Supporting Information for

Ionic Side-Chain Engineering in Conjugated Polyelectrolytes for High-Performance Pseudocapacitors

Jinesh Lalitkumar Chouhan^a, Haim Kwon^a, Jung Min Ha^a, Wonho Lee^{b,*}, Han Young Woo^{a,*}

^aDepartment of Chemistry, Korea University, Seoul, Republic of Korea, 02841

^bDepartment of Polymer Science and Engineering, Kumoh National Institute of Technology, Gumi, Gyeongbuk, Republic of Korea, 39177

*Corresponding Authors

Wonho Lee (<u>1holee@kumoh.ac.kr</u>), and Han Young Woo (<u>hywoo@korea.ac.kr</u>)

1. General

¹H-NMR and ¹³C-NMR spectra were recorded using a Bruker Advance III HD system operating at 500 and 125 MHz. The number-average (M_n) and weight-average molecular weights (M_w) of the polymers were determined using an Agilent 1200 Series Gel Permeation Chromatography (GPC) system, with o-dichlorobenzene as the eluent and calibration based on polystyrene standards. UV-Vis-NIR absorption spectra were measured both in solution and in film form using a JASCO V-630 spectrophotometer. Scanning Electron Microscopy (SEM) images were obtained using a Hitachi SU5000 FE-SEM (Japan). Contact angle measurements were conducted at room temperature with a Phoenix10 system (SEO Co.).

2. Electrochemical Characterization

All electrochemical measurements (CV, GCD, EIS, and rate performance) were performed using a VersaSTAT-3 electrochemical workstation with a conventional three-electrode setup and 2 M NaCl in water as the electrolyte. The electrolyte solutions were purged with dry argon for at least 15 minutes to deoxygenate the system. A platinum mesh, an ITO-coated glass deposited with CPEs or CPEs-SWCNT composites, and a Saturated Calomel Electrode (SCE) (Sat'd KCl + 0.01 M AgCl) were used as the counter, working, and reference electrodes, respectively. The CPE films were prepared by dissolving the active CPE materials at a concentration of 5 mg/mL. Specifically, CPE-K was dissolved in water, while CPE-Br was dissolved in methanol. For each film, 200 μ L of the prepared solution was drop-cast onto a clean ITO substrate. The films were allowed to dry in air, which were used directly for subsequent electrochemical testing. A similar procedure was used to fabricate CPE/SWCNT composite films. CPE and SWCNT were mixed in weight ratios of 1:2, 1:1, and 2:1, and dispersed in 5 mL of solvent (deionized water for CPE-K and methanol for CPE-Br). The composite solution was then drop-cast onto ITO substrates, yielding films with an active mass loading of approximately 1.0 mg.

3. Spectroelectrochemical Characterizations

For spectroelectrochemical analysis, a three-electrode system was combined with a UV-Vis-NIR spectrometer to monitor optical transitions during electrochemical doping and dedoping. The working electrode consisted of the active film, with a reference electrode and a counter electrode completing the circuit. Chronoamperometry was performed at different applied potentials to induce doping (charging) and dedoping (discharging) of the film. During doping, a potential of 0.1 V was applied for 300 seconds, and the corresponding UV-Vis-NIR spectra were recorded. This process was repeated at different step potentials to track the spectral evolution. The potential was stepwise increased from 0 V to 0.8 V (0.1 V per step), with each step held for 300 seconds before measuring the UV-Vis-NIR absorption at each stage. For dedoping, the applied potential was stepped down from 0.8 V, resulting in a decrease in NIR absorption and an increase in visible absorption, indicating the transition from a doped to a dedoped state. The reverse trend was observed during doping, where NIR absorption increased and visible absorption decreased.¹

4. Materials

4H-cyclopenta-[2,1-b;3,4-b']-dithiophene (CDT) was purchased from BLD pharma. 2,1,3-Benzothiadiazole-4,7-bis(boronic acid pinacol ester) was purchased from solarmer, Inc. SWCNTs were purchased from TCI chemicals. All the other reagents and solvents used were purchased from Sigma Aldrich. All these were used without any further purifications.

4-1. Synthesis

The synthesis of the monomers, precursor neutral polymer and conjugated polyelectrolytes studied in this study are shown in Scheme S1.

CPE-K: CPE-K was synthesized according to previously reported methods.² The ¹H NMR of CPE-K in D_2O only showed non informative broad peaks, probably due to the presence of paramagnetic radical cations. Therefore, ion exchange with excess tetrabutylammonium bromide (TBABr) provided a DMSO-soluble polyelectrolyte CPE-TBA with tertbutylammonium as the counterions, of which NMR was possible to analyse.

