

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/229975267>

Hexyl-Derivatized Poly(3,4-ethylenedioxy-selenophene): Novel Highly Stable Organic Electrochromic Material with High Contrast Ratio, High Coloration Efficiency, and Low-Switching Vo...

ARTICLE in ADVANCED MATERIALS · MAY 2009

Impact Factor: 17.49 · DOI: 10.1002/adma.200802259

CITATIONS

70

READS

59

4 AUTHORS, INCLUDING:



Mao Li

National Institute for Materials Science

40 PUBLICATIONS 1,192 CITATIONS

SEE PROFILE



Asit Patra

National Physical Laboratory - India

33 PUBLICATIONS 772 CITATIONS

SEE PROFILE



Michael Bendikov

Weizmann Institute of Science

106 PUBLICATIONS 4,220 CITATIONS

SEE PROFILE

Hexyl-Derivatized Poly(3,4-ethylenedioxy-selenophene): Novel Highly Stable Organic Electrochromic Material with High Contrast Ratio, High Coloration Efficiency, and Low-Switching Voltage

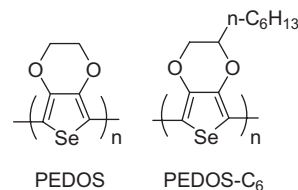
By Mao Li, Asit Patra, Yana Sheynin, and Michael Bendikov*

Currently, there is significant interest in the design of new electrochromic (EC) materials exhibiting a high contrast ratio (a large change in percent transmittance between the colored and bleached states), high coloration efficiency (efficient color changes in response to applied charge) and long-term stability.^[1–4] EC materials could be employed in the fabrication of efficient displays and EC windows if they could be made to exhibit a large change in transmittance upon application of a small charge. While considerable research was performed on inorganic EC materials, better performance has been reported recently using conducting polymers, mostly based on poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives.^[3–10] Conducting polymers offer better processability and better color tunability than their inorganic and molecular counterparts.^[1e,5b,9,11]

PEDOT film can be quite rapidly switched between the absorptive (neutral) and transmissive (doped) states at low switching potentials. The neutral PEDOT film shows a band gap of around 1.6 eV and a light sky blue appearance as a doped film.^[5,12] The coloration efficiency (CE) of PEDOT is 137 cm² C^{−1} at full switch, 183 cm² C^{−1} at 95% of full switch, 206 cm² C^{−1} at 85% of full switch,^[8] and the dibutyl derivative of poly(3,4-propylenedioxythiophene) (PProDOT(Bu)₂)^[13] obtained by Reynolds' group achieves a CE of 1365 cm² C^{−1}, which is currently the highest CE value reported for an electropolymerized EC film measured in liquid electrolyte. The stability of the electrochromic materials is another crucially important feature for practical application. Reynolds' group studied PEDOT, PEDOT-C₈, and PEDOT-C₁₄ films and found that the films retained 65%, 50%, and 62% of their electroactivity after 6000, 9000, and 16000 switching cycles, respectively.^[6d] However, the contrast ratios were less than 65%.^[6d] Kumar's group obtained a dibenzyl poly(3,4-propylenedioxythiophene) (PProDOT-Bz₂) that has the highest known contrast ratio (89%), a CE of 575 cm² C^{−1} and high stability after 5000 switching cycles.^[3] The poly(1,4-bis(2-(3',4'-ethylenedioxy)thienyl)-2-methoxy-5-2''-ethylhexyloxybenzene) (P(BEDOT-MEHB)) reported by Wudl's group has a CE of 680 cm² C^{−1} and also exhibits high stability after 5000 switching cycles, though it has a contrast ratio of only 57%.^[4,14] Catellani et al. reported that poly(3-butylthiophene) can

be cycled 20000 times without significant modification of its optical properties, however, its contrast ratio was low and its coloration efficiency was not reported.^[15]

Recently, our group developed a synthetic method for poly(3,4-ethylenedioxy-selenophene) (PEDOS),^[16] which contains a novel building block for electron-rich π -conjugated polymers. PEDOS has a smaller band gap (~ 1.4 eV) than PEDOT (~ 1.6 eV) and its HOCO (highest occupied crystal orbital) lies 0.1 eV lower than that of PEDOT.^[17]



Here, we report on novel polyselenophenes as EC materials. We find that polyselenophenes are excellent electrochromic materials in terms of their contrast ratios and CEs, while retaining stability and switching time characteristics comparable to those of PEDOT derivatives. In particular, here we find that poly(hexyl-3,4-ethylenedioxy-selenophene) (PEDOS-C₆) has one of the highest reported contrast ratios and CEs while maintaining excellent electrochemical stability and a fast switching time.

