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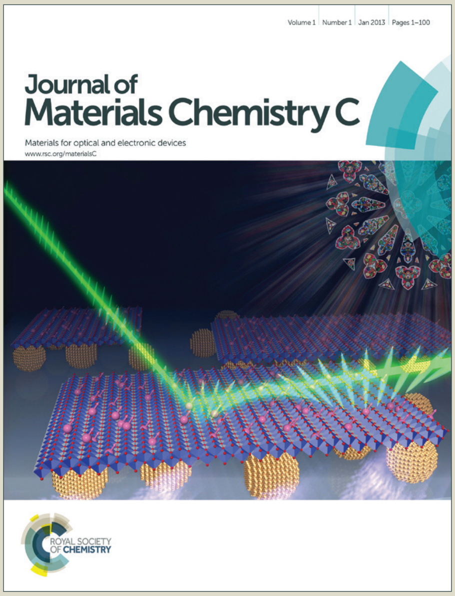

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Synthesis and characterization of novel electrochromic and photoresponsive materials based on azobenzene-4,4'-dicarboxylic acid dialkyl ester

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Novel electrochromic and photoresponsive materials based on azobenzene-4,4'-dicarboxylic acid dialkyl ester derivatives (ADDEDs) were successfully prepared and characterized through nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy, and high–performance liquid chromatography–mass spectrometry. The electrochromic behavior, electrochromic mechanism, electro–optical properties, and photoresponsive properties of ADDEDs were investigated through cyclic voltammetry and ultraviolet–visible absorption spectra. ADDEDs displayed not only outstanding electrochromic behavior but also good and reversible photoisomerization properties even under electrochromic conditions. Electrochromic devices (ECDs) based on ADDEDs were fabricated, and their electrochromic performance was analyzed. The ECDs presented a color change from colorless to magenta between 0.0 V (bleached state) and ±3.0 V (colored state). In addition, the ECDs exhibited fast switching time, reasonable contrast, satisfactory optical memories, and redox stability. The novel redox–active azobenzene derivatives are promising candidates for full–color EC display devices, electronic paper, smart window, optical memory devices, dual–stimuli–responsive systems, as well as other potential new scopes.

1 Introduction

Stimuli responsive materials (SRMs), which are also known as environmental responsive materials or smart materials, are special materials that respond to specific external stimuli with a considerable change in their properties,[1] such as molecular chain structure,[2] solubility,[3] surface structure,[4] swelling,[5] or dissociation behavior.[6] External stimuli include electrochemistry,[7] light intensity,[8] temperature,[9] pH,[10] ionic and/or solvent composition of the media,[11] magnetic field,[12] and ultrasound.[13] In view of these interesting properties, the potential application of SRMs in various fields, including drug delivery,[14] biotechnology,[15] separation sciences,[16] and chemosensor,[17] is gaining considerable research attention. Thus, new materials that have improved properties or that produce new responses to designated stimuli must be developed.

Electrochromic materials (ECMs) possess the ability to change their optical properties as persistent and reversible response through the alternation of the applied potential. ECMs are employed in numerous practical applications, such as electronic paper,[18] smart windows[19,20] and optical memory devices.[21] Organic ECMs have unique advantages over their inorganic counterparts; these advantages include fast response time, flexible device fabrications, relatively narrow absorption band in displaying diverse, and clear colors large–scale processability. Previous studies have mainly focused on organic polymer materials.[22] The electrochromic properties and color change of the polymer material were modified by the electronic structure of the monomers.[23] To induce a multi–stimuli responsive, more than two monomers were incorporated into conducting polymers.[24] Single molecular electrochromic and stimuli–responsive materials have recently attracted significant attention because of their ability to be chemically engineered into nanosized electrode materials.[25]

Azobenzene derivatives have gained popularity in recent years because of their unique photophysical properties and extensive applications in photoresponsive materials,[26–28] supramolecular structure construction,[29,30] and non–linear optics.[31] The azobenzene chromophore has two isomeric states, namely, the more thermodynamically stable *trans* isomer and the less stable *cis* isomer. Upon irradiation at an appropriate wavelength, azobenzene and a range of its derivatives undergo photoisomerization. The *trans*↔*cis* photoisomerization of azobenzene results in a significant change in color, refractive index, dielectric constant, and dipole moment, etc., suggesting that azobenzene and its derivatives show great potential as functional materials.[26–28,32]

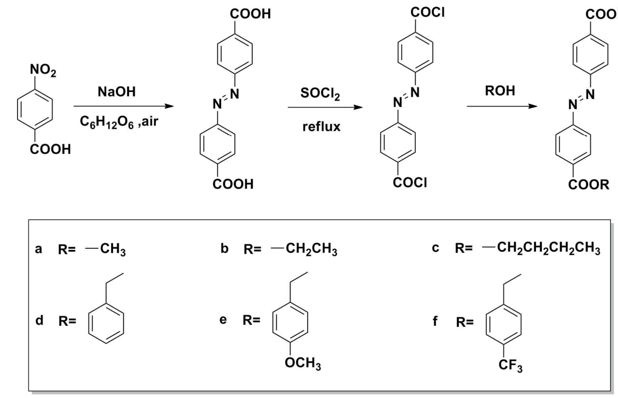
Although there are some reports on dual–stimuli–responsive materials,[33–35] to the best of our knowledge, the report about electrochromism of azobenzene and its application to ECD is scarce. In this paper, we developed dual–stimuli–responsive materials based on azobenzene-4,4'-dicarboxylic acid dialkyl ester derivatives (ADDEDs). ADDEDs showed not only outstanding electrochromic behaviors but also good and reversible photoisomerization properties even under electrochromic conditions. Electrochromic devices (ECDs) based on ADDEDs exhibited fast switching time, reasonable contrast, satisfactory optical memories, and redox stability. The novel redox–active azobenzene derivatives are promising candidates for full–color EC display systems, dual–stimuli–responsive materials, electronic paper, smart window, and optical memory devices.

