Supplementary Information

Electrodeposited Copolymers Based on 9,9′-(5-Bromo-1,3-Phenylene)Biscarbazole and Dithiophene Derivatives for High-Performance Electrochromic Devices

Chung-Wen Kuo [1], Jui-Cheng Chang [2,3], Jeng-Kuei Chang [4], Sheng-Wei Huang [1], Pei-Ying Lee [2] and Tzi-Yi Wu [2,*]

[1] Department of Chemical and Materials Engineering, National Kaohsiung University of Science and Technology, Kaohsiung 80778, Taiwan; welly@nkust.edu.tw (C.-W.K.); bill4794@gmail.com (S.-W.H.)
[2] Department of Chemical Engineering and Materials Engineering, National Yunlin University of Science and Technology, Yunlin 64002, Taiwan; d700215@gmail.com (J.-C.C.); leepeiying1018@gmail.com (P.-Y.L.)
[3] Bachelor Program in Interdisciplinary Studies, National Yunlin University of Science and Technology, Yunlin 64002, Taiwan
[4] Department of Materials Science and Engineering, National Yang Ming Chiao Tung University, No. 1001 University Road, Hsinchu 30010, Taiwan; jkchang@nctu.edu.tw
* Correspondence: wuty@gemail.yuntech.edu.tw; Tel.: +886-5-534-2601 (ext. 4626)

Figure S1 showed the infrared spectra of PBPBC, P(BPBC-*co*-BT), P(BPBC-*co*-CDT), and P(BPBC-*co*-CDTK) films. As displayed in Figure S1(a), the infrared peak at 1065 cm^{-1} implied the doping of PBPBC with the electrolyte (ClO_4^-). The infrared peak at ca. 1593 cm^{-1} stands for the C=C stretching vibration of phenyl group. The peak at ca. 1451 cm^{-1} can be attributed to the C–N stretching of the carbazole group.

There was no noticeable -C-S-C- stretching peak of PBPBC at around 790-803 cm^{-1}. Figure S1b–d displayed the infrared peaks of PBPBC and -C-S-C- stretching vibration of P(BPBC-*co*-BT), P(BPBC-*co*-CDT), and P(BPBC-*co*-CDTK), the presence of new peaks at 790, 803, and 797 cm^{-1} could be attributed to the existence of BT, CDT and CDTK in P(BPBC-*co*-BT), P(BPBC-*co*-CDT), and P(BPBC-*co*-CDTK) films, respectively. The peak at ca. 1708 cm^{-1} can be ascribed to the C=O stretching of P(BPBC-*co*-CDTK).

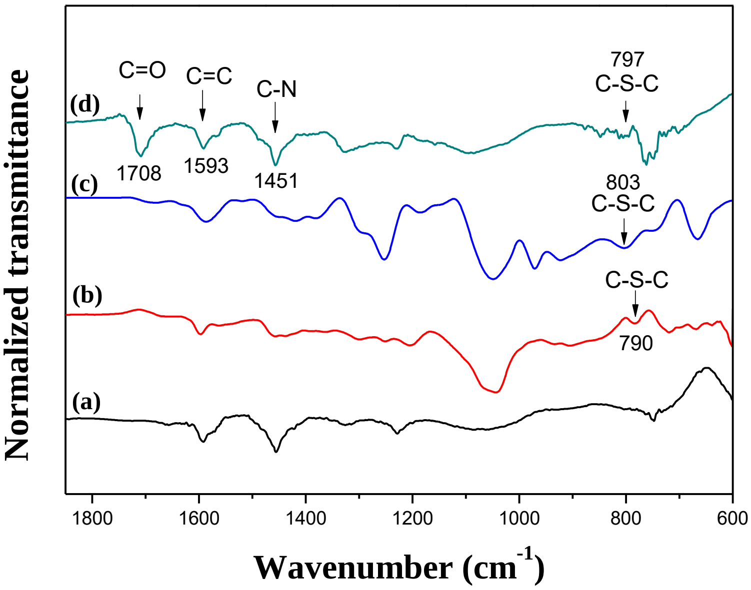

Figure S1. FT-IR spectra of (a) PBPBC, (b) P(BPBC-*co*-BT), (c) P(BPBC-*co*-CDT), and (d) P(BPBC-*co*-CDTK).

