Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Side Chain effect on the electrochemical and optical properties of thieno[3,4-c]pyrrole-4,6-dione based donor acceptor donor type monomers and polymers

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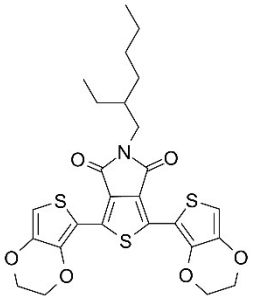
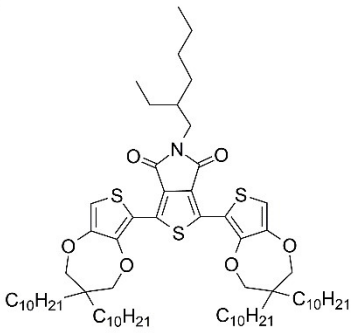
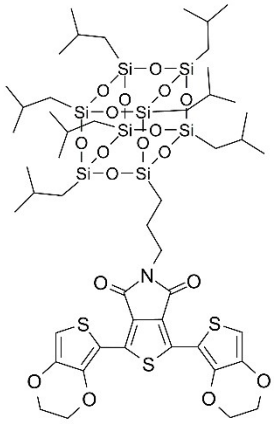
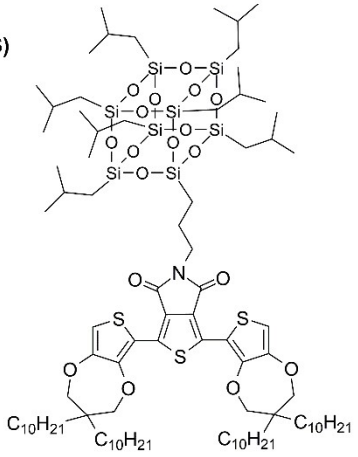
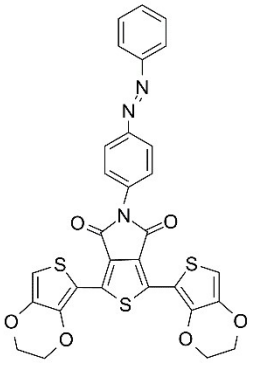
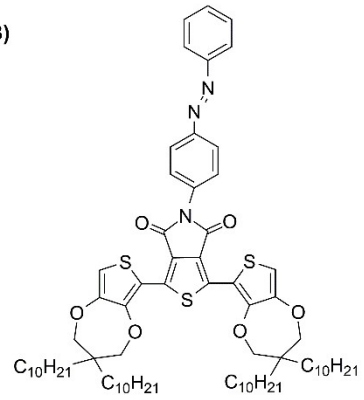
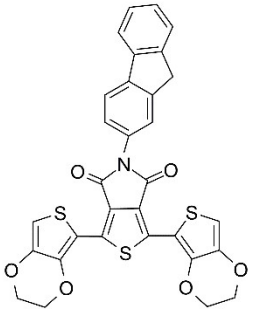
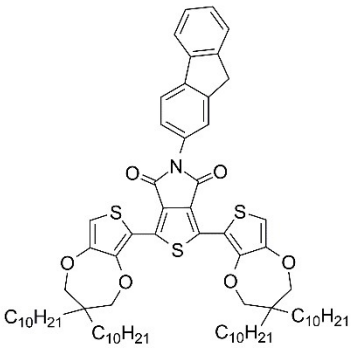
E(EH) 	**P(EH)** 
E(POSS) 	**P(POSS)** 
E(AB) 	**P(AB)** 
E(FI) 	**P(FI)** 

Scheme S1. The structures of TPD based donor acceptor donor monomers with different side chains.

Table S1. The calculated band transitions in Fl-appended unsubstitued ProDOT based D-A-D monomer.

