Appendix A. Supplementary data

S1 Instruments and measurements

Infrared spectra in the range of 4000-400 cm⁻¹ were recorded on the PerkinElmer Spectrum 100 model FT-IR spectrometer. The ¹H NMR and ¹³NMR spectra of tetramethylsilane were measured at Bruker AC-400 MHz and AC-100 MHz respectively. Uv-vis spectra were measured at Shimadzu UV-3600. The fluorescence spectra were recorded with JASCO FP-6200 PL spectrometer. The thermogravimetric analyses by PerkinElmer Pyris 6 thermogravimetric analyzer were carried out in nitrogen atmosphere. The inherent viscosities of the polymers were determined at 0.5 g/dL concentration using an Ubbelohde viscometer at 30 °C. The thicknesses of the PIs films were determined on a profile-system XP-100 (KLA-Tencor) by comparing them to the thickness of a blank ITO-coated glass slide. Devices were prepared to operate in glove box model JMS-1X. The experiments were conducted on about 6-8 mg powder samples heated in flowing nitrogen or air (flow rate: $20 \text{ cm}^3 \cdot \text{min}^{-1}$) at a heating rate of 10 °C·min⁻¹. The manufacturing process and measurement of the device were performed in room temperature air. Before being used, ITO was washed by ultrasonic for 30 minutes in detergent, deionized water and dichloromethane successively. CV and spectroelectrochemical analysis were performed using a three-electrode electrochemical cell in 0.1M tetramethylammonium perchlorate (TBAP) solution at room temperature of 50 mV \cdot s⁻¹. Ultraviolet tube used as a holder and indium tin oxide (ITO, $1.0 \text{ cm} \times 4.0 \text{ cm}$), platinum wire and Ag/AgCl (0.1 M) are used as working electrode, the electrode and reference electrode, respectively. Theoretical studies were carried out on the 6-31G basis set in Gaussian 09 using density functional theory (DFT), which was approximated by B3LYP.

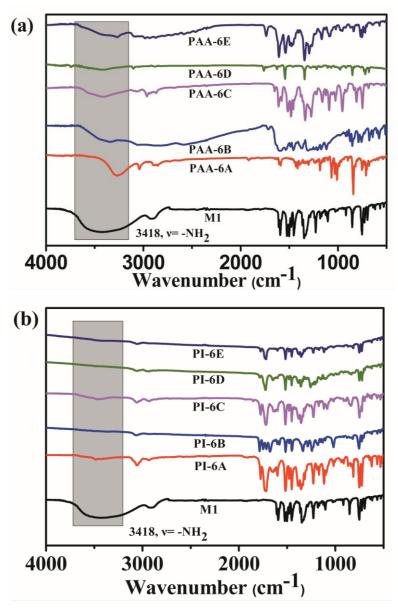


Fig. S1 FTIR spectra of (a) PAAs and (b) PIs.

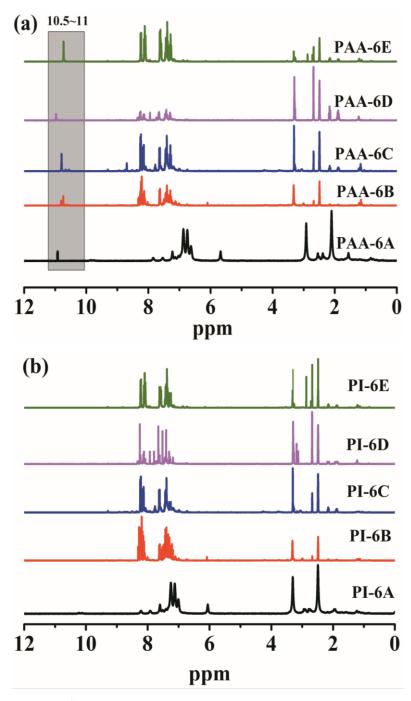
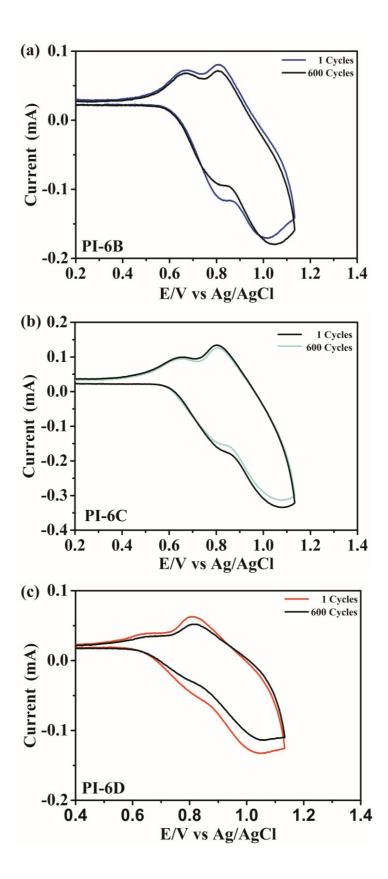


Fig. S2 ¹H NMR spectra of (a) PAAs and (b) PIs and in DMSO- d_6 .



