Cite this: New J. Chem., 2011, 35, 1327–1334

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### PAPER

## Electrochromic devices and thin film transistors from a new family of ethylenedioxythiophene based conjugated polymers<sup>†</sup><sup>‡</sup>

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*Received (in Gainesville, FL, USA) 28th October 2010, Accepted 7th January 2011* DOI: 10.1039/c0nj00837k

New electrochromic conjugated polymers and their corresponding devices based on EDOT (ethylenedioxythiophene) are described. The best of these polymers display response times on the order of 1s and high switchable contrast in the visible and near-infrared (Vis-NIR) spectral regions. Thin films (70 nm) of these new polymers displayed optical band gaps on the order of 1.73 eV (7a) < 2.19 eV (7b) < 2.23 eV (7c) < 2.31 eV (4) < 2.34 eV (2) as calculated from their extrapolation of the absorption edges. Polymers 4 and 7a show field effect hole mobilities of *ca*.  $6.7 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> (on/off ratio 10<sup>4</sup>) and  $2.5 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> (on/off ratio10<sup>3</sup>), respectively, related to their highly ordered inter-chain packing as confirmed by XRD analyses of polymer 4. Electrochromic characterizations show that polymers 7a–c exhibit significant absorption changes in the infrared at low voltage. The resulting solid-state devices offer promise for electrochromic shutters and filters in the IR, since their high charge transfer mobility and ion injection efficiency permits relatively rapid switchable contrast, while their robustness exceeds that of aqueous devices.

#### Introduction

Electrochromic materials were brought to public attention 35 years ago in seminal work on tungsten oxide films by Deb.<sup>1</sup> In essence, the optical absorption changes between widely separated extrema as charge is inserted or extracted. Electrochemical manipulation of the redox processes in thin films of these materials thus allows modulation of their transmittance spectra. Over the past few years, electrochromic devices (ECDs) utilizing electroactive conjugated polymers have received increasing attention owing to their fast response time, high optical contrasts, low fabrication cost and easy functional modifications.<sup>2</sup> Conjugated polymers, such as polyanilines, polypyridines, polypyrroles, polythiophenes, and in particular, poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives have thus far proved most useful. Reynolds and some other groups have investigated the electrochromic properties of PEDOT and other EDOT containing polymers.<sup>2,3</sup>

Research on conjugated polymer electrochromics has focused on increasing switching speed and optical contrast in the visible, as well as on device design.<sup>4</sup> These materials can be induced by modest voltages to change reversibly between a colored neutral state and a transparent doped state.<sup>5</sup> Although relatively few investigations have explored the electrochromic properties of conjugated polymers in the infrared, these materials are known to offer potential for device applications in these wavelengths ranging from variable attenuators for optical information technology,<sup>6</sup> and infrared camouflage in low-light environments,<sup>7</sup> to shutters or filters for infrared detection and imaging.<sup>8</sup>

Our group previously designed and fabricated transmissive infrared electrochromic devices (ECDs) based on poly-(3-hexylthiophene) (P3HT) and solid gel electrolytes.<sup>8</sup> We varied the salt type, salt concentration and polymer film thicknesses and discussed the effects these changes made on the devices' optical contrast and response time. Although those devices exhibited high optical contrast in the infrared, their switching speeds were on the order of tens of seconds.

We report here the synthesis and use of a series of conjugated polymers (Scheme 1), namely poly(5-(9,9-didodecyl-7-methyl-9*H*-fluoren-2-yl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine) **2**, poly((2-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-9-(heptadecan-9-yl)-9*H*-carbazole) **4**, poly((4,7-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)benzo[*c*][1,2,5]thiadiazole)-9-(heptadecan-9-yl)-9*H*-carbazole) **7a**, poly((5,6-bis(octyloxy)-4,7-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)benzo[*c*][1,2,5]thiadiazole)-9-(heptadecan-9-yl)-9*H*-carbazole) **7b** and poly((5,6-bis(dodecyloxy)-4,7-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)benzo[*c*][1,2,5]thiadiazole)-9-(heptadecan-9-yl)-9*H*-carbazole) **7b** and poly((5,6-bis(dodecyloxy)-4,7-(2,3-dihydrothieno[3,4,7-(2,3-dihydrot

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<sup>†</sup> This article is part of a themed issue on Molecular Materials: from Molecules to Materials, commissioned from the MolMat2010 conference.
‡ Electronic supplementary information (ESI) available. See DOI: 10.1039/c0nj00837k.



