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Supplementary Information

Benzotriazole-EDOT electrochromic conjugated polymers perform sub-second response time and 774 cm^2C^{-1} coloration efficiency

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EXPERIMENTAL

Electrochemistry

All the electrochemical experiments were performed in a one-compartment cell with the use of spectroelectrochemical workstation of Xi Pu Guang Dian (XP-SEC-BAC). For electrochemical tests, the working and counter electrodes were both Pt wires with a diameter of 1 mm, while the reference electrode (RE) was Ag/AgCl. The Ag/AgCl was prepared by chronoamperometry method at potential of 1.5 V for 100 s in hydrochloric acid (6 mol L^{-1}) and calibrated with the SCE system. Bu_4NPF_6 as electrolyte was dissolved in anhydrous CH_3CN (0.1 mol L^{-1}). All the solutions were distilled in a dry nitrogen stream before use. Polymer films were obtained by spray-coating. After polymerization, the films were washed repeatedly with anhydrous CH_3CN to remove the electrolyte and monomer.

Electrochromic study

Spectroelectrochemistry and kinetic studies of polymers were recorded on a spectroelectrochemical workstation of Xi Pu Guang Dian (XP-SEC-BAC). The spectroelectrochemical cell consisted of a quartz cell, an Ag/AgCl electrode as reference electrode, a Pt wire as counter electrode, and an indium tin oxide (ITO) coated glass as the transparent working electrode. All measurements were carried out in

CH_3CN containing Bu_4NPF_6 (0.1 mol L^{-1}).

Spectroelectrochemical analyses were performed by recording the changes in the absorption spectra using diverse voltage pulses. Under the applied potential, an electrochromic polymer will perform oxidation behavior with producing radical cations (polarons) and further oxidation produce dications (bipolarons), allowing new electronic transition thereby changing absorption spectra. Upon stepwise oxidation of the electrochromic polymers, the formation of polaron and bipolaron leads to new absorption bands at larger wavelength. Additionally, the CIE 1931 color coordinates (L* a* b*, where L* represents lightness, a* the red/green balance, and b* the yellow/blue balance) of the polymer film were determined in both its neutral and oxidized states.

The potentials were alternated between the reduced and oxidized states with a residence time of 2 s, 5 s, 10 s, and 20 s. The optical contrast at the specific wavelength (λ) was determined by $\Delta T\%$ values of polymer films, using the following equation:

$$\Delta T = \left| T_{ox} - T_{red} \right|$$

The colouration efficiency (*CE*) is defined as the relation between the injected/ejected charge as a function of electrode area (Q_d) and the change in optical density (ΔOD) at the specific wavelength (λ) of the sample as illustrated by the following equation:

$$\Delta OD = \log(T_{ox}/\ T_{red})$$

$$CE = \Delta OD / Q_d$$

Flexible electrochromic devices (ECDs)

Flexible electrochromic devices were fabricated as device structure of indium tin oxide/polyethylene terephthalate (ITO/PET) /electrochromic active layer/gel electrolyte/ ITO/PET. The electrochromic layer was carried out via spray-coating onto ITO glass from a $CHCl_3$ solution (ca. 1.5 mg mL^{-1}). As a vital component of flexible ECDs, gel electrolyte displays unique advantages over liquid and solid electrolyte, such as no risk of leakage, high chemical stability and fast switching time. To prepare the gel electrolyte in this work, chemicals including Lithium perchlorate ($LiClO_4$, 1.35 g), CH_3CN (1.5 mL) and propylene carbonate (PC, 15 mL) were added in the flask. Then, polymethyl methacrylate (PMMA, 1.25 g) was slowly added in the mixture, followed by stirring of 12 h along with reflux condensation at 65 °C. The gel electrolyte was obtained with a composition of CH_3CN: PC: $LiClO_4$: PMMA (5.4 wt%: 82.7 wt%: 6.2 wt%: 5.7 wt%).

Fig. S1 ^{1}H NMR spectrum of $C_{23}H_{37}Br_2N_3$.