Poly[4,4-bis(6-bromohexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-alt-2,1,3-

Benzothiadiazole] (PCPDTBT): All monomers required for the synthesis of the neutral polymer PCPDTBT were synthesized according to previously reported procedures.³ Compound 3 (0.2 g, 0.302 mmol), 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (0.117 g, 0.302 mmol), and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄, 0.018 g, 0.015 mmol, 5 mol%) were dissolved in toluene (4 mL) under a nitrogen atmosphere. An aqueous solution of potassium carbonate (2 M, 2 mL) was added, and the reaction mixture was stirred at 80 °C for 1.5 h. After completion, the reaction mixture was cooled to room temperature and precipitated into methanol. The crude polymer was purified via Soxhlet extraction using methanol, acetone, n-hexane, and chloroform in sequence. The chloroform fraction was collected and concentrated under reduced pressure, yielding a dark blue polymer

(0.072 g, 37%). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.15 – 7.85 (m, 2H), 7.78 – 7.44 (m, 2H), 3.34 (s, 4H), 2.15 – 1.69 (m, 8H), 1.45 – 1.06 (m, 12H). M_n = 5.4 kg/mol (D = 1.33).

CPE-Br: PCPDTBT (0.048 g, 0.072 mmol) and trimethylamine (30 equiv.) were dissolved in THF and stirred at room temperature for 2 days. After completion, THF was removed under reduced pressure, and methanol was added to dissolve the resulting precipitate, yielding the intermediate CPE-Br. The reaction mixture was stirred overnight to ensure complete quaternization. Subsequently, the solvents were evaporated under vacuum, and the crude product was redissolved in methanol and precipitated into diethyl ether. The resulting dark blue solid was collected by filtration and dried under vacuum to afford the final product (0.055 g, 93%). ¹H NMR (500 MHz, DMSO) δ (ppm): 8.36 – 8.12 (m, 2H), 7.65 – 7.05 (m, 2H), 3.24-3.17 (m, 4H), 3.08 – 2.89 (m, 18H), 2.19 – 1.93 (m, 4H), 1.56 (s, 4H), 1.32 – 0.82 (m, 12H).

5. Supporting Figures



Scheme S1. Synthesis of (a) CPE-K and (b) CPE-Br.



Fig. S1 ¹H NMR spectrum of CPE-TBA in DMSO-d6.



Fig. S2 ¹H NMR spectrum of PCPDTBT in CDCl₃.



Fig. S3 ¹H NMR spectrum of CPE-Br in DMSO-d6.



Fig. S4 ¹H and ¹³C NMR spectra of compound 1 in D₂O.



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Fig. S5 ¹H and ¹³C NMR spectra of compound 3 in CDCl₃.



Fig. S6 Photographs of CPE-K (in water) and CPE-Br (in methanol) solutions.



Fig. S7 GCD profiles of CPE-K and CPE-Br at different current densities ranging from 1 A/g to 5 A/g.



Fig. S8 Spectroelectrochemical analysis of (a) CPE-K and (b) CPE-Br films by electrochemical doping.



Fig. S9 (a) The equivalent circuit model and (b) Z' versus $\omega^{-1/2}$ plots with extracted Warburg factor (σ) values for CPE-K and CPE-Br.



Fig. S10 Electrochemical analysis of SWCNTs films: (a) cyclic voltammograms, (b) GCD, (c) EIS, and (d) calculated *b*-value.



Fig. S11 SEM images of (a) SWCNTs, (b) CPE-K, and (c) CPE-Br films.



Fig. S12 Water contact angle measurements of (a) SWCNTs, (b) CPE-K, (c) CPE-Br, (d) CPE-K/SWCNT and (e) CPE-Br/SWCNT films.



Fig. S13 Cyclic voltammograms of CPE/SWCNT composites at different ratios.



Fig. S14 GCD profiles of 2:1 CPE/SWCNT composites at different current densities ranging from 1 A/g to 10A/g.



Fig. S15 Nyquist plots from EIS measurements of (a) CPE-K/SWCNT and (c) CPE-Br/SWCNT composites at weight ratios of 1:2, 1:1, and 2:1 (inset shows the zoomed-in spectra). Capacitance retention and CE uring 1000 charge–discharge cycles at a current density of 5 A/g for (b) CPE-K and CPE-K/SWCNT composites, and (d) CPE-Br and CPE-Br/SWCNT composites.

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