

Supporting Information

Furan and Benzochalcogenodiazole Based Multichromic Polymers via Donor-Acceptor Approach

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Experimental

Reagents, materials and instrumentations

Toluene was refluxed over CaH₂ during 1 h and then distilled over CaH₂ for the synthesis of the monomers. For the purification of monomers, thin layer chromatography (TLC) and column chromatography techniques were used. For this aim, TLC aluminum sheets (Merck, 20x20, Silica gel 60 F₂₅₄) and silica gel (SiO₂) (Acros, 0.060-0.200 mm, 60 A^o) were used. 2-(tributylstannyl)furan (Sigma-Aldrich), 4,7-dibromobenzo[c]-1,2,5-thiadiazole (Sigma-Aldrich), 4,7-dibromobenzo[c]-1,2,5-selenadiazole (Sigma-Aldrich), dichlorobis(triphenylphosphine)palladium (II) (Pd(PPh₃)₂Cl₂) (Aldrich, ≥99 %) were used without further purification methods.

For electrochemical synthesis and analysis, tetrabutylammonium hexafluorophosphate (TBAH) (Fluka, ≥98 %), the supporting electrolyte, was used without further purification. Acetonitrile (ACN) (Merck) was refluxed over CaH₂ (Acros, ≥99 %) during 1 h and then distilled over CaH₂ via simple distillation method.

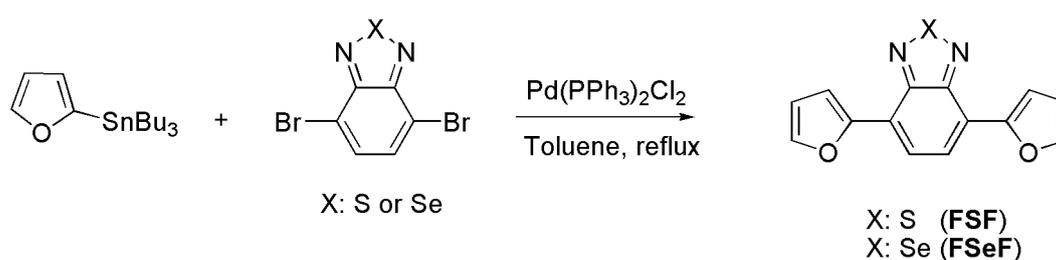
Polished platinum disc (electrode area: 0.02 cm^2) and platinum wire electrodes were used as working (WE) and counter electrodes (CE), respectively. As well as a silver wire was used as a pseudo-reference electrode (calibrated externally using 1.5 mM solution of ferrocene/ferrocenium couple, ferrocene exhibit an oxidation peak at 0.610 mV) or Ag/AgCl (ferrocene exhibits an oxidation peak at 0.496 mV with an onset potential of oxidation at 0.362 V) in 1.0 M NaCl reference electrode. In order to carry out electro-optical analysis, indium tin oxide coated quartz glass slide (ITO, Delta Tech. $8\text{-}12 \ \Omega$, $0.7 \text{ cm} \times 5 \text{ cm}$) was used as WE as well as a platinum wire as CE and a Ag wire as a pseudo-reference electrode. Repetitive cycling or constant potential electrolysis was used to obtain the polymer films. In endeavors to equilibrate the redox behavior of the polymer film, that is, to break-in the film, and to obtain reproducible results, the coated polymer films were switched between their neutral and oxidized states several times before electroanalytical and optical studies. Electrolytic solution was purged with Ar gas to eliminate the degradative effect of O_2 during the cathodic scan of the monomers and polymers. Stability tests were carried out under air atmosphere and the system was not sealed (sealing would further increase the long-term stability of the material upon cycling) in order to show both operational stability and environmental robustness under ambient conditions. The HOMO and LUMO levels are calculated from the onset potentials of oxidation and reduction with respect to the energy level of ferrocene/ferrocenium couple, which was taken as -4.8 eV below the vacuum level.

Electroanalytical measurements were performed using a Gamry PCI4/300 potentiostat-galvanostat. The electro-optical spectra were monitored on a Hewlett-Packard 8453A diode array spectrometer. FTIR spectra were recorded on Nicolet 510 FT-IR with attenuated total reflectance. High resolution mass spectrometry analysis of the monomer was done using a Water Synapt HRMS instrument. ^1H and ^{13}C NMR analysis were done via Bruker Spectrospin

Avance DPX-400 Spectrometer at 400 MHz and chemical shifts were given relative to tetramethylsilane as the internal standard. Calorimetric measurements were recorded on Specord S 600 (standart illuminator D65, field of with 10° observer), color space were given by (CIE) Luminance (L), hue (a) and intensity (b). Platinum cobalt DIN ISO 621, iodine DIN EN 1557 and Gardner DIN ISO 6430 are the references of colorimetric measurements.