In order to evaluate the EC properties of polyselenophenes, the PEDOS films were electrodeposited onto indium-tin-oxide (ITO) coated glass having dimensions of 3.2 cm \times 0.7 cm at a constant potential of 0.93 V versus Ag/AgCl and passing charge of 0.03 C to form a film with a thickness of ~ 100 nm. PEDOS film obtained under these conditions has a band gap of ca. 1.42 eV (873 nm, see Fig. S1) as determined by the onset of the π -to- π^* transition from the UV-vis-NIR spectrum.^[16,18] It also exhibits a high contrast ratio of 55% (see Fig. 1a) at 666 nm (λ_{max}) and a CE of 212 cm² C^{−1}.^[19–21] The measured bleached and colored times are 0.4 s and 0.6 s, respectively (at 95% of the maximum value of the contrast ratio). Both the contrast ratio and the coloration efficiency of PEDOS are better than those of PEDOT,^[8] which has a contrast ratio of 54% and a CE of 137 cm² C^{−1} at full switching.

Introduction of alkyl chains onto the polymer backbone significantly improves the EC properties of PEDOT derivatives, as shown by Reynolds et al.^[6d,g,7–9] Inspired by their work, we have synthesized hexyl-3,4-ethylenedioxy-selenophene (EDOS-C₆). For spectroelectrochemical measurement, EDOS-C₆ was electro-

[*] Dr. M. Bendikov, Dr. M. Li, Dr. A. Patra, Dr. Y. Sheynin
Department of Organic Chemistry, Weizmann Institute of Science
Rehovot 76100 (Israel)
E-mail: michael.bendikov@weizmann.ac.il

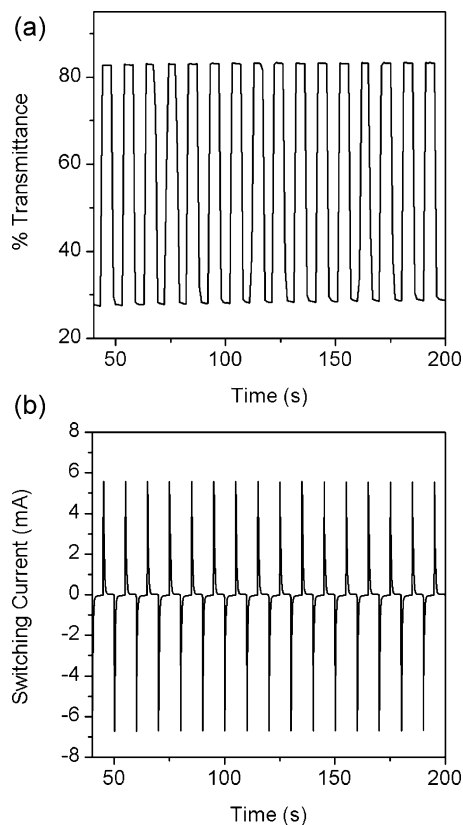


Figure 1. The simultaneous monitoring of a) transmittance and b) switching current for PEDOS film monitored at 666 nm, when it was switched between its neutral (-0.9 V vs. Ag/AgCl) and oxidized ($+0.5$ V vs. Ag/AgCl) states at 5-s intervals.

polymerized onto ITO-coated glass using a constant potential of 0.98 V versus Ag/AgCl in 0.1 M LiBF_4 /propylene carbonate (PC). As shown in Figure 2a, a series of spectra were collected from the resultant PEDOS- C_6 film at various potentials ranging from -0.9 V to 0.5 V. Importantly, PEDOS- C_6 film switches between an absorbing pure-blue neutral state and a highly transmissive nearly colorless oxidized state. At an applied potential of -0.9 V, the neutral form of the polymer shows a distinctive π -to- π^* interband transition that is split into two sharp peaks at 686 nm and 763 nm (λ_{max}) and one shoulder peak at 632 nm. As the applied potential increases, the absorption peaks at 686 nm and 763 nm decrease while the polaron (~ 1100 nm) and bipolaron peaks (that peak in the NIR beyond the limits of the spectrophotometer) increase. As the potential (doping level) increases, the polaron peak reaches a maximum intensity and then begins to decrease, while the bipolaron peak continues to increase.

