Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Side-Chain Engineering of Green Color Electrochromic Polymer Materials: Toward Adaptive Camouflage Application

Hongtao Yu,[a,+] Shan Shao,[a,+] Lijia Yan,[b] Hong Meng,*[,a,b] Yaowu He,[a] Chao Yao,[a] Panpan Xu,[a] Xiaotao Zhang,[c,d] Wenping Hu,[c] Wei Huang,*[,b]

Fabrication. Acetonitrile (ACN), dichloromethane (DCM), toluene (TOL), Propylene carbonate (PC), polymethyl methacrylate (PMMA) and other chemicals were purchased from Aldrich. 2,3-Bis(3-methoxyphenyl)-5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline (G1),[1] 2,3-Bis(3,4-bis(decyloxy)phenyl)-5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline (G2),[2] and 2,3-Bis(3,4-bis((2-octyldodecyl)oxy)phenyl)-5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline (G3)[2] were synthesized according to the reported methods. ACN and DCM were dried and distilled over calcium hydride under nitrogen. All electrochemical studies were accomplished with a CHI620E electrochemical workstation. Electropolymerizations (PG1, PG2 and PG3) were performed in a three-electrode cell that consisted of a platinum button or ITO-coated glass as the working electrode, a platinum wire as the counter electrode, and a Ag wire as the pseudo-reference electrode. Electrodeposition was performed from a 0.1 M of $TBAPF_6$ in DCM or in a mixture of DCM and ACN (50/50, v:v) system at a scan rate 100 mV s^{-1} for 15 cycles. Cyclic voltammograms of the polymers were obtained using the same electrode setup using monomer-free ACN solution with 0.1 M $TBAPF_6$. UV Vis-NIR spectra were recorded on a Shimadzu UV-2600 spectrophotometer at a scan rate of 2000 nm min^{-1}. A three-electrode cell was utilized that consisted of a silver wire reference electrode, a Pt wire counter electrode, and an ITO-coated glass working electrode. The potentials were controlled using a CHI620E electrochemical workstation. Colorimetry measurements were achieved with a Minolta CS-100A Chroma Meter with a 0/0 (normal/normal) viewing geometry as recommended by CIE. The sample was illuminated from behind by a D50 (5000 K) light source in a light booth specially designed to exclude external light and to illuminate from behind.

2,3-Bis(3-methoxyphenyl)-5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline (G1): ^{1}H-NMR (300M, $CDCl_3$): δ[ppm] 8.59 (s, 2H), 7.73 (d, 4H), 6.92 (d, 4H), 6.56 (d, 2H), 4.36 (d, 8H), 3.86 (s, 6H) ^{13}C-NMR (300 M, $CDCl_3$): δ 160.13, 150.19, 141.29, 131.92, 113.58, 102.90, 99.94, 64.93, 64.89, 55.23 [ppm]. MS (*m/z*): 621 [M^+].

2,3-Bis(3,4-bis(decyloxy)phenyl)-5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline (G2): ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS, d): 0.88 (t, 12H, J = 6.0 Hz), 1.1-1.4 (m, 72 H), 1.75-1.86 (m, 8H), 3.94 (t, 4H, J = 6.0 Hz), 4.02 (t, 4H, J = 6.0 Hz), 4.30 (m, 4H), 4.39 (m, 4H), 6.05 (s, 2H), 6.81 (d, 2H, J = 9 Hz), 7.28 (d, 2H, J = 3 Hz), 7.48 (s, 2H), 8.58 (s, 2H). 13C NMR (300 MHz, 25 °C, TMS, $CDCl_3$, d): 14.09, 22.66, 26.01, 26.05, 29.12, 29.20, 29.35, 29.42, 29.44, 29.62, 29.68, 31.90, 64.30, 64.89, 69.00, 69.09, 76.55, 76.98, 77.40, 102.64, 112.57, 113.36, 115.63, 123.49, 127.55, 128.31, 131.24, 136.65, 140.19, 141.35, 148.50, 149.76, 150.21. MS (*m/z*): 1298.8 [M^+].