Wavelength (nm)	**Osc. Strength**	**Major contribs**
405.72	**0.52**	**HOMO->LUMO (99%)**
375.35	0.19	H-1->LUMO (49%), H-1->L+1 (43%)
301.83	0.23	H-4->LUMO (87%)
281.94	0.42	H-6->LUMO (13%), H-1->L+2 (56%)
279.26	0.23	H-6->LUMO (59%), H-1->L+2 (18%)

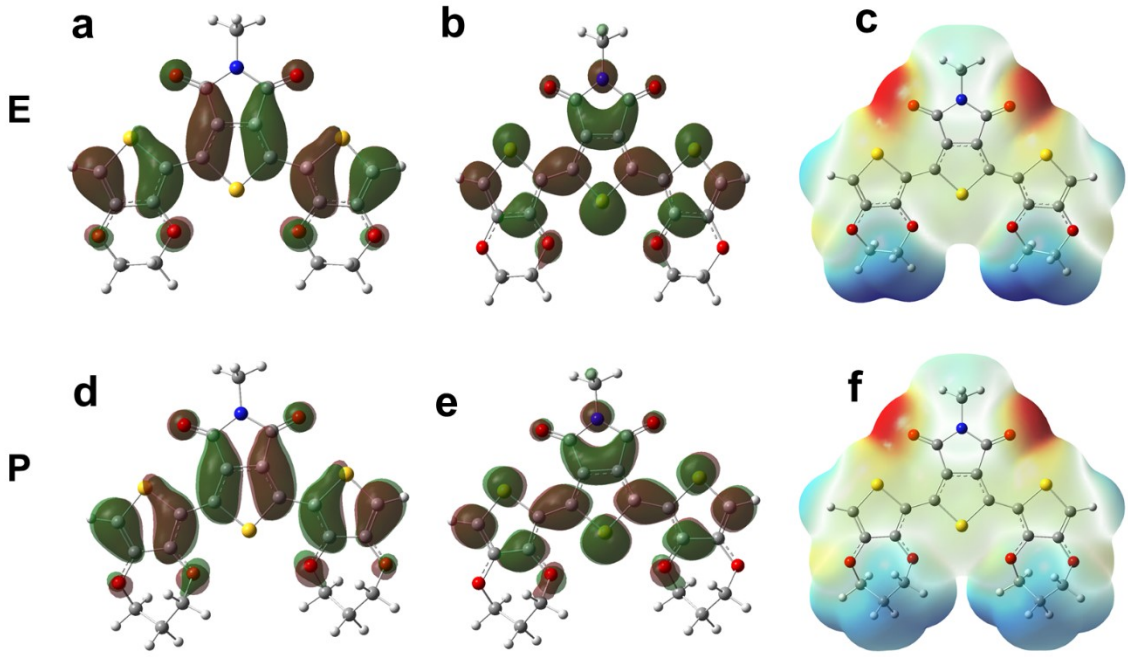


Figure S1. HOMO, LUMO and ESP surfaces for the pristine methyl substituted EDOT **(E)** and ProDOT **(P)**.

