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## A low cost, all-organic Na-ion Battery Based on Polymeric Cathode and Anode

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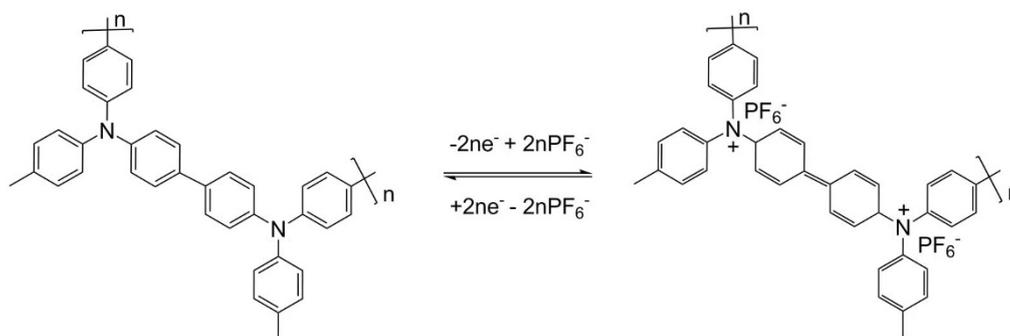
Current battery systems have severe cost and resource restrictions, difficultly to meet the large scale electric storage applications. Herein, we report an all-organic Na-ion battery using p-dopable polytriphenylamine as cathode and n-type redox-active poly(anthraquinonyl sulphide) as anode, excluding the use of transition-metals as in conventional electrochemical batteries. Such a Na-ion battery can work well with a voltage output of 1.8 V and realize a considerable specific energy of 92 Wh kg<sup>-1</sup>. Due to the structural flexibility and stability of the redox-active polymers, this battery has a superior rate capability with 60% capacity released at a very high rate of 16 C (3200 mA g<sup>-1</sup>) and also exhibit an excellent cycling stability with 85% capacity retention after 500 cycles at 8 C rate. Most significantly, this type of all-organic batteries could be made from renewable and earth-abundant materials, thus offering a new possibility for widespread energy storage applications.

Existing battery technologies are all based on redox chemistry of less-common metals and their oxides, which face severe cost and resource restrictions for widespread applications of electric energy storage such as in electric vehicles and renewable power stations<sup>1-3</sup>. To meet growing demands for green and sustainable electric power storage, Na-ion batteries are recently revisited as a promising alternative to current Li-ion technology, due to their material abundance, low-cost and environmental benignity<sup>4,5</sup>.

Recent researches on Na-ion battery are mostly directed on the development of inorganic Na intercalation materials<sup>6</sup>. Several types of layered transition metal oxides<sup>7,8</sup>, phosphates<sup>9</sup>, and hexacyanides<sup>10,11</sup> were demonstrated to have certain reversible capacities as Na-insertion cathodes, these materials suffer from their low capacity utilization or sluggish kinetics, due to the stronger coordination of larger Na ions in the rigid inorganic lattices than their lithium counterpart. Meanwhile, a number of Na-alloyable metals such as Sn<sup>12</sup> and Sb<sup>13</sup> were recently revealed as high capacity Na-storage anodes<sup>14</sup>, these metals are also scarce resources and difficult to support large scale electric storage applications.

Redox-active polymers<sup>15-17</sup> seem to be a good choice of electrode-active materials for Na-ion batteries because their structural diversity and materials sustainability. As a flexible framework, organic polymers can accommodate larger Na ions reversibly without much spatial hindrance, thus facilitating to achieve a fast kinetics for Na<sup>+</sup> insertion and extraction reactions<sup>18-20</sup>. More significantly, organic polymers are potentially low-cost, environmentally friendly and possibly accessible from abundant biomass resources. However, despite tremendous work has been done on developing polymeric electrode materials for Li-ion batteries and electrochemical supercapacitors, very few of them have been devoted for Na-ion batteries. Very recently, Hong et al.<sup>18</sup> and Hu et al.<sup>19</sup> demonstrated reversible Na<sup>+</sup> insertion behaviour of organic carboxylate, Na<sub>2</sub>C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>, with a nearly 2 Na storage capacity ~ 300 mAh g<sup>-1</sup> as an anode material. Meanwhile, our group has also revealed feasible applications of p-doped polymers such as nitro-substituted polyaniline<sup>20</sup> and Fe(CN)<sub>6</sub><sup>4-</sup>-doped polypyrrole<sup>21,22</sup>, as cathode materials and n-type polythiophene<sup>23</sup> as an anodic host for Na-ion batteries, all of which exhibit considerable redox capacity and cyclability in Na<sup>+</sup> electrolyte. Unfortunately, these organic cathodes and anodes were all singly tested in half cell experiments and have not been paired for a Na-ion battery.