2,3-Bis(3,4-bis((2-octyldodecyl)oxy)phenyl)-5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline (G3): ^{1}H NMR (400 MHz, $CDCl_3$): d (ppm) 0.86-0.88 (m, J = 6 Hz, 24H), 1.25-1.54 (m, 128 H), 1.76-1.83 (m, 4H), 3.84-3.87 (m, 8H, J = 6.0 Hz), 4.31 (m, 4H), 4.40 (m, 4H),6.48 (s, 2H), 6.79 (d, 2H, J = 9 Hz), 7.19 (d, 2H, J =3 Hz), 7.60 (d, 2H，J =3 Hz), 8.58 (s, 2H). ^{13}C NMR (300 MHz, $CDCl_3$): d (ppm) 14.08, 22.67, 26.87, 26.05, 29.34, 29.36, 29.38, 29.44, 29.66, 29.68, 29.71, 29.74, 29.79, 31.91, 64.29, 64.90, 71.76, 71.90, 76.55, 76.97, 77.39, 102.59, 112.38, 113.40, 115.68, 123.40, 127.45, 128.28, 131.17, 136.61, 140.17, 141.36, 149.14, 150.19, 150.27. MS (*m/z*): 1748.1 (M^+)

Polymerization.[3] Poly(2,3-bis(3-methoxyphenyl)-5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline) (PG1); Poly(2,3-bis(3,4-bis(decyloxy)phenyl)-5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline) (PG2); Poly(2,3-bis(3,4-bis((2-octyldodecyl)oxy)phenyl)-5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline) (PG3). A solution of G1, G2 and G3 (3.15 g, 0.01 M) dissolved in dry chloroform (50 mL) was added (via syringe) under an argon atmosphere to a suspension of $FeCl_3$ (6.48 g, 0.04 M) in 100 mL of chloroform at room temperature. The polymerization started immediately with the appearance of a brown-black color. The reaction mixture was stirred at room temperature for 24 h and then heated to 50 °C for a further 24 h. After cooling to room temperature, the mixture was poured into 400 mL of methanol. The precipitated black polymer was isolated by centrifugation.

Poly(2,3-bis(3,4-bis((2-octyldodecyl)oxy)phenyl)-5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline) (PG3): ^{1}H NMR (400 MHz, $CDCl_3$): d (ppm) 2.17-0.44 (m, 84H), 4.69-3.46 (m, 16H), 6.83 (s, 2H), 7.26 (s, 4H), 8.68 (s, 2H).

Device Assembly. Conductive cloth electrodes were used as-cut from large Ag woven cloth (composed by fiber (55%), Ni (15%), Cu (15%) and Ag (15%)). A gel electrolyte comprising 0.3 g of $LiCLO_4$, 2 g of PC, 7 g of ACN, and 0.7 g of PMMA was used for all devices. The clothes for working electrodes were spray-coated with PG3 polymer from toluene or dichloromethane using OW-130 spray coater. A fiberglass separator soaked with a gel electrolyte was placed between the working and counter cloth electrodes. The measurements are done before the solvents of gel electrolyte was evaporated totally.