Synthesis of the monomers

4,7-Dibromobenzo[c]-1,2,5-selenadiazole or 4,7-dibromobenzo[c]-1,2,5-thiadiazole (0.735 mmol), 2-(tributylstannyl)furan (0.294 mmol) and bis(triphenylphosphine) palladium(II)dichloride (0.0588 mmol) which is used as catalyst were dissolved in toluene (Scheme S1). The reaction mixture was refluxed for 4 h at 110 °C under inert atmosphere and monitored by TLC. After removal of the solvent by evaporation, the residue was dissolved in dichloromethane and extracted with water. The organic extract was dried over MgSO₄ and the solvent was evaporated under reduced pressure. Column chromatography on silica gel was performed to obtain 4,7-di(furan-2-yl)benzo[c][1,2,5]selenadiazole (**FSeF**) or 4,7-di(furan-2-yl)benzo[c][1,2,5]thiadiazole (**FSF**).



Scheme S1. Synthesis reactions of monomers **FSF** and **FSeF**.

FSeF: ¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.86 (s, 2H), 7.58 (d, J= 3.2 Hz, 2H), 7.48 (d, J= 2.0 Hz, 2H), 6.53 (dd, J= 1.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃, δ, ppm): 156.91, 150.48, 142.61, 123.92, 123.24, 112.76, 112.48; FTIR (ATR, cm⁻¹): 3144, 2925, 1728, 1603, 1522,

1478, 1356, 1263, 1078, 1016, 940, 882, 797, 725; MS: $m/z = 315.98$ (Calculated) and 316.00 (Found).

FSF: ^1H NMR (400 MHz, CDCl_3 , δ , ppm): 7.99 (s, 2H), 7.62 (d, $J = 2.8$ Hz, 2H), 7.52 (d, $J = 0.8$ Hz, 2H), 6.57 (dd, $J = 1.6$ Hz, 2H), ^{13}C NMR (100 MHz, CDCl_3 , δ , ppm): 151.34, 150.16, 142.82, 123.54, 121.81, 112.49, 112.17; FTIR (ATR, cm^{-1}): 3150, 2922, 2857, 2172, 2038, 1979, 1469, 1260, 1078, 1012, 944, 800, 719; MS: $m/z = 268.03$ (Calculated) and 268.00 (Found).

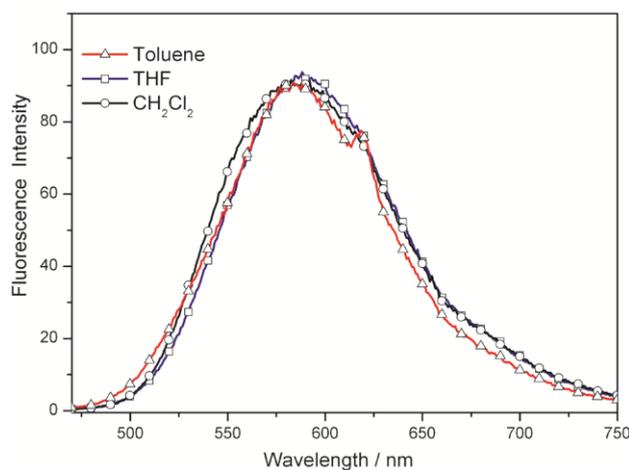


Figure S1. Emission spectra of **FSF** in toluene, THF and CH_2Cl_2 .