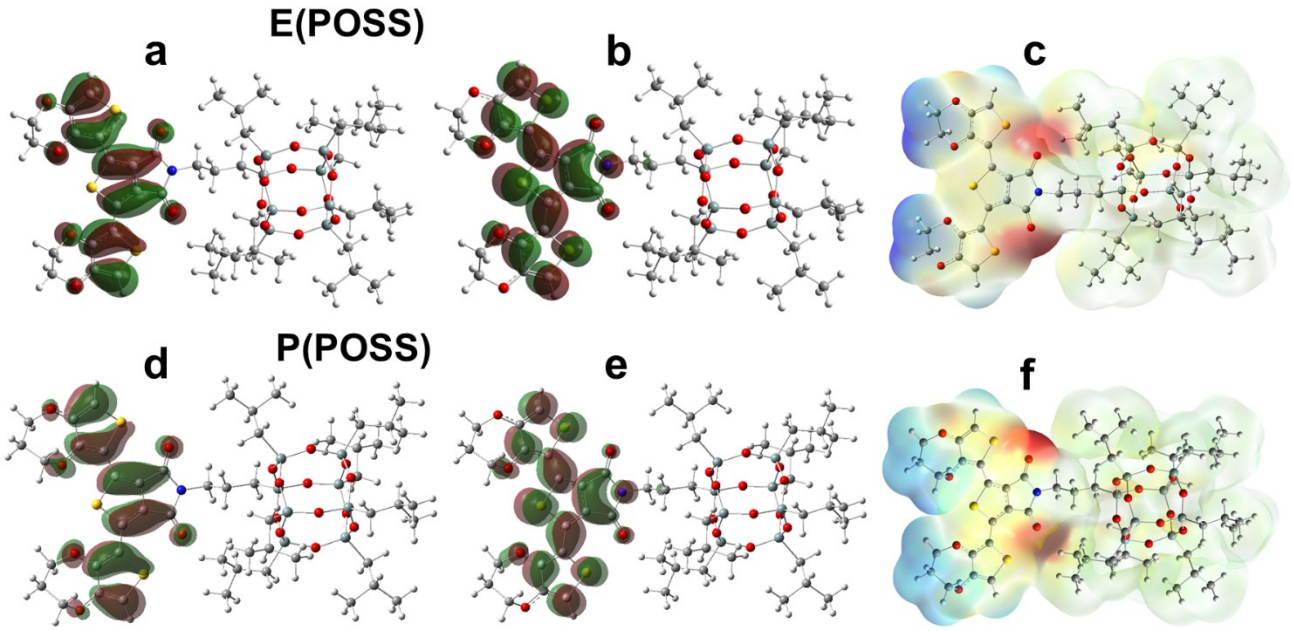


Figure S2. HOMO, LUMO and ESP surfaces for the pristine methyl substituted **E(POSS)** and **P(POSS)**.

