

Communication

Balance cathode-active and anode-active groups in one conjugated polymer towards high-performance all-organic lithium-ion batteries[☆]

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ABSTRACT

Organic electrode materials are promising for future rechargeable batteries owing to their potential high capacity, tunable structure, flexibility and sustainability. Thus, developing high-performance all-organic batteries is highly demanded. But so far it is still a great challenge to achieve simultaneously such desired capacities and cycling stability, particularly for the case of all-organic symmetric batteries. Here, we design and report a polymer, named Poly-BQ1, which can be used as both cathode and anode materials for high-performance all-organic symmetric Lithium-ion battery. Such a two-fold electrode material was designed and optimized by balancing/maximizing abundant cathode-active groups (C[•]O, C[•]N) and anode-active groups (C[•]C) in one stable conjugated polymer for both the purposes of achieving high capacity and cycling stability. Thus, owing to optimized integration of redox-active C[•]O, C[•]N and C[•]C groups in a stable conjugated backbone and minimized redox-inactive units, the all-organic battery using this single material exhibits the highest capacity (351.5 mA h g⁻¹ at 50 mA g⁻¹) among all previously reported all-organic batteries with also remarkable cycling stability (99.96% retention per cycle up to 400 cycles) and rate performance (203.4 mA h g⁻¹ at 1 A g⁻¹).

1. Introduction

Rechargeable lithium-ion batteries (LIBs) have been used widely in many areas for the past decades [1–4]. Conventional LIBs usually use lithium transition metal oxides (such as LiMn₂O₄ and LiCoO₂) as the cathode material and graphite as the anode material. But there have been some serious issues including low capacities, scarce resources, toxicity and energetically expensive fabrications [5]. In contrast to metal-containing inorganic materials, organic electrode materials are endowed with various merits, such as mainly consisting of naturally abundant and light elements (C, H, O, N, S), less energy input for synthesizing such materials and truly intrinsic flexibility required for integrated devices. Together with their high chemically structural diversity and potential reusability, it's possible to design eco-friendly organic battery materials with high theoretical gravimetric capacities, energy densities and intrinsic flexibility [6,7].

Though there have been many studies for using organic materials as a single electrode material (cathode or anode) [8–13], it is believed much better to use the same material as both cathode and anode materials simultaneously to construct an all-organic symmetric battery [14–16]. But this is clearly more challenging as such one material needs to consider and balance many factors all together, including potentials, capacities and cycling stability of both electrodes. Furthermore, these should be above that all the cathode-active and anode-active groups need to be merged into one stable structure for long cycling capability together with minimum redox-inactive units. All-organic batteries by using organic small molecules with abundant redox-active groups as both cathode and anode materials show high capacities (> 200 mA h g⁻¹) but short cycle life (≤ 200 cycles) due to the unwanted dissolution of active materials in the aprotic electrolytes [14–16]. On the contrary, all-organic batteries based on polymers usually display improved cycling stability (>200 cycles) because of the stable

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backbones of polymers, but most of them come with the sacrifice of capacities due to too much loading of redox-inactive units in the structures ($< 150 \text{ mA h g}^{-1}$) [17–20]. These reveal the imbalance between high capacities and good cycling stability of current all-organic symmetric batteries. Another issue for polymer-based all-organic symmetric batteries is that their cathode materials generally have lower capacities than that of anode materials [20–22]. Thus, delicate and balanced consideration is needed to design such all-organic symmetric batteries materials with both high capacities and cycling life.

To solve these problems and design an all-organic symmetric batteries material with simultaneously high capacities and good cycling stability, it is crucial to merge maximum redox-active groups with high and low redox potentials and minimum redox-inactive units into one stable backbone of polymer and use it as both cathode and anode materials. Organic materials with $\text{C}=\text{O}$ or $\text{C}=\text{N}$ groups (as in quinones, anhydrides, Schiff bases and heteroaromatic compounds) show relatively high redox potentials ($> 2.0 \text{ V vs Li/Li}^+$) and high specific capacities, so they are promising active cathode materials for all-organic symmetric batteries [23–25]. Unsaturated organic compounds containing $\text{C}=\text{C}$ groups (as in benzene ring) display relatively low redox potentials ($< 1.0 \text{ V vs Li/Li}^+$) and high specific capacities, and they are good choice of active anode materials for all-organic symmetric batteries [26,27]. Ladder polymers possessing stable backbones have been used as active electrode materials with remarkable cycling stability and rate performance [28–30]. There have been reports that cathode-active $\text{C}=\text{N}$ linkages and stable backbones of polymers can form through direct condensation reaction between reactants containing aminos and carbonyls, which can also improve capacities and cycling stability of all-organic symmetric batteries synergistically [8,29,31,32]. Thus, it would be possible by maximizing cathode-active and anode-active groups ($\text{C}=\text{O}$, $\text{C}=\text{N}$ and $\text{C}=\text{C}$) and minimizing redox-inactive units and merging them into one stable ladder polymer to obtain high-performance all-organic symmetric batteries with balanced potentials, high capacities and long cycling stability of both cathode and anode.