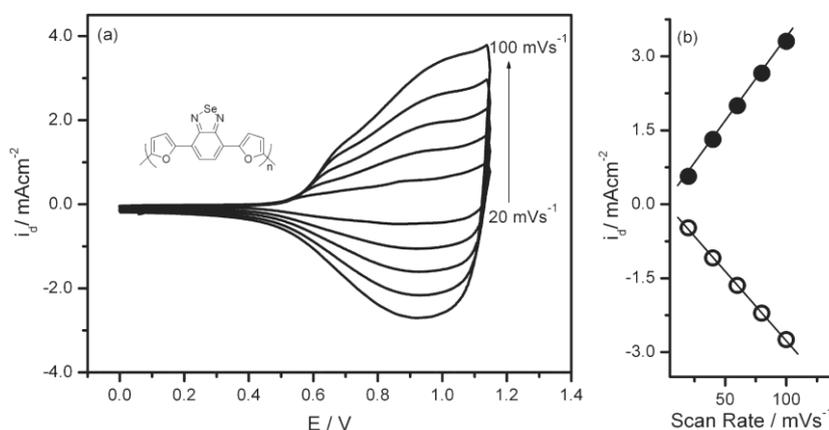


Figure S2. (a) Scan rate dependence of **PFSeF** film on a Pt disk electrode in 0.1 M TBAH/ACN at different scan rates between 20 mV/s and 100 mV/s with an increment of 20 mV/s. (b) Relationship of anodic and cathodic peak currents as a function of scan rate between neutral and oxidized states of **PFSeF** film in 0.1M TBAH/ACN.

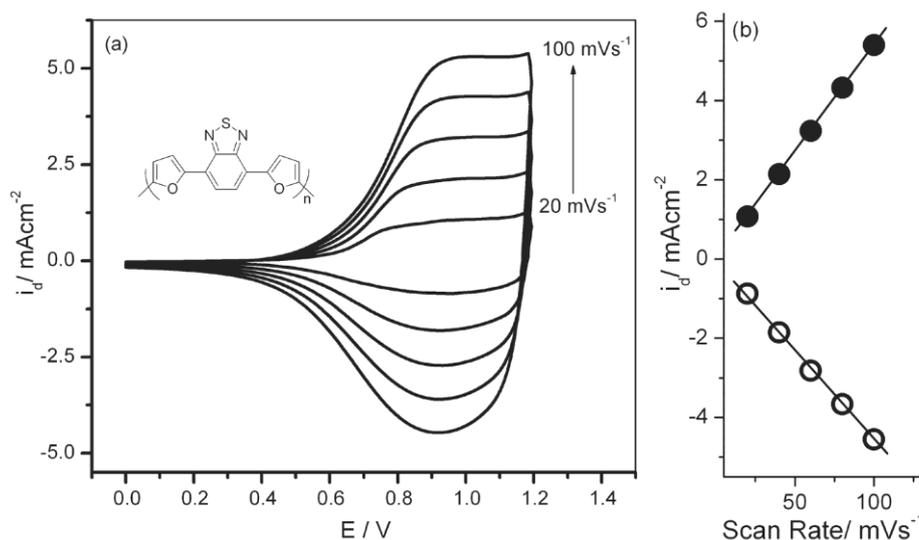


Figure S3. (a) Scan rate dependence of **PFSF** film on a Pt disk electrode in 0.1 M TBAH/ACN at different scan rates between 20 mV/s and 100 mV/s with an increment of 20 mV/s. (b) Relationship of anodic and cathodic peak currents as a function of scan rate between neutral and oxidized states of **PFSF** film in 0.1M TBAH/ACN.

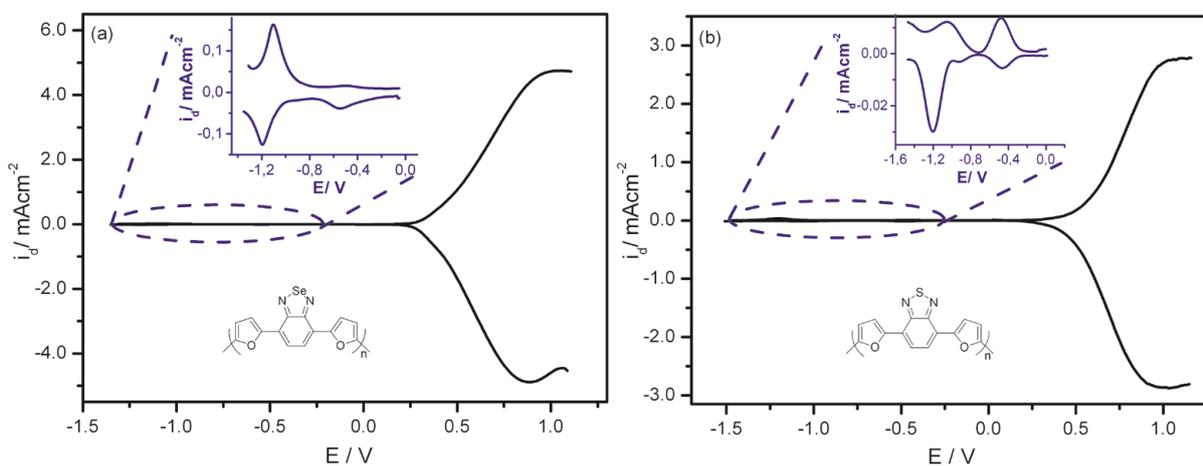


Figure S4. DPV of n- and p-doped (a) **PFSeF** and (b) **PFsF** films in 0.1 M TBAH/ACN.