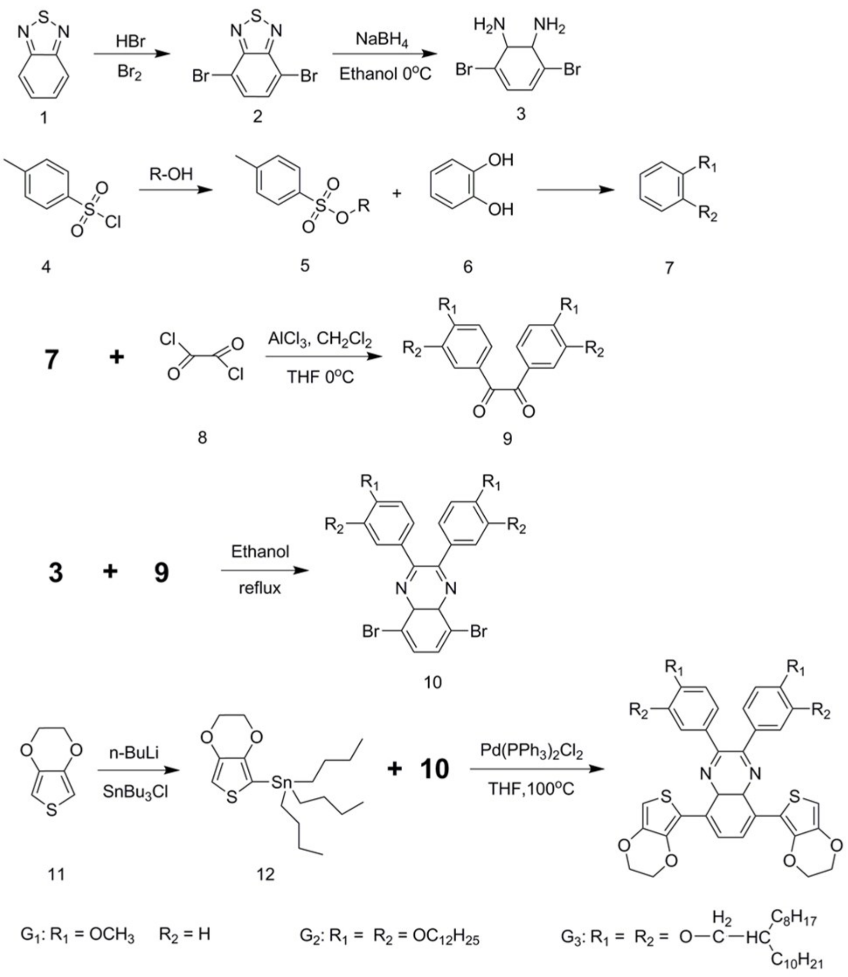

Figure S1. Synthesis of G1, G2 and G3.

Table 1. The solubility of G1, G2 and G3 monomer in common solvents

	G1	G2	G3
Acetonitrile	S	InS	InS
Ethanol	InS	InS	InS
Acetone	S	S	S
DMSO	S	InS	InS
DMF	S	S	S
$CHCl_3$	S	S	S
PC	S	InS	InS
DCM	S	S	S
Toluene	S	S	S

(S = Soluble; InS = Insoluble)

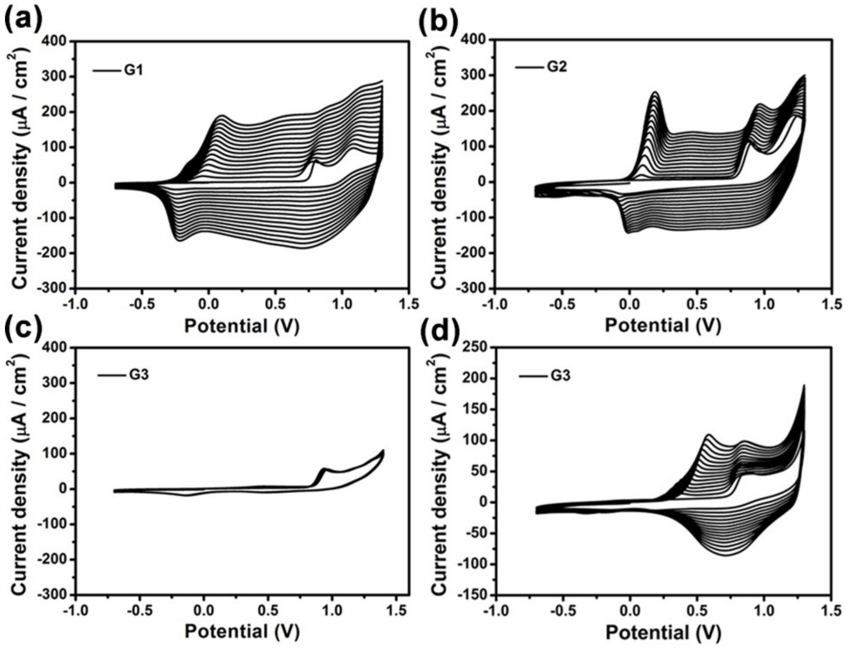

Figure S2. (a) (b) (c) Repeated potential scan electropolymerization of G1, G2 and G3 in 0.1 M $TBAPF_6$/DMC at 100 mV s^{-1} on a Pt electrode; (d) G3 in 0.1 M $TBAPF_6$/DMC/ACN (V:V = 1:1) at 100 mV s^{-1} on a Pt electrode.

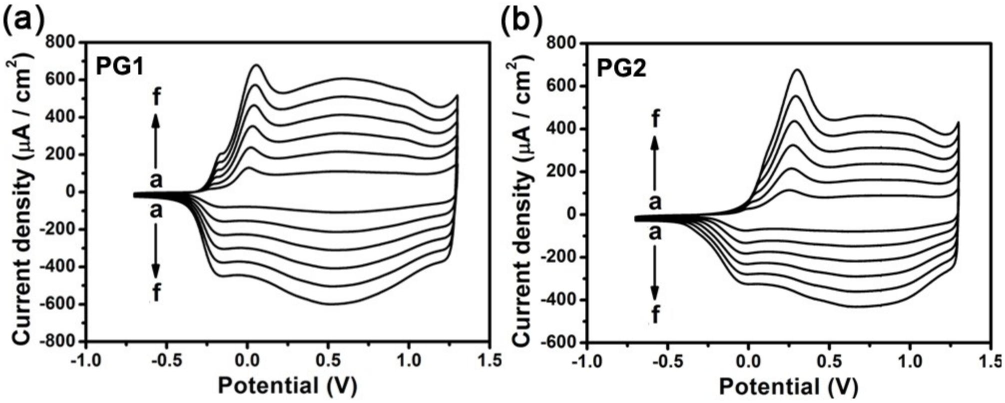

Figure S3. (a) (b) Scan rate dependence of PG1, and PG2 film in 0.1 M TBAPF$_6$/ACN at a) 50, b) 100, c) 150, d) 200, e) 250 and f) 300 mV/s, respectively.

