Supporting Information

Mechanically Robust and Superior Conductive n-Type Polymer Binders for High-performance Micro-Silicon Anodes in Lithium-Ion Batteries

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Experimental Procedures

Materials and Synthesis:

Raw Materials: All starting chemicals used to synthesize conductive polymers were purchased from Chengdu Kelong Chemical Co., Ltd. Sulfuric acid fuming 20% was received from Yangzhou Lubao Chemical Reagent Co., Ltd. Nitromethyl pyrrolidone (NMP) and dimethyl sulfoxide (DMSO) with a purity greater than 99% were bought from Shanghai Titan Scientific Co., Ltd. Super C65 and CMC were acquired from Shenzhen Kejing Zhida Technology Co., Ltd. PAALi (4 wt.%) and the electrolyte (1.0 M $LiPF_6$ in carbonate (EC) and dimethyl carbonate (DMC) (1:1 v/v) with 5 wt.% fluoroethylene carbonate (FEC)) were obtained from Guangdong Candlelight New Energy Technology Co., Ltd. The silicon powder (particle size 0.5 μm) were provided by Innovative Nano Co., Ltd. and used without purification. Freshly deionized water was utilized in experiments.

Synthesis of PODs: First, 4-4'diphenyl ether dicarboxylic acid (7.53 g, 29.15 mmol) and hydrazine sulfate (5.69 g, 47.73 mmol) were mixed with terephthalic acid (2.08 g, 12.49 mmol), isophthalic acid (2.08 g, 12.49 mmol), 4,4'diphthalic acid (3.03 g, 12.49 mmol), 2,6-naphthalene dicarboxylic acid (2.70 g, 12.49 mmol), respectively, and then 20% oleum was used as a solvent to prepare the sulfonated POD, which was then neutralized by 0.05 mol L^{-1} lithium hydroxide solution. Finally, the synthesized polymers were soaked in deionized water, washed to neutrality, and dried in an oven to obtain four PODs. The resultant PODs were dissolved in deuterium band-DMSO (DMSO-d6) to identify their chemical structures via ^1H NMR tests as shown in **Figure S1** with the assistance of elemental composition. GPC (DMF, PS standard): p-POD (Mn=140701, PDI = 2.2); m-POD (Mn=141234, PDI=2.2); b-POD (Mn=142063, PDI=2.2); n-POD (Mn=143013, PDI=2.2).

Characterization:

Fourier Transform Infrared Spectroscopy: The PODs were dissolved in NMP to prepare 10 wt.% solutions, which were then coated with a 500 μm applicator and dried to generate POD films. Attenuated Total Reflectance (ATR-FTIR) spectra of POD films were collected by a Tracer100 spectrometer (Shimadzu Corporation, Japan).

Tensile Test: Tensile strength was measured by the INSTRON 5982 electronic universal testing machine with a drawing speed of 20 mm min^{-1} and a gauge length of 20 mm.

Elemental Analysis: Elemental analysis was performed on EA3000 Elemental Analyzer (Euro Vector, Italy). The mass percentages of C, H, O, and S elements were characterized respectively, as summarized in **Table S1**. The SD is defined as 100% when each benzene or naphthalene ring is grafted with one sulfonate, which can be calculated according to the following equation:

$SD=W_S'/W_S= (W_S'\cdot m_C)/ (W_C\cdot m_S)$

where W_s' and W_s represent the actual S quality score and the theoretical S quality score, m_S is corresponding to the theoretical S quality, and m_C is the theoretical C quality.

Thermogravimetric Analysis: A TGA2 Thermogravimetric Analyzer (METTLER TOLEDO, China) was utilized to analyze the thermal stability of the PODs under N_2 atmosphere with a heating rate of 10 °C min^{-1}. The temperature was first increased from room temperature to 150 °C and maintained at 150 °C for 60 min to remove the bound water in the molecule, and then continued to increase the temperature to 800 °C.