In principle, a Na-ion battery can be constructed by use of a pair of organic cathode and anode, as long as this pair of organic electrodes has sufficient potential difference and can be coupled well to carry out a battery reaction. Such an all-organic Na-ion battery would be greatly attractive for large scale electric storage applications because of its low cost and eco-friendliness. In this paper, we report an all-organic Na-ion battery based on polytriphenylamine (PTPAn) cathode and poly(anthraquinonyl sulfide) (PAQS) anode, where the charge/discharge reactions go through the doping/dedoping of electrolyte cations into/from PTPAn cathode simultaneously with the



**Figure 1** | Redox mechanism of PTPAn.

association/disassociation of Na ions into/from the PAQS anode. Since the PTPAn cathode and PAQS anode operate at a quite high potential of 3.6 V and at a lower potential of 1.8 V (vs.  $\text{Na}^+/\text{Na}$ ), this all-organic battery can output a discharge voltage of  $\sim 1.8$  V with superior rate capability and cyclability.

## Results

The selection of the PTPAn/PAQS redox couple for a Na-ion battery is mainly based on the reversible p-dopability of PTPAn at a high potential and the strong n-type redox activity of PAQS at relatively low potentials, which enable an effective voltage output. In addition, these two redox polymers are highly electroactive and structurally stable, possibly achieving a Na-ion battery with high rate capability and long term cyclability.

**p-Type redox behaviors of PTPAn cathode.** PTPAn and its derivatives have been actively investigated as a fast hole-transport material for organic optoelectronic devices<sup>24</sup>. Because of its unique structure with electroactive polyaniline units embedded on highly conductive polyparaphenylene chains, we tried to use PTPAn as polymer cathode for Li-ion batteries and found its superior capacity utilization, stable cyclability and high rate capability<sup>25</sup>. As shown in Figure 1, the cathodic reaction of PTPAn takes place through the reversible redox process between triphenylamine and triphenylamine radical cation, accompanying with the association/dissociation of the electrolyte anion ( $\text{PF}_6^-$ ) into/from the polymer chains. However, the p-type redox property of PTPAn in Na-containing electrolytes is not clear up to date.

Figure 2 shows electrochemical response of PTPAn in a  $\text{NaPF}_6$  electrolyte. The structural characterization of the synthesized PTPAn sample is given in Electronic Supplementary Information (Figure S1). As shown in the cyclic voltammograms (CV) of Fig. 2a, a pair of well-defined redox peaks with almost similar peak areas appear at 3.4 and 3.7 V (vs.  $\text{Na}/\text{Na}^+$ ), characterizing the reversible p-doping reaction of the PTPAn polymer. Accordingly, galvanostatic charge/discharge curves of the Na/PTPAn cells as shown in Fig. 2b exhibit sloping charge and discharge curves at a quite high voltage of  $\sim 3.6$  V and the reversible discharge capacity reaches 98 mAh/g, corresponding to a 90% utilization of its theoretical 1e redox capacity ( $109 \text{ mA g}^{-1}$ ). Cycled at various high rates (Fig. 2c), the PTPAn cathode can still displays a surprisingly high rate capability, giving a reversible capacity of  $96 \text{ mA h g}^{-1}$  and  $88 \text{ mA h g}^{-1}$  at 2 C and 20 C rate ( $1 \text{ C} = 100 \text{ mA g}^{-1}$ ), respectively. On continuous cycling at a constant current of 5 C rate, the PTPAn cathode shows a stable reversible capacity of  $88 \text{ mA h g}^{-1}$  with 97% capacity retention after 200 cycles (Fig. 2d).