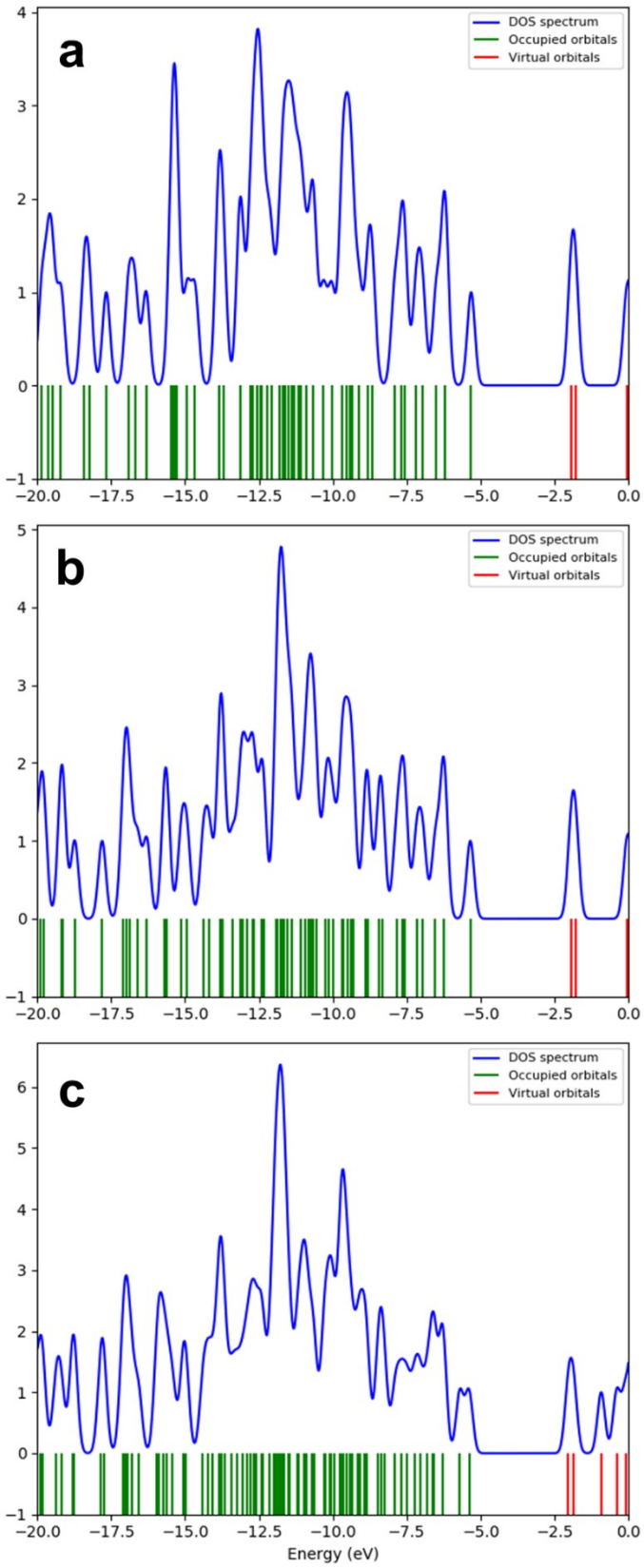


Figure S3. Density of states for the (a) pristine EDOT **(E)**, (b) pristine ProDOT **(P)**, (c) **P(Fl)**.