Energy Level Calculation and Contact Angle Test: In order to evaluate the cyclic voltammetry (CV) curves of the materials, PODs were coated on a stainless steel electrode and dried as working electrodes, the counter electrode was lithium metal sheet and a ceramic separator was used in the middle to assemble into a coin-type cell with 50 μL electrolyte, which consisted of 1.0 M $LiPF_6$ in EC, DMC and DMSO (5:5:3 v/v/v) with 5 wt.% FEC. The CHI660E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China) was used to carry out the CV tests with the potential sweep between 2.5 V and 0 V at 1 mV s^{-1} sweep rate. The 10 wt.% POD solutions with 0.18 mm thickness were sandwiched

between two ITO quartz conductive glass sheets to assemble electrochromic devices. The ultraviolet-visible (UV-Vis) spectra of the devices in doping state were obtained by applying 3.5 V voltage to the devices to change their colors, where the undoing device as background was subtract. The UV-vis spectra were recorded by TU-1900 UV–Vis spectrometer (Beijing Purkinje General Instrument Co., Ltd., China) with a scan wavelength range from 400 to 900 nm. Next, a small amount of POD was dissolved in water to generate a 0.01 wt.% solution, which was then tested UV-vis as the undoped material. The contact angle test of the POD film to electrolyte solvent was completed via a DSA100 Optical Contact Angle Measuring Instrument (Germany). The electrolyte solvent consisted of EC and DMC (1:1 v/v) with 5 wt.% FEC.

Cell Assembling and Testing: The electrode slurry was made by dispersing a certain amount of SiMPs and the conductive additive C65 in the POD NMP solution with a weight ratio of 6:2:2 (SiMPs to C65 to POD), which was then coated on a copper foil. After that, the coated copper foil was put into a vacuum oven and dried at 80 °C for 48 h to fabricate the bonded SiMP electrode. In the same way, a reference SiMP electrode with either PAALi or CMC as a binder was prepared. The average loading of active materials was 0.4− 0.6 mg cm^{-2}. All the cell data reported are based on lithium metal as a counter electrode in coin cells with a testing voltage range of 0.01-1.6 V.

Nanoindentation and Morphology Measurements: The nanoindentation of the electrode sheet was measured on the UNHT ultra-nano indentation instrument (Switzerland) with a speed of 3000 nm min^{-1}. Through the test, the indentation modulus, Vickers hardness, maximum indentation depth, and residual indentation depth parameters of various binder-bonded SiMP anodes were obtained, as shown in **Table S3**. SEM images of the anode surface and cross-section were collected by JSM-5900LV Scanning Electron Microscope (Japan) with an accelerating voltage of 15 kV and 5 kV, respectively, using the high vacuum mode at room temperature.