CD_2Cl_2 and CF_3COOD are deuterated solvents with strong dissolving ability. CD_2Cl_2 and CF_3COOD solvents are used to dissolve as-prepared polymer films. However, only less than 5% as-prepared polymer films are soluble in CD_2Cl_2 and CF_3COOD (Figure S2).

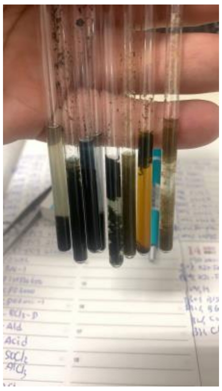

Figure S2. The NMR tubes of PBPBC, P(BPBC-*co*-BT), P(BPBC-*co*-CDT), and P(BPBC-*co*-CDTK) in CD_2Cl_2 and CF_3COOD solvents. More than 95% polymer samples are insoluble in CD_2Cl_2 and CF_3COOD.

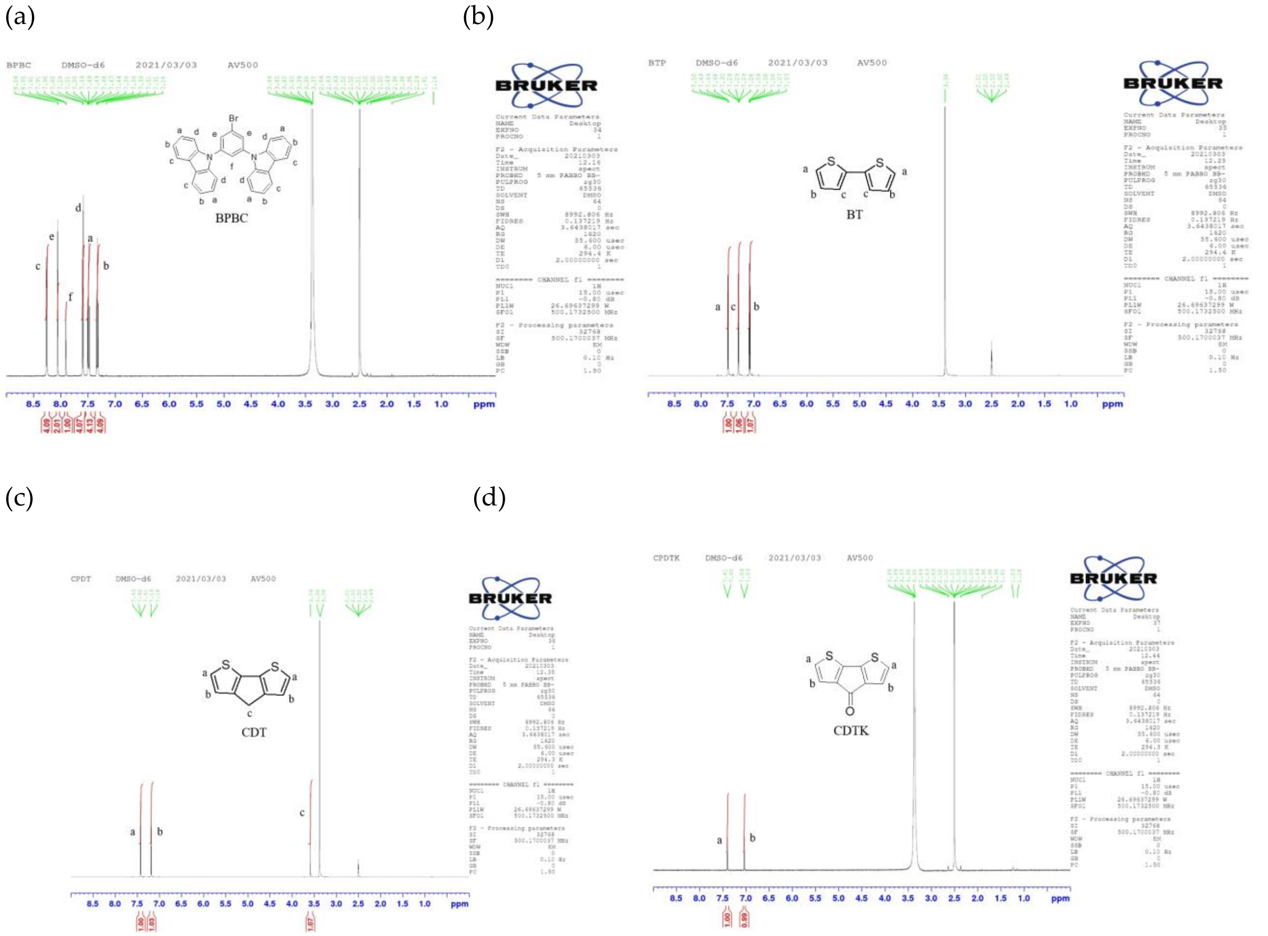

Figure S3. The ^1H NMR spectra of (a) BPBC, (b) BT, (c) CDT, and (d) CDTK in deuterated solvent.

The ^1H NMR spectrum does not display any significant signal for less than 5% soluble polymers in CF_3COOD. Nevertheless, less than 5% soluble polymers in CD_2Cl_2 reveal some weak ^1H NMR signals. Figure S3 shows the ^1H NMR spectra of monomers (BPBC, BT, CDT, and CDTK) and Figure S4 shows the ^1H NMR spectra of less than 5% soluble polymers (PBPBC, P(BPBC-*co*-BT), P(BPBC-*co*-CDT), and P(BPBC-*co*-CDTK)) in deuterated solvents. The ^{1}H NMR peaks of partial soluble polymers are broader than those of monomers in deuterated solvents, indicating the formation of polymers after electrochemical polymerization. However, less than 5% polymer samples are soluble in CD_2Cl_2, the ^{1}H NMR results do not clearly indicate all structures of polymers. The ^{1}H NMR spectra only display the signals of soluble bicarbazole-based homomers. Bithiophene-based homopolymers (PBT, PCDT, and PCDTK) and three copolymers (P(BPBC-*co*-BT), P(BPBC-*co*-CDT), and P(BPBC-*co*-CDTK)) are almost insoluble in CD_2Cl_2. More than 95% insoluble polymer samples are not presented in ^{1}H NMR spectra.