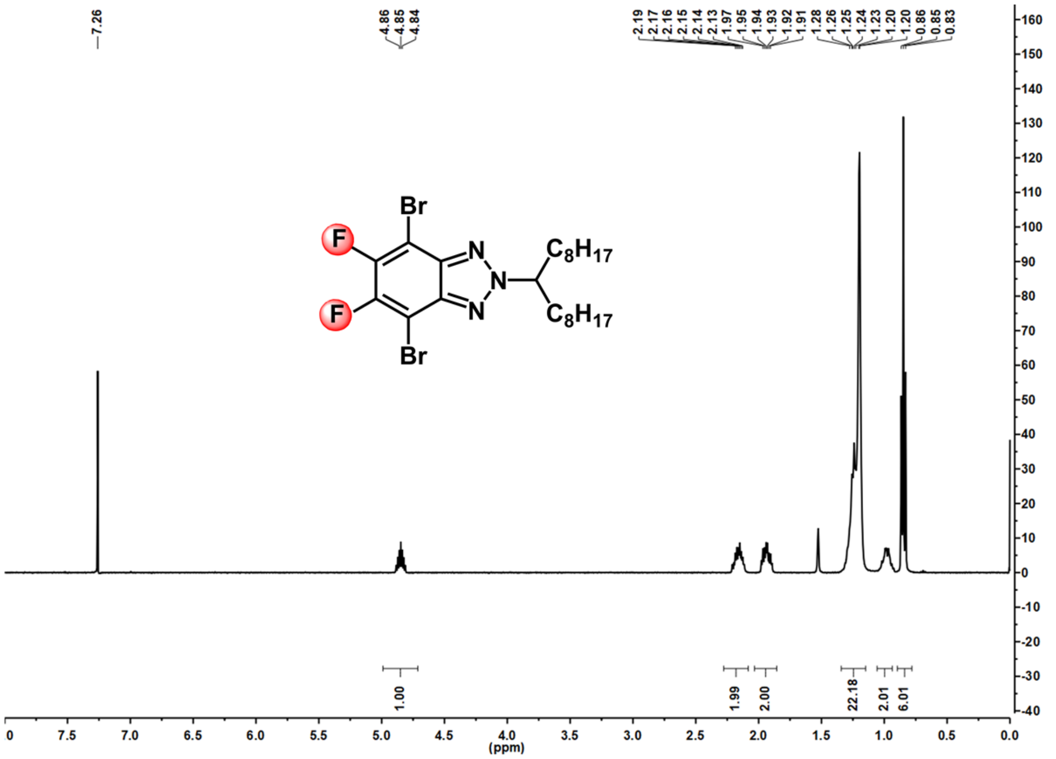

Fig. S2 ^{1}H NMR spectrum of $C_{23}H_{35}Br_2F_2N_3$.