Results and Discussion

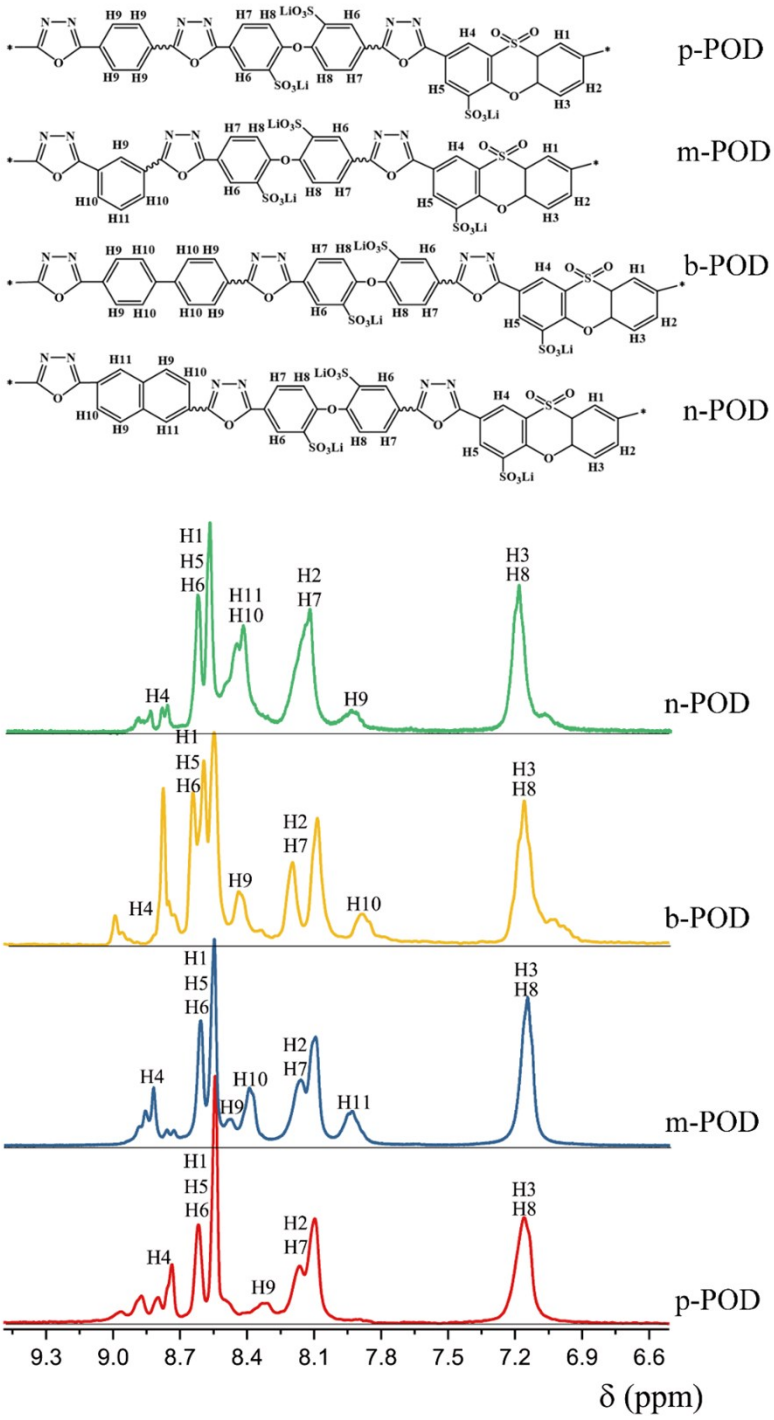

Figure S1. The corresponding chemical structures and ^{1}H NMR spectra of PODs.

Parameter / Polymer	200~400 ℃ Weight loss (%)	N (%)	C (%)	H (%)	S (%)

Table S1. Thermal and chemical stability and composition of PODs.

p-POD	3.86	6.59	35.04	3.68	10.61
m-POD	2.49	6.50	34.86	3.68	10.41
b-POD	2.39	5.56	33.18	3.86	11.09
n-POD	2.79	5.90	36.56	3.67	10.58