It should be mentioned that the electrochemical performance of the PTPAn polymer observed in a  $\text{NaPF}_6$  electrolyte is very much similar to that measured from a  $\text{LiPF}_6$  electrolyte (Supplementary Fig. S2) except for a slight decrease in the working potential, suggesting that the cathodic reaction proceeds through reversible p-doping/

dedoping of the  $\text{PF}_6^-$  anions. Though this p-doped polymer is not a Na host material, it can still serve as an effective cathode for Na ion batteries by hosting concomitant  $\text{PF}_6^-$  anions along with  $\text{Na}^+$  insertion into the anodic material.

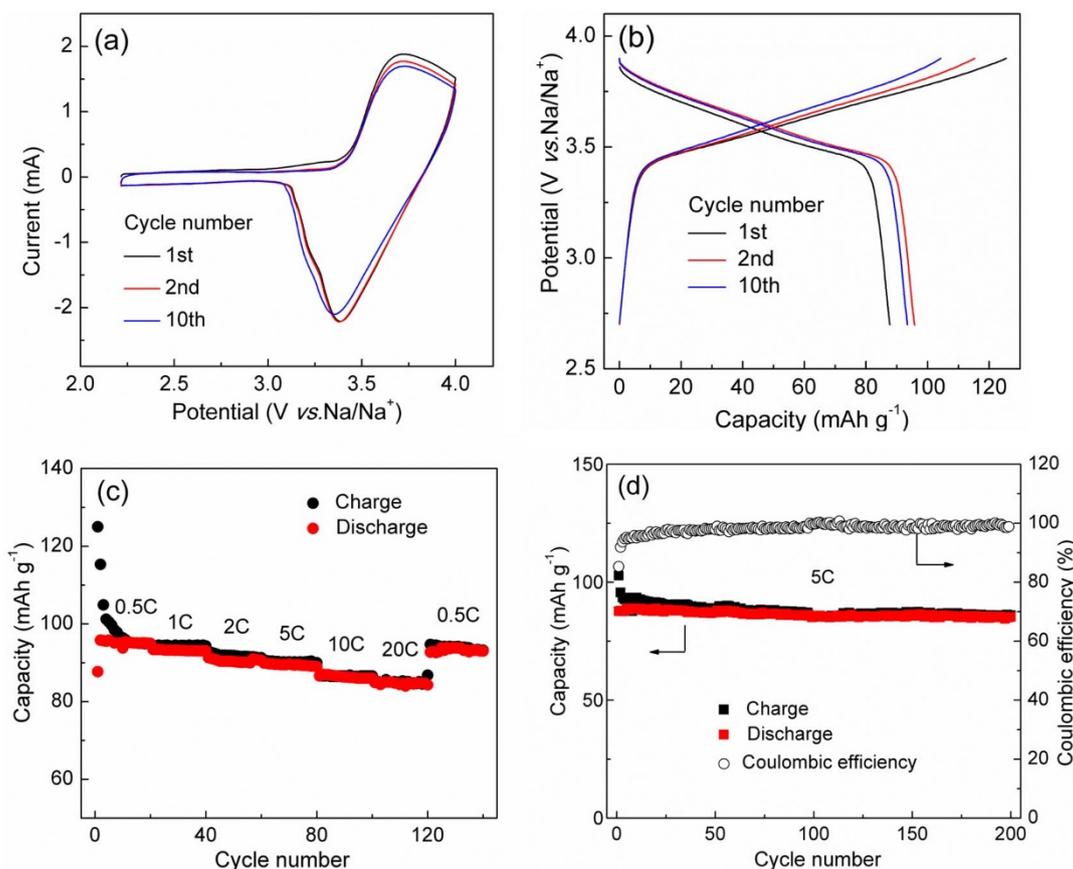
**Anodic Na storage in PAQS polymer.** PAQS was known to have n-type redox activity through reversible electrochemical association of cations with its redox-active anthraquinonyl groups<sup>26–28</sup>, as shown in Figure 3. In previous studies, Song et al. discovered the Li-storage reaction of the PAQS polymer with a reversible capacity of  $185 \text{ mA h g}^{-1}$  and a stable cyclability during 200 cycles when used as an anodic host for Li-ion batteries<sup>26</sup>. Considering that the replacement of smaller  $\text{Li}^+$  by larger  $\text{Na}^+$  ions may facilitate the redox reaction of the anthraquinonyl groups<sup>29</sup>, we tested electrochemical feasibility of PAQS polymer as a possible Na-storage anode.