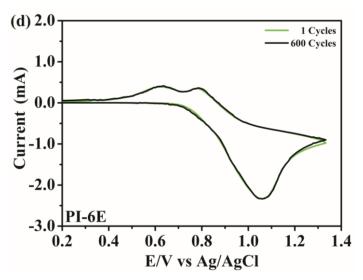
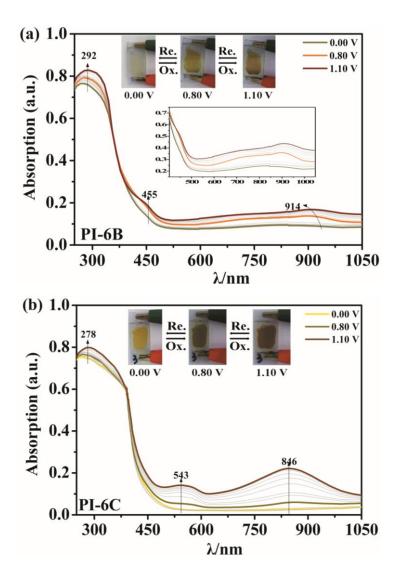


Fig. S3 Electrochemical stability of (a) **PI-6B**, (b) **PI-6C**, (c) **PI-6D** and (d) **PI-6E** films on an ITO-coated glass substrate in 0.1 M TBAP/CH₃CN solution at the scan rate of 50 mV·s⁻¹ after 1000 switching by the CV method.



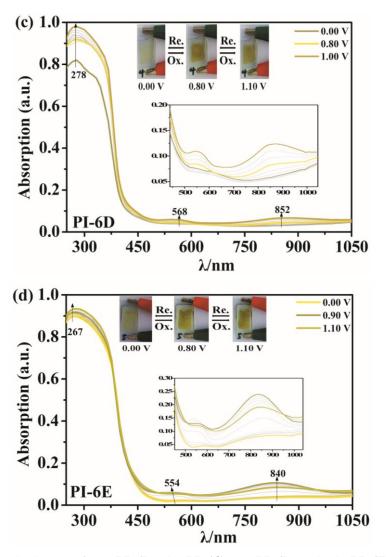
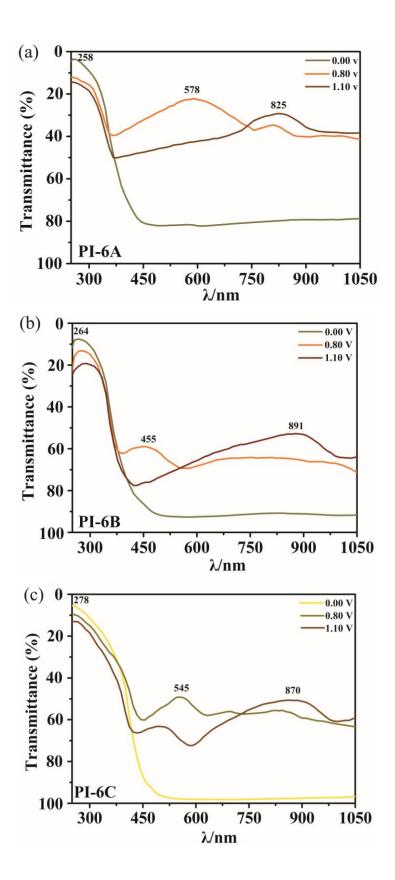


Fig. S4 Spectral change of (a) **PI-6B**, (b) **PI-6C**, (c) **PI-6D** and (d) **PI-6E** films on the ITO-coated glass substrate (0.1 M TBAP/CH₃CN solution as the supporting electrolyte) at different applied (V vs Ag/AgCl). The inset shows the photographic images of the film at indicated applied voltages.