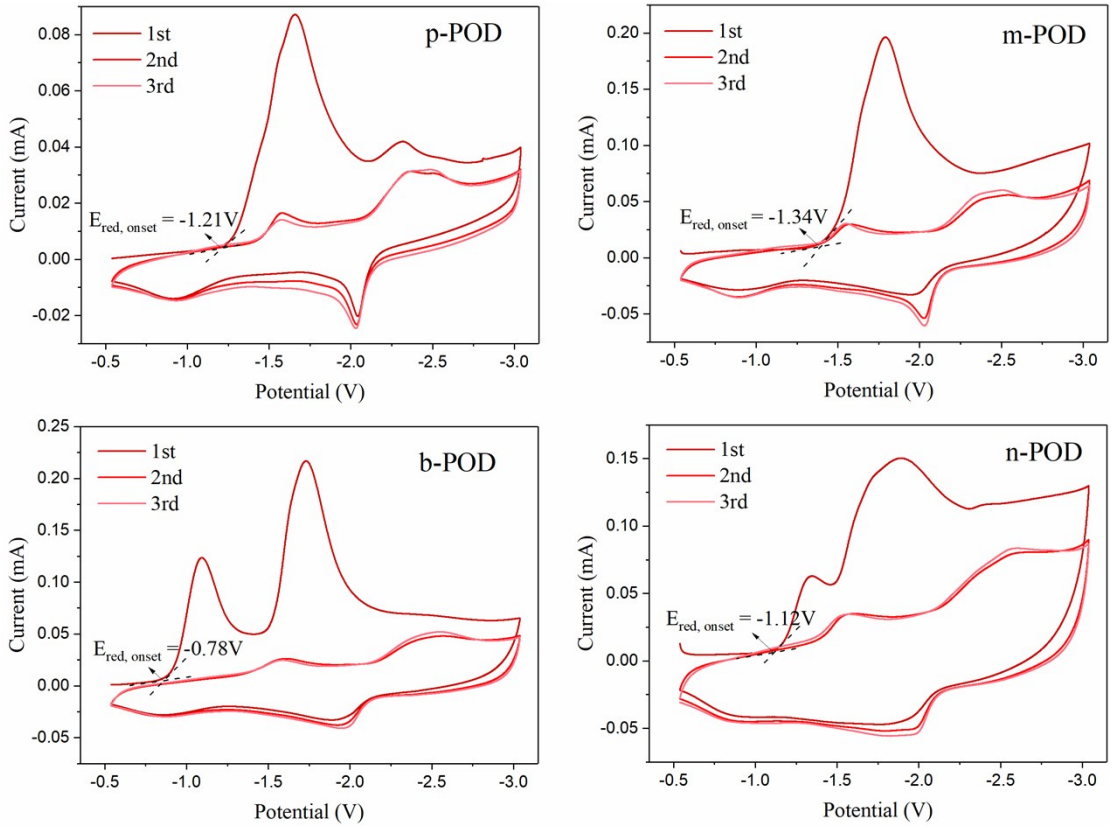

Figure S2. CV profiles of PODs.