The band gap (E_g) of PEDOS- C_6 was estimated to be 1.54 eV (805 nm), which is about 0.12 eV higher than for PEDOS. The calculated (PBC/B3LYP/6-31G(d)) band gap for PEDOS- C_6 is 1.64 eV, which is practically identical to the calculated band gap of PEDOS (1.66 eV).^[22,23] So, the observed experimental difference of 0.12 eV between the band gaps of PEDOS and PEDOS- C_6 is a result of the sharper UV spectrum of PEDOS- C_6 relative to PEDOS and not result from different conjugation in polysele-nophene backbone. Indeed, the λ_{max} (666 nm) of PEDOS is very similar to (and at an even shorter wavelength than) the λ_{max} of the

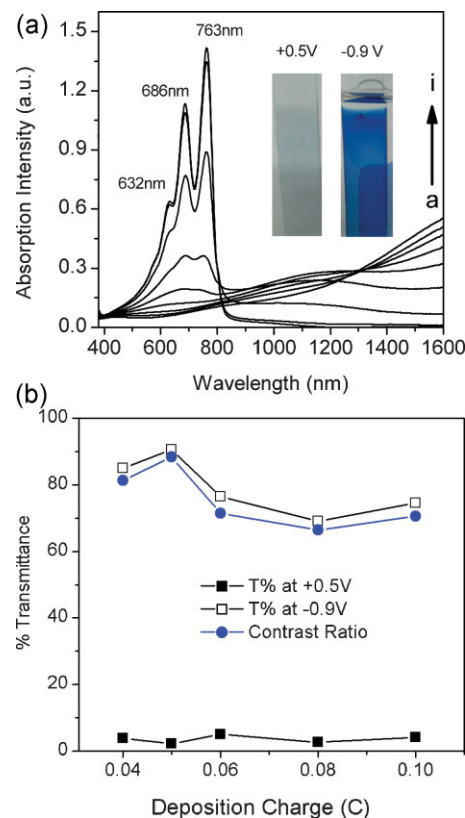


Figure 2. a) Spectroelectrochemical data and photos (inset) for a PEDOS- C_6 film (ca. 100 nm thick) on ITO-coated glass at applied potentials of a) -0.9 , b) -0.7 , c) -0.5 , d) -0.3 , e) -0.1 , f) 0 , g) 0.1 , h) 0.3 , i) 0.5 V versus Ag/AgCl; b) Transmittance values (at 763 nm) of PEDOS- C_6 films on ITO-coated glass as a function of film deposition charge as obtained by switching the voltage between -0.9 V (neutral colored state) and $+0.5$ V versus Ag/AgCl (oxidized bleached state) at 3-s intervals.

second vibronic peak (686 nm) of PEDOS- C_6 . The significantly weaker interaction between the polymer chains in PEDOS- C_6 compared to PEDOS can result in a sharper UV spectrum and lead to observed increase in band gap. The vibronic splitting and sharper UV band can also be attributed to solid-state order of PEDOS- C_6 backbones compared to PEDOS, due to the presence of the alkyl chain, as was suggested for alkyl-substituted PEDOT derivatives.^[6g,9] The low-absorption intensity at 900 – 1600 nm for doped PEDOS- C_6 film compared to doped PEDOS film is also indicative of a weak interaction between PEDOS- C_6 backbones.

PEDOS- C_6 films obtained through electropolymerization (in 0.1 M LiBF_4 /PC on ITO-coated glass) at increasing deposition charges (of 30 , 40 , 50 , 60 , 80 , and 100 mC) at a constant potential of 0.98 V versus Ag/AgCl were switched between -0.9 and 0.5 V versus Ag/AgCl at 3-s intervals. Transmittance values at 763 nm as a function of the film's electropolymerization charge are given in Figure 2b. While the films were switched, the percentage transmittance ($T\%$) at λ_{max} (763 nm) was simultaneously monitored as a function of time (Fig. 3). The highest contrast ratio ($\Delta T\%$) was achieved using a charge of 50 mC. Significantly, PEDOS- C_6 films exhibit an unusual combination of a very high contrast ratio, one and best CEs, a fast switching time and excellent long-term stability. The $\Delta T\%$ of PEDOS- C_6 films achieves a maximum of 88 – 89% (see Fig. 3a and c), which is the