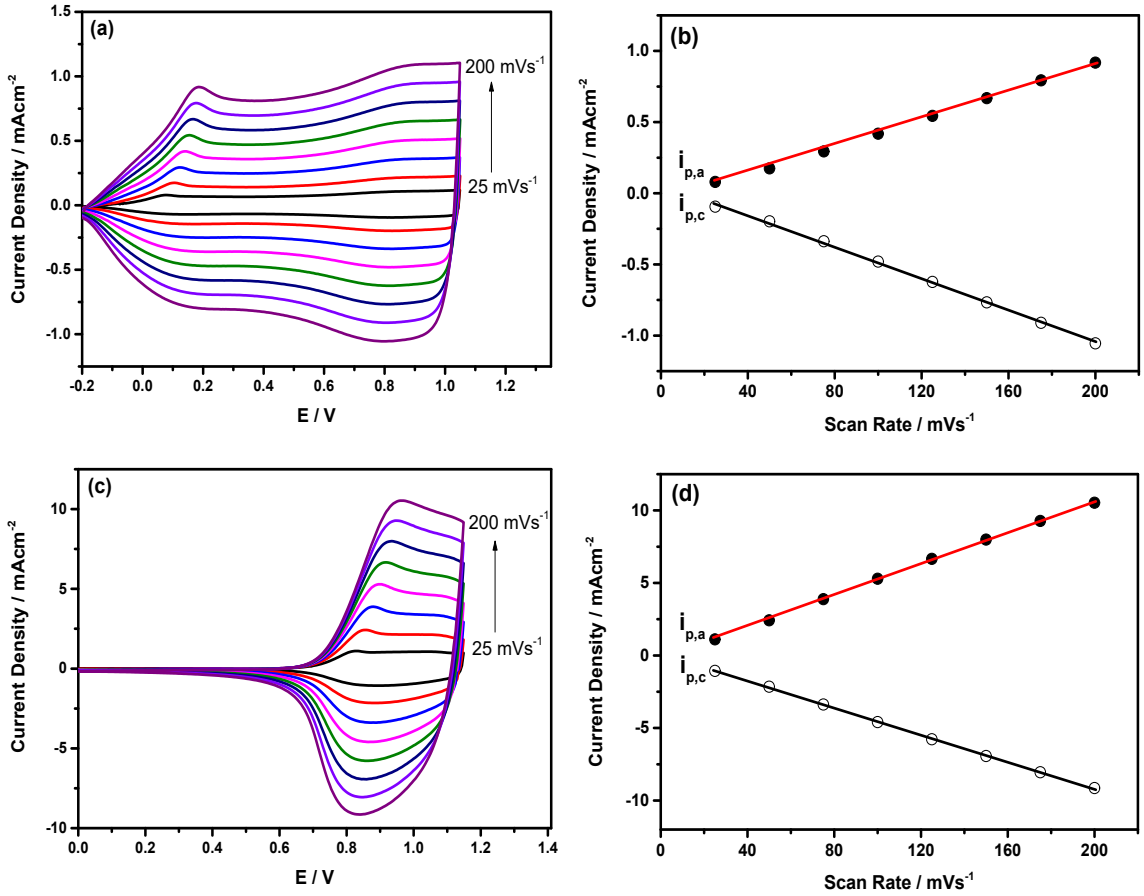
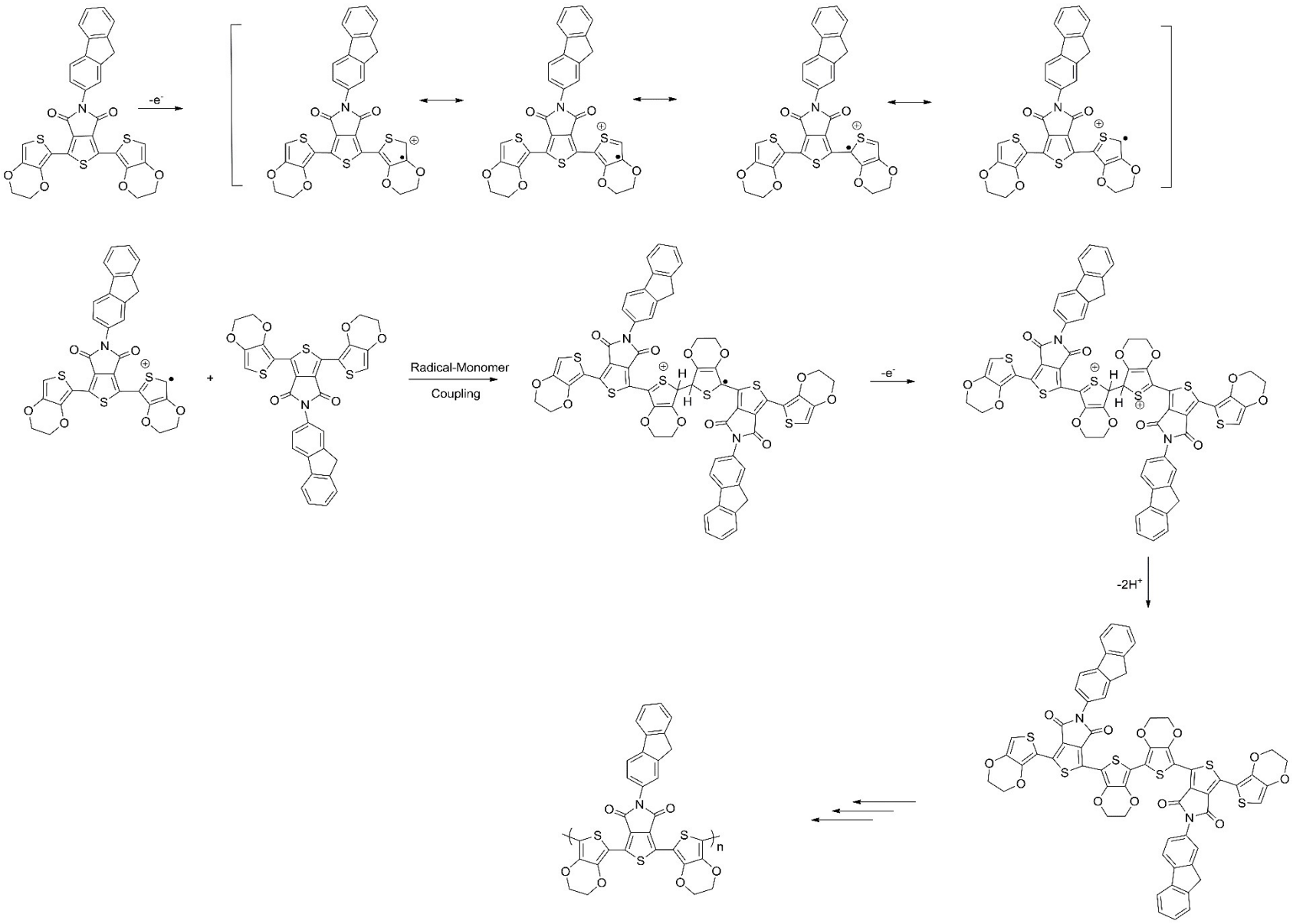