Scheme 1 Synthetic routes to polymers 2, 4 and 7a-c.

(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)benzo[c][1,2,5]thiadiazole)-9-(heptadecan-9-yl)-9H-carbazole) 7c, with different functional groups that enable us to further explore the relationship between electrochromic properties and chemical structures. The charge transfer mobility of these polymers was also measured to determine the relationship between the structure and electrochromic switching. These polymers contain ethylenedioxythiophene (EDOT) units, which provide exceptional stability in the oxidation state combined with a low energy requirement for oxidation.9 9,9-Didodecyl-9Hfluorene and 9-(heptadecan-9-yl)-9H-carbazole are introduced into the polymer chains to improve ECDs' performance through the adjustment of spacing between the polymer chains to facilitate ion injection.<sup>10</sup> The introduction of the acceptor unit benzo[c][1,2,5]thiadiazole (BT) and its derivations was used to decrease the lowest unoccupied molecular orbital (LUMO) level and to narrow the band gap, thereby extending absorbance to longer wavelengths.11

#### Experiment

#### Materials

All reagents were purchased from commercial sources and were used without further purification, unless otherwise noted. The solvents were distilled and dried using known methods.<sup>12</sup> All reactions were carried in an air atmosphere unless otherwise mentioned. The following acceptor and donor blocks were prepared according to literature procedures: 4,7-dibromo-2,1,3-benzothiodiazole (DB-BT),13 tributyl(2,3-dihydrothieno-[3,4-b][1,4]dioxin-5-yl)stannane (EDOT-T),<sup>14</sup> 5,7-dibromo-2,3-dihydrothieno[3,4-b][1,4]dioxine (DB-EDOT),15 4,7-dibromo-(DB-BTC8),<sup>11</sup> 5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole 4,7-dibromo-5,6-bis(dodecyloxy)benzo[c][1,2,5]thiadiazole (DB-BTC12),<sup>11</sup> 2,2'-(9,9-didodecyl-9*H*-fluorene-2,7-diyl)bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 1<sup>16</sup> and 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9Hcarbazole 3.<sup>17</sup> ITO/glass electrodes were obtained from Delta Technologies, Ltd., and rinsed successively with distilled water, acetone and isopropanol before use.

### General procedures of polymerization through Suzuki cross-coupling

The general synthesis protocols used to produce the conjugated copolymers are shown in Scheme 1. The dibromomonomer (1.0 mol ratio), bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1.0 mol ratio), Pd(PPh\_3)<sub>4</sub> (0.02 mol ratio), and toluene were placed into a two neck-bottle under argon. After complete dissolution of the reagents, a degassed 2 M K<sub>2</sub>CO<sub>3</sub> solution was added under argon to the mixture. The reaction was refluxed under stirring for 48 h. The mixture was poured into methanol. The precipitates were collected, extracted with methanol, acetone and hexane using a Soxhlet apparatus, and then dried under vacuum.

#### Poly(5-(9,9-didodecyl-7-methyl-9*H*-fluoren-2-yl)-2,3dihydrothieno[3,4-*b*][1,4]dioxine) 2

150 mg **1** (0.20 mmol), 60 mg DB-EDOT (0.20 mmol), 5 ml toluene and 0.5 ml 2 M K<sub>2</sub>CO<sub>3</sub> solution were used to afford 80 mg yellow solid (yield 61%).  $M_{\rm n}$ , 16 620;  $M_{\rm w}$ , 31 445; PDI, 1.89. <sup>1</sup>H NMR (500 MHz CDCl<sub>3</sub>),  $\delta$  = 7.85–7.77 (m, 6H), 4.47 (s, 4H), 2.08 (br, 4H), 1.22–1.13 (m, 40H), 0.79 (s, 6H); Anal. calcd for C<sub>43</sub>H<sub>60</sub>O<sub>2</sub>S (%): C, 80.32; H, 9.72. Found: C, 80.16, H, 9.58.