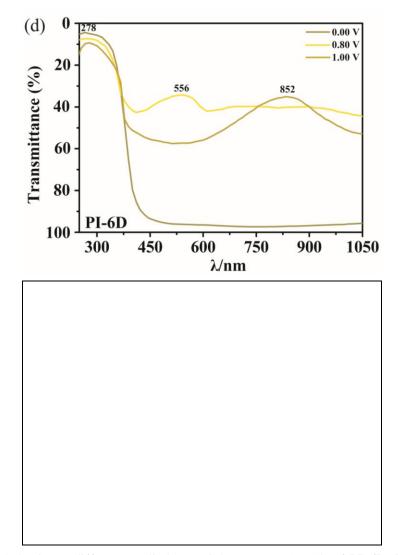
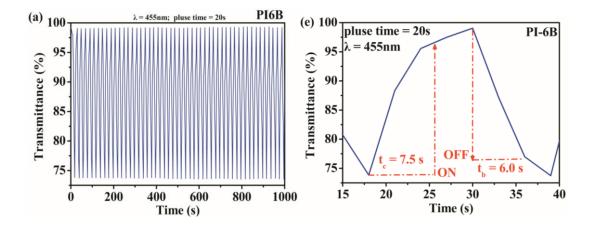


Fig. S5 EC behavior at different applied potentials (V vs Ag/AgCl) of **PI-6B**, **PI-6B**, **PI-6C**, **PI-6D** and **PI-6E** films (~210 nm in thickness) on the ITO-coated glass substrate (coated area: 1.0 cm× 4.0 cm) in 0.1 M TBAP/CH₃CN.



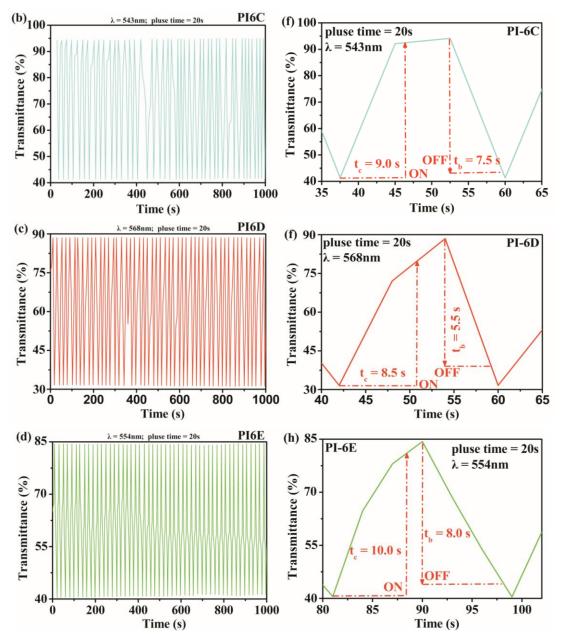
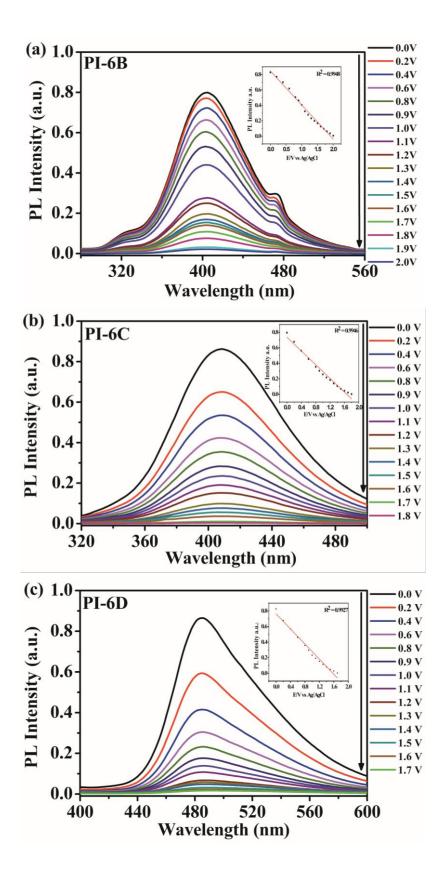


Fig. S6 Square-wave potential step absorptiometry and optical switching of **PI-6B - PI-6E** films.



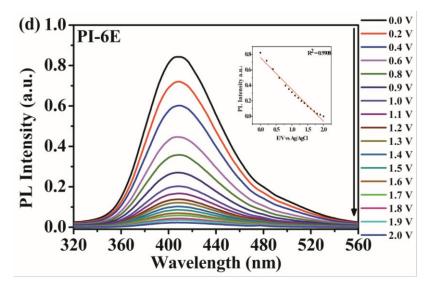


Fig. S7 PL spectra changes of (a) PI-6B, (b) PI-6C, (c) PI-6D and (d) PI-6E films upon different applied potentials.