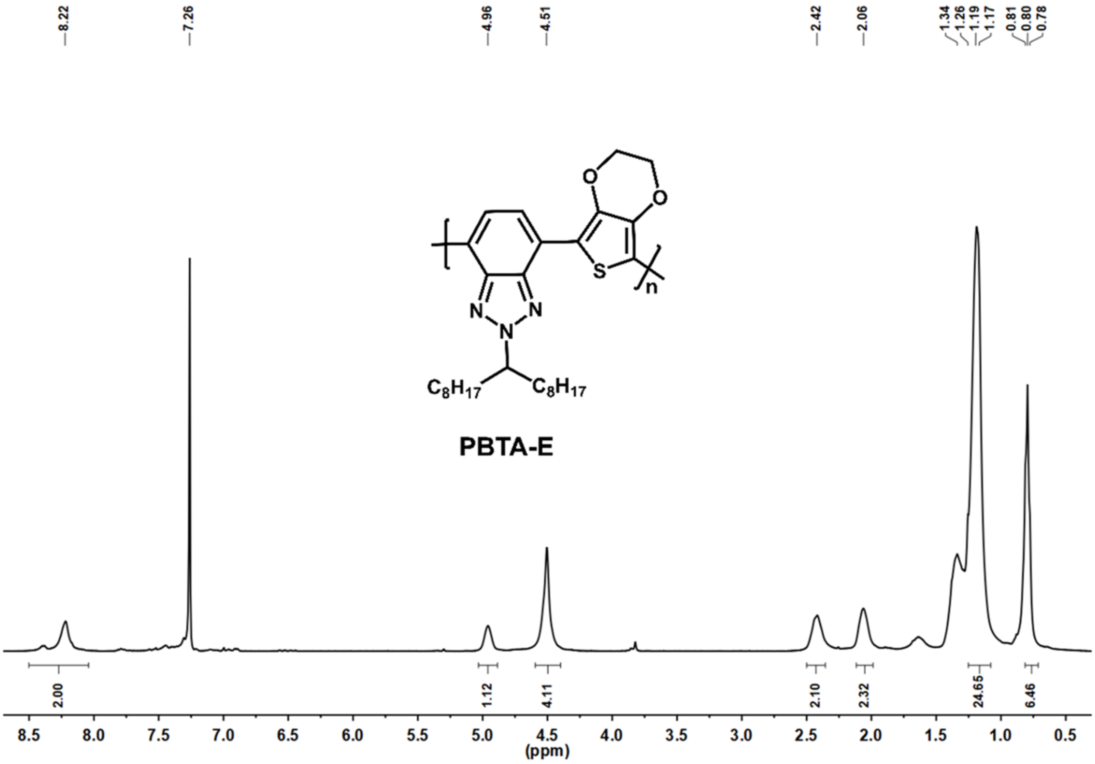

Fig. S3 ^{1}H NMR spectrum of PBTz-E.

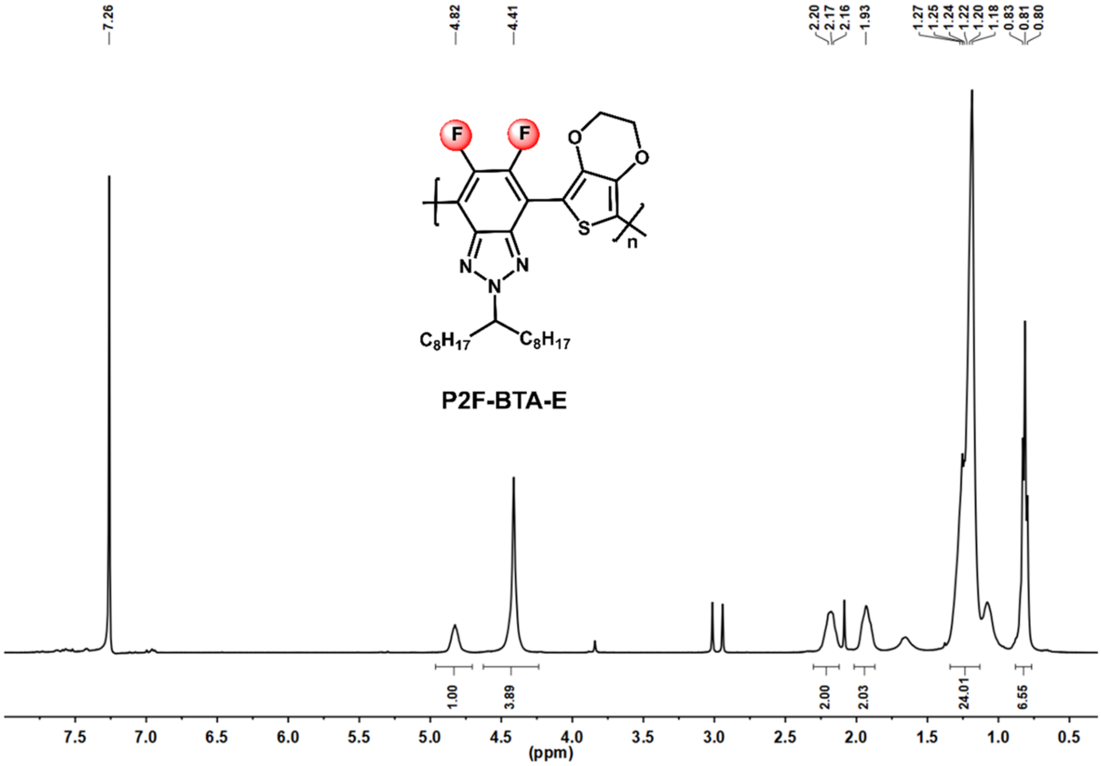

Fig. S4 ^{1}H NMR spectrum of P2F-BTz-E.