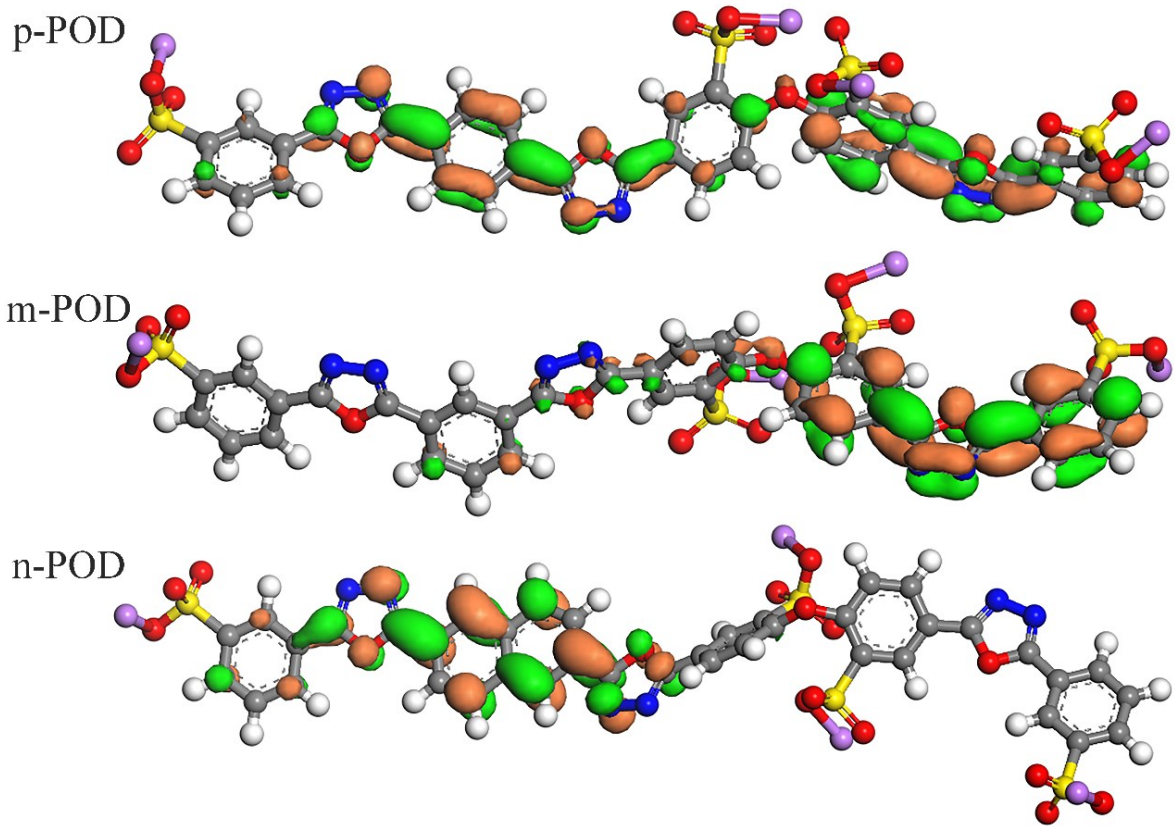

Figure S3. Calculated LUMO energy levels of PODs.

Table S2. Simulated energy level parameters of the PODs.

Polymer \ Parameter	ELUMO* (eV)	Eg* (eV)
p-POD	-2.89	3.12
m-POD	-2.81	3.59
b-POD	-2.99	2.80
n-POD	-2.95	2.91

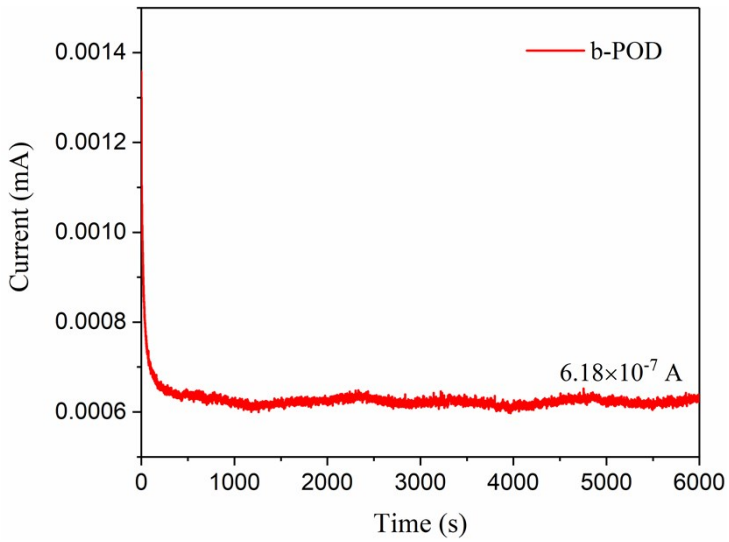

Figure S4. The i-t curve of b-POD in the eigenstate state.

Table S3. Related parameters of PODs' conductivity.

Polymer \ Parameter	D (cm)	R(eigenstate) (Ω)	R(doping) (Ω)	i(eigenstate) (A)	i(doping) (A)
p-POD	0.0032	22.1	16.2	6.09×10^{-7}	3.22×10^{-6}
m-POD	0.0034	36.1	22.2	6.22×10^{-7}	1.94×10^{-5}
b-POD	0.0030	11.4	5.2	6.18×10^{-7}	1.97×10^{-5}
n-POD	0.0032	16.8	11.4	6.24×10^{-7}	2.23×10^{-6}