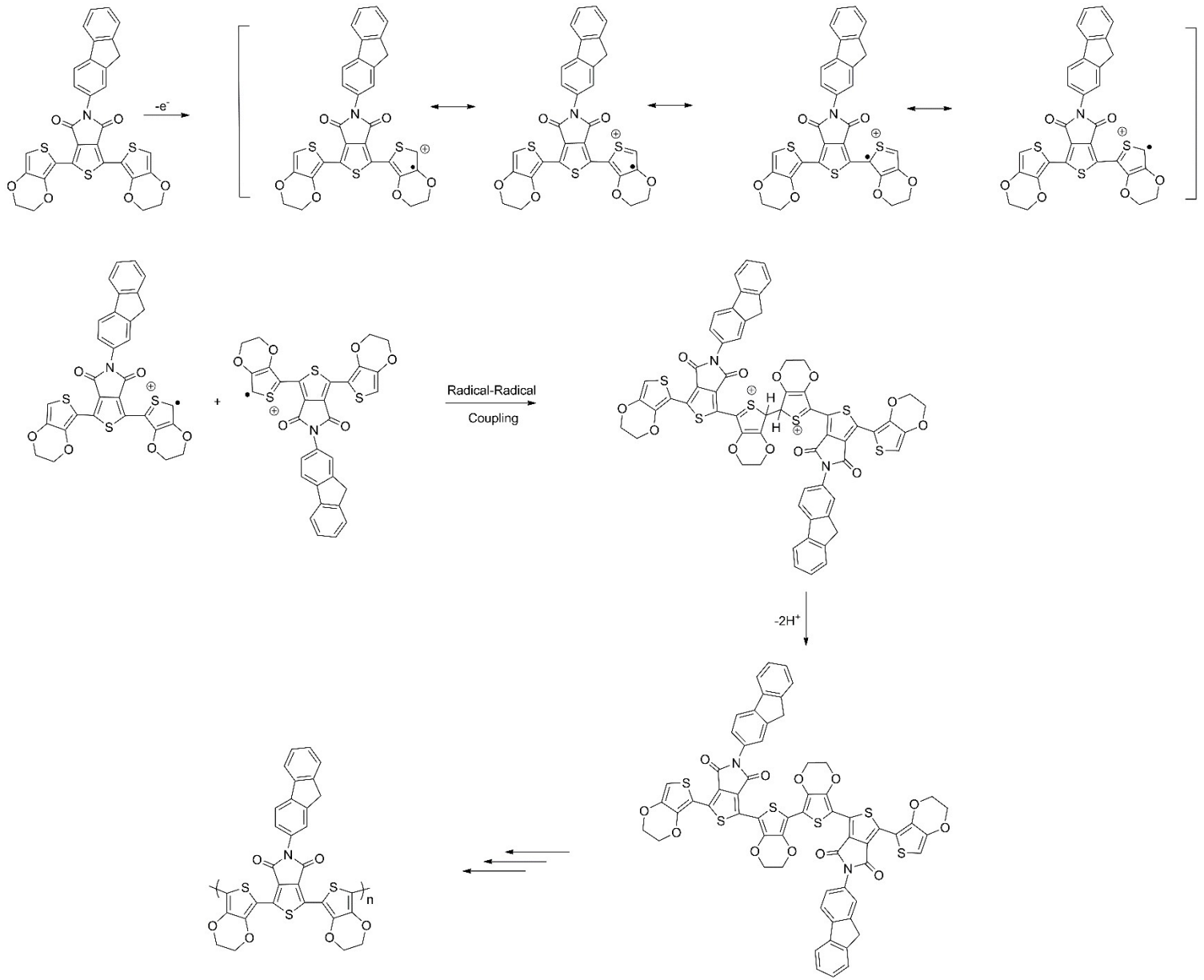


