Electronic Supplementary Information

Poly(phenanthrenequinone) as a Conductive Binder for Nano-sized Silicon Negative Electrodes

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Synthesis of 3,6-poly(phenanthrenequinone) (PPQ)

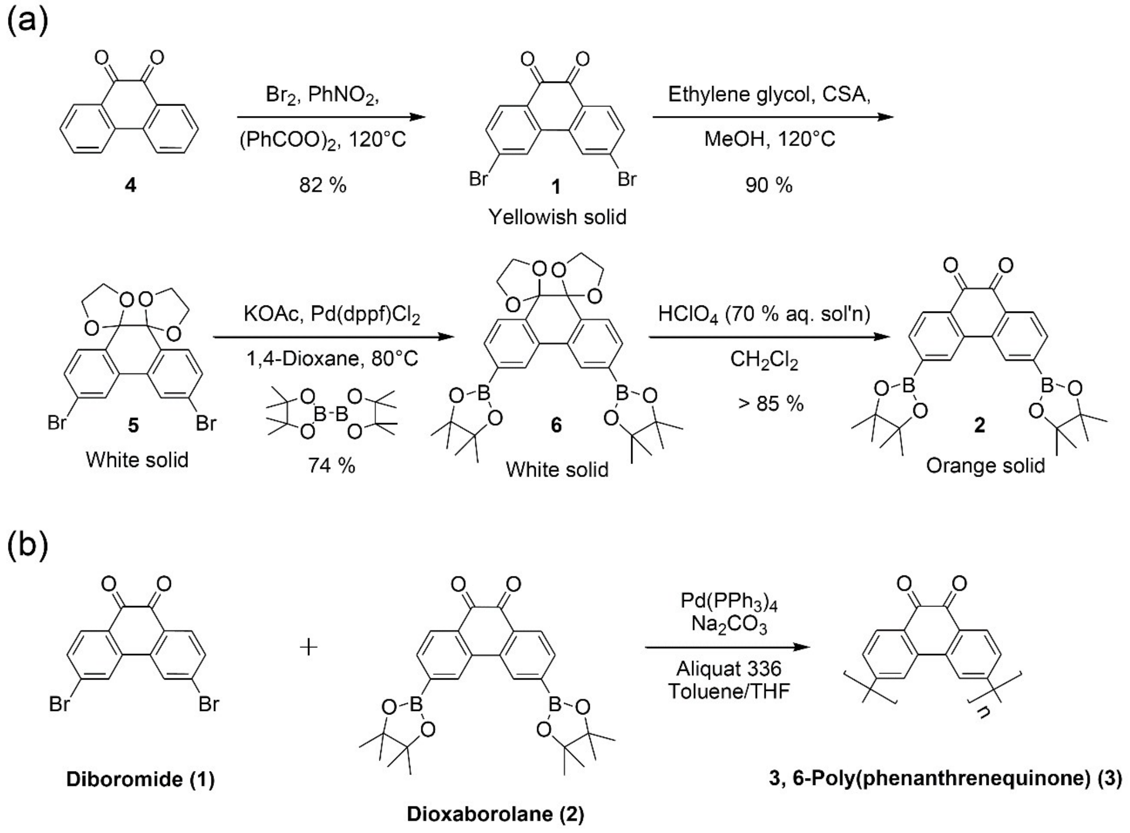

Fig. S1. Synthetic procedure for monomers (a) and polymer (b).

General

Materials for synthesis of PPQ were purchased from commercial suppliers and used without further purification except solvents. Tetrahydrofuran (THF) was distilled in the presence of sodium with benzophenone and 1,4-dioxane, toluene were distilled in the presence of calcium hydride under N_2 atmosphere.