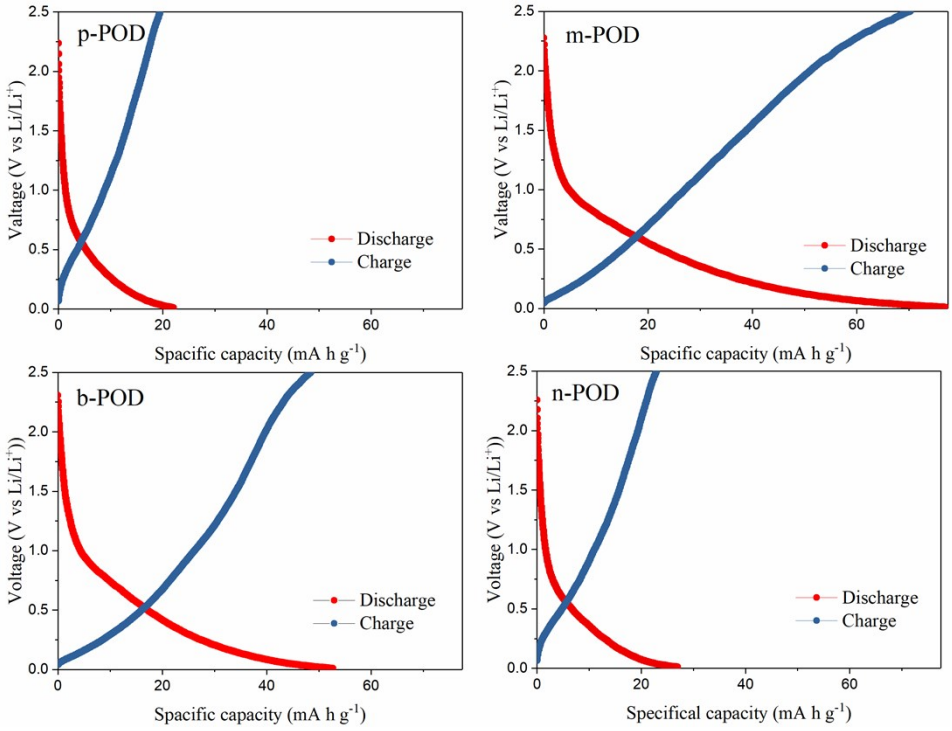

Figure S5. Charge and discharge profiles of the cells with various PODs at the current density of 10 mA g^{-1}

Table S4. Nano-indentation test data of SiMP anodes with various binders.

Anodes \ Parameter	Indentation modulus (MPa)	Vickers hardness (MPa)	Maximum indentation depth (nm)	Residual indentation depth (nm)
Si/C65/CMC	4.939	4.896	1978	1718
Si/C65/PAA	10.278	10.043	1376	1216
Si/C65/p-POD	5.069	6.965	1677	1418
Si/C65/m-POD	4.051	5.993	1821	1517
Si/C65/b-POD	9.135	13.795	1188	980
Si/C65/n-POD	8.377	15.735	1271	1040

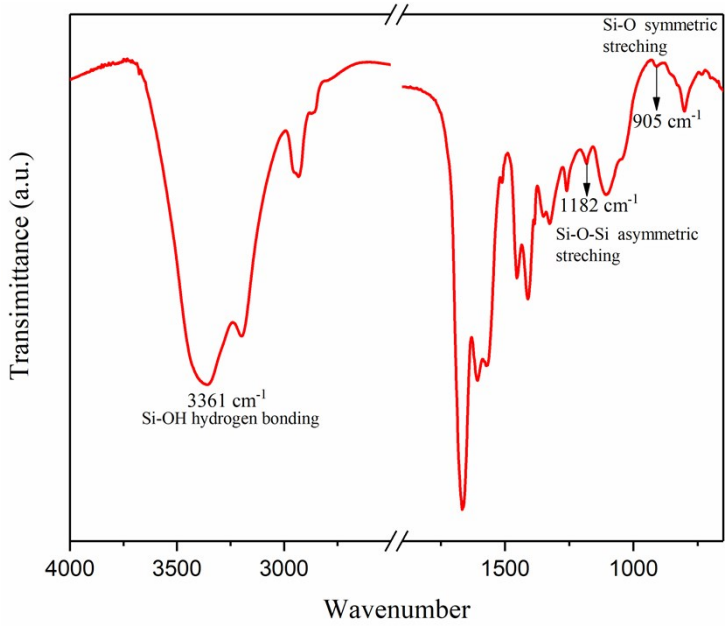

Figure S6. The FTIR spectra of raw SiMPs.