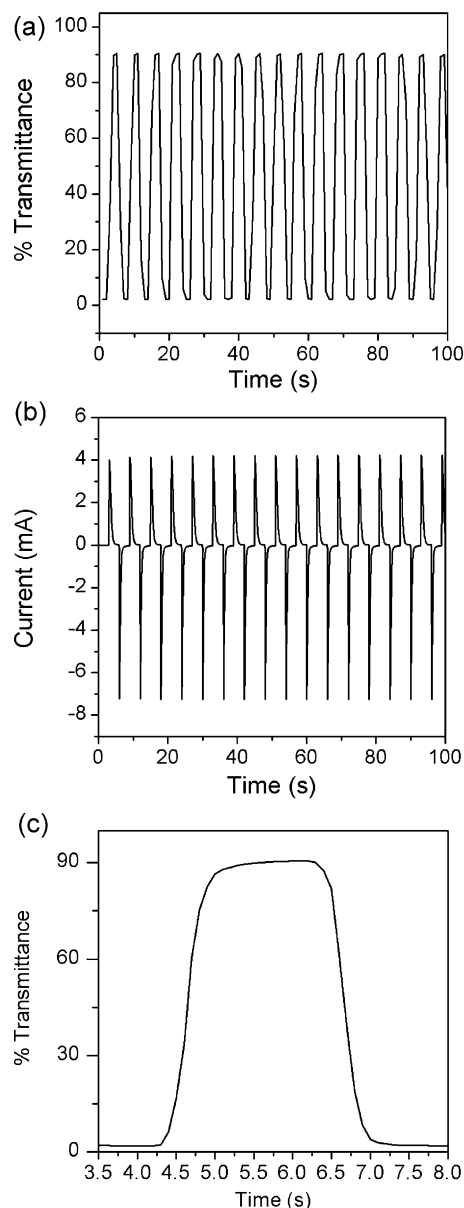


Figure 3. The simultaneous monitoring of a) transmittance monitored at 763 nm and b) current for PEDOS- C_6 film, when it was stepped between its neutral (-0.9 V) and oxidized ($+0.5$ V) states at 3-s intervals; c) Electrochromic switching studies for PEDOS- C_6 film monitored at 763 nm at 2-s intervals (second cycle).

same as the $\Delta T\%$ of PProDOT-Bz $_2$ ^[3] and is the highest reported $\Delta T\%$ for any electrochromic material. The measured switching time is 0.7 s when the contrast ratio reaches 95% of its maximum (Fig. 3c). So, PEDOS- C_6 film has a switching time comparable with the alkyl PEDOT derivatives.^[9] Coloration efficiency is one of most important characteristics of EC materials. The CE value of PEDOS- C_6 on ITO-coated glass in solution, as calculated on the basis of Figure 3a and b, achieves up to $773 \text{ cm}^2 \text{ C}^{-1}$.^[19,21,24,25] Both the contrast ratio and the CE of PEDOS- C_6 are amongst the highest reported, making it a unique electrochromic material. The high CE of PEDOS- C_6 is probably due to the switching voltage for PEDOS and PEDOS- C_6 films lying between -0.9 V

and 0.5 V, while the switching voltage for the PEDOT analogs is usually between -1.0 V and $+1.0$ V.^[3,6d,8,9]

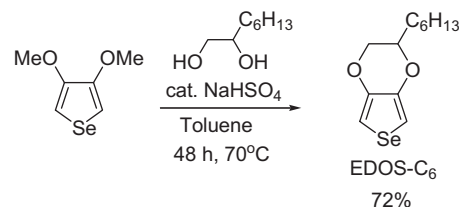
Stability studies for PEDOS- C_6 films were carried out by measuring the contrast ratio as a function of the number of switching cycles for the films on ITO-coated glass in an electrochemical cell that was open to the air without purging inert gas. The contrast ratio remains 48% (55% of its initial value) after 10000 cycles at full switching potentials between -0.9 V and 0.5 V at a 3 s interval, indicating that PEDOS- C_6 film is highly stable. We note that EC lifetimes for EDOS-based practical devices may greatly exceed this measured value due to device construction methods, operating conditions, etc.

In conclusion, we have shown that polyselenophene derivatives exhibit excellent characteristics for EC applications. The electropolymerized PEDOS- C_6 film switches in color between a highly absorbing pure-blue and a nearly colorless states, has a high contrast ratio of 88–89%, a high CE of up to $773 \text{ cm}^2 \text{ C}^{-1}$ and a fast switching time at a low switching voltage of -0.9 to 0.5 V versus Ag/AgCl, with this switching range being smaller than that of PEDOT and its derivatives. PEDOS- C_6 films show remarkable stability, with the contrast ratio remaining at 48% after 10000 cycles. Applications of other PEDOS derivatives as EC materials are currently being investigated in our laboratory.