With this in mind, we design and report such a ladder polymer named Poly-BQ1, which can be made by a simple condensation reaction between two commercial compounds, namely 2,3,5,6-tetramino-1,4-benzoquinone (TABQ) and 2,5-dihydroxy-1,4-benzoquinone (DHBQ), with the aim of maximizing balanced cathode-active ($\text{C}=\text{O}$ and $\text{C}=\text{N}$) and

anode-active groups ($\text{C}=\text{C}$) and minimizing redox-inactive units in a stable ladder polymer backbone. Owing to abundant redox-active $\text{C}=\text{O}$, $\text{C}=\text{N}$ and $\text{C}=\text{C}$ groups, the constructed all-organic symmetric battery by using Poly-BQ1 as both cathode and anode materials exhibits the highest capacity of $351.5 \text{ mA h g}^{-1}$ at 50 mA g^{-1} among all the previous all-organic batteries (Table S1). It also shows superior rate capacity of $203.4 \text{ mA h g}^{-1}$ at 1 A g^{-1} and remarkable cycling stability up to 400 cycles with a capacity retention of 99.96% per cycle. Noticeably, the electrochemical performance of our flexible all-organic battery keeps almost unchanged under a wide range of bending states ($0\text{--}180^\circ$), which shows good flexibility of our battery.

2. Results and discussion

Poly-BQ1 is prepared by a simple condensation reaction between TABQ and DHBQ (Fig. 1a), and the detailed synthesis process is shown in Section S2 of the Supporting Information. Fig. 1b displays the solid state ^{13}C NMR spectrum of Poly-BQ1, in which the peaks at 174 and 146 ppm are contributions from carbon atoms of cathode-active $\text{C}=\text{O}$ and $\text{C}=\text{N}$ bonds, respectively (1 and 2 in orange color in Fig. 1a and 1b). The shift values at 142, 134, 130 and 108 ppm are ascribed to carbon atoms of anode-active $\text{C}=\text{C}$ bonds at different chemical environments (3–6 in orange color in Fig. 1a and 1b) [10,31]. Note due to the fact that the ^{13}C NMR spectrum is recorded in solid state and also the large conjugated system of Poly-BQ1, their/some peaks could be weak/broad as observed in many literatures [10,33–35]. Peaks of $\text{C}=\text{O}$ (1626 cm^{-1}) and $\text{C}=\text{N}$ (1545 cm^{-1}) groups of Poly-BQ1 can be observed in the FT-IR spectra (Fig. S1) [10,31]. The high-resolution X-ray photoelectron spectroscopy (XPS) spectra of C1s, N1s and O1s of Poly-BQ1 exhibit the deconvoluted peaks of redox-active $\text{C}=\text{O}$, $\text{C}=\text{N}$ and $\text{C}=\text{C}$ groups (Fig. S2) [10,35]. The energy dispersive spectroscopy (EDS) mapping images show that carbon, nitrogen and oxygen are homogeneously distributed throughout (Fig. S4). The thermogravimetric analysis (TGA) shows no significant weight loss (2%) before 300°C , and 60% of its weight still maintains up to 703°C in N_2 (Fig. 1c), revealing the formation of the polymer structure and its outstanding thermal stability. Peaks of G band (1513 cm^{-1}) and D band (1375 cm^{-1}) can be observed from the Raman spectroscopy of Poly-BQ1 (Fig. S5) [10,36]. These characterizations of Poly-BQ1 indicate that cathode-active $\text{C}=\text{O}$ and $\text{C}=\text{N}$ groups and

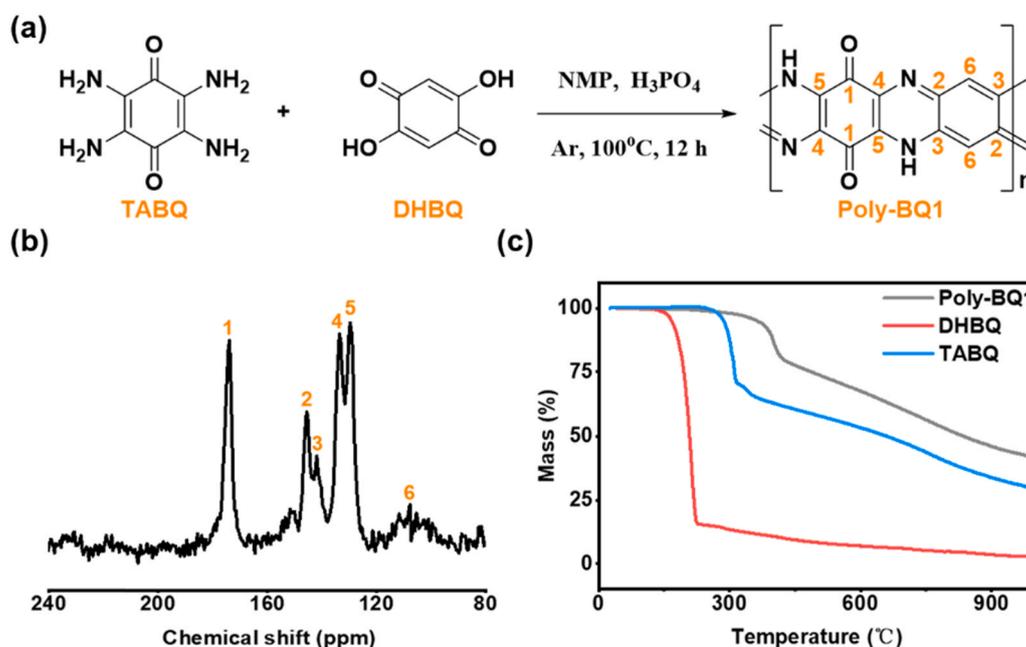


Fig. 1. Synthesis and structural characterizations of Poly-BQ1. (a) The synthesis route of Poly-BQ1. (b) The solid state ^{13}C NMR spectrum of Poly-BQ1. (c) The TGA characterization of reactants and products.