2 Experimental

2.1 Materials and Instruments

All chemical reagents were purchased from Aladdin Co., Shanghai, China, and used as received. All of the solvents were of analytic reagent grade, commercially available and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were measured with a Bruker AV 300 (300 MHz) spectrometer at ambient temperature using tetramethylsilane as an internal standard. HPLC–MS was performed with a Bruker Esquire 2000 HCT LC/MS system. FT–IR spectra (400–4000 cm^{-1}) were recorded on a Perkin–Elmer Model GX Spectrometer through KBr pellet method. UV–vis spectra were obtained with a UV–4802 spectrophotometer [UNICO (Shanghai) Instruments Co. Ltd., China]. Cyclic voltammetry was performed with a CHI 650B electrochemical workstation using a three–electrode system, and Ag/AgCl was used as the reference electrode. The concentrations of tetrabutylammonium perchlorate (TBAP) and ferrocene (Fc) for all experiment were 20 mmol L^{-1} and 10 mmol L^{-1}, respectively. All of the ECDs were fabricated, sealed, and tested at room temperature.

2.2 General procedure for ADDEDs synthesis



Scheme 1 Synthesis of ADDEDs

ADDEDs were synthesized in two steps in accordance with Ref. 36, with slight modification. The synthetic route is shown in Scheme 1.

In a typical experiment, 4-nitrobenzoic acid (2.0 g, 12 mmol) and NaOH (5.75 g, 144 mmol) were mixed in 30 mL of water and heated until the solid dissolved. Glucose (13.0 g, 72 mmol) aqueous solution (20 mL) was added dropwise at 70 □, yielding initially a yellow precipitate and subsequently a brown solution upon further addition of glucose. A stream of air was bubbled into the mixture overnight, resulting in a light brown precipitate. The precipitate was filtered. The cake was dissolved in 10 mL of water, and acetic acid was used to adjust the pH of the solution in the range of 5 to 6. Approximately 1.06 g azobenzene-4,4'-dicarboxylic acid as light pink powder was obtained by filtration, washed with 25 mL of distilled water, and finally dried to constant weight in an oven at 80 □. Yield: 65.6%. ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 8.26 (d, 4H, J=8.37), 8.10 (d, 4H, J=8.37). ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm): 123.7, 131.6, 134.3, 155.0, 167.5.

Azobenzene-4,4'-dicarboxylic acid (5.4 g, 20 mmol) was refluxed in 50 mL of thionyl chloride for 5 h, yielding a clear yellow solution. Excess thionyl chloride was removed by distillation, and the remainder was recrystallized in toluene. Approximately 5.8 g 4,4-bis(chlorocarbonyl)azobenzene as a red crystal was obtained. Yield: 92.0%. ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 8.43 (d, 4H, J=8.52), 8.16 (d, 4H, J=17.88).

4,4-Bis(chlorocarbonyl)azobenzene (0.62 g, 2.0 mmol) was dissolved in dry 20 mL of THF, to which 2.5 times of alkyl alcohols was added dropwise while being stirred. Triethylamine (2.0 mL) was subsequently added. Then, the reaction mixture was stirred at room temperature for 12 h, and the reaction was monitored by thin layer chromatography. Afterward, the mixture was evaporated to remove the solvent, and the crude product was purified by column chromatography on silica gel with the use of 2:1 petroleum ether and dichloromethane (v:v) as eluents. The corresponding yields and characterized data for a series of ADDEDs are listed as follows:

Azobenzene-4,4'-dicarboxylic acid methyl ester (compound **a**): Orange powder, 0.45 g. Yield: 78.0%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.32 (d, 4H, J=8.31), 8.10 (d, 4H, J=8.31), 4.09 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 166.35, 154.85, 132.36, 130.62, 122.86, 128.4, 52.37. MS(m/z) cal.: 298.29; found: 298. FT–IR (KBr, cm^{-1}): 1725, 1623, 1493, 1409, 1278, 1112, 865, 777, 697.

Azobenzene-4,4'-dicarboxylic acid ethyl ester (compound **b**): Orange red powder, 0.53 g. Yield: 82.0%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.33 (d, 4H, J=8.40), 8.10 (d, 4H, J=8.40), 4.53 (m, 4H, J=21.27), 1.55 (t, 6H, J=14.19). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 165.89, 154.80, 132.69, 130.57, 122.82, 61.31, 14.27. MS (m/z) cal.: 326.35; found: 326. FT–IR (KBr, cm^{-1}): 1716, 1617, 1388, 1269, 1098, 1008, 870, 779, 699.

Azobenzene-4,4'-dicarboxylic acid butyl ester (compound **c**): Orange red powder, 0.53 g. Yield: 75.0%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.32 (d, 4H, J=8.40), 8.09 (d, 4H, J=8.40), 4.48 (t, 4H, J=13.14 Hz), 1.85–1.92 (t, 4H, J=21.3), 1.58–1.66 (m, 4H, J=22.35), 1.09–1.14 (t, 6H, J=14.67). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 165.94, 154.78, 132.70, 130.56, 122.84, 65.19, 30.69, 19.24, 13.74. MS (m/z) cal. 382.45; found: 382. FT–IR (KBr, cm^{-1}): 1714, 1639, 1400, 1313, 1147, 874, 779, 698.