Figure S4. Scan rate dependence of the polymer films on Pt disc electrode recorded in 0.1 M n-Bu_4NPF_6 solution (a) **PE(Fl)** in DCM and (c) **PP(Fl)** in MeCN at different scan rates from 25 mVs^{-1} to 200 mVs^{-1} with 25 mVs^{-1} increments. The relationship of anodic and cathodic current peaks as a function of scan rate for (b) **PE(Fl)** and (d) **PP(Fl)** polymer films



Sheme S2. The proposed mechanism for electrochemical polymerization of **E(Fl)** via radical-monomer coupling.



Scheme S3. The proposed mechanism for electrochemical polymerization of **E(Fl)** via radical-radical coupling.

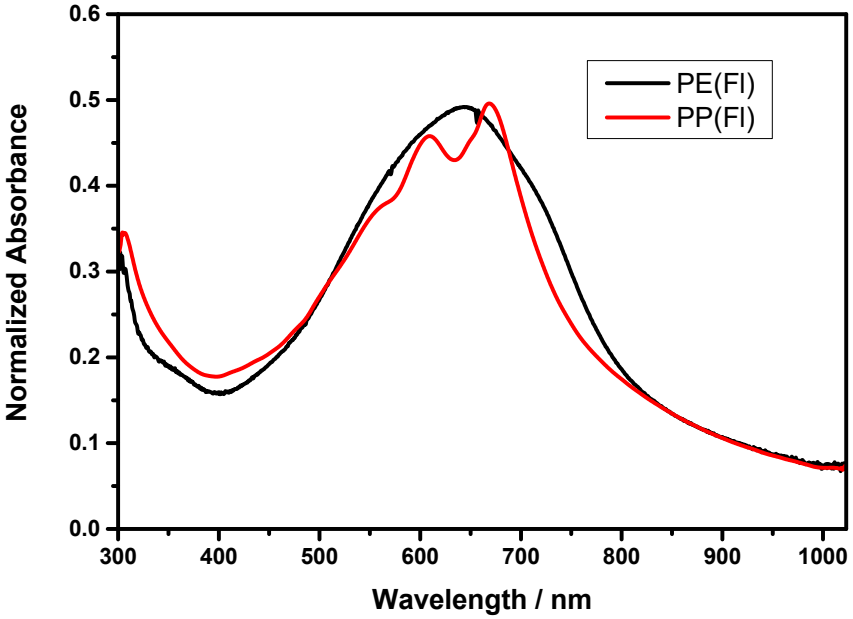


Figure S5. Neutral state absorption spectra of **PE(Fl)** and **PP(Fl)** films coated on ITO electrode in 0.1 M n-Bu_4NPF_6/MeCN.