anode-active C=C groups are successfully merged into the stable backbone of Poly-BQ1.

The electrochemical performance was investigated by using half-cells with lithium metal as the reference electrode. Poly-BQ1 was first evaluated as active cathode material in the optimized relatively high potential window of 1.2–3.6 V (vs Li/Li⁺). In the cyclic voltammetry (CV) curves of cathode half cell (Fig. 2a), redox peaks at 2.62, 2.74 and 3.04 V (vs Li/Li⁺) are contributions from C=O groups, peaks at 2.24 and 2.40 V (vs Li/Li⁺) are ascribed to C=N groups, respectively [10,31]. The galvanostatic charge/discharge profiles of Poly-BQ1 cathode half-cell show slopes corresponding to the peaks of CV curves (Fig. 2b), revealing that C=O and C=N are cathode-active groups as expected. The CV curves and charge/discharge curves overlap well during the 2–3 cycles, confirming good stability and reversibility of the cathode half-cell. A high initial discharge capacity of 427.5 mA h g⁻¹ (94.1% of its theoretical capacity) can be obtained at 50 mA g⁻¹, which is higher than the capacities of most previous organic cathode materials (Fig. S9, Table S2) [37,38]. The Poly-BQ1 cathode half-cell maintains reversible capacity of 268.9 mA h g⁻¹ at 100 mA g⁻¹ after 100 cycles with a capacity retention of 78.6% (Fig. 2c). Even at a large current density of 500 mA g⁻¹, it remains a discharge capacity of 182.6 mA h g⁻¹ after 1500 cycles with an average capacity loss of only 0.028% per cycle (Fig. 2e). Some capacity decay during the early stage of cycling may be caused by some irreversible side reactions and the formation of SEI layers [12]. The Coulombic efficiency (CE) of neat unity can be

maintained throughout the cycling under different current densities, revealing remarkable cycling stability. After activation under 50 mA g⁻¹, it displays reversible capacities of 360.5, 359.1, 333.3 and 322.8 mA h g⁻¹ at current densities of 100, 200, 500 and 1000 mA g⁻¹, respectively (Fig. 2d). A high capacity recovers when the current density is reduced after the back-and-forth large current densities, indicating its superior rate performance. The energy density of Poly-BQ1 cathode half-cell is estimated to be 301.0 W h kg⁻¹ (Section S5, Fig. S10), which is much higher than that of conventional LIBs based on inorganic cathode materials (100–140 W h kg⁻¹) [31,39]. These results suggest that Poly-BQ1 is a promising active cathode material for all-organic symmetric batteries with high capacity and cycling stability simultaneously.

Based on previous studies [10,31] two-step redox processes of Poly-BQ1 were proposed in the relatively high potential range of 1.2–3.6 V (vs Li/Li⁺) (Fig. 3a). This was supported by density functional theory (DFT) calculations for the optimized structures at different stages of lithiation (Section S6, Supporting Information). Simulation studies are carried out on oligomer of Poly-BQ1 (n = 3), 3BQ1 for short, the edges of which are saturated with hydrogen atoms, and the optimized structures of 3BQ1-xLi (x = 0, 6, 12) are shown in Fig. 3b. The optimized result of 3BQ1-6Li reveals that every Li⁺ coordinates with oxygen atom and the adjacent nitrogen atom to form a five-membered ring (C-O-Li-N-C) during the lithiation process of the C=O groups [31,40]. The optimized structure of 3BQ1-12Li indicates that another six