Experimental

The synthesis of EDOS was reported earlier [16].

Synthesis of EDOS- C_6 :



A mixture of 3,4-dimethoxyselenophene (250 mg, 1.31 mmol) [16], 1,2-octanediol (400 mg, 2.74 mmol, racemic) and a catalytic amount of NaHSO_4 (50 mg) in dry toluene (35 mL) was stirred for 48 h at 70°C . The completion of the reaction was monitored by thin layer chromatography (TLC). Toluene was removed under reduced pressure and the residue was diluted with water (50 mL). The mixture was extracted with hexane (3×50 mL). The combined organic layers were washed with H_2O , brine, dried (MgSO_4), and then concentrated. Purification of the crude residue by chromatography on silica gel (60–230 mesh; hexanes as eluent) gave EDOS- C_6 (255 mg, 72%) as a colorless liquid. ^1H NMR (250 MHz, CDCl_3 , δ): 6.76 (s, 2H), 4.04–4.14 (m, 2H), 3.84 (dd, $J = 11.7$ Hz, 8.5 Hz, 1H), 1.48–1.71 (m, 2H); 1.24–1.42 (m, 8H), 0.89 (t, $J = 6.5$ Hz, 3H); ^{13}C NMR (62.5 MHz, CDCl_3 , δ): 143.1, 142.6, 101.2, 101.1, 73.4, 68.0, 31.6, 30.6, 29.1, 24.9, 22.5, 14.0; HRMS (Electrospray, $\text{EDOS-}C_6\text{H}^+$): calcd for $\text{C}_{12}\text{H}_{19}\text{O}_2\text{Se}$, 275.0551; found, 275.0550; EA: Anal. calcd for $\text{C}_{12}\text{H}_{18}\text{O}_2\text{Se}$: C 52.75, H 6.64; found: C 53.22, H 6.78.

Electrochemistry: Electropolymerization was carried out with a Princeton Applied Research VF263A potentiostat, employing an ITO-coated glass as the working electrode ($7 \text{ mm} \times 50 \text{ mm} \times 0.7 \text{ mm}$, $R_s \leq 12 \text{ } \Omega \square^{-1}$, Delta Technologies Inc.), a gold flag as the counter electrode, and Ag/AgCl as the reference electrode (an AgCl coated Ag wire was directly dipped in electrolyte solution [26], the $E_{1/2}$ of the Fc/Fc^+ couple is 0.24 V versus Ag/AgCl under these conditions). The electrolyte used was 0.1 M LiBF_4 in PC. PEDOS and PEDOS- C_6 films were prepared on ITO-coated glass ($7 \text{ mm} \times 32 \text{ mm}$) at constant potentials of 0.93 V and 0.98 V versus Ag/AgCl, respectively. Before examining the optical properties of PEDOS and

PEDOS-C₆ films, the films were rinsed with acetonitrile after electropolymerization and placed into a quartz cell for subsequent UV-vis-NIR experiments. The solution was bubbled with nitrogen to remove any incipient oxygen. UV-vis-NIR spectra were recorded on a V-570 JASCO UV-vis-NIR spectrophotometer. A three-electrode cell assembly was used for all electrochemical experiments. The working electrode was ITO-coated glass, the counter electrode was a platinum wire, and Ag/AgCl was used as the pseudo-reference electrode. The thickness of the films was measured by a Dektak 6M Manual Veeco Instrument.

Acknowledgements

We thank Prof. D. F. Perepichka (McGill University) for helpful discussions and Mr. Yair Haim Wijsboom and Ms. Natalia Zamoshchik (Weizmann Institute) for their assistance. We thank the Israel Science Foundation, the BARD Research and Development Fund and the Helen and Martin Kimmel Center for Molecular Design for financial support. M.B. is the incumbent of the Recanati career development chair, a member *ad personam* of the Lise Meitner-Minerva Center for Computational Quantum Chemistry and acknowledges support from a DuPont Young Professor Award. Supporting Information is available online from Wiley InterScience or from the author and includes the spectroelectrochemistry of PEDOS and computational details.