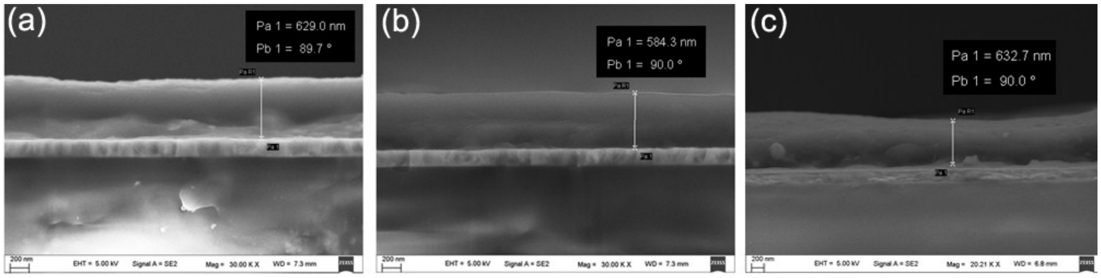

Figure S4. (a) (b) (c) SEM images of PG1, PG2 and PG3 on an ITO substrate. PG1 and PG2 are coated by potentiodynamic method and PG3 by the spray-coating method.

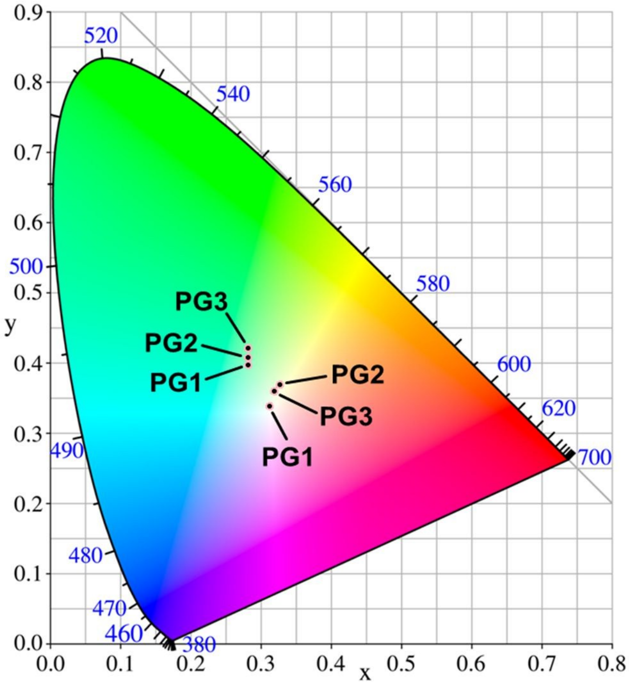

Figure S5. Representation of the hue and saturation *x-y* track for PG1, PG2 and PG3 film at their fully neutral and oxidized state.

Movie S1. Water droplets on PG3 modified surface of a rough paper by spray-coating.

Movie S2. Reversible change of electrochromic letters in the fully neutral (-1.5 V) and oxidized state (+1.5 V).

Movie S3. Reversible change of electrochromic fabric device in the fully neutral (-1.5 V) and oxidized state (+1.5 V).

Movie S4. Reversible change of chameleonic electrochromic device between the green (-2.0 V for half pieces) and sand color (+2.0 V for half pieces).

References:

(1) G. E. Gunbas, A. Durmus, L. Toppare. Could Green be Greener? Novel Donor–Acceptor-Type Electrochromic Polymers: Towards Excellent Neutral Green Materials with Exceptional Transmissive Oxidized States for Completion of RGB Color Space. *Advanced Materials* **2008**, *20*, 691.

(2) G. E. Gunbas, A. Durmus, L. Toppare. A Unique Processable Green Polymer with a Transmissive Oxidized State for Realization of Potential RGB-Based Electrochromic Device Applications. *Advanced Functional Materials* **2008**, *18*, 2026.

(3) H. Meng, F. Wudl. A Robust Low Band Gap Processable n-Type Conducting Polymer Based on Poly (isothianaphthene). *Macromolecules* **2001**, *34*, 1810.