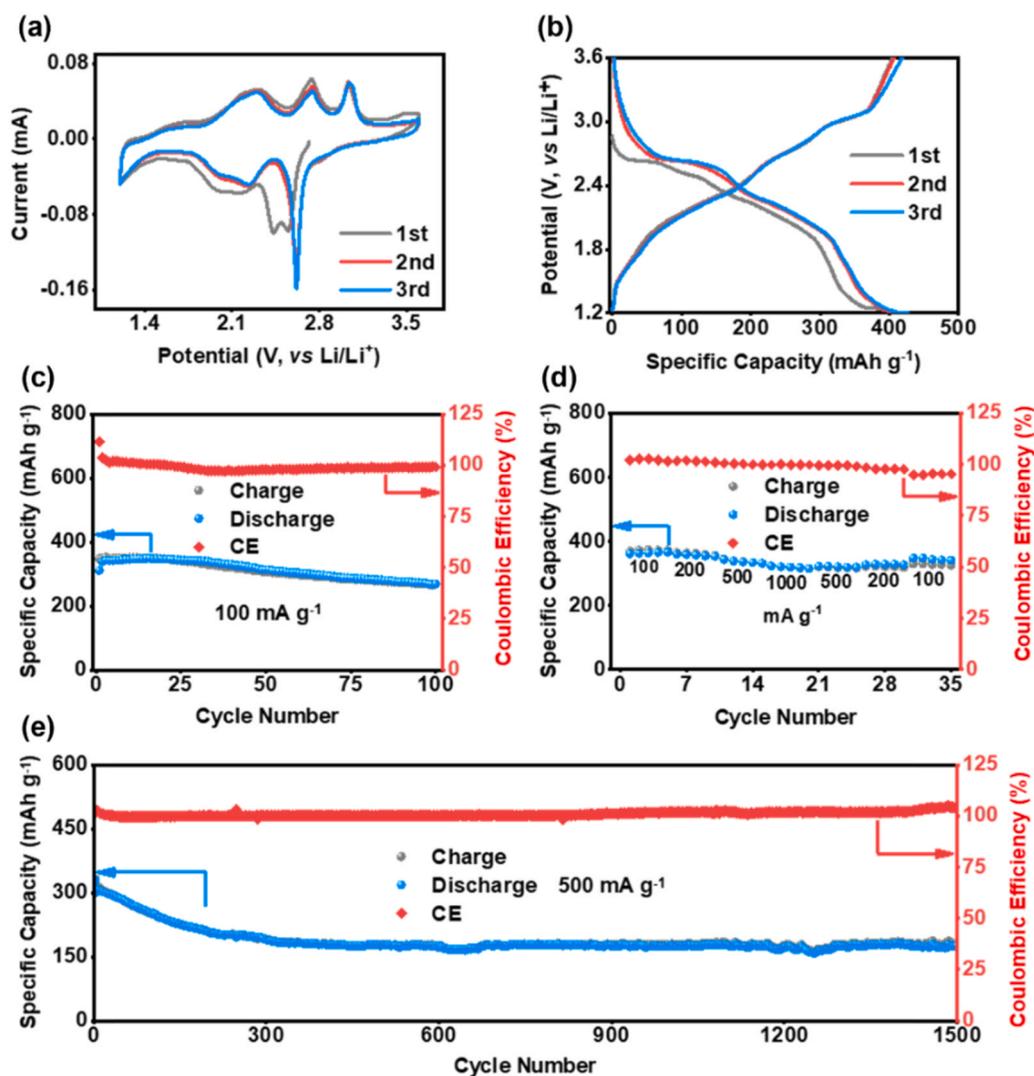


Fig. 2. Electrochemical performance of Poly-BQ1 cathode half-cell between 1.2 and 3.6 V (vs Li/Li⁺), the electrolyte is 1 M LiTFSI in the mixed solvent of DOL and DME (1:1, v/v). (a) Cyclic voltammetry (CV) curves at a scan rate of 0.1 mV s⁻¹ in the initial 3 cycles. (b) Capacity-voltage profiles at 50 mA g⁻¹ in the initial 3 cycles. (c) Cycling performance at 100 mA g⁻¹ for 100 cycles. (d) Rate capacities at current densities of 100, 200, 500, 1000 mA g⁻¹. (e) Long-term cycling performance at 500 mA g⁻¹ for 1500 cycles.