#### Poly((2-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-9-(heptadecan-9-yl)-9*H*-carbazole) 4

150 mg **3** (0.23 mmol), 68 mg DB-EDOT (0.23 mmol), 5 ml toluene and 0.5 ml 2 M K<sub>2</sub>CO<sub>3</sub> solution were used to afford 75 mg yellow solid (yield 56%).  $M_{\rm n}$ , 32 649;  $M_{\rm w}$ , 73 570; PDI, 2.25. <sup>1</sup>H NMR (500 MHz CDCl<sub>3</sub>),  $\delta = 8.10$  (s, 3H), 7.87 (s, 1H), 7.67 (s, 2H), 4.68 (s, 1H), 4.51 (s, 4H), 2.43 (br, 2H), 2.02 (br, 2H), 1.30–1.19 (m, 28H), 0.84 (tr, 6H). Anal. calcd for C<sub>35</sub>H<sub>45</sub>NO<sub>2</sub>S (%): C, 77.02; H, 8.68. Found: C, 77.26, H, 8.43.

#### Poly((4,7-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)benzo[*c*]-[1,2,5]thiadiazole)-9-(heptadecan-9-yl)-9*H*-carbazole) 7a

150 mg **6a** (0.26 mmol), 170 mg **3** (0.26 mmol), 5 ml toluene and 0.5 ml 2 M K<sub>2</sub>CO<sub>3</sub> solution were used to afford 105 mg black solid (yield 65%).  $M_{\rm n}$ , 20800;  $M_{\rm w}$ , 48117; PDI, 2.31. <sup>1</sup>H NMR (500 MHz CDCl<sub>3</sub>), <sup>1</sup>H NMR (500 MHz CDCl<sub>3</sub>),  $\delta = 8.53$  (s, 2H), 8.17–8.11 (m, 3H), 7.92 (br, 1H), 7.77–7.75 (br, 2H), 4.71 (s, 1H), 4.56–4.53 (d, 8H), 2.44 (br, 2H), 2.03 (br, 2H), 1.31–1.20 (m, 28H), 0.82 (tr, 6H). Anal. calcd for C<sub>33</sub>H<sub>25</sub>N<sub>3</sub>O<sub>4</sub>S<sub>3</sub> (%): C, 63.54; H, 4.04. Found: C, 63.76, H, 4.52.

#### Poly((5,6-bis(octyloxy)-4,7-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)benzo[*c*][1,2,5]thiadiazole)-9-(heptadecan-9-yl)-9*H*carbazole) 7b

150 mg **6b** (0.18 mmol), 118 mg **3** (0.18 mmol), 5 ml toluene and 0.5 ml 2 M K<sub>2</sub>CO<sub>3</sub> solution were used to afford 114 mg red solid (yield 71%).  $M_n$ , 16128;  $M_w$ , 26648; PDI, 1.65. <sup>1</sup>H NMR (500 MHz CDCl<sub>3</sub>), <sup>1</sup>H NMR (500 MHz CDCl<sub>3</sub>),  $\delta = 8.08$  (s, 3H), 7.85 (s, 1H), 7.67 (br, 2H), 4.65 (s, 1H), 4.47 (s, 4H), 4.38 (s, 4H), 4.17 (s, 4H), 2.39 (br, 2H), 2.00 (br, 2H), 1.80 (br, 4H), 1.41–1.19 (m, 48H), 0.83 (tr, 12H). Anal. calcd for  $C_{49}H_{55}N_3O_6S_3$  (%): C, 66.86; H, 6.53. Found: C, 67.03, H, 6.81.

# Poly((5,6-bis(dodecyloxy)-4,7-(2,3-dihydrothieno[3,4-*b*][1,4]-dioxin-5-yl)benzo[*c*][1,2,5]thiadiazole)-9-(heptadecan-9-yl)-9*H*-carbazole) 7c

150 mg **1** (0.16 mmol), 104 mg **3** (0.16 mmol), 5 ml toluene and 0.5 ml 2 M K<sub>2</sub>CO<sub>3</sub> solution were used to afford 100 mg red solid (yield 63%).  $M_n$ , 18836;  $M_w$ , 34286; PDI, 1.82. <sup>1</sup>H NMR (500 MHz CDCl<sub>3</sub>), <sup>1</sup>H NMR (500 MHz CDCl<sub>3</sub>),  $\delta = 8.08$  (s, 3H), 7.85 (s, 1H), 7.68 (br, 2H), 4.65 (s, 1H), 4.47 (s, 4H), 4.37 (s, 4H), 4.16 (s, 4H), 2.40 (br, 2H), 1.98 (br, 2H), 1.79 (br, 4H), 1.43–1.17 (m, 64H), 0.88–0.83 (tr, 12H). Anal. calcd for C<sub>57</sub>H<sub>71</sub>N<sub>3</sub>O<sub>6</sub>S<sub>3</sub> (%): C, 68.99; H, 7.41. Found: C, 68.79, H, 7.05.