Azobenzene-4,4'-dicarboxylic acid benzyl ester (compound **d**): Orange pink solid, 0.59 g. Yield: 68.0%. ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.36 (d, 4H, J=8.37), 8.10 (d, 4H, J=8.37), 7.60 (d, 6H, J=6.99), 7.55 (d, 2H, J=6.36), 7.50 (d, 2H, J=8.01), 5.53 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 165.70, 154.89, 135.72, 132.33, 130.76, 128.45, 122.91, 67.02. MS(m/z) cal.: 450.49; found: 450. FT–IR (KBr, cm^{-1}): 1712, 1638, 1309, 1101, 865, 778, 697.

Azobenzene-4,4'-dicarboxylic acid p-methoxylbenzyl ester (compound **e**): Light pink solid, 0.57 g. Yield: 62.0%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.33 (d, 4H, J=8.40), 8.08 (d, 4H, J=8.40), 7.54 (d, 4H, J=8.49), 7.05 (d, 4H, J=8.46), 5.45 (s, 4H), 3.95 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 165.53, 159.48, 154.62, 132.24, 130.48, 129.96, 127.60, 122.61, 113.74, 66.67, 55.03. MS (m/z) cal. 510.54; found: 509. FT–IR (KBr, cm^{-1}): 1710, 1614, 1379, 1247, 1099, 866, 779, 698.

Azobenzene-4,4'-dicarboxylic acid p-trifluoromethylbenzyl ester (compound **f**): Light pink solid, 0.71 g. Yield: 64.0%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.36 (d, 4H, J=8.43), 8.12 (d, 4H, J=8.40), 7.79 (d, 4H, J=8.13), 7.71 (d, 4H, J=8.04), 5.58 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 165.50, 155.00, 139.69, 131.96, 130.78, 128.21, 125.63, 122.99, 66.05. MS (m/z) cal.: 586.48; found: 586. FT–IR (KBr, cm^{-1}): 1719, 1266, 1113, 866, 777, 695.

2.3 ECDs construction

ECDs generally consist of two–electrode electrochemical cells. ECDs include an ion–conducting liquid or solid electrolyte medium sandwiched between two electrode surfaces coated with organic or inorganic electrochromic materials, which are selected on the basis of their electrical and optical properties. In this paper, ECDs based on ADDEDs embedded in a sandwich matrix were prepared in accordance with a previous technology.[37] An indium tin oxide (ITO)–coated glass surface (conductive side inward) and a reflective metallic surface that are spaced a fraction of a millimeter apart (35 mm × 40 mm × 0.7 mm, 50 Ω/sq) form the two electrodes of the cell. The electrolyte solution was prepared by dissolving ADDEDs (10 mmol L^{-1}), Fc, and TBAP in DMF. Then, the prepared electrolyte was injected into the electrochromic device with the use of a syringe. The device is hereafter referred to as the conductive ITO glass|| ADDEDs + Fc + TBAP|| DMF|| conductive ITO glass device.

3 Results and discussion

3.1 Electrochemical properties

Cyclic voltammetry is a widely used electrochemical technique for acquiring qualitative information about electrochemical reactions. This method rapidly provides the location of redox potentials of electro–active species. The redox properties of ADDEDs were investigated by cyclic voltammetry in DMF containing TBAP (0.05 mol L^{-1}) as supporting electrolyte. As shown in Fig. 1, only compound **c** (Fig. 1C) showed quasi–reversible one–electron reduction, illustrating that compound **c** had only a pair of redox peaks. The probable reason for this phenomenon is that the second reduction required a higher energy than the first one. Meanwhile, compounds **a**, **b**, **d, e**, and **f** (Figs. 1A, 1B, 1D, 1E, and 1F) showed two pairs of separated redox peaks, indicating that two quasi–reversible redox peaks would be observed due to substituent effect. Taking compound **d** (Fig. 1D) for example, the first reduction peaks at > –1.0 V can be attributed to the reduction of ADDEDs to ADDEDs$^{\cdot-}$, and the second redox couple at ca. –1.555 V (2) and –1.510 V ca. (2') can be attributed to the reduction of ADDEDs$^{\cdot-}$ to ADDEDs^{2-}. Cyclic voltammogram analysis revealed that these compounds showed excellent electrochemical reversibility and stability after more than 100 cycles.

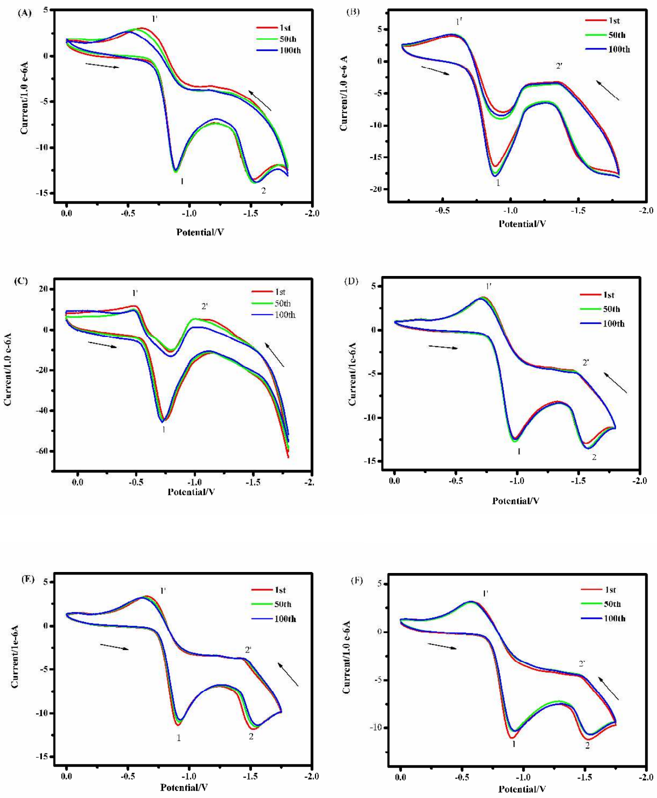
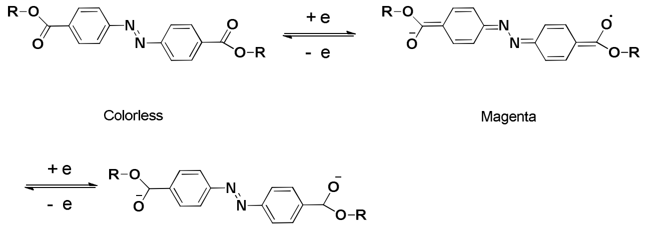