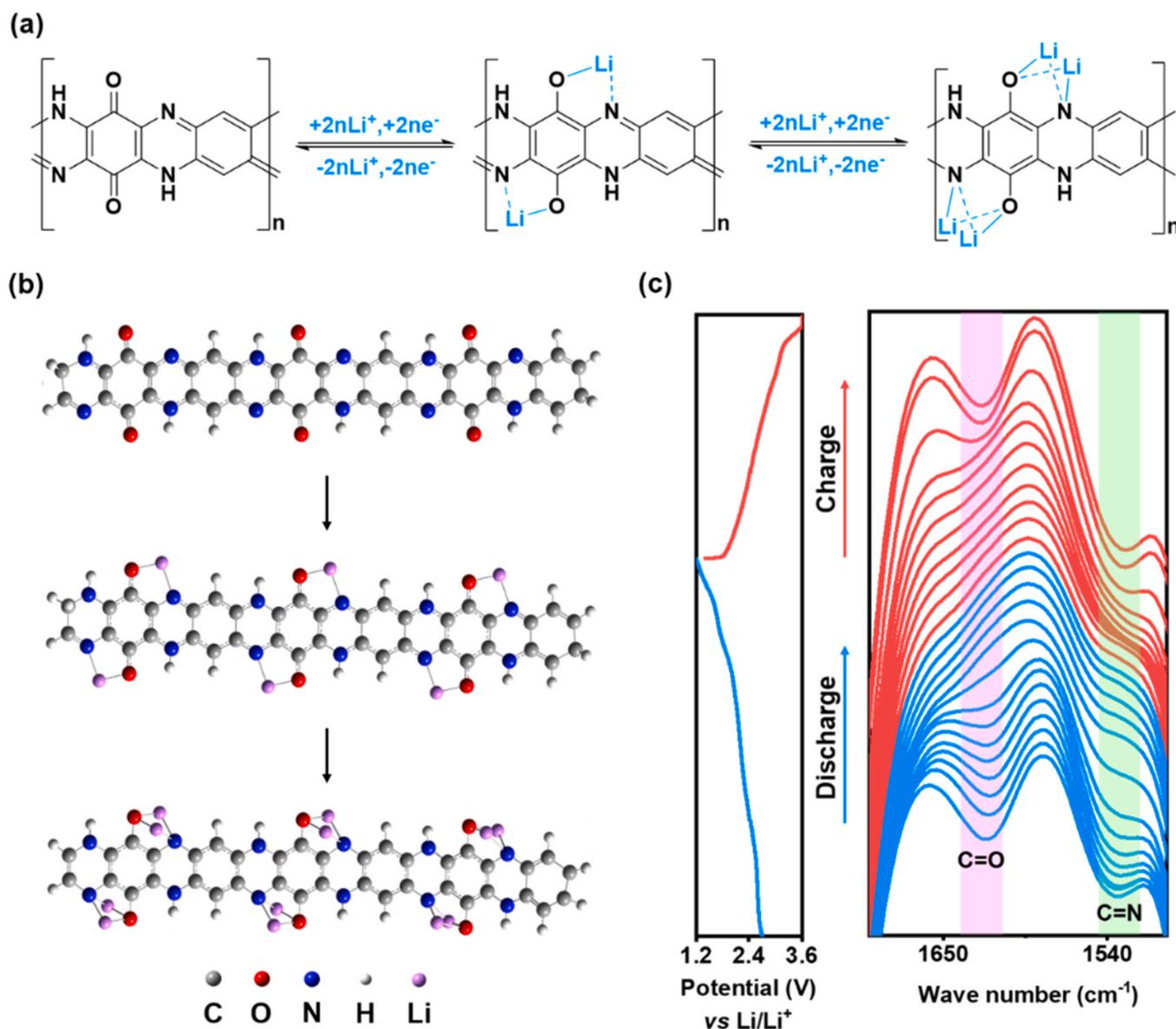


Fig. 3. Reaction mechanism of Poly-BQ1 cathode half-cell between 1.2 and 3.6 V (vs Li/Li^+). (a) The structural evolutions of active sites of Poly-BQ1 cathode half-cell during lithiation/delithiation processes. (b) The schematic diagram of two-step lithiation/delithiation processes of 3BQ1 obtained via the DFT calculations. (c) Charge/discharge profiles at 50 mA g^{-1} and the *in situ* ATR-IR spectra collected during the first cycle.

five-membered rings ($\text{C}-\text{O}-\text{Li}-\text{N}-\text{C}$) could form during the reaction between $\text{C}=\text{N}$ groups and additional six Li^+ , and each ring shares the same C, N and O atoms with one ring formed in advance [10,41]. Such evolutions of optimized structures support the two-step lithiation processes of Poly-BQ1 cathode half-cell.

With the aim to further confirm the lithium storage mechanism of Poly-BQ1 between 1.2 and 3.6 V (vs Li/Li^+), the discharge/charge processes were *in situ* monitored by attenuated total reflection infrared spectroscopy (ATR-IR) (Fig. S12). The absorption peaks situated at 1623 and 1535 cm^{-1} can be assigned to $\text{C}=\text{O}$ and $\text{C}=\text{N}$ groups, respectively. Their intensities also gradually decrease with discharging and gradually increase with charging, corresponding to the intercalation/deintercalation of Li^+ into/from the cathode-active $\text{C}=\text{O}$ and $\text{C}=\text{N}$ bonds of Poly-BQ1 (Fig. 3c) [10,42]. Note that the observed reversible changes of the ATR-IR spectra also illustrate the good reversibility and stability of Poly-BQ1 cathode half-cell.

The electrochemical tests were then performed within the relatively low potential window of $0.01\text{--}3.0 \text{ V}$ (vs Li/Li^+) by using Poly-BQ1 as an active anode material. Fig. 4a proposes the lithiation/delithiation

processes of Poly-BQ1 anode half-cell, in which Li^+ combine with $\text{C}=\text{O}$ and $\text{C}=\text{N}$ groups and then $\text{C}=\text{C}$ groups [28,29]. As expected, the peaks of the CV profiles of anode half-cell are similar to that of cathode half-cell in the potential range of $1.2\text{--}3.0 \text{ V}$ (vs Li/Li^+), corresponding to the redox reactions between Li^+ and $\text{C}=\text{O}$ and $\text{C}=\text{N}$ groups. In the lower potential range of $0.01\text{--}1.2 \text{ V}$ (vs Li/Li^+), a pair of new broad redox peak appears, which can be ascribed to the redox reaction between Li^+ and the anode-active $\text{C}=\text{C}$ bonds of aromatic rings (Fig. S13a) [28,29]. A reversible discharge capacity of $1143.4 \text{ mA h g}^{-1}$ can be observed from the charge/discharge curves (Fig. S13b), of which a capacity of $232.2 \text{ mA h g}^{-1}$ is the contribution from Super P (Fig. S14b). It can be calculated that $\sim 8 \text{ Li}^+$ can reversibly insert into each repeating unit of Poly-BQ1 anode material, corresponding to 50% of its theoretical capacity (Section S7, Supporting Information). It shows high capacities and good cycling stability up to hundreds of cycles under different current densities (Fig. 4b, Fig. S15). The observed gradual/slight capacity increase with cycling as shown in Fig. 4b is believed due to the electrochemical activation process as reported for many organic battery materials [33,43]. Notably, high reversible capacities of 1898.6 and