#### Characterization

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were collected on a Mercury 500 MHz NMR spectrometer using CDCl<sub>3</sub> and referenced to the solvent residual peak (CDCl<sub>3</sub>: <sup>1</sup>H:  $\delta$  = 7.26 ppm, <sup>13</sup>C:  $\delta = 77.23$  ppm). Gel permeation chromatography (GPC) was performed using a Waters Associates GPCV2000 liquid chromatography system with its internal differential refractive index detector (DRI) at 150 °C. Cyclic voltammetry (CV) was performed using a CIH 500/A electrochemical workstation from CH Instruments, Inc. These analyses were carried out using a three-electrode cell with a Pt wire as the counter electrode, a Ag/AgCl reference electrode calibrated with a 5 mM solution of Fc/Fc+ in 0.1 M TBAP/acetonitrile (ACN) as electrolyte solution and a glassy carbon working electrode. All absorption spectra were collected with a Jasco 670 UV-vis-NIR spectrophotometer at room temperature using a quartz cuvette with a path length of 1 cm and chlorobenzene as solvent. For the thin film spectra, polymers were first dissolved in chlorobenzene (1 mg mL<sup>-1</sup>), and spin-coated at a speed rate of 1500 rpm for 30 s onto the glass slides. Optical bandgaps were calculated from the edge of the visible-absorption bands in the thin films spectra. X-ray diffraction (XRD) was performed by Philips X'PERT MPD X-ray diffractometer, using Cu K $\alpha$  radiation ( $\lambda = 1.5405$  Å) with a typical scan range from  $2^{\circ}$  to  $35^{\circ}$ ,  $1^{\circ}$  step size, and 120 s per step on the drop-cast polymer film.

#### Fabrication and characterization of field effect transistors

Transistors were fabricated using a bottom gate-top electrode device structure. 150 nm thick SiO<sub>2</sub> with an area capacitance of  $\sim 2.33 \times 10^{-4}$  F m<sup>2</sup> was used as the gate dielectric under which a highly n-type doped Si layer functions as the gate. All the materials studied here were dissolved in chlorobenzene with a concentration of 8 mg ml<sup>-1</sup> and the solution was sufficiently stirred at 110 °C on a hotplate. The SiO<sub>2</sub> substrates were sonicated with acetone and 2-isopropanol for 30 min and dried at 140 °C, then immediately transferred in a UV-ozone oven for 1 hour to remove surface impurities. Subsequently the SiO<sub>2</sub> substrates were soaked in octadecyltrichlorosilane/ hexane dilute solution (1 : 750 vol. ratio) for 30 min to enhance surface hydrophobicity. The active layers were spun-coat from chlorobenzene with a spin-speed of 2000 RPM

leading to film thickness typically of ~40 nm. A thermal annealing of 140 °C for 20 min was also applied to the cast films. At last 90 nm of the Au top electrode was evaporated through a shadow mask on the active layers under a pressure of  $2 \times 10^{-7}$  Torr resulting in a channel width of 1 mm and length of 40 µm.

Transistor characteristics were analyzed with in a Lakeshore probe station under a pressure of  $\sim 10^{-4}$  Torr and electrical measurements taken with a Keithley 4200 semiconductor parameter analyzer.

#### Fabrication and characterization of electrochromic devices

The polymer films (thicknesses *ca.* 70 nm) were spun-cast from chlorobenzene (1% wt.) solution onto the ITO/glass electrode at 1500 rpm for 30 s and vacuum annealed at 120 °C overnight. The gel electrolyte base prepared from an acetonitrile solution of poly(methyl methacrylate) (PMMA), propylene carbonate and ethylene carbonate in weight ratios of 1 : 0.1 : 0.4 : 0.4, and tetrabutyl ammonium tetrafluoroborate TBABF<sub>4</sub> was added in a 0.9 M concentration relative to the acetonitrile. After spin-coating a given polymer and the gel electrolyte on two separate ITO/glass substrates, the coated surfaces were manually sandwiched together and sealed with epoxy.