The FTIR and  $^{13}\text{C}$  NMR spectra of the as-synthesized PAQS are displayed in Supplementary Fig. S3 and S4, confirming that the polymer chains consist of regular arrangement of anthraquinonyl sulfide unit. To further enhance electric conductivity, the PAQS polymer was composited with a highly conductive carbon by ball milling before electrochemical applications.

Figure 4 displays the electrochemical characteristics of PAQS in  $\text{NaPF}_6$  electrolyte. As shown in Fig. 4a, the CV responses of the PAQS anode are quite different between initial and subsequent cathodic scans. At initial cathodic scan, the first reduction peak at 1.85 V appeared weaker and the second reduction peak at 1.49 V was relatively larger, suggesting an electrochemical activation process for PAQS as observed previously for Li-storage anode<sup>28</sup>. After the first activation cycle, two pairs of symmetric redox peaks at 1.85/2.18 V and at 1.46/1.8 V emerged with similar intensities and areas, and kept almost unchanged at subsequent cycles, implying a two-step redox reaction of the anthraquinonyl groups in the PAQS chains. In contrast with the CV feature in  $\text{Li}^+$  electrolyte (Supplementary Fig. S6)<sup>28</sup>, the two pairs of redox peaks from the PAQS anode are well separated with  $\sim 300$  mV potential difference, possibly due to a larger coulombic or steric repulsion for the second step  $\text{Na}^+$  association when the first  $\text{Na}^+$  ion is associated with the anthraquinonyl group of the polymer.

Fig. 3b shows the charge-discharge curves of the PAQS polymer with respect to Na. In accord with the CV data, the PAQS electrode shows two stepped charge and discharge at 2 V and at 1.5 V, respectively, revealing a two-step redox reaction. The total discharge capacity is  $220 \text{ mA h g}^{-1}$ , corresponding to a 98% utilization of its theoretical 2 Na storage capacity.

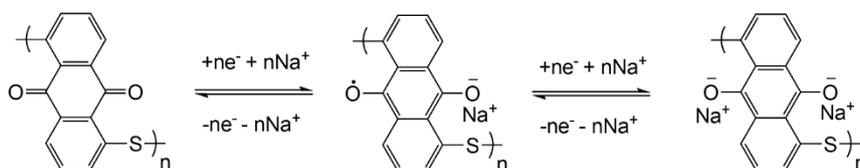
The PAQS anode has demonstrated not only a high capacity, but also a high rate capability. As displayed in Fig. 4c, the PAQS anode delivers a surprisingly high capacity of  $210 \text{ mA h g}^{-1}$  and  $175 \text{ mA h g}^{-1}$  at considerably high rate of 2 C ( $400 \text{ mA g}^{-1}$ ) and 16 C ( $3200 \text{ mA g}^{-1}$ ), respectively. Even at a very high rate of 30 C, the discharge capacity can still reach  $160 \text{ mA h g}^{-1}$ , corresponding to a 73% utilization of its reversible capacity, which is very rarely



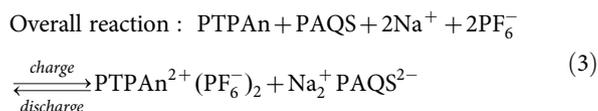
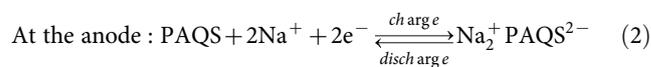
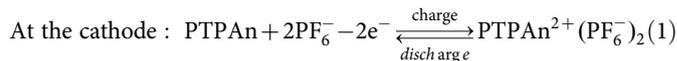
**Figure 2** | Electrochemical redox properties of PTPAN in a mixed DOL/DME electrolyte saturated with NaPF<sub>6</sub>. (a) CV curves at a scan rate of 5 mV s<sup>-1</sup>; (b) Charge and discharge profiles at a constant current of 50 mA g<sup>-1</sup>; (c) Cycling performance of PTPAN at different C-rates (1C = 100 mA g<sup>-1</sup>); (d) Cycling performance of PAQS at 5C rate. The charge-discharge capacities were derived from 2032 coin type Na-PTPAN cells, measured at voltage interval of 2.7–3.9 V.