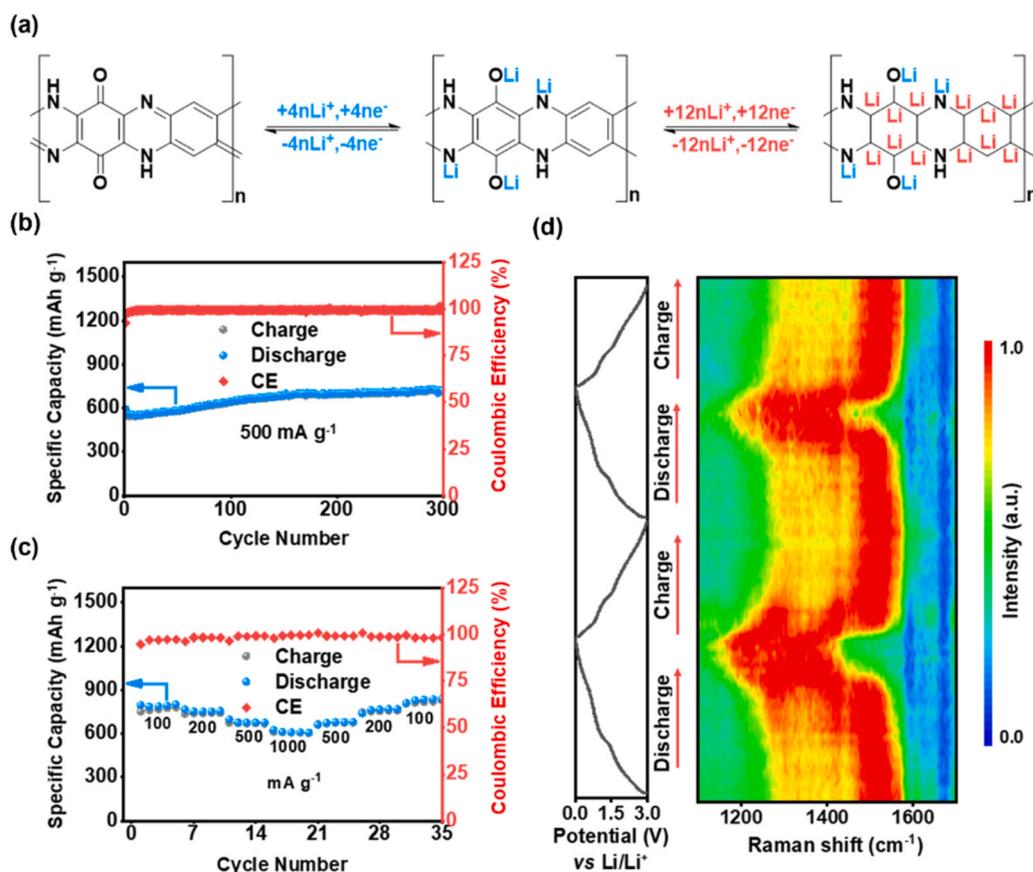


Fig. 4. Electrochemical performance of Poly-BQ1 anode half-cell between 0.01 and 3.0 V (vs. Li/Li^+), the electrolyte is 1 M LiPF_6 in the mixed solvent of EC and DEC (1:1, v/v). (a) The proposed electrochemical redox reaction processes. (b) Cycling performance. (c) Rate capacities at current densities of 100, 200, 500 and 1000 mA g^{-1} after activation under 50 mA g^{-1} . (d) Charge/discharge profiles at 50 mA g^{-1} and the *in situ* Raman spectra collected during 2 cycles.

1716.7 mA h g^{-1} can be obtained when cycling under 60 °C at 500 and 1000 mA g^{-1} , respectively, which are close to its theoretical capacity (Fig. S16 and S17). The anode half-cell shows capacity of 623.1 mA h g^{-1} (~24% is contribution from Super P) under large current density of 1 A g^{-1} , which suggests good rate performance (Fig. 4c). The superior electrochemical performance of anode half-cell in the relatively low potential range indicates that Poly-BQ1 is also a good candidate for active anode material of all-organic symmetric batteries with simultaneously high capacities and cycling stability.