#### **Result and discussion**

#### **Optical properties**

The normalized (to the maximum absorption value) UV-visible absorption spectra of the studied copolymers in dilute chlorobenzene  $(1.0 \times 10^{-3} \text{ mg ml}^{-1})$  and thin films are shown in Fig. 1a and b, respectively. The corresponding maximum absorption wavelengths ( $\lambda_{max}$ ) and optical band gaps ( $E_g^{\text{opt}}$ ) are summarized in Table 1. The  $\lambda_{max}$  of polymers **2**, **4**, and **7a–7c** in solution are observed at 442 nm, 468 nm, 591 nm, 465 nm and 460 nm, respectively, while those of the thin films are at 450 nm, 475 nm, 600 nm, 473 nm and 468 nm. The solid films show similar absorption spectra to those in chlorobenzene solutions, but the peaks are broadened. The  $\lambda_{max}$  of the polymer films are slightly red-shifted relative to those of the same polymers in solution, suggesting  $\pi$ – $\pi$  inter-chain association and aggregation in the solid state.

The optical band gaps ( $E_g^{opt}$ , eV) obtained from extrapolation of the absorption edges of the polymer film spectra are in the order of 7a (1.73 eV) < 7b (2.19 eV) < 7c (2.23 eV)< 4 (2.31 eV) < 2 (2.34 eV). Lacking the acceptor-donor structure, polymers 2 and 4 have shorter  $\lambda_{max}$  absorbances relative to those of polymers 7a-c. Introduction of the acceptor benzothiodiazole (BT) also effectively reduces the polymer band gap. Polymer 7a exhibits the longest  $\lambda_{max}$ absorbance, largely as a result of the intramolecular charge transfer effect between the donor and acceptor and the extension of the conjugated system. On the other hand, the incorporated bulky side chains (dodecyloxy or octyloxy) on acceptors in polymers 7b and 7c lead to a blue shift of absorption. Even though there are donor-acceptor structures in these polymer backbones, the non-planarity of the extended conjugated system also leads to a smaller band gap.<sup>18</sup> The above results indicate that the band gap and the molecular



**Fig. 1** Normalized optical absorption spectra of polymers **2**, **4**, **7a–c** in (a) dilute chlorobenzene solutions and (b) thin films on a glass plate.

energy level of the EDOT based polymers can be efficiently tuned by combination with different subunits and polymer backbone planarity.

#### **Electronic properties**

Cyclic voltammetry (CV) curves of the polymers were obtained with drop-cast polymer films under 0.1 M TBAP/ acetonitrile electrolyte solutions scanned at a rate of 100 mV s<sup>-1</sup> The HOMO and LUMO energy levels and electrochemical band gaps (E<sup>ec</sup><sub>g</sub>) were estimated from the onset oxidation potentials (Eoset) and onset reduction potentials (Ered based on the following equations: HOMO =  $-[E_{onset}^{ox} - E_{1/2}^{ferrocene} +$ 4.8] eV and LUMO =  $-[E_{\text{onset}}^{\text{red}} - E_{1/2}^{\text{ferrocene}} + 4.8]$  eV, with the potentials referenced to an Ag/AgCl reference electrode.  $E_{1/2}^{\text{ferrocene}} = 0.26 \text{ V}$  versus Ag/AgCl. The results are summarized in Table 1. All the polymers exhibited both reversible p-doping/dedoping (oxidation/rereduction) and n-doping/dedoping (reduction/reoxidation) processes. The corresponding HOMO energy levels of 2, 4, and 7a-c are -5.52, -5.04, -5.28, and -5.17 eV, respectively, while their LUMO energy levels are -3.24, -3.38, -3.22, and -3.62 eV. Although the band gap values show the same trend as a function of polymer structure, the Ege values are up to 0.3 eV larger than the  $E_{g}^{opt}$  values, an effect probably due to the exciton binding energy of the conjugated polymers.<sup>19</sup> Polymer 7a exhibits the lowest HOMO and highest LOMO. Apparently, intramolecular charge transfer renders this polymer