observed for Na insertion reactions. Fig. 4d shows the cycle performance of a Na/PAQS cell at a constant current of 8 C rate (1600 mA g<sup>-1</sup>). The cell exhibited very stable cycling performance with almost indiscernible capacity decay and kept its coulombic efficiency around 100% during successive 200 cycles. Such an excellent cyclability arises apparently from the electrochemical reversibility of the anthraquinone units and the structural stability of the PAQS chains.

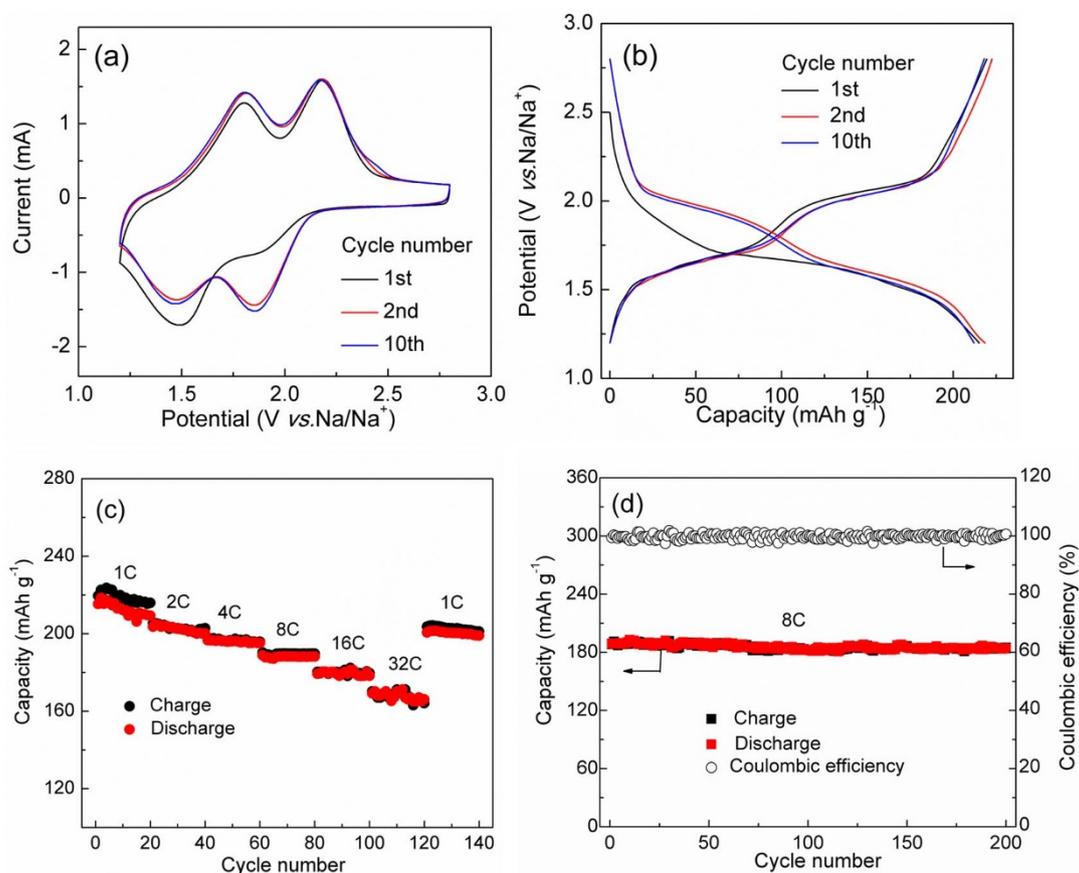
**A prototype all-organic Na-ion battery.** Encouraged by the suitable p- and n-type redox activities of PTPAN and PAQS polymers, we used these two polymers to construct an all-organic Na-ion battery. The cell reaction of such an all-organic battery is expressed in Eq. (1) – (3). During the charge process, the PAQS anode is n-type redox-active to accept electrons from an external circuit with Na<sup>+</sup> association, while the PTPAN cathode is p-doped to donate its electrons to an external circuit with PF<sub>6</sub><sup>-</sup> association for charge counterbalance. At reversed discharge, Na<sup>+</sup> cations and PF<sub>6</sub><sup>-</sup> anions are disassociated from the anodic PAQS and cathodic PTPAN chains, respectively, while the electrons flow from the anode to the cathode through the external circuit.