Fig. 1 Cyclic voltammetry of ADDEDs [(A), (B), (C), (D), (E), and (F) for compounds **a**, **b**, **c**, **d**, **e**, and **f**, respectively] in DMF/TBAP (0.05 mol L^{-1}) vs. Ag/AgCl at room temperature. The 1st, 50th, and 100th cycles are showed and the scan rate is 50 mV s^{-1}.

Thus, the redox mechanism and states of ADDEDs were proposed accordingly. The three redox states and accepting–donating e^{-} process of ADDEDs are presented in Scheme 2.[38]



Scheme 2 Three redox states of ADDEDs in electrolyte solution

Fig. 3 Colors of a sandwich–type ADDEDs [(A) bleached state and (B) colored state at 3.0 V] in ECDs.

3.2 Spectroelectrochemistry properties

Spectroelectrochemistry was applied to elucidate the electronic structure of ADDEDs and to examine the spectral changes that occurred during redox switching.[39] Fig. 2 illustrates the UV-vis spectra of the ADDEDs obtained in DMF containing Fc and TBAP at various applied potentials. Only an absorption band was observed for ADDEDs when no potential was applied.

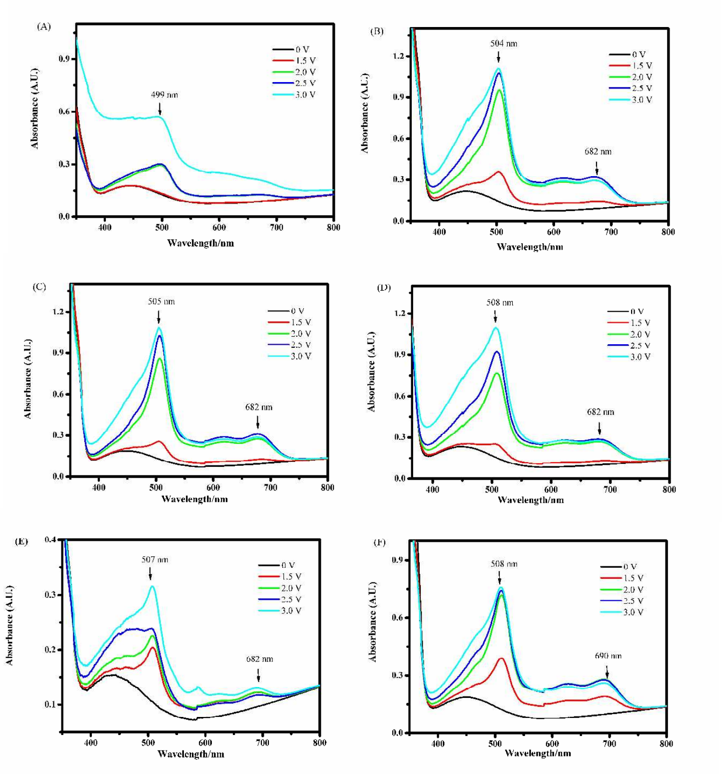


Fig. 2 UV-vis/NIR spectroelectrochemistry for ADDEDs [(A), (B), (C), (D), (E), and (F) for compounds **a**, **b**, **c**, **d**, **e**, and **f**, respectively] on ITO glass at different potential stepping from 1.5 V to 3.0 V with 0.5 V increment.

However, the absorption intensity at ca. 475 nm increased, and a new absorption band appeared for compounds **b**, **c**, **d**, **e,** and **f** as the result of the electrochemical reduction of ADDEDs. Taking compound **d** for example (Fig. 2D), without applied potential (0 V), only an absorption band centered at 446 nm was present. After the application of potential (2.0 V), the previous absorption intensity increased and a new broadband centered at 682 nm appeared. With the applied voltage increased up to 3.0 V, the intensity of the band located at 508 nm increased, whereas minimal change was observed for the band centered at 682 nm.

During electrochemical reduction, the color of ECDs changed from colorless to magenta (see ESI). Taking compound **d** for example, Fig. 3 shows the photographs of the as–prepared ECD based on compound **d** in the bleached (Fig. 3A) and colored states when the applied potential was +3.0 V (Fig. 3B).

The corresponding electrochromic mechanism (from colorless to magenta) was as follows. When potential was charged, the possible process for the conversion of ADDED to ADDED$^{\cdot-}$ between +3.0 V and − 3.0 V in ECD was given by the reaction with the oxidized or reduced form of the anodic compound (Eq. 1).[40]

$$\text{ADDED} + \text{Fc(II)} \rightleftharpoons \text{ADDED}^{\bullet-} + \text{Fc(III)} \qquad (1)$$

At the coloration of the present sandwich–type ECD with a 50 Ω separator between two ITO electrodes, Fc(II) was oxidized to Fc(III) at the counter electrode (anode) to maintain a balance charge, because ADDEDs as electrochromic materials were reduced at the working electrode (cathode). In ADDED$^{\cdot-}$–Fc complex, as counter ions of ADDED$^{\cdot-}$, the anodic compounds Fc(II) and Fc(III) promoted the conversation between ADDED to ADDED.-, which further improved the performance of color change from colorless to magenta.