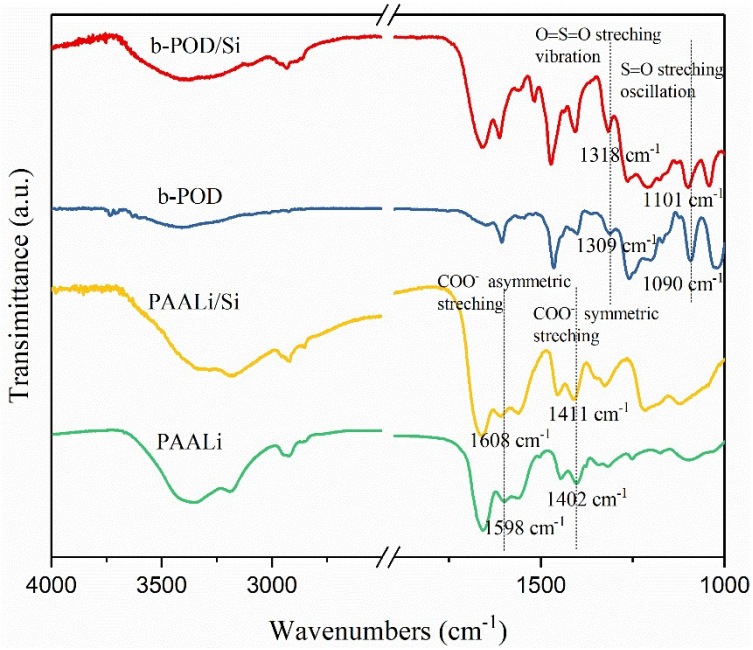

Figure S7. The FTIR spectra of PAALi, PAALi/Si composite, b-POD and b-POD/Si composite.