**Figure 3** | Possible redox mechanism of PAQS in Na<sup>+</sup>- electrolytes.



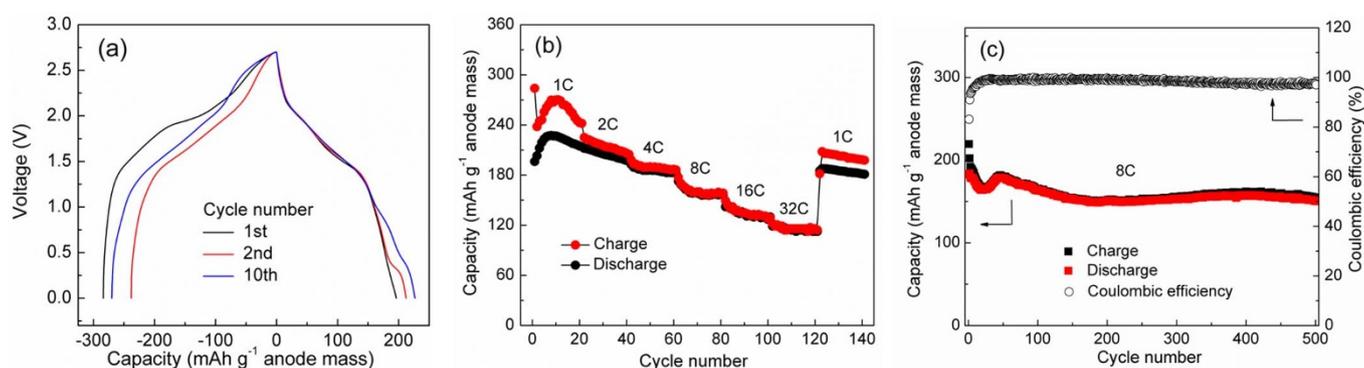
Electrochemical performances of coin type PAQS/PTPAN cells are demonstrated in Figure 5. As shown in Fig. 5a, the cell works very well with an average voltage of ~ 1.8 V. As an anode-limited design, the reversible capacity of the cell is determined by the mass of anode material and the realized capacity of the cell reaches 220 mAh g<sup>-1</sup> (the full capacity of the PAQS anode) after a few cycles, suggesting a complete electrochemical utilization of the polymer materials. More strikingly, this all-organic cell displays a surprisingly high rate capability with a reversible capacity of 130 mAh g<sup>-1</sup> and 118 mAh



**Figure 4** | Electrochemical characterizations of PAQS. (a) CV curves at a scan rate of  $5 \text{ mV s}^{-1}$ ; (b) Charge and discharge profiles at a constant current of  $180 \text{ mA g}^{-1}$ ; (c) Cycling performance of PAQS at different C-rates; ( $1\text{C} = 200 \text{ mA g}^{-1}$ ); (d) Cycling performance of PAQS at  $8 \text{ C}$  rate ( $1600 \text{ mA g}^{-1}$ ). The electrolyte was a mixed DOL/DME solution saturated with  $\text{NaPF}_6$ . The charge-discharge capacities were derived from 2032 coin type Na-PAQS cells, measured at the voltage interval of  $1.2\text{--}2.8 \text{ V}$  vs  $\text{Na}^+/\text{Na}$ .