All the experimental glassware, syringes, and magnetic stirring bars were oven-dried at 120°C for at least 4 h and stored in desiccator prior to use. Air or moisture sensitive reactions were conducted under Ar atmosphere. The reactions were checked by thin layer chromatography plate. Analytical thin layer chromatography (TLC) was performed with Merck 60 F_{254} glass plates pre-coated with a 0.25-mm thickness of silica gel and then monitored under UV light (254 nm) and visualized with phosphomolybdic acid staining solution. Column chromatography was performed on Kiesel gel 60 (70~230 mesh) silica gel.

^1H and ^{13}C NMR spectra were measured at 400 MHz and 100 MHz, respectively, using $CDCl_3$ as a solvent on a Bruker Avance III spectrometer unless stated otherwise. The data were reported as follows in ppm (δ) from the internal standard (TMS, 0.0 ppm): chemical shift (multiplicity, integration, coupling constant in Hz). Gel permeation chromatography (GPC) analysis against poly(methyl methacrylate) standards was performed in DMF on Ultimate 3000 GPC with LPG-3400SD pump, Shodex KD-801 columns and Refracto Max 520, a refractive index detector. High resolution mass spectra were obtained on JEOL JMS-600W (mass system), Agilent 6890 (GC system) with electron ionization mode. Melting points were measured on a Meltemp apparatus in an open capillary tube.

3,6-Dibromophenanthrene-9,10-dione (1)

9,10-Phenanthrenequinone **(4)** (4.00 g, 19.2 mmol) was placed in a round bottom flask and nitrobenzene (30 ml) was added. Bromine (5 ml, 96.0 mmol) and dibenzoyl peroxide (0.15 g, 0.96 mmol) was additionally added and the reaction mixture was heated under reflux at 120°C for 15~16 h with Na_2SO_3 trap apparatus.[1–3] After cooling the reaction mixture, solid precipitate was filtered and washed with ethanol or methanol. Further purification was conducted by a recrystallization in xylene to give **1** as a yellowish solid (5.16 g, 82 %): mp 290°C; ^1H NMR $\delta = 8.12$ (d, 2H), 8.07 (d, 2H), 7.67 (dd, 2H); ^{13}C NMR $\delta =$ 178.8, 135.9, 133.4, 132.1, 129.8, 127.4; HRMS (EI) calcd for $C_{14}H_6Br_2O_2$ $[M]^+$ 365.8714, found 365.8714.

3,6-Dibromophenanthrene-9,10-di(ethyleneglycol)ketal (5)

1 (1.00 g, 2.73 mmol) was placed in a pressure tube and methanol (15 ml) was added. (±)-camphorsulfonic acid (0.82 g, 0.82 mmol) and ethylene glycol (4.57 ml, 81.9 mmol) were added to reaction mixture and heated at 120°C for 12 h.[4,5] Reaction mixture was converted into white color after 12 h and cooled to room temperature. Crude mixture was filtered and washed with diethyl ether to give **5** as a white solid (1.12 g, 90 %): mp 305°C; ^{1}H NMR δ = 7.96 (s, 2H), 7.62 (d, 2H), 7.56 (d, 2H), 4.16, 3.63 (br, 8H); ^{13}C NMR δ = 133.8, 132.2, 132.1, 128.2, 127.0, 124.4, 92.1, 61.3; HRMS (EI) calcd for $C_{18}H_{14}Br_2O_4$ $[M]^+$ 451.9258, found 451.9268.

3,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenanthrene-9,10-di(ethyleneglycol)ketal (6)