The optical band gap of ADDEDs were calculated from their low energy absorption edges (λ_{onset}) according to Planck Eq. ($E_g = 1241/\lambda_{onset}$).[41] Redox couple ($E_{ox}$), $E_{p,1/2}$, λ_{max}, and E_g for ADDEDs are shown in Table 1.

Table 1 Electrical and optical data of six ADDEDs

compound	E_{ox} (V)	$E_{p,1/2}$ (V)	λ_{onset} (nm)	E_g (eV)	0 V	±3 V
a	-0.616	-0.892, -1.520	499	2.49	coloress	light magenta
b	-0.650 -1.258	-0.886	504	2.46	coloress	magenta
c	-0.531 -1.010	-0.750	505	2.46	coloress	magenta
d	-0.725 -1.510	-0.977, -1.555	508	2.44	coloress	magenta
e	-0.654 -1.501	-0.908 -1.521	507	2.45	coloress	light magenta
f	-0.584 -1.518	-0.902 -1.522	511	2.45	coloress	magenta

3.3 Switching and stability

Switching and stability are two important properties of an electrochromic material and its corresponding ECD.[42] ECDs based on ADDEDs were switched under ambient conditions by repeated potential steps between the oxidized and reduced states with a residence time of 4 s at around 505 nm.

Optical contrast (ΔT%) was the transmittance difference between the reduced and oxidized states and was monitored as a function of time at the specified wavelength. Fig. 4 shows the the electrochromic switching properties of ADDEDs. The maximum ΔT% of compounds **a**, **b**, **c**, **d**, **e**, and **f** were 15% at 499 nm, 66% at 504 nm, 65% at 505 nm, 62% at 508 nm, 21% at 507 nm, and 67% at 511 nm, respectively. After 1000 s (250 cycles), the transmittance changes of compounds **a** and **e** were 13% and 16%. After 4000 s (1000 cycles), the transmittance changes of compounds **b**, **c**, **d**, and **f** were 8%, 9%, 10%, and 3%, respectively. These results illustrated that compounds **b**, **c**, **d**, and **f** exhibited superior stability and highly optical transparency over 10^3 cycles, indicating that these ECDs are good candidates for electrochromic applications. However, compounds **a** and **e** were unstable and their optical transparency were low. Moreover, their colors (in reduced states) were significantly lighter than that of compounds **b**, **c**, **d**, and **f** (see ESI). The possible reason is the substituent effect on electrochromism.

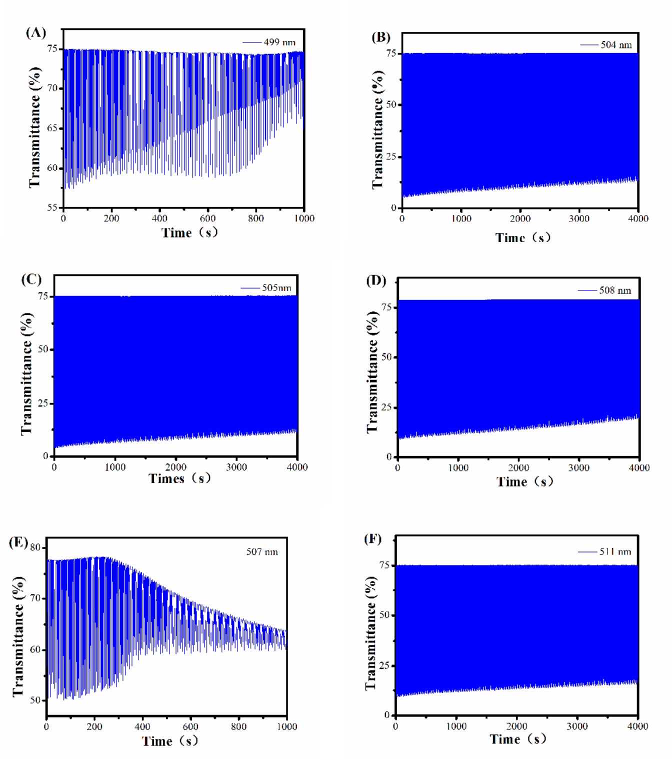


Fig. 4 Electrochromic switching response for ADDEDs monitored at (A) 499 nm, (B) 504 nm, (C) 505 nm, (D) 508 nm, (E) 507nm, and (F) 511 nm for compounds **a**, **b**, **c**, **d**, **e**, and **f**, respectively, between −3.0 V and +3.0 V with a residence time of 4 s.

Response time, which is an important characteristic of ECMs, refers to the time needed to perform a switching between the two colored states of the materials. Switching time quantification was performed by defining a change in 95% of the total absorbance span, as the naked eye could not distinguish the color change beyond this point.[43] As shown in Fig. 5, the optical response time for the coloring and bleaching processes were 1.28 and 0.83 s for compound **a**, 0.92 and 0.86 s for compound **b**, 1.21 and 1.06 s for compound **c**, 0.82 and 0.78 s for compound **d**, 1.24 and 1.02 s for compound **e**, 0.87 and 0.83 s for compound **f,** respectively. These values indicate that the six compounds had fast switching time. The time required for bleaching process was faster than that for coloring process because of the inhibition of the discharging current flowing in the external circuit; this finding is consistent with a previous report.[37]

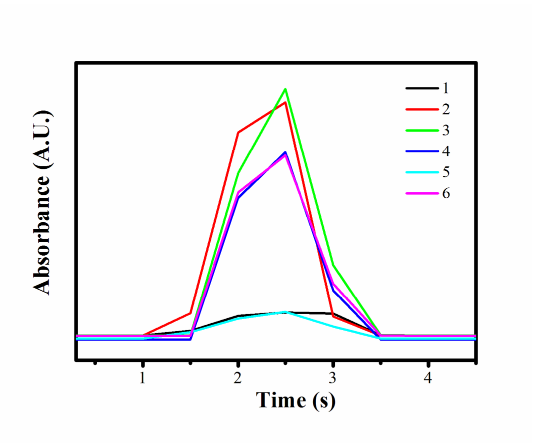


Fig. 5 Optical switching studies of ECDs based on ADDEDs monitored at (1) 499 nm, (2) 504 nm, (3) 505 nm, (4) 508 nm, (5) 507nm, and (6) 511 nm for compounds **a**, **b**, **c**, **d**, **e**, and **f**, respectively.