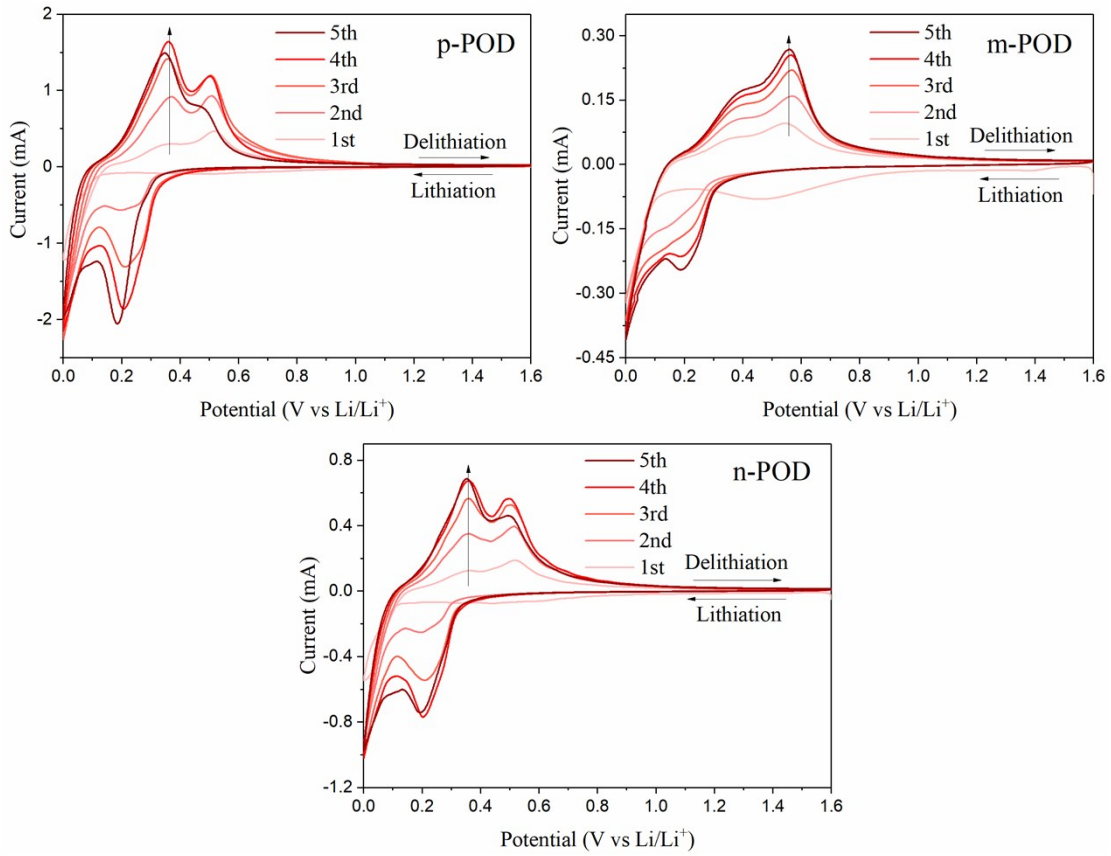

Figure S8. CV profiles of the cells with SiMP anodes prepared by PODs.

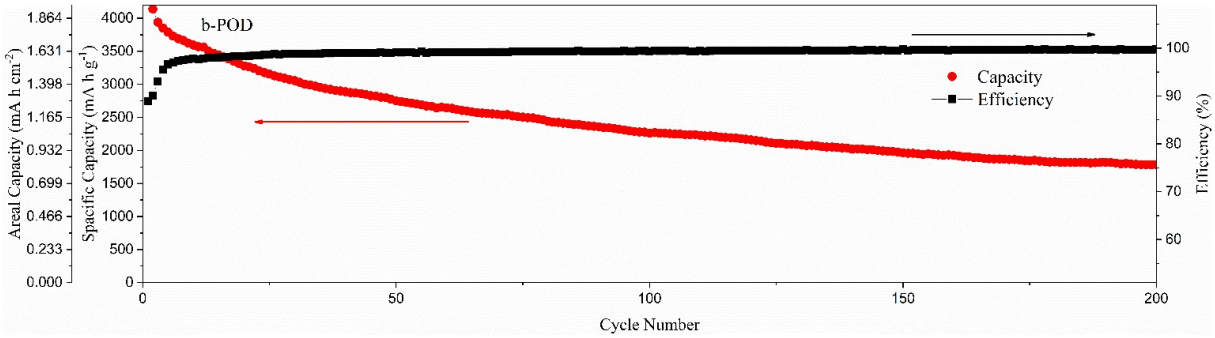

Figure S9. Cycling performance of Si/C65/b-POD for 200 cycles at 0.1 C.

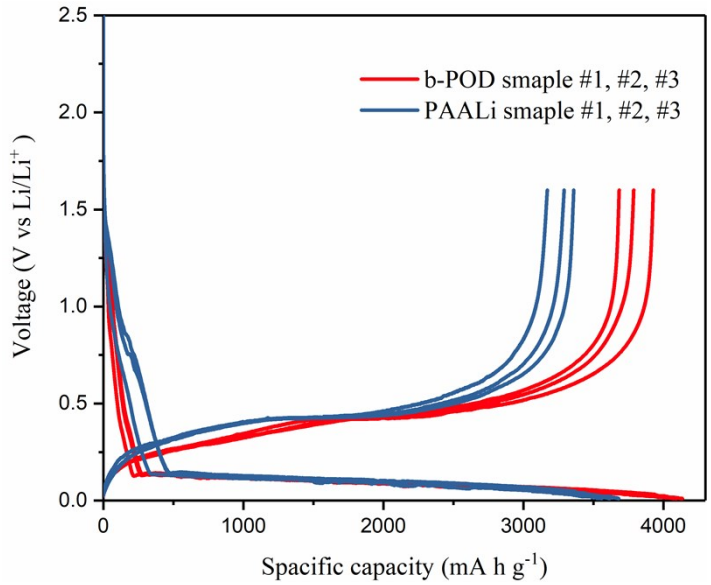

Figure S10. The first-cycle capacities of SiMP anodes prepared by using b-POD and PAALi binders at 0.02 C.