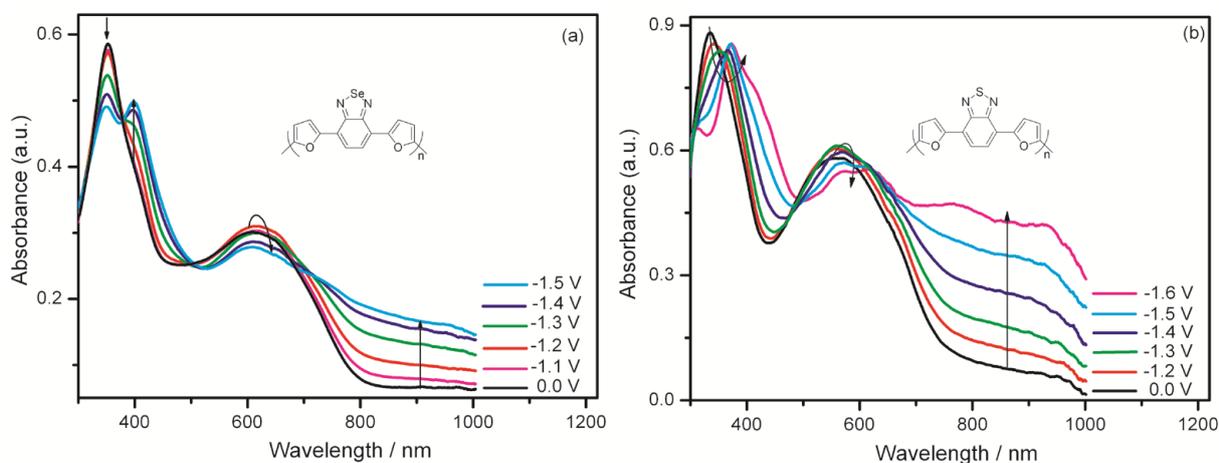


Figure S5. Electronic absorption spectra of the (a) **PFSeF** and (b) **PFsF** on ITO in 0.1 M TBAH/ACN at various applied potentials along the cathodic region.

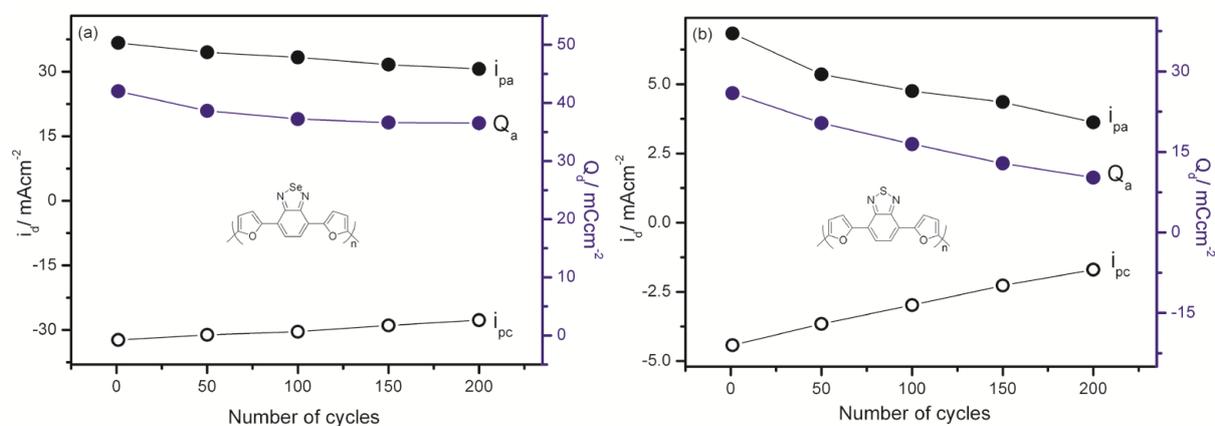


Figure S6. Stability test for (a) **PFSeF** and (b) **PFsF** films in 0.1 M TBAH/ACN at a scan rate of 100 mVs⁻¹ under ambient conditions by cyclic voltammetry as a function of the number of cycles: Q_a (anodic charge stored), I_{pa} (anodic peak current), I_{pc} (cathodic peak current).