) to illustrate the solvato-electrochromic effect. In the neutral state, **1** showed a typical positive solvatochromic effect. This is derived from the 20 nm absorbance red-shift in DMSO compared to THF. The solvent induced spectral changes are consistent with the solution solvatochromic studies (vide supra). The neutral state of **1** in THF was red-orange and purple in DMSO. An interesting electrochromic color shift was observed when it was oxidized. In THF, the oxidized state of **1** was deep blue in color, whereas when it was oxidized in DMSO, it was colorless. The color bleaching is a result of a red-shift in the absorbance into the near infrared (NIR) and not from decomposition. The associated spectral shifts when oxidized were 99 and 199 nm for THF and DMSO, respectively. The large solvatochromic difference arises from the intramolecular charge transfer in the oxidized states, being 616 and 735 nm compared to 517 and 536 nm for the neutral states in THF and DMSO, respectively (Figure 6B). While significant solvent induced spectral changes were observed, the color change was much slower in DMSO compared to THF with electrochemical oxidation. Subsequently, the change between the neutral and oxidized states could spectroscopically be followed (Figure S4, Supporting Information). It should be noted that two clear isosbestic points were observed in the spectroelectrochemistry of **1** in DMSO. These imply that three distinct species are present, most likely the neutral, radical cation, and dication. The concise isosbestic points further confirm that robustness of the azomethine and that it does not decompose under the spectroelectrochemical conditions.

Solid state spectroelectrochemistry of electrochromic organic polymers is usually done in organic electrolyte solvents. Unfortunately, solid state spectroelectrochemistry of organic electrochromic materials that are soluble in these commonly used solvents is not feasible. Therefore, spectroelectrochemical measurements in water with organic compounds immobilized on the electrode as thin films provide an interesting alternative. While this is beneficial, only a limited number of studies have successfully demonstrated this approach with conjugated polymers.[8,27−34] This is because most conjugated polymers do not show the desired electrochemical switching under these conditions.[28] The solid state spectroelectrochemistry of **1** in water was nonetheless examined to evaluate its color switching under electrochromic device-type conditions. **1** was chosen because it showed the desired reversible oxidation in solution. It was subsequently spray-coated from dichloromethane onto an ITO coated glass electrode, resulting in transparent purple thin films. These were insoluble in the spectroelectrochemical water electrolyte solution. A 4:1 water/acetonitrile solvent mixture was chosen because spectroelectrochemical changes were not observed when salt water was used exclusively as the electrolyte. In contrast, electrochromic switching was observed with the water/acetonitrile mixture (Figure 7). As seen in the inset of Figure 7, the neutral and oxidized states switched between purple and dark blue in color. It is noteworthy that the absorbance spectrum of **1** is broader in thin film than in solution. This is a result of increased π-stacking in the solid state. Meanwhile, the oxidized state of **1** in thin film uniformly absorbs across the visible, resulting in a dark blue color. The spectroelectrochemical studies in the water/acetonitrile mixture confirm that desired electrochromic spectral and reversible switching properties are possible with highly conjugated azomethine triads.

Electrochromic Devices. Window-type electrochromic devices were prepared from **1** and **2** to validate the spectroelectrochemical studies. These compounds were targeted because of their preliminary optical−electrochemical properties that were found to be suitable for use in electrochromic devices. The fabricated devices were successfully switched between their neutral and oxidized states at +3 and −3 V, respectively, for **1** and **2**. The absorbance spectra of devices in their neutral and oxidized states were measured, and the color coordinates were calculated, as per Figure 8C. The device prepared from **1** switched from deep purple to dark blue, whereas **2** changed from bright yellow to bright orange (Table 1). Color switching between the neutral and oxidized states was possible upwards of five times before the intensity of oxidized state began to wane. These visibly detectable colors to the naked eye are desired properties for ultimate use in large scale display-type applications, and they demonstrate the robustness and suitability of azomethines as electrochromic materials.

■ CONCLUSIONS

In summary, a series of symmetric and unsymmetric highly conjugated azomethine triads were prepared that strongly absorbed in the visible spectral region. The spectral properties could further be adjusted in solvents of varying polarity. The strongest solvatochromism was observed with the symmetric azomethine containing two terminal *N*,*N*-dimethylamines, with the absorbance varying some 31 nm with this electronic *push*–*push* system. In contrast, little solvatochromic effect was seen with the conjugated π-donor–acceptor system. Strong electron donating groups must therefore be conjugated with the inherent strong electron withdrawing azomethines. This strong donor–acceptor system gives rise to bold colors in the visible. Moreover, the absorbance of the electrochemically produced oxidized intermediate can be extensively red-shifted into the NIR contingent on solvent polarity. While preliminary electrochromic devices were prepared with the azomethines, the working device nonetheless serve as a proof-of-principle that these often overlooked conjugated heteroatomic compounds are viable electrochromic materials. The knowledge gained is of importance for the design and subsequent preparation of new conjugated azomethines having targeted color changes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra of all compounds, COSY NMR spectra of **3** and **4**, absorbance and fluorescence spectra, and cyclic voltammograms. This information is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

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