Received: August 4, 2008

Published online: February 6, 2009

- [1] a) P. M. S. Monk, R. J. Mortimer, D. R. Rosseinsky, in *Electrochromism: Fundamentals and Applications*, Wiley-VCH, Weinheim, Germany **1995**. b) A. L. Dyer, J. R. Reynolds, in *Handbook of Conducting Polymers. Conjugated Polymers: Theory, Synthesis, Properties, and Characterization*, 3rd ed. (Eds: T. A. Skotheim, J. R. Reynolds), CRC Press, Boca Raton, FL, USA **2007**, Ch. 20. c) R. J. Mortimer, *Chem. Soc. Rev.* **1997**, 26, 147. d) D. R. Rosseinsky, R. J. Mortimer, *Adv. Mater.* **2001**, 13, 783. e) K. Bange, T. Bamble, *Adv. Mater.* **1990**, 2, 10.
- [2] a) A. A. Argun, A. Cirpan, J. R. Reynolds, *Adv. Mater.* **2003**, 15, 1338. b) S. I. Cho, W. J. Kwon, S. Choi, P. Kim, S. Park, J. Kim, S. J. Son, R. Xiao, S. Kim, S. B. Lee, *Adv. Mater.* **2005**, 17, 171. c) H. Meng, D. Tucker, S. Chaffins, Y. Chen, R. Helgeson, B. Dunn, F. Wudl, *Adv. Mater.* **2003**, 15, 146. d) A. L. Dyer, C. R. G. Grenier, J. R. Reynolds, *Adv. Funct. Mater.* **2007**, 17, 1480. e) D. M. DeLongchamp, M. Kastantin, P. T. Hammond, *Chem. Mater.* **2003**, 15, 1575.
- [3] K. Krishnamoorthy, A. V. Ambade, M. Kanungo, A. Q. Contractor, A. J. Kumar, *J. Mater. Chem.* **2001**, 11, 2909.
- [4] a) G. Sonmez, H. Meng, F. Wudl, *Chem. Mater.* **2004**, 16, 574. b) G. Sonmez, H. Meng, Q. Zhang, F. Wudl, *Adv. Funct. Mater.* **2003**, 13, 726.
- [5] a) L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, J. R. Reynolds, *Adv. Mater.* **2000**, 12, 481. b) L. Groenendaal, G. Zotti, P. H. Aubert, S. M. Waybright, J. R. Reynolds, *Adv. Mater.* **2003**, 15, 855.
- [6] a) G. Heywang, F. Jonas, *Adv. Mater.* **1992**, 4, 116. b) G. A. Sotzing, J. R. Reynolds, P. J. Steel, *Adv. Mater.* **1997**, 9, 795. c) H. W. Heuer, R. Wehrmann, S. Kirchmeyer, *Adv. Funct. Mater.* **2002**, 12, 89. d) B. Sankaran, J. R. Reynolds, *Macromolecules* **1997**, 30, 2582. e) I. Schwendeman, C. L. Gaupp, J. M. Hancock, L. Groenendaal, J. R. Reynolds, *Adv. Funct. Mater.* **2003**, 13, 541. f) C. Wang, J. L. Schindler, C. R. Kannewurf, M. G. Kanatzidis, *Chem. Mater.* **1995**, 7, 58. g) D. M. Welsh, A. Kumar, E. W. Meijer, J. R. Reynolds, *Adv. Mater.* **1999**, 11, 1379. h) D. M. Welsh, L. J. Kleppner, L. Madrigal, M. R. Pinto, B. C. Thompson, K. S. Schanze, K. A. Abboud, D. Powell, J. R. Reynolds, *Macromolecules* **2002**, 35, 6517. i) B. D. Reeves, B. C. Thompson, K. A. Abboud, B. E. Smart, J. R. Reynolds, *Adv. Mater.* **2002**, 14, 717.
- [7] C. L. Gaupp, D. M. Welsh, J. R. Reynolds, *Macromol. Rapid Commun.* **2002**, 23, 885.
- [8] G. L. Gaupp, D. M. Welsh, R. D. Rauh, J. R. Reynolds, *Chem. Mater.* **2002**, 14, 3964.
- [9] A. Kumar, D. M. Welsh, M. C. Morvant, F. Piroux, K. A. Abboud, J. R. Reynolds, *Chem. Mater.* **1998**, 10, 896.
- [10] Recently, a fast switching, dual color non-PEDOT type polythiophene with a coloration efficiency of 381 cm² C⁻¹ at 95% of a full switch was reported by Skabara's group. R. Berridge, S. P. Wright, P. J. Skabara, A. Dyer, T. Steckler, A. A. Argun, J. R. Reynolds, R. W. Harrington, W. Clegg, *J. Mater. Chem.* **2007**, 17, 225.