Coloration efficiency (*CE*) is another important characteristic for ECMs, that facilitates the comparison between electrochromic materials and devices.[44] *CE* value can be calculated by Eqs. 2 and 3[45]:

$$\Delta OD = \log\left(\frac{T_b}{T_c}\right) \qquad (2)$$

$$CE(\eta) = \frac{\Delta OD}{Q_d} \qquad (3)$$

where T_c and T_b are the light transmittances of the colored and bleached states of the ECD at a certain wavelength (λ), respectively; *ΔOD* is the change in optical density, which is proportional to the amount of created color centers; η denotes the *CE*; and Q_d is the amount of injected/ejected charge per unit sample area. *ΔOD* and *CE* were calculated to be 0.14 and 150 cm^2/C at 499 nm for compound **a**, 0.87 and 935 cm^2/C at 504 nm for compound **b**, 1.02 and 1096 cm^2/C at 505 nm for compound **c**, 0.88 and 946 cm^2/C at 508 nm for compound **d**, 0.15 and 161 cm^2/C at 507 nm for compound **e**, 0.89 and 957 cm^2/C at 511 nm for compound **f**, respectively. The coloration efficiency data showed that compounds **b**, **c**, **d**, and **f** exhibited higher *CE*.**Table 1** Electrical and optical data of six ADDEDs

In comparison with extensively used ECD materials such as poly/oligothiophene, triphenyamine, viologen, Prussian blue,[44-51] compounds **b**, **c**, **d**, and **f** displayed slightly better stability, comparable or slightly higher color efficiency, slightly shorter response time, and slightly higher optical contrast. This render them very prospective for application as electronic paper, smart windows, optical memory devices, full–color EC display devices, and dual–stimuli–responsive systems.

Table 2 Electrochromic properties of in comparison with ECMs containing poly/oligothiophene, triphenyamine, viologen, and Prussian blue.

compound	CE (cm^2/C)	Response time (s)	Applied voltage	Ref.No
ADDEDS	946	0.82	±3 V vs. Ag/AgCl	This work
poly/oligothiophene	125	>2	±1.2 V vs. Ag/AgCl	44,50
Triphenyamine	320	>2	±1.0 V vs. Ag/AgCl	46
Viologen	725	>2	±4.0 V vs. Ag/AgC	47
Prussian blue	117.26	>2	-0.2-(+0.6) V vs. Ag/AgCl	48,49

3.4 Photoisomerization analysis of ADDEDs

The photoisomerization of ADDEDs (2.0×10^{-5} mol L^{-1}) in DMF was studied by UV–vis. Taking compound **d** for example, Figs. 6A and 6B show the spectroscopic responses at room temperature upon alternate irradiation at 365 and 440 nm. The dark incubation of the DMF solution of compound **d** served to maximize the absorption at 331 nm corresponding to the π–π* transition of *trans* azobenzene chromophore and a weak band at 450 nm corresponding to the n–π* transition of azo units.[52] Kinetics of the photoisomerization were analyzed by kinetic Eq. 4.[32]

$$\ln\frac{A_0 - A_\infty}{A_t - A_\infty} = kt \qquad (4)$$

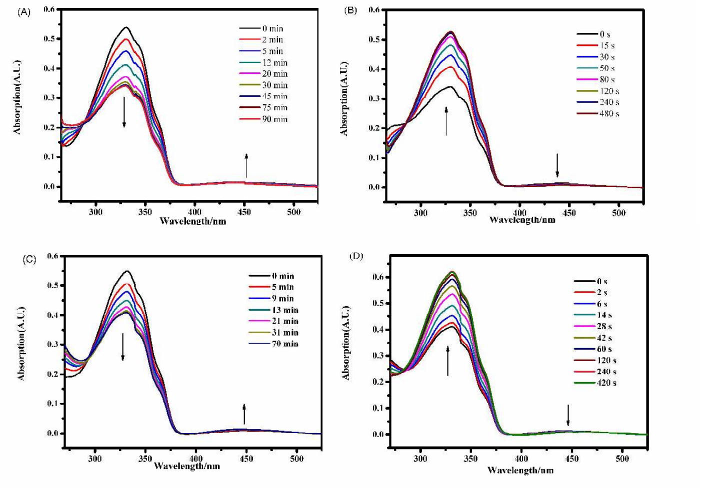


Fig. 6 UV–vis spectra and spectral changes of compound **d** (2.0×10^{-5} mol L^{-1}) in DMF solution (A) upon irradiation at 365 nm, and then (B) upon irradiation at 440 nm. UV–vis spectra and spectral changes of compound **d** (2.0×10^{-5} mol L^{-1}) in TBAP and ferrocene in DMF solution (C) upon irradiation at 365 nm, and then (D) upon irradiation at 440 nm.