In situ Raman spectra were collected to study the intercalation/deintercalation of Li^+ into/ from the Poly-BQ1 anode material when cycling (Fig. S19). In the range of G band (1500–1630), the weak peak at 1615 cm^{-1} attributes to the $\text{C}=\text{O}$ groups, and the broad band from 1510 to 1600 cm^{-1} attributes to the $\text{C}=\text{N}$ and $\text{C}=\text{C}$ groups of redox-active aromatic rings in backbone of Poly-BQ1 [44,45]. The broad band from 1280 to 1400 cm^{-1} can be assigned to the disordered carbon (D band) of poly-BQ1 (Fig. 4d). The peaks of $\text{C}=\text{O}$, $\text{C}=\text{N}$ and $\text{C}=\text{C}$ groups gradually weaken during the discharge process, while the band of disordered carbon gradually enhances due to the increased amount of sp^3 carbon atoms, which indicates the intercalation of Li^+ into $\text{C}=\text{O}$, $\text{C}=\text{N}$ and $\text{C}=\text{C}$ bonds and the reduction of these unsaturated bonds. The changes of these peaks are opposite during the following charge process, indicating the deintercalation of Li^+ from $\text{C}=\text{O}$, $\text{C}=\text{N}$ and $\text{C}=\text{C}$ bonds, which reveal good reversibility and stability of Poly-BQ1 anode half-cell. To further confirm the chemical bonding states and composition changes of the Poly-BQ1 anode material, *ex situ* C1s XPS spectra were collected at different stages of lithiation processes during the first cycle. The reversible changes between $\text{C}=\text{C}$ and $\text{C}-\text{C}$ bonds along with the reversible formation of $\text{C}-\text{Li}$ bonds can be observed, which indicates the reversible insertion of Li^+ into aromatic rings. These results also suggest that $\text{C}=\text{O}$,

$\text{C}=\text{N}$ and $\text{C}=\text{C}$ bonds undergo reversible redox processes between 0.01 and 3.0 V (vs Li/Li^+) (Fig. S20).

In theory, four and twelve Li^+ can be stored in each repeating unit of Poly-BQ1 in the potential ranges of 1.2–3.6 and 0.01–1.2 V (vs Li/Li^+), respectively. Four Li^+ can combine with $\text{C}=\text{O}$ and $\text{C}=\text{N}$ groups, and four Li^+ can combine with $\text{C}=\text{C}$ groups in our experiments. With this two-fold property, Poly-BQ1 at different redox states was thus used as both cathode material and anode material (prelithiated) to fabricate an all-organic symmetric battery. The cathode-active $\text{C}=\text{O}$ and $\text{C}=\text{N}$ bonds of cathode material uptake four Li^+ , while the anode-active lithiated carbon atoms of anode material release four Li^+ when discharging, and the opposite processes take place while charging (Fig. 5a). The full cell displays an open circuit voltage of ~2.3 V and an average work voltage of ~1.4 V. Compared to the cathode half-cell (Fig. 2a and 2b), the positions of redox peaks and voltage plateaus are ~1 V lower (Fig. S21 and S22), corresponding to the redox potential of the $\text{C}=\text{C}$ groups of the anode (Fig. S13). These results indicate that the proposed reaction processes of symmetric full cell based on Poly-BQ1 are reasonable.

The all-organic symmetric battery exhibits superb electrochemical performance with the highest capacity of 351.5 mA h g^{-1} at 50 mA g^{-1} among all the previously reported all-organic batteries (Fig. S23, Table S1). It also displays remarkable cycling stability at 500 mA g^{-1} for 400 cycles with an average capacity loss of 0.038% per cycle (Fig. 5b). After activation at 50 mA g^{-1} , it delivers high capacities of 277.3, 253.8, 227.6 and 203.4 mA h g^{-1} at current densities of 100, 200, 500 and 1000 mA g^{-1} , respectively (Fig. 5c). As far as we are aware, these are the highest rate capacities among almost all the all-organic rechargeable batteries reported (Fig. 5d, Table S1). Our all-organic symmetric battery exhibits a high energy density of 147.9 W h kg^{-1} , which is higher than almost all the all-organic batteries ($\leq 90 \text{ W h kg}^{-1}$) (Fig. S25) [46,47].