- [11] a) S. A. Sapp, G. A. Sotzing, J. R. Reynolds, *Chem. Mater.* **1998**, 10, 2101. b) G. Sonmez, H. B. Sonmez, K. F. Shen, R. W. Jost, Y. Rubin, F. Wudl, *Macromolecules* **2005**, 38, 669. c) I. Schwendeman, R. Hickman, G. Sonmez, P. Schottland, K. Zong, D. M. Welsh, J. R. Reynolds, *Chem. Mater.* **2002**, 14, 3118.
- [12] a) Q. Pei, G. Zuccarello, M. Ahlsgog, O. Inganäs, *Polymer* **1994**, 35, 1347. b) M. Dietrich, J. Heinze, G. Heywang, F. Jonas, *J. Electroanal. Chem.* **1994**, 369, 87. c) J. C. Gustafsson, B. Liedberg, O. Inganäs, *Solid State Ionics* **1994**, 69, 145.
- [13] B. D. Reeves, C. R. G. Grenier, A. A. Argun, A. Cirpan, T. D. McCarley, J. R. Reynolds, *Macromolecules* **2004**, 37, 7559.
- [14] Recently, a contrast ratio of 60% and a CE of 932 cm² C⁻¹ were obtained by spin-coating a solution processable conducting polymer: C. G. Wu, M. I. Lu, S. J. Chang, C. S. Wei, *Adv. Funct. Mater.* **2007**, 17, 1063.
- [15] M. Catellani, C. Arbizzani, M. Mastragostino, A. Zanelli, *Synth. Met.* **1995**, 69, 373.
- [16] A. Patra, Y. H. Wijsboom, S. S. Zade, M. Li, Y. Sheynin, G. Leitun, M. Bendikov, *J. Am. Chem. Soc.* **2008**, 130, 6734.
- [17] The calculated (PBC/B3LYP/6-31G(d)) HOCO and LUCO levels for PEDOS at k = 0 are -3.45 eV and -1.79 eV, respectively. For comparison, the HOCO and LUCO levels of PEDOT at k = 0 are -3.54 eV and -1.69 eV, respectively (ref. 16).
- [18] We note that LiBF₄ in propylene carbonate (PC) was used as a supporting electrolyte, and the PEDOS film was obtained using a constant potential mode in PC, while in reference [16], LiClO₄ was used as a supporting electrolyte in acetonitrile and the polymer was obtained by cyclic voltammetry.
- [19] T_b = 82.5, T_c = 27.6 and Q_d = 2.25 mC cm⁻² based on the data in Figure 1.
- [20] The CE (in units of cm² C⁻¹) at a specified wavelength is expressed as CE(λ) = ΔOD/Q_d, ΔOD = log[T_b(λ)/T_c(λ)] where Q_d is the injected/ejected charge density (in units of C cm⁻²), OD is an optical density, and T_b and T_c are the transmittance in the bleached and colored states, respectively. For more details, see ref. [1a,e].
- [21] All CE values reported in this paper were measured at 100% of a full switch, which corresponds to the highest contrast ratio. We note that even higher CE values can be obtained by narrowing the switching potential window; however the contrast ratio will be compromised. See ref. [8] for details.
- [22] All Calculations were performed using the Gaussian 03 program. *Gaussian 03, Revision C.02*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski,

- P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, USA 2004. See Supporting Information for details.
- [23] The calculated (PBC/B3LYP/6-31G(d)) HOCO and LUCO levels for PEDOS-C₆ at $k=0$ are -3.30 eV and -1.67 eV, respectively. For comparison, the HOCO and LUCO levels of PEDOT-C₆ at $k=0$ are -3.38 eV and -1.55 eV, respectively.
- [24] $T_b\% = 90.4$, $T_c\% = 2.23$ and $Q_d = 2.08$ mC cm⁻² based on the data in Figure 3a and b.
- [25] A coloration efficiency of $686\text{--}773$ cm² C⁻¹ was routinely obtained in several experiments.
- [26] F. Yalcinkaya, E. T. Powner, *Med. Eng. Phys.* **1997**, *19*, 299.
-