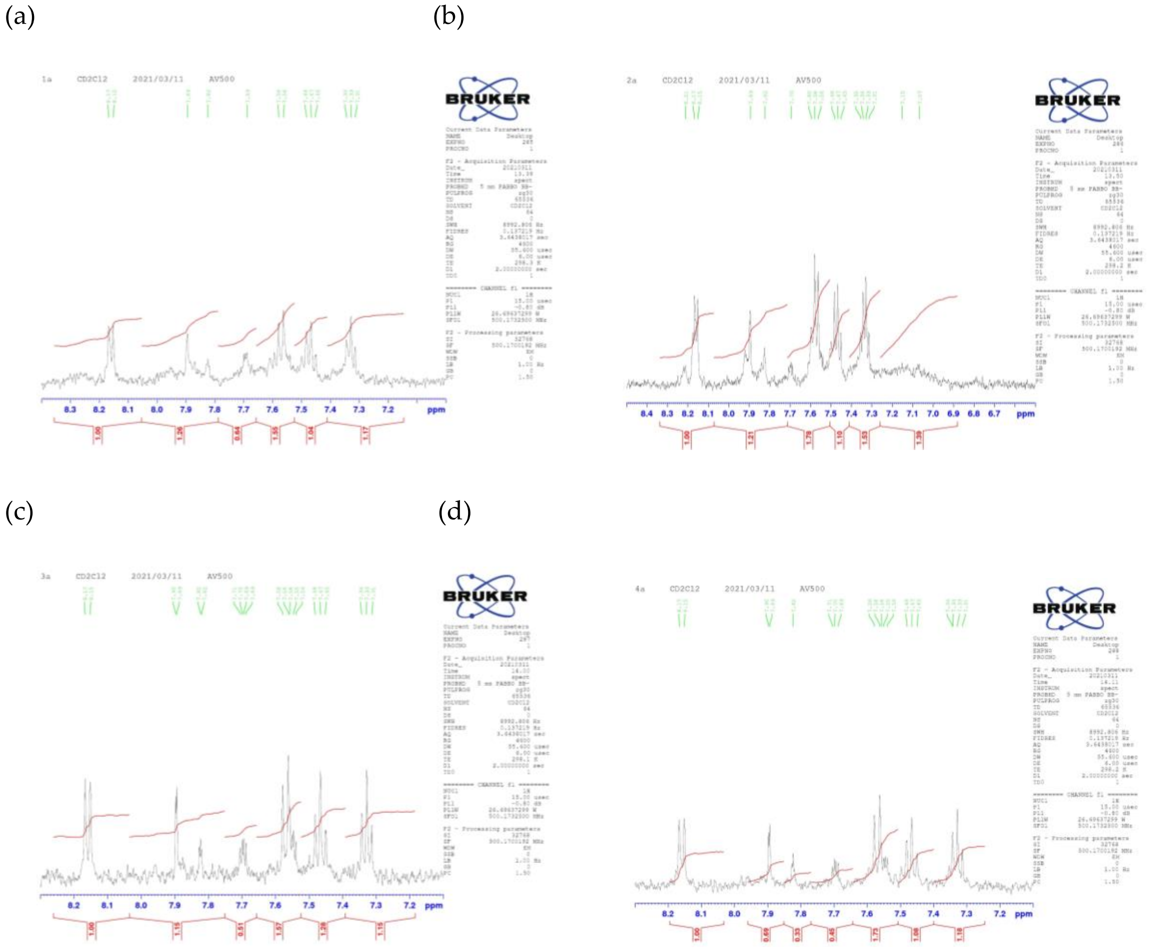

Figure S4. The ^{1}H NMR spectra of (a) PBPBC, (b) P(BPBC-*co*-BT), (c) P(BPBC-*co*-CDT), and (d) P(BPBC-*co*-CDTK) in CD_2Cl_2. Less than 5% polymer samples are soluble in deuterated solvent, the ^{1}H NMR results are not clearly indicate all structures of polymers. More than 95% insoluble polymer samples are not presented in ^{1}H NMR spectra.

Figure S5 showed the electrochromic switching plot of PBPBC after under dark (or light) environment for 30 hr, the Δ*T* of PBPBC under light conditions was 98.7% of that under dark conditions. It implied that PBPBC revealed sufficient Δ*T* stability when exposed to light.

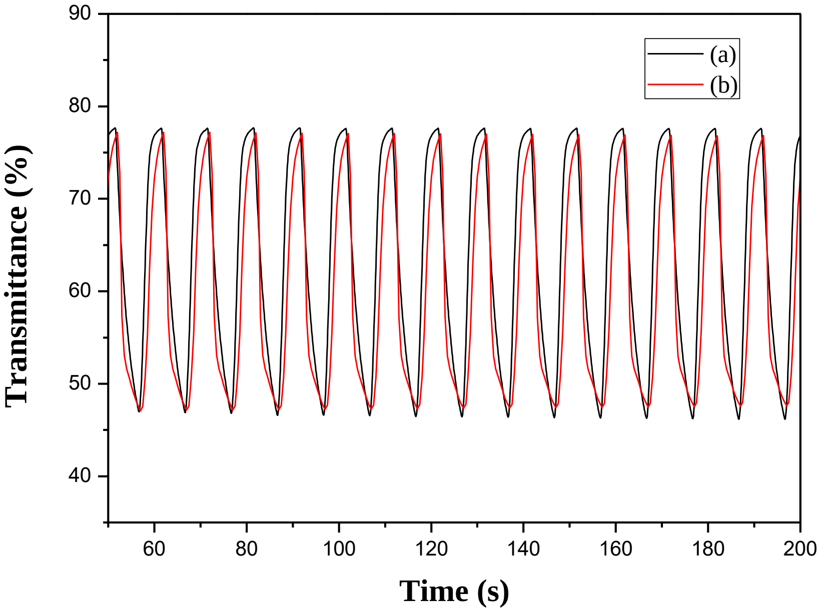

Figure S5. Transmittance-time profiles of PBPBC under (a) dark environment and (b) AM 1.5 irradiation (100 mW cm^{-2}) with a residence time of 5 s. The measurements were carried out after under dark (or light) condition for 30 h.

