Elemental Analysis

The formation of PAQS was verified by elemental analysis. It indicates that the measured value of the C, H and S content in PAQS is 67.95 %, 2.60 % and 13.44 %, respectively, approximating to the calculated value of 70.57 %, 2.54 % and 13.43 %. The difference between the measured carbon content and calculated one is mostly caused by the residual NMP solvent, whose existence was also detected in the form of nitrogen.

Solid-state $^{13}$C NMR Spectrum

As PAQS is completely insoluble in any solvent, the solid-state $^{13}$C NMR spectrum (Fig. S1) was obtained to determine its structure. Due to the strong rigidity of the polymer chains, the spectral line is greatly widened and four spinning side bands appear around the main characteristic bands. However, we can still get the needed information from the three peaks between 100 and 150 ppm. For AQ, there are four types of carbon atoms (shown as a, b, b’, c’, d, d’ in Fig. S1). From Spectral Database for Organic Compounds, SDBS, the corresponding chemical shifts are as follows: $\delta_a=183.1$ ppm (2C), $\delta_b=\delta_{b'}=133.6$ ppm (4C), $\delta_c=\delta_{c'}=127.2$ ppm (4C), $\delta_d=\delta_{d'}=134.1$ ppm (4C). When carbon atom c bonds with sulfur atom, the electron withdrawing effect of sulfur will obviously shift $\delta_b$ and $\delta_c$ to more positive value, while other bands remain almost unchanged. Based on this knowledge, we can assign the characteristic bands of PAQS as follows: band of carbon a is hidden in the spinning side bands; the additional band at 145.5 ppm that is absent for AQ should be ascribed to carbon b according to above analysis (thioether bond formation leads to notable variation of $\delta_b$); band of carbon c’ remains at 127.1 ppm; considering the positive shift of $\delta_c$ and very insignificant difference between $\delta_{b'}$, $\delta_d$ and $\delta_{d'}$, the band at 134.3 ppm can be reasonably assigned to carbon b’, d, d’, and c. Rough comparison indicates that the ratio of the area of each band matches the number of carbon atoms deduced from above assignment. These results supply complementary and supporting proof for the formation of thioether bond between the anthracene rings.

XRD patterns and SEM micrographs

X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) observation of AQ and PAQS were conducted in order to compare their crystalline states and particle morphologies. As known, anthraquinone has a good monoclinic crystal structure, mainly due to its $\pi-\pi$ stacking between the anthracene ring layers. So in its XRD profile (Fig. S2a), strong diffraction peaks indexed by monoclinic structure can be observed. Comparing with AQ, PAQS shows a totally different XRD pattern in Fig. S2b. The quite broadened and low-intensity XRD peaks all suggest that the PAQS polymer is amorphous. It seems likely that importing thioether bond in the polymer backbone has destroyed the ordered stacking between the anthracene ring layers. The SEM micrographs of AQ and PAQS (Fig. S2c and Fig. S2d) also
show great differences. Comparison of the particles of AQ and PAQS tells that, the latter is less angular than the former, and has a more uniform size distribution. Regarding the average particle size, both of the monomer and polymer particles are with micron dimension, but the latter seems a little smaller.

**Experimental Details**

**Synthesis of PAQS**

All chemicals were of reagent grade and used as received. Na₂S·9H₂O (4.80 g, 0.02 mol) was added into 50 mL N-methyl pyrrolidone (NMP). The crystal water was removed by azeotropic dehydration using benzene as an entrainer at 150 °C. After distilling the residual benzene, 1,5-dichloranthraquinone (5.54 g, 0.02 mol) was added into the solution and reacted with anhydrous sodium sulfide at 200 °C overnight. The product was filtrated, washed with hot water and acetone for several times, and then dried at 120 °C for 12h, obtaining 4.43g (yield 93%) brown powder.

**Characterization of AQ and PAQS**

The FT-IR spectra of AQ and PAQS were recorded using KBr pellets on AVATAR 360 spectrometer (Nicolet Instrument Corp., USA) in range of 400-4000 cm⁻¹. Elemental analysis of PAQS was conducted on Vario EL III elemental analysis instrument (Elementar Inc., Germany). Solid-state ¹³C NMR spectra of PAQS were preformed on Varian Infinity Plus 400 spectrometer (Varian Inc., USA) with spin rate of 5000 kHz. XRD analysis of the powders were carried out on Shimadzu XRD 6000 X-ray diffractometer (Shimadzu Corp., Japan) using Cu Kα (λ= 0.15406 nm) radiation. SEM micrographs were observed on Quanta 200 environmental scanning electron microscope (FEI Company, Holland).

**Electrochemical measurements**

CR2016 type coin cells consisting of the cathode and the lithium anode separated by a Celgard 2300 microporous membrane were used for cycling tests. The cathode were prepared by mixing the active material with 40 wt% acetylene black and 20 wt% polytetrafluoroethylene (PTFE) binder, then compressing the mixture onto a stainless steel mesh current collector. The electrolyte was 1 M LiN(CF₃SO₂)₂ (LiTFSI) solution in a mixed solvent of 1,3-dioxolane (DOL) and dimethoxyethane (DME) (2:1 by weight) or 1 M LiClO₄ solution in that of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume). The cells were assembled in an argon-filled glove box. The charge-discharge experiments were performed on LAND battery test system (China) in the potential range of 1.4~3.5 V, using different current rates.

CV measurements were conducted on a three-electrode cell on CH1660A electrochemical workstation (CH Instruments Inc., USA). The working electrode had the same composition as the above description, lithium foil acted as both the reference and counter electrode. The scan potential range is 1.4~3.2 V and the scan rate is 0.1 mV s⁻¹. All the electrochemical tests were operated at room temperature.
Fig. S1. Solid-state $^{13}$C NMR Spectrum of PAQS. Spin rate = 5000 kHz.

Fig. S2. XRD patterns of (a) AQ and (b) PAQS, and SEM micrographs of (c) AQ and (d) PAQS.