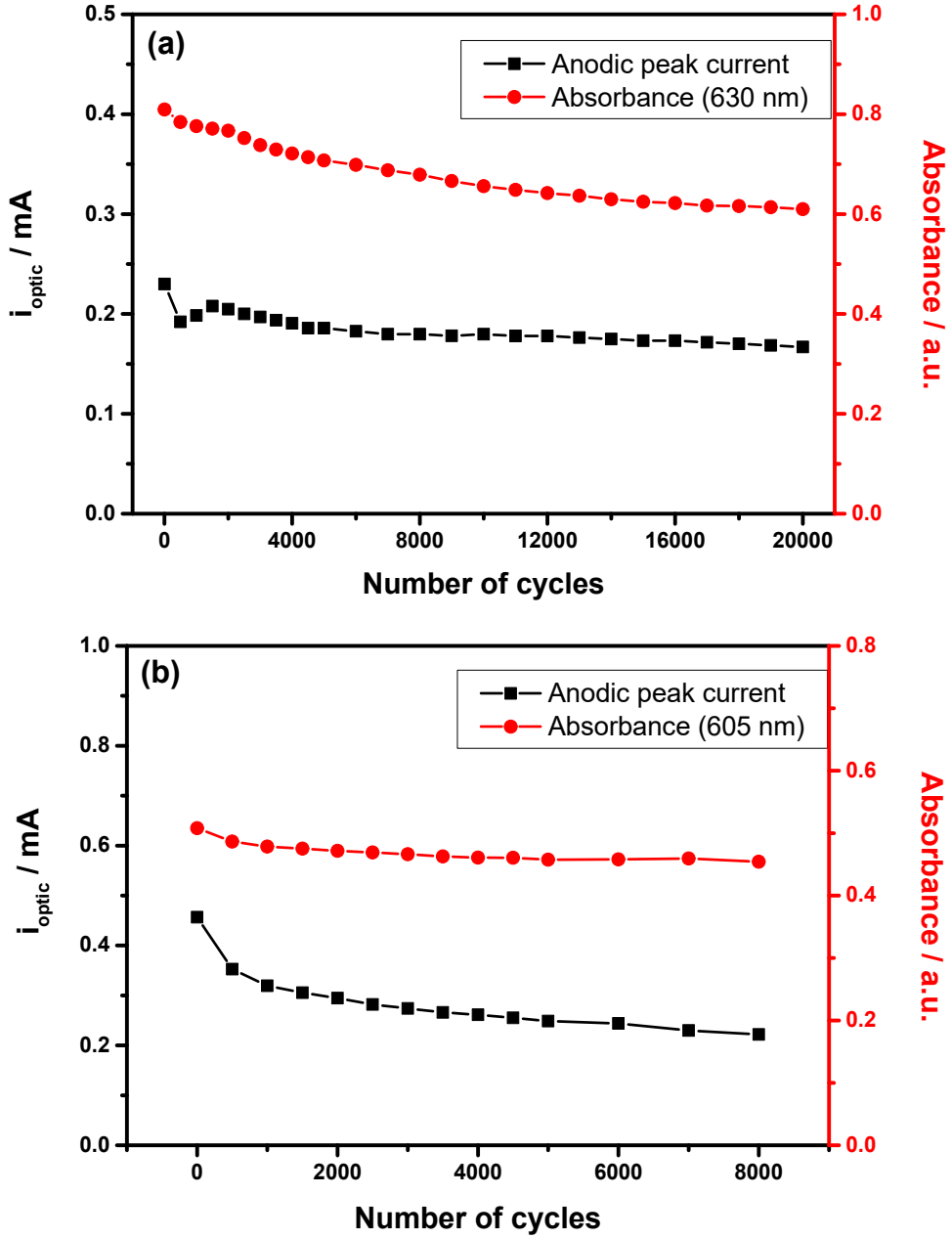


Figure S6. Electrochemical and optical stability tests for the polymer films on ITO in 0.1 M n-Bu_4NPF_6/MeCN when the films switched between redox states (-0.5 V and +1.1 V) at 630 nm for (a) **PE(Fl)** and (0.0 V and +1.1 V) at 605 nm for (b) **PP(Fl)** with an interval of 1 s.