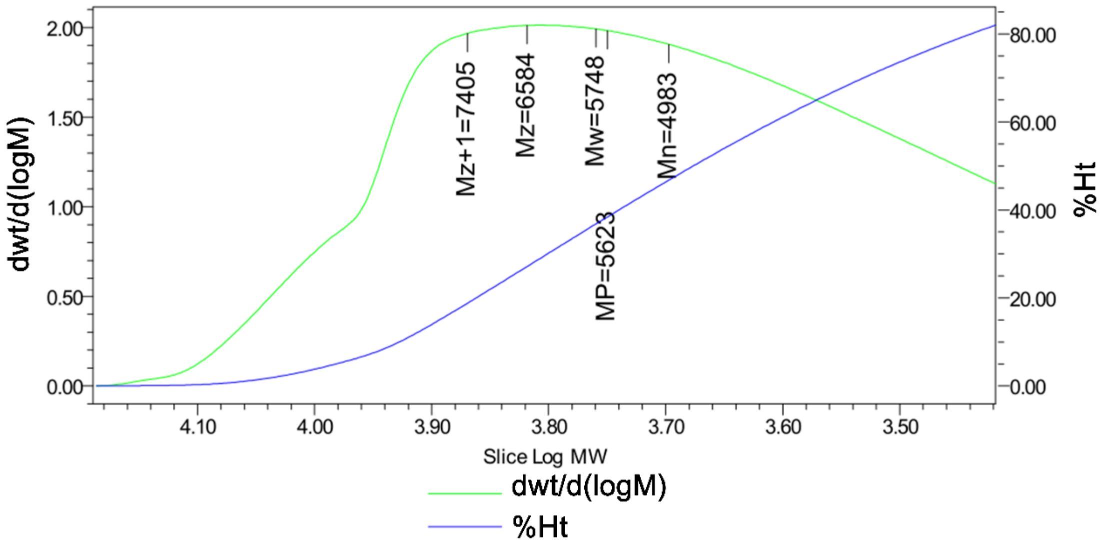

Fig. S5 GPC of PBTz-E.

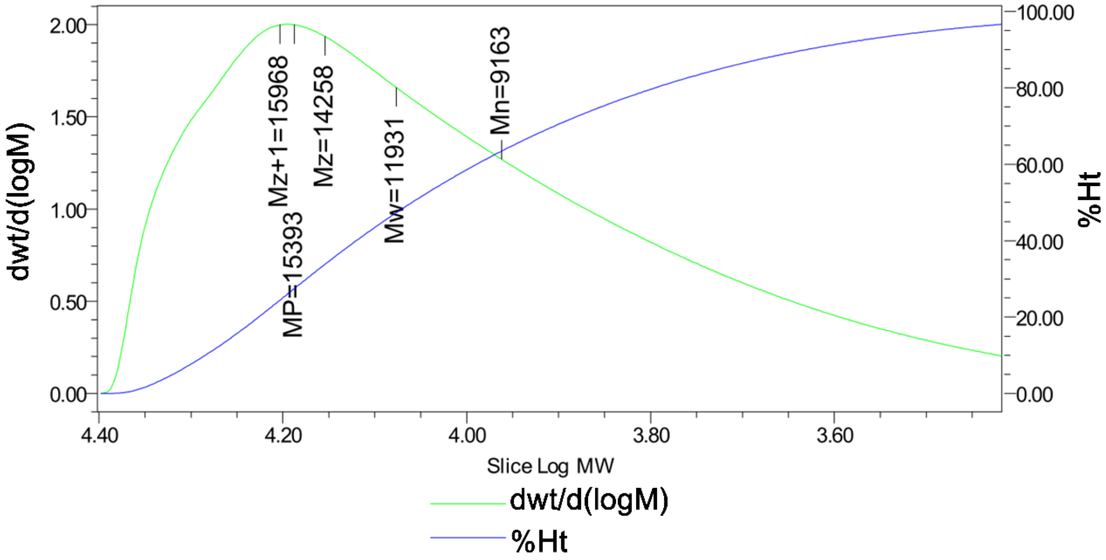

Fig. S6 GPC of P2F-BTz-E.