$\text{g}^{-1}$  at very high rate of  $16 \text{ C}$  and  $32 \text{ C}$ , respectively (Fig. 5b). In addition, this cell also exhibit a superior cycling stability with  $85\%$  capacity retention and  $99\%$  coulombic efficiency over  $500$  cycles at  $8 \text{ C}$  rate (Fig. 5c), which far exceed all the organic-based batteries reported so far<sup>30,31</sup>. Taking into account the total mass weight of the cathode and anode materials, the theoretical energy density of cell attains to  $92 \text{ Wh kg}^{-1}$ . In general, electrode materials possess about  $60\%$  of the total weight of the practical batteries. Thus, our organic battery may achieve a practical specific energy of  $\sim 55 \text{ Wh kg}^{-1}$ , which is competitive with the specific energy densities of conventional Pb acid, Ni-Cd and Ni-MH batteries ( $25 \sim 50 \text{ Wh kg}^{-1}$ ).

It should be pointed out that several types of all-organic rechargeable batteries have been proposed very recently and demonstrated electrochemical feasibility<sup>30–33</sup>. For instance, Nishide's group firstly utilized a p-type poly(TEMPO-substituted norbornene) cathode in conjunction with an n-type poly(galvinoxystyrene) anode to construct a totally radical polymer-based battery<sup>30</sup>. Also, their group found some radical polymers bearing pendant nitroxide groups to have bipolar (p- and n-dopable) redox activities, capable to be used as both cathode and anode for constructing a symmetric all-organic battery<sup>33</sup>. However, these radical batteries have very low specific energy densities, because of their low working voltage ( $<1 \text{ V}$ ) and small redox capacity ( $\sim 50 \text{ mAh g}^{-1}$ ). Very recently, our group have



**Figure 5** | Electrochemical performances of the all-organic PAQS/PTPAn cells with an optimized mass ratio of PTPAn: PAQS =  $2.5 : 1$ . (a) Charge and discharge curves at  $1\text{C}$  rate ( $1\text{C} = 200 \text{ mA g}^{-1}$ ); (b) Cycling capacities at varies C-rates; (c) Cycling performance of PAQS at  $8 \text{ C}$  rate. The charge-discharge capacities were derived from 2032 coin type cells, measured at the voltage interval of  $0\text{--}2.7 \text{ V}$ .



revealed an all-organic lithium ion battery using bipolar polypara-phenylene (PPP) as both cathode- and anode-active materials<sup>31</sup>. This new battery can operate at a high voltage of 3.0 V with fairly high capacity, benefiting from the large voltage gap between its p-type reaction and n-type reaction of PPP electrode. However, the capacity utilization and cycleability of the PPP-based cell is relatively poor, possibly due to a mismatching between the anode and the cathode. In comparison, the PTPAn/PAQS battery developed in this work demonstrates greatly enhanced electrochemical performance both in terms of energy density and long-term cyclability. More significantly, this battery system uses natural abundant Na<sup>+</sup> electrolyte rather than expensive Li<sup>+</sup> electrolyte, thus offering a low cost and environmentally friendly alternative to the existing batteries.

## Discussion

Though our organic Na-ion battery has a much lower specific energy than the advanced Li-ion batteries due to its low voltage, this deficiency could be overcome by exploring suitable electrode-active polymers with higher p-doping potential and lower n-doping potential. Undoubtedly, a large diversity of organic structures would enable the feasibility of finding and developing such electrode-active polymers, therefore achieving high voltage and high capacity organic batteries.

It should be noted that the organic battery has an instinct drawback of low volumetric energy density. As far as we know, organics usually have much lower mass density than inorganics, because of its highly branched structure and large porosity. However, this may not be a problem where the volume issue is not the strict limitation, such as in thin film flexible electronics and grid-scale energy storage applications.

Another problem with our organic Na-ion battery is that the electrolyte participates in the battery reaction, causing a consumption of electrolyte. As illustrated in Fig. 1 and Fig. 3, each PTPAN unit combines with 2 PF<sub>6</sub><sup>-</sup> during the charge process, while each PAQS unit combines with 2 Na<sup>+</sup>. Thus, for practical battery applications, excessive electrolyte is needed to allow fast electric storage reactions and high ion conduction.