5 (2.00 g, 4.40 mmol) was dissolved in distilled 1,4-dioxane (150 ml) in a round bottom flask and $Pd(dppf)Cl_2$ (0.32 g, 0.44 mmol), bis(pinacolato)diboron (2.4 g, 2.1 mmol) and KOAc (2.59 g, 26.4 mmol) were added into the solution.[6,7] The reaction mixture was heated under reflux for 17 h under Ar atmosphere. After cooling, crude solution was filtered out through Celite with dichloromethane (DCM) and ethyl acetate (EtOAc). This organic solution was concentrated by rotary evaporator, and the crude solid was purified with silica gel column chromatography (Hexane:EtOAc = 2:1 → 1:1). Further purification was conducted with silica gel column chromatography (Hexane:EtOAc = 8:1 → 4:1) to give **6** as a white solid (1.79 g, 74 %): mp 309°C; ^{1}H NMR δ = 8.41 (s, 2H), 7.87 (d, 2H), 7.74 (d, 2H), 4.15, 3.67 (br, 8H), 1.35 (s, 24H); ^{13}C NMR δ = 135.5, 135.1, 132.5, 130.4, 125.3, 92.6, 84.0, 61.3, 24.8; HRMS (EI) calcd for $C_{30}H_{38}O_8B_2$ $[M]^+$ 548.2753, found 548.2743.

3,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenanthrene-9,10-dione (2)

6 (1.94 g, 3.53 mmol) was dissolved in DCM (120 ml) and perchloric acid (70% aq. solution, 2.5 ml, 35.3 mmol) was added into the solution.[8] The reaction mixture was stirred vigorously for 1 h at room temperature. The reaction mixture was quenched by saturated $NaHCO_3$ solution and the organic layer was dried over $MgSO_4$, filtered and concentrated by rotary evaporator. The obtained product was purified by washing with ethanol to give **2** as an orange solid (1.38 g, 85 %): mp 285°C; ^1H NMR $\delta = 8.52$ (s, 2H), 8.16 (d, 2H), 7.89 (d, 2H), 1.42 (s, 24H); ^{13}C NMR $\delta = 180.8$, 135.6, 135.0, 132.5, 130.3, 84.6, 24.9; HRMS (EI) calcd for $C_{26}H_{38}O_6B_2$ $[M]^+$ 460.2228, found 460.2236.

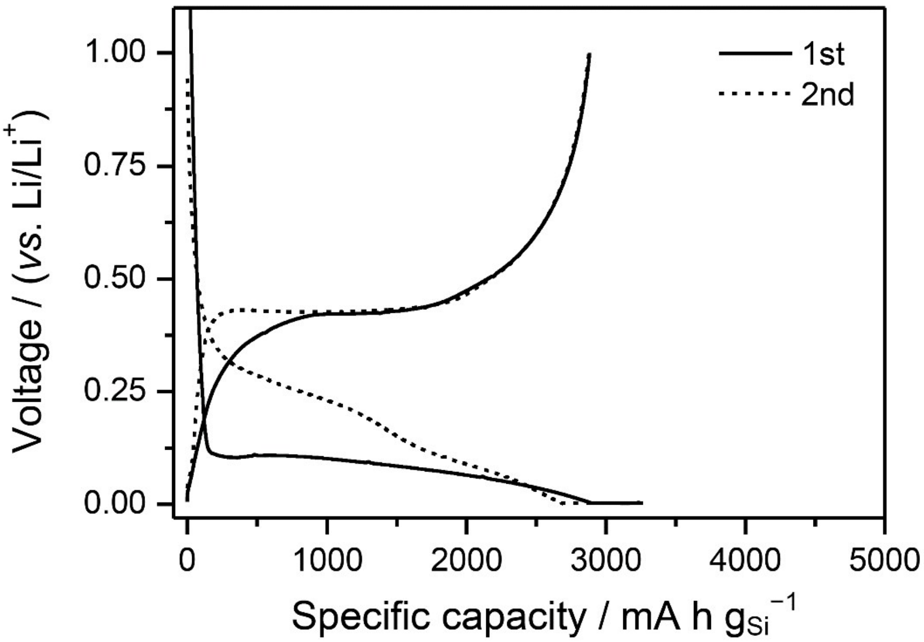

Fig. S2. The charge/discharge voltage profiles of Li/nano-Si cell fabricated with LiPAA binder. The composite electrode was prepared from nano-Si powder, conductive carbon (Super P) and LiPAA (5:2:3, weight ratio). Current density = 100 mA g_{Si}^{-1} (0.028 C).

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