The isomerization rate constants of *trans*→*cis* and *cis*→*trans* were $(7.41 \pm 0.58) \times 10^{-3}$ and $(2.96 \pm 0.07) \times 10^{-2}$ s^{-1}. Figs. 6C and 6D show the spectroscopic responses of compound **d** (2.0×10^{-5} mol L^{-1}) containing TBAP (4.0×10^{-5} mol L^{-1}) and Fc (2.0×10^{-5} mol L^{-1}) (under electrochromic conditions) at room temperature upon alternate irradiation at 365 and 440 nm. The *trans*→*cis* and *cis*→*trans* isomerization rate constants were $(1.75 \pm 0.07) \times 10^{-3}$ and $(9.15 \pm 1.20) \times 10^{-2}$ s^{-1}. Comparison of the photoisomerization process of compound **d** in DMF and in the electrochromic condition revealed that TBAP and Fc in the electrochromic condition had insignificant effect on the photoisomerization behavior of azobenzene.

Reversibility of photoisomerization of the azobenzene chromophores is an important factor for photoresponsive materials. Fig. 7 shows the modulation of the absorbance of compound **d** in the electrochromic condition upon alternate irradiation at 365 and 440 nm. No obvious change in absorbance at 331 nm was observed after 3 cycles, illustrating that the photoisomerization of the azobenzene chromophores was reversible and robust.[27,28]

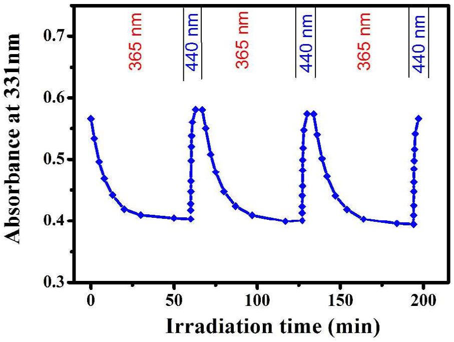


Fig. 7 Reversibility of the photoisomerization processes of the azobenzene chromophores in DMF upon alternate irradiation at 365 and 440 nm, respectively.

The photoisomerization and reversibility of other ADDEDs (compounds **a**, **b**, **c**, **e** and **f**) were similar to that of compound **d** (see ESI). To investigate the influence of *trans*↔*cis* photoisomerization of azobenzene on the electrochromic behaviors of ADDEDs, ADDEDs in both *trans* and *cis* forms were used as electrochromic materials, and both *cis* and *trans* forms produced similar results. This finding also proved that the electrochemical mechanism of ADDEDs was through the formation of dianions, as proposed in Scheme 2.[38]

Conclusions

In this paper, a series of electrochromic and photoresponsive materials ADDEDs were synthesized and characterized. In comparison with extensively used ECD materials such as poly/oligothiophene, triphenyamine, viologen, Prussian blue, ADDEDs showed not only outstanding electrochromic behaviors but also good and reversible photoisomerization properties even under electrochromic conditions. ECDs based on ADDEDs exhibited good stabilities, well–defined reversible redox processes, and superior electrochromic behaviors. These results suggest that the prepared electrochromic and photoresponsive materials are effective for applications in full–color EC display devices and stimuli responsive systems, as well as other potential new scopes.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: Colors of sandwich-type ECDs based on ADDEDs; Optical transmittance for ECDs based on ADDEDs; UV–vis spectra and spectral changes of compounds **a**, **b**, **c**, **e** and **f** in DMF and electrochromic conditions. These materials are available free of charge via the Internet at http://pubs.rsc.org. See DOI: 10.1039/b000000x/