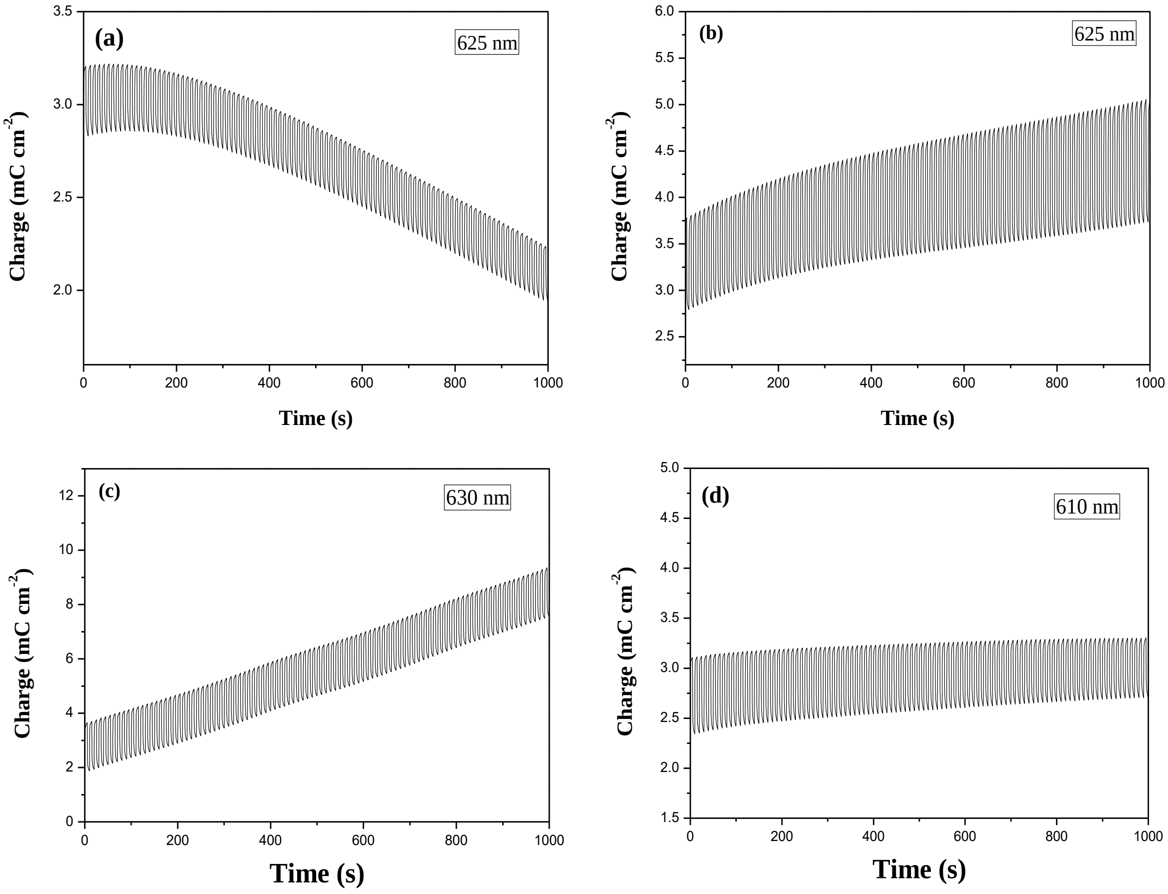

Figure S6. Charge-time plots of (a) PBPBC/PEDOT, (b) P(BPBC-*co*-BT)/PEDOT, (c) P(BPBC-*co*-CDT)/PEDOT, and (d) P(BPBC-*co*-CDTK)/PEDOT ECDs with a residence time of 5 s.