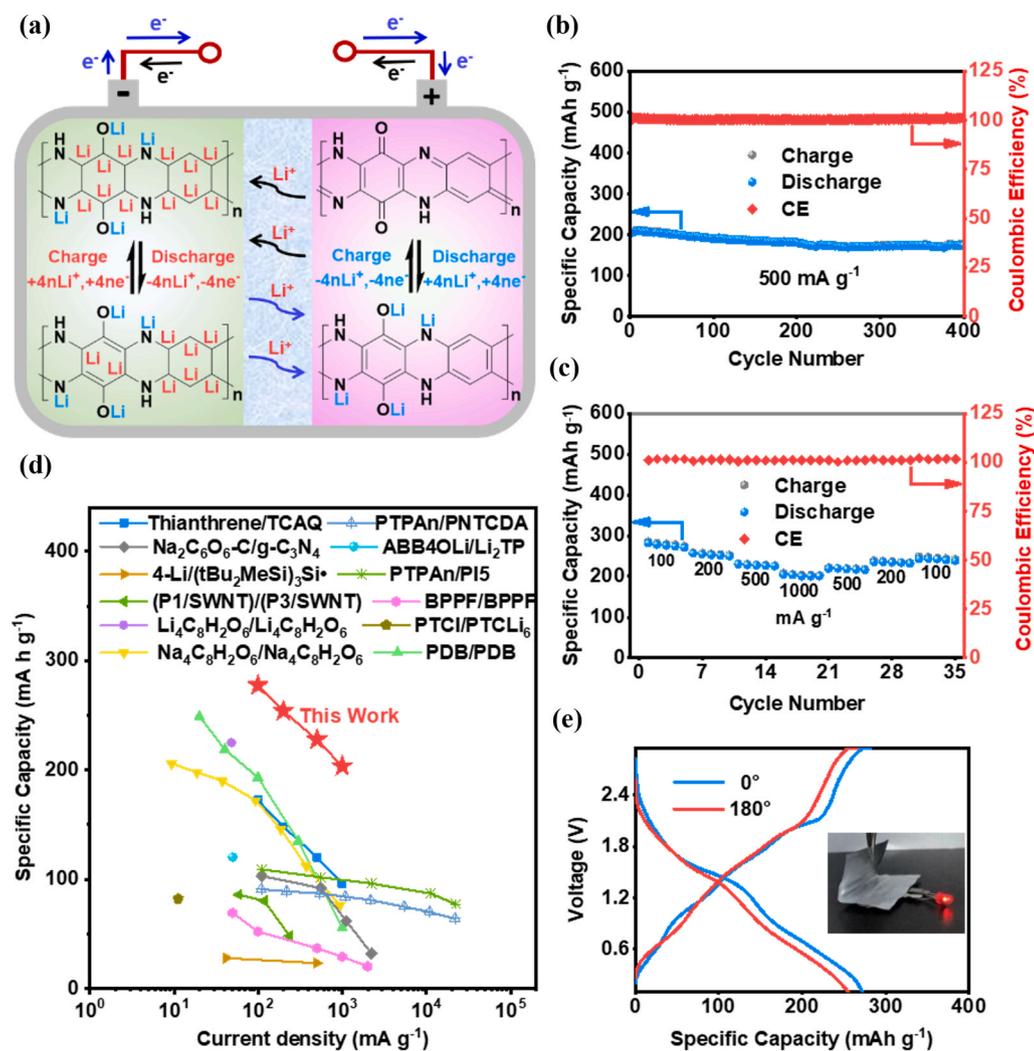


Fig. 5. All-organic symmetric battery based on Poly-BQ1, the electrolyte is 1 M LiTFSI in the mixed solvent of DOL and DME (1:1, v/v). (a) The diagram of the full cell. (b) Cycling performance from 0.1 to 2.9 V for 400 cycles. (c) Rate capacities of the full cell at current densities of 100, 200, 500 and 1000 mA g⁻¹ from 0.1 to 2.95 V. (d) Comparison of rate capacities with some previously reported all-organic batteries. (e) Capacity-voltage profiles of the flexible symmetric cell at different states from 0.1 to 2.95 V at 100 mA g⁻¹ under bending states of 0° and 180° (the inset shows that the pouch cell is powering a red LED under bending state of 90°).

These results indicate that Poly-BQ1 is a promising candidate for both cathode and anode materials of high-performance all-organic symmetric batteries.

Organic materials possess an advantage of intrinsically flexible, and thus we fabricated an all-organic symmetric pouch cell with aluminum plastic packing film. The charge/discharge curves of the pouch cell in the voltage range of 0.1–2.95 V under flat (0°) and bending (180°) states show discharge capacities of ~280 mA h g⁻¹ without obvious decay (Fig. 5e), which verifies the flexibility and high capacity of Poly-BQ1. Fig. S26 and S27 show the cycling performance under different bending states. The flexible symmetric pouch cell based on Poly-BQ1 can successfully power a red light-emitting diode (LED) continuously from 0° to 180° with constant brightness (inset of Fig. 5e, Movie S1). The flexible all-organic symmetric pouch cell can supply power steadily and is promising for flexible wearable devices.

Supplementary material related to this article can be found online at [doi:10.1016/j.nanoen.2021.106055](https://doi.org/10.1016/j.nanoen.2021.106055).

3. Conclusion

In conclusion, we designed and synthesized a stable ladder polymer with high performance by merging minimum redox-inactive units and maximum cathode-active and anode-active groups into one stable ladder backbone and used it as both cathode and anode materials for all-organic symmetric battery. By balancing multiple optimized redox-active groups in the stable ladder backbone of Poly-BQ1, the all-

organic symmetric battery displays the highest capacity (351.5 mA h g⁻¹ at 50 mA g⁻¹) among all the previous all-organic batteries, together with a remarkable cycling stability (capacity retention of 99.96% per cycle for 400 cycles), superior rate performance (203.4 mA h g⁻¹ at 1 A g⁻¹) and high flexibility. The results suggest that our strategy offers a possible approach for designing and synthesizing flexible next-generation all-organic symmetric batteries materials with both high capacities and cycling stability simultaneously.

CRediT authorship contribution statement

Yang Zhao: Conceptualization, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing. **Manman Wu:** Validation, Formal analysis, Investigation, Writing - review & editing. **Hongbin Chen:** Formal analysis. **Jie Zhu:** Formal analysis. **Jie Liu:** Formal analysis. **Zhantong Ye:** Formal analysis. **Yan Zhang