1 J. H. Holtz and S. A. Asher, *Nature*, 1997, **389**, 829.
2 J. F. Lutz, *Adv. Mater*., 2011, **23**, 2237.
3 S. Aluri, M. K. Pastuszka, A. S. Moses and J. A. MacKay, *Biomacromol*., 2012, **13**, 2645.
4 A. C. Rinkenauer, A. Schallon, U. Gunther, M. Wagner, E. Betthausen, U. S. Schubert and F. H.Schacher, *ACS Nano*, 2013, **7**, 9621.
5 A. Grigoryev, V. Sa, V. Gopishetty, I. Tokarev, K. G.Kornev and S. Minko, *Adv. Funct. Mater*., 2013, **23**, 5903.
6 J. M. Hu and S. Y. Liu, *Macromolecules*, 2010, **20**, 8315.
7 J. Ge, E. Neofytou, T. J. Cahill, R. E. Beygui, R. N. Zare, *ACS Nano*, 2012, **6**, 227.
8 Y. Takashima, S. Hatanaka, M. Otsubo, M. Nakahata, T. Kakuta, A. Hashidzume, H. Yamaguchi and A. Harada, *Nat. Commun*., 2012, **3**, 1270.
9 K. J. Mackenzie and M. B. Francis, *J. Am. Chem. Soc*., 2013, **135**, 293.
10 X. Hao, H. Liu, Z. Lu, Y. J. Xie, H. Y.Yang and S. G. J. Boyes, *Mater. Chem A*, 2013, **1**, 6920.
11 P. Kaewsaiha, K. Matsumoto and H. Matsuoka, *Langmuir*, 2007, **23**, 7065.
12 P. Llg, *Soft Matt*., 2013, **9**, 3465.
13 J. Wang, M. Pelletier, H. Zhang, H. Xia and Y. Zhao, *Langmuir*, 2009, **25**, 13201.
14 S. Mura, J. Nicolas and P. Couvreur, *Nat. Mater*., 2013, **12**, 991.
15 H. Nandivada, A. M. Ross and J. Lahann, *Prog. Polym. Sci*., 2010, **35**, 141.
16 C. C. Hsu, C. S. Wu and Y. L. Liu, *J. Memb. Sci*., 2014, **450**, 257.
17 Q. Tang, Y. T. Nie, C. B. Gong, C. F. Chow, J. D. Peng and M. H. Lam, *J. Mater. Chem*., 2012, **22**, 19812.
18 Y. Kondo, H. Tanabe, H. Kudo, K. Nakano and T. Otake, *Materials*, 2011, *4*, 2171.
19 S. M. Wang, L. Liu, W. Chen, Z. M. Zhang, Z. M. Su and E. B. Wang, *J. Mater. Chem. A*, 2013, **1**, 216.
20 R. D. Rauh, *Electrochimi. Acta*., 1999, **44**, 3165.
21 Y. G. Ko, W. Kwon, H. J. Yen, C. W. Chang, D. M. Kim, K. Kim, S. G. Hahm, T. J. Lee, G. S. Liou and M. Ree, *Macromolecules*, 2012, **45**, 3749.
22 P. Beaujuge, S. Ellinger and J. R. Reynolds, *Nat. Mater*., 2008, **7**, 795.
23 A. Patra, Y. H. Wijsboom, S. S. Zade, M. Li, Y. Sheynin, G. Leitus and M. Bendikov, *J. Am. Chem. Soc*., 2008, **130**, 6734.
24 A. A. Argun, P. H. Aubert, B. C. Thompson, I. Schwendeman, C. L. Gaupp, J. Hwang, N. J.Pinto, D. B.Tanner, A. G. MacDiarmid and J. R. Reynolds, *Chem. Mater*., 2004, **16**, 4401.
25 W. Sharmoukh, K. C. Ko, C. H. Noh, J. Y. Lee and S. U. Son, *J. Org. Chem*., 2010, **75**, 6708.
26 L. X. Liao, F. Stellacci and D. V. McGrath, *J. Am. Chem. Soc*., 2004, **126**, 2181.
27 C. B. Gong, M. H. W. Lam and H. X. Yu, *Adv. Funct. Mater*., 2006, **16**, 1759.
28 C. B. Gong, Y. Z.Yang, C. Gao, Q. Tang, C. F. Chow, J. D. Peng and M. H. W. Lam, *J. Sol*‑*Gel Sci. Technol*., 2013, **67**, 442.
29 K. S. M. Nalluri and B. J. Ravoo, *Angew. Chem. Int. Ed*., 2010, **49**, 5371.
30 Y. P. Wang, N. Ma, Z. Q. Wang and X. Zhang, *Angew. Chem. Int. Ed*., 2007, **46**, 2823.
31 M. M. M. Raposo, A. M. C. Fonseca, M. C. R. Castro, M. Belsley, M. F. S. Cardoso, L. M. Carvalho and P. J. Coelho, *Dyes Pigm*., 2011, **91**, 62.
32 Q. Tang, X. Z. Meng, H. B. Jiang, T. Y. Zhou, C. B. Gong, X. K. Fu and S. Q. Shi, *J. Mater. Chem*., 2010, **20**, 9133.
33 A. Peters and N. R. Branda, *J. Am. Chem. Soc.*, 2003, **125**, 3404.
34 M. Nakagawa, M. Rikukawa, M. Watanabe, K. Sanui and N. Ogata, *Bull. Chem. Soc. Jpn*, 1997, **70**, 737.
35 J. F. Zhi, R. Baba, K. Hashimoto and A. Fujishima, *J. Photochem. Photobio. A-Chem*, 1995, 92, 91.
36 T. Bartosz, P. Malgorzata, J. Emilia, G. V. Ricard and G. Marta, *Eur. Polymer*, 2009, **45**, 1420.
37 J. Deng, X. K. Fu, G. Wang and J. Huang, *Electrochim. Acta*., 2012, **85**, 195.
38 W. Sharmoukh, K. C. Ko, S. Y. Park, J. H. Ko, J. M. Lee, C. Noh, J. Y. Lee and S. U. Son, *Org. Lett*., 2008, **10**, 5365.
39 C. S. Cui, C. X. Xu, L. Y. Xu, J. S. Zhao, R. M. Liu, J. F. Liu, Q. P. He and H. S. Wang, *Opt. Mater*., 2011, **33**, 1792.
40 G. Wang, X. K. Fu, J. Huang, C. L. Wu, L. Wu and Q. L. Du, *Org. Electron*., 2011, **12**, 1216.
41 X. Tu, X. K. Fu and Q. L. Jiang, *Displays*, 2011, **31**, 150.
42 G. M. Wang, X. K. Fu, J. Deng, X. M. Huang and Q. Miao, *Chem. Phys. Lett.*, 2013, **579**, 105.
43 G. M. Wang, X. K. Fu, L. H. He, X. M. Huang and Q. Miao, *Org. Electron*., 2014, **15**, 622.
44 G. Wang, X. K. Fu, J. Hang, C. L. Wu, L. Wu, J. Deng, Q. L. Du and X. C. Zou, *Electrochim. Acta*, 2011, **56**, 6352.
45 B. Hu, Y. J. Zhang, X. J. Lv, M. Ouyang, Z. Y. Fu and C. Zhang, *Electroanal. Chem*., 2013, **689**, 291.
46 S. H. Hsiao and Y. T. Chou, *Polymer*, 2014, **55**, 2411.
47 R. Sydam, M. Deepa and A. G. Joshi, *Organic Electronics*, 2013, **14**, 1027.

48 P. M. S. Monk, R. J. Mortimer and D. R. Rosseinsky, Electrochromism: Fundamentals and Applications, VCH, Weinheim, Germany, 1990.

49 B. Seelandt and M. Wark, *Microporous and Mesoporous Materials*, 2012, **164**, 67.

50. G. Gunbasab and Levent Toppare, *Chem. Commun.*, 2012, **48**, 1083.

51. P. R. Somani and S. Radhakrishnan, *Mater. Chem. Phys.*, 2002, **77**, 117.

52 S. Ghosh, A. K. Banthia and Z. Chen, *Tetrahedron*, 2005, **61,** 2889.

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351x140mm (96 x 96 DPI)