Nevertheless, our work has demonstrated, for the first time, a viable Na-ion battery using polymeric cathode and anode. This battery offers new possibilities to create high energy/power density, cost-effective, environmentally friendly energy storage system for future large scale applications.

In summary, we have successfully constructed an all-organic Na-ion battery by use of PTPAn cathode and PAQS anode. Different from “rocking-chair” type batteries, this Na-ion battery works through reversible Na<sup>+</sup>-doping/dedoping reactions at the anode with simultaneous PF<sub>6</sub><sup>-</sup>-doping/dedoping reactions at the cathode during charge/discharge processes. Because the cathodic p-doping reaction and anodic n-type reaction are well separated and have excellent redox reversibility, the organic battery can be discharged at 1.8 V with a considerable specific energy of 92 Wh kg<sup>-1</sup>, stable cyclability and superior rate capability. Most significantly, this type of battery is made from low cost and environmentally benign organic polymers, offering a new possibility for widespread energy storage applications.

## Methods

**Material preparation.** PAQS was synthesized by a polycondensation reaction of Na<sub>2</sub>S and 1,5-Dichloroanthraquinone. Anhydrous Na<sub>2</sub>S was obtained by removing the hydrated water from Na<sub>2</sub>S·9H<sub>2</sub>O (Lingfeng Chemical reagent co., Ltd, Shanghai, China) through azeotropic dehydration in benzene at 135°C. After evaporation of benzene, a stoichiometric quantity of 1,5-Dichloroanthraquinone (Alfa Asser) and N-methyl-2-pyrrolidone (NMP) was added into the mixture and then refluxed at 150°C for 10 h under magnetic stirring. After the reaction was completed, the solid was filtered, then washed alternately with de-ionized water and acetone, and finally dried in vacuum oven over night at 60°C. PTPAn was obtained by an oxidative polymerization of triphenylamine monomer (purity ≥ 99.0%, Zhenjiang Haitong Chemical Industry Co., Ltd., Jiangsu, China) using FeCl<sub>3</sub> oxidant and under the purge of dry N<sub>2</sub>, in a similar way as described in ref. 25.

**Physical characterizations.** Infrared (IR) absorption measurements were conducted using KBr pellets on AVATAR 360 spectrometer (NICOLET 5700 FTIR Spectrometer) in range of 400–4000 cm<sup>-1</sup>. Solid-state <sup>13</sup>C NMR was performed with Inova 300 MHz Spectrometer (Varian Inc., USA). SEM micrographs were observed on a nova nanosem 450 scanning electron microscope (FEI Company, Holland).

**Electrochemical measurements.** Electrochemical characterization of the PAQS and PTPAn materials was separately evaluated in a half-cell configuration of CR2032-type coin cells using sodium disks as counter electrodes. The electrolyte was a mixed solution of 1,2-dimethoxy ethane (DME) and 1,3-dioxolane (DOL) (1 : 1 by volume) saturated with NaPF<sub>6</sub>. The separator was a microporous membrane (Celgard 2400). The PAQS anode were prepared by mixing 40% PAQS powders, 50% Ketjen Black (KB) and 10% polytetrafluoroethylene (wt.%) and rolling the electrode mixture into a ~ 0.1 mm thick film. The anode was finished by pressing the electrode film onto aluminium mesh, then punching the electrode into φ2 mm disks and drying the anodic disks in vacuum for 24 h at 60°C. The PTPAn cathode consisted of 60% active material, 30% Super P carbon, and 10% polytetrafluoroethylene (wt.%), made in the same way as the PAQS anode. Prototype all-organic Na-ion cells were constructed using the PAQS anode and PTPAn cathode with an anode-limited design, where a slightly excess of the cathode material was used, so that the cell capacity was determined by the anode material.

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## Author contributions

J.Q. and H.Y. proposed the conceptual idea. W.D. prepared the electrode materials, constructed the all-organic Na-ion battery, tested its performance and wrote the first draft of the manuscript. X.L. and J.F. supported the solid NMR test. X.W. assisted for the IR test. Y.C. and X.A. contributed to discussions of results. All authors read and approved the final manuscript.

## Additional information

**Supplementary information** accompanies this paper at <http://www.nature.com/scientificreports>

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