Polymer	UV-visible absorption spectra				Cyclic voltammetry	
	$\lambda_{\max}^{a}$ (solution)/nm	$\lambda_{\max}{}^a$ (film)/nm	$E_{\rm g}^{ m opt}/ m ev$	E <sup>red</sup> /LUMO/ev	E <sup>ox</sup> /HOMO/ev	$E_{ m g}^{ m ec}/ m ev$
2	442	450	2.31	-1.41/-3.13	0.99/-5.53	2.40
4	468	475	2.34	-1.43/-3.12	0.98/-5.52	2.41
7a	591	600	1.73	-1.18/-3.36	0.56/-5.10	1.74
7b	465	473	2.19	-1.37/-3.17	1.01/-5.55	2.38
7c	460	468	2.23	-1.43/-3.12	1.02' - 5.56	2.45
<sup>a</sup> Chlorobenz	zene as processing solution.					

Table 1 Optical and electrochemical properties of polymers 2, 4, 7a-c



Fig. 2 XRD pattern of a polymer 4 film drop-cast on glass from chlorobenzene.

more able to capture electrons at higher reduced potential and lose electrons at lower oxidized potential, resulting in a narrower band gap. Compared to the HOMO/LUMO energy levels of 7a (-5.52/-3.24 eV), those of **7b** (-5.04/-3.38 eV) and **7c** exhibit a higher HOMO level by 0.48 eV, and a lower LUMO level by 0.14 eV, apparently the result of the reduced electron withdrawing activity of the BT units. The stabilization of the HOMO level and destabilization of the LUMO level thus increase the band gaps of 7b and 7c.<sup>20</sup> Polymers 2 and 4 exhibit similar HOMO/ LOMO levels to those of polymers 7b and 7c. Even though there are no donor-acceptor structures in these polymer backbones, the co-planarity of the extended conjugated system also leads to a smaller band gap. The above results indicate that the band gap and the molecular energy level of the EDOT based polymers can be efficiently tuned by combination with different subunits and polymer backbone planarity.

#### X-Ray diffraction analysis

To further understand the molecular organization and morphology in the film, X-ray diffraction (XRD) was used to analyze polymer **4** (in Fig. 2). Films were drop-cast from chlorobenzene onto glass plates and annealed at 180 °C overnight for X-ray analysis, as shown in Fig. 2. The higher angle peak of the  $d_3$  spacing at 22.2° corresponds to a distance of approximately 4.03 Å that can be assigned to the  $\pi$ - $\pi$ stacking between aromatic rings. The higher intensity 11.1° peak of the second-order diffraction peak  $d_2$  corresponds to a distance of 8.03 Å, which may be related to the spacing between co-planar chains caused by the solubilizing groups. The distinct



Fig. 3 p-Type output characteristics of FETs and transfer characteristics of polymer 4 prepared by spin-coating from chlorobenzene onto the ODTS modified substrates.

diffraction peak at  $2\theta \approx 5.4^{\circ}$  corresponds to the  $d_1$  spacing value of 16.3 Å, which is assigned to the interchain spacing between polymer main chains, where the alkylcarbazole substituents are segregated similar to those of  $\pi$ -conjugated polymers with long side chains.<sup>21</sup> The  $d_1$ ,  $d_2$  and  $d_3$  spacings exhibit a proportionality ( $d_1 : d_2 : d_3 \approx 4 : 2 : 1$ ) that suggests a highly organized packing of polymer chains. Hence, the 16.3 Å out-of-plane spacing (100) in the polymer **4** film suggests partial interdigitation of the side chains, indicative of the formation of a lamellar structure that may enhance charge transport. XRD analyses of the other polymers failed to detect any peaks.