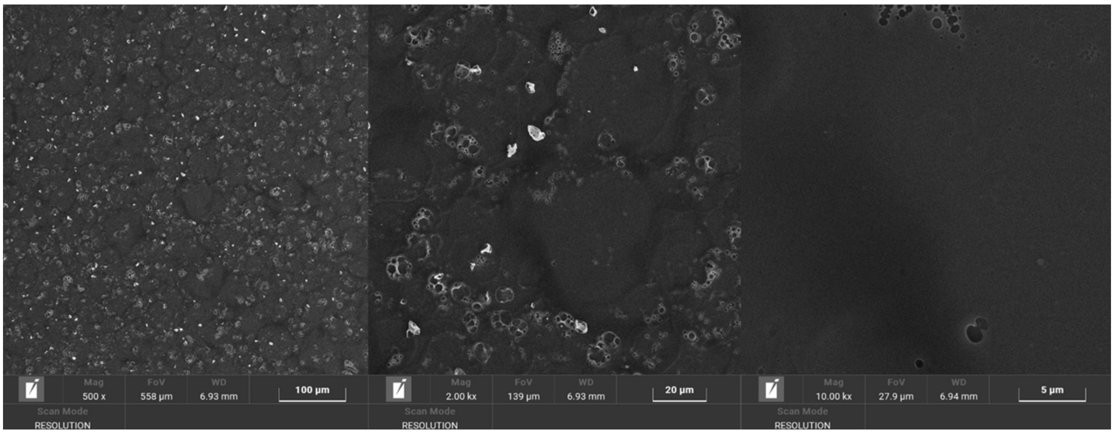

Fig. S7 SEM images of PBTz-E

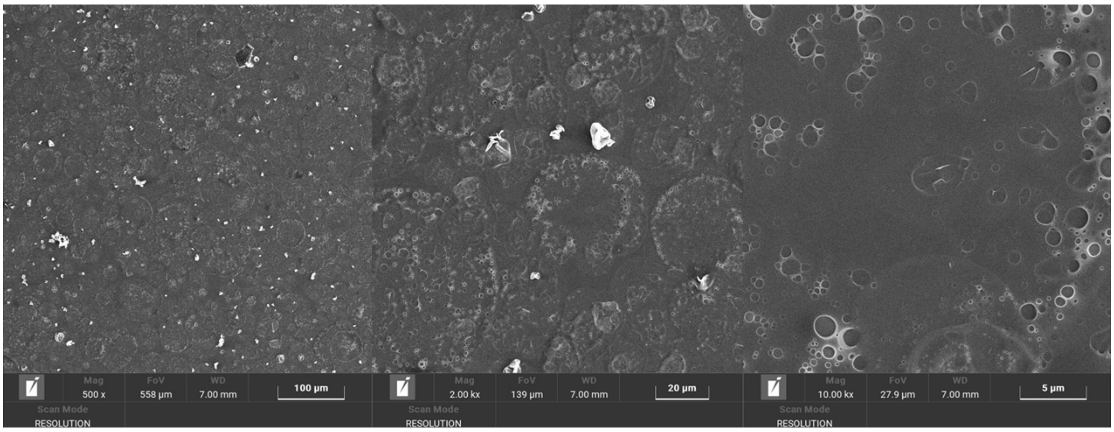

Fig. S8 SEM images of P2F-BTz-E

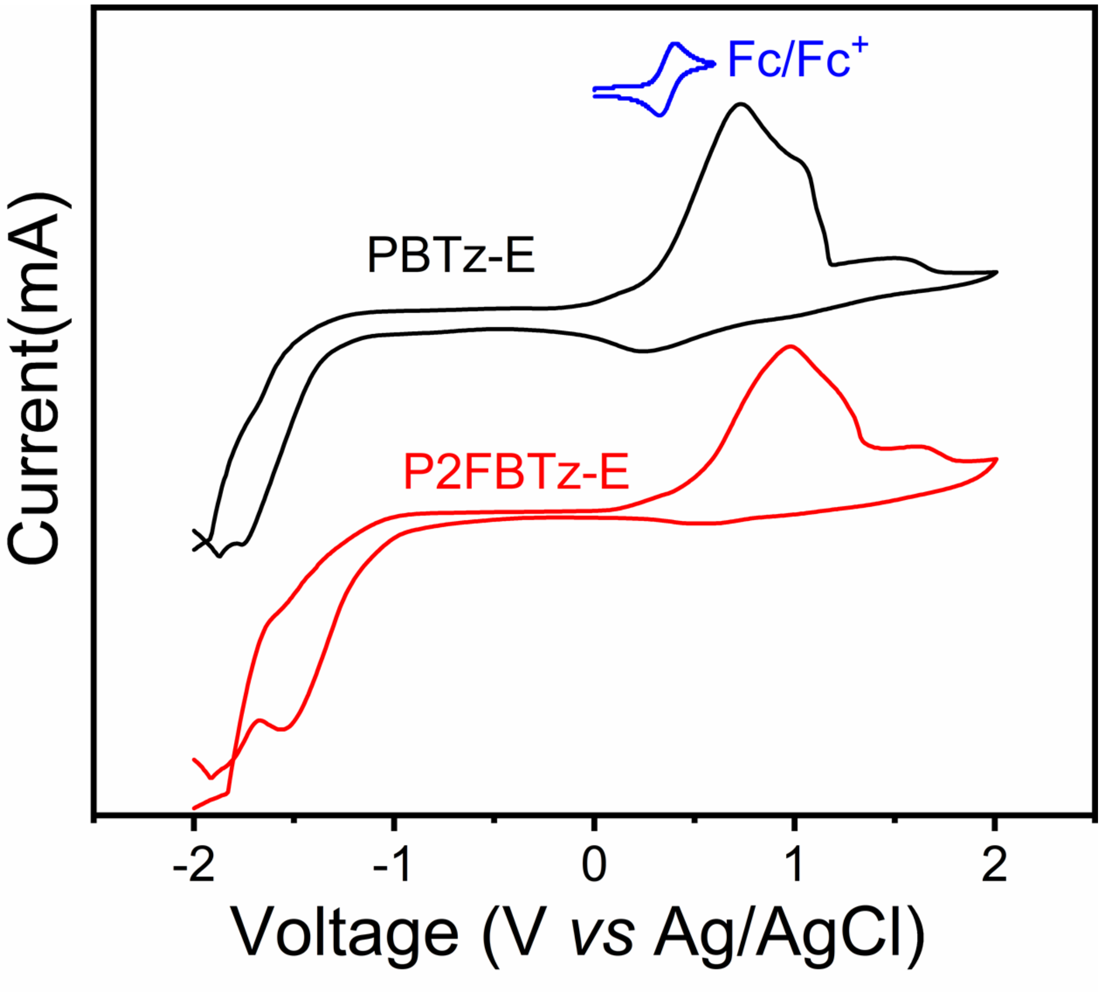

Fig. S9 CVs of PBTz-E and P2F-BTz-E in MeCN-Bu4NPF6 (0.1 M) at the scan rate of 250 mV s^{-1}.

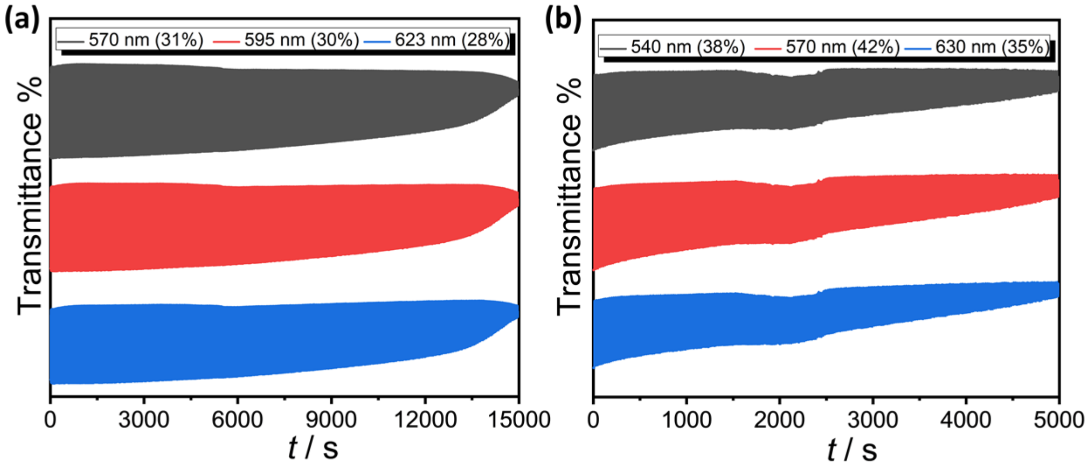

Fig. S10 Time-transmittance profiles of PBTz-E (a) and P2F-BTz-E (b) recorded during double step chronoamperometry for the switching time of 10 s under indicated wavelengths.

Table S1 Molecular weights of PBTz-E, P2F-BTz-E.

	*M*n	*M*w	*M*w/*M*n
PBTz-E	4983	5748	1.15
P2FBTz-E	9163	11931	1.30