#### Field-effect transistor (FET) characteristics

Fig. 3a shows the output characteristics of the FETs in terms of the hole transport in polymer **4**. The steep curves in the



**Fig. 4** p-Type output characteristics of FETs and transfer characteristics of polymer **7a** prepared by spin-coating from chlorobenzene onto the ODTS modified substrates.

linear regime are an indication of a relatively low contact resistance between the Au and polymer. Upon application of -60 V, the drain current becomes saturated. Fig. 3b represents the transfer curves of the FETs. Varying the drain voltage from -40 V to -60 V results in identical drain currents, suggesting that the channel is totally pinched off under at this bias. The current when the FETs are fully turned on and off exhibits an on/off ratio of  $10^4$ . From the extrapolation of  $\sqrt{I_{\text{drain}} vs. V_g}$  a threshold voltage of -23 V is obtained. Using the standard FET equation as follows:

$$\mu_{\rm sat}({\rm FET}) = \frac{2L}{WC_i} \frac{\partial \sqrt{I_{\rm drain}}}{\partial V_{\rm g}} \tag{1}$$

where W and L are the width and length of the FET channels, and  $C_i$  is the area capacitance, the estimated hole mobility of polymer **4** amounts to  $6.7 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. This value negligibly varies with device and dimensions due to slight differences in the gate-source leakage.

The output characteristics and transfer curves of the FETs based on polymer **7a** are shown in Fig. 4. This device shows a hole mobility of  $2.5 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and an on/off ratio of  $10^3$ , roughly similar to of the values for polymer **4**. Polymers **2** and **7b** and **7c** did not exhibit FET behavior, possibly due to the weak intermolecular interactions and decreased crystallinity in their thin films.



**Fig. 5** Spectroelectrochemistry of polymer **2** and **4** films on the ITO-coated glass substrate; UV-vis-NIR absorption spectra were monitored while different potentials were applied to the films: (a) polymer **2**; (b) polymer **4**; a 0 V, b 2.0 V, c 2.5 V, d 2.8 V, e 3.0 V, f 0 V, g 2.0 V, h 2.5 V, i 2.7 V, j 3.0 V.

#### **Electrochromic properties**

Oxidation and reduction of the polymer films are accompanied by remarkable color changes depending on the chemical structure of the polymers. To analyze these color changes in detail, we carried out a spectro-electrochemical study, monitoring the absorption spectra while different potentials were applied to the films.

Polymers 2 and 4 display similar electrochromic spectral properties (Fig. 5). The films change color from yellow to blue when the applied bias drives oxidation. The first doping states occur at 2.5 V. The color changes in these two polymers are marked by a decrease in the bands at around 450 nm and 470 nm, respectively, and the formation of new peaks at 710 nm and 700 nm. At 3.0 V, oxidation intensifies and the films become light blue and more transparent. The different colors of the films can be ascribed to different oxidation states, radical delocalization, and formation of a quinoid structure in the polymer backbone.<sup>22</sup>

The color transitions in both polymers are accompanied by an absorption decrease at around 700 nm and the appearance of a very broad absorption starting at 900 nm with a long wavelength tail extending to the infrared. Absorption also decreases below 500 nm upon oxidation. These spectral changes are highly reversible and do not necessitate special precautions to protect the films against oxygen or humidity.



Fig. 6 Switching property of EC devices based on polymers 2 and 4. (a) polymer 2; (b) polymer 4.

Fig. 6 shows the NIR switching behavior of devices based on polymers **2** and **4**. Switching times are determined by monitoring the absorption intensity changes at 700 nm with the applied voltage switching between -2.5 V and 2.5 V. By expanding the time scale of a single operating cycle, the switching time could be determined. Devices based on polymer **2** need over 10 s for turning on and approximately 1-2 s for turning off (85% of total transformation). The response time of polymer **4** is much quicker, requiring only 1.8 s on and 0.6 s off; this is considerably faster than previously reported.<sup>8,23</sup>

The dynamics of color switching of an electrochromic device are typically limited by the ionic conductivities of the electrolyte and polymer film, electron and hole transfer at the electrodes and charge mobility in the polymer film. In our case, when the EC device turns on, the polymers lose their electrons and become electropositive as a result of electron transfer from the polymer layer into the contacting electrode. At the same time, oppositely charged ions in the electrolyte gel are separated under the influence of the external field, and these anions are injected into the polymer, oxidizing it and maintaining electrical neutrality. Polymer 4 has much higher charge transfer mobility than polymer 2. When turning on the devices, electrons are more easily transferred into the electrode from polymer 4 as a result of this high charge transfer mobility. The carbazole in polymer 4 also plays an important role in stabilizing polymer oxidization. However, this oxidation proceeds through the  $\alpha$  positions of the external heterocyclic rings since the 2, 7, and 9 positions of the carbazole are blocked. The external rings contain a higher electron density and thus result in rapid oxidation.<sup>24</sup>

When the device is turned off, the process is reversed. Electrons flow back from the electrode into the polymer and anions flow from the polymer into the electrolyte. The injection of the smaller electrons from the electrode into the polymer layer is much faster than of the movement of the bulk ions from the electrolyte, leading to a higher turn-off speed.

As shown in Fig. 7a, when positive voltage is applied to devices based on polymer 7a, the polymer switches from a dark teal-green in the neutral state to a pearl blue in the



**Fig.** 7 Spectroelectrochemistry of coordination polymer 7a and 7b films on the ITO-coated glass substrate; UV-vis-NIR absorption spectra were monitored while different potentials were applied to the films: (a) polymer 7a; (b) polymer 7b; a 0 V, b 2.0 V, c 2.25 V, d 2.5 V, e 0 V, f 1.5 V, g 2.0 V, h 2.5 V.



Fig. 8 Switching property of EC devices based on polymers 7a and 7b. (a) polymer 7a; (b) polymer 7b.

oxidized state. The depletion of both of these transitions occurs with a decrease in the absorbance at 600 and 410 nm. The doping-induced infrared absorption bands begin to emerge at intermediate oxidation levels with an absorbance centered at 800 nm and a broad absorbance beginning at 950 nm and extending into the IR (Fig. 7a).

Polymers **7b** and **7c** (see ESI<sup>‡</sup>) exhibit similar EC properties. Decreases in absorbance occur at 473 nm and 390 nm and an increased broad absorbance starts at 800 nm. Unlike polymers **2** and **4**, polymers **7a–c** show significant absorption changes in the IR at low voltage related to their donor–acceptor properties (Fig. 8).

The switching times of polymers 7a and 7b were determined by monitoring the absorption intensity changes at 1100 nm with the applied voltage switching between -2.5 V and 2.5 V. The response time of devices based on polymer 7a is 2 s for turning on and 0.7 s for turning off. The color change time of polymer 7b is much longer, requiring tens of seconds to turn on and several seconds to turn off. This marked difference in behavior probably stems from the introduction of the long side chains in 7b. Polymer 7a has similar charge transfer mobility to that of 4, and also contains the carbazole unit to accelerate ion injection, leading (as described above) to high switching speeds. But while the substitutions on BT in polymers 7b and 7c improved the polymers' solubility (making them readily soluble in common solvents at room temperature), the flexible bulky side-chains evidently disrupt molecular planarity and block the access of anions to the polymer backbone. The low charge transfer mobility of the 7b and 7c also will have a negative effect on switching speed.

#### Conclusion

We have synthesized and investigated the optical properties of a new series of electrochromic polymers. These polymers contain EDOT units and fluorene (2), carbazole (4), carbazolebenzothiadiazole (7a), carbazole-benzothiadiazoles (7b and 7c) formed by cross-linking though the Suzuki reaction. The experimental data reveal that the materials' optical and electrical properties can be tuned by copolymerization with different subunits. The donor-acceptor polymer 7a has the longest maximum absorbance and narrowest band gap. Polymers 4 and 7a exhibit the highest hole mobility at around  $10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, mainly attributable to the enhanced intermolecular packing in the solid state. The much lower hole mobilities of polymers 2, 7b and 7c apparently are due to the bulk steric substitution twisting the polymer backbone, leading to poorer interchain interaction. Polymers 7a-c show significant absorption changes in the IR at lower voltages, reflecting their donor-acceptor structures. Devices based on polymers 4 and 7a can be operated in seconds due to their high charge transfer mobility and ion injection efficiency. Solid-state devices based on polymer 7a offer promise for electrochromic applications in the IR, since its high charge transfer mobility and ion injection efficiency permits relatively rapid switching and good switchable contrast, while their robustness exceeds that of some aqueous devices.

#### Acknowledgements

We gratefully acknowledge support from DARPA through ARO (grant W911NF-08-1-0494), the Army Research

Laboratory (grant W911NF-09-D-0001) and the University of California Discovery Program (IUCRP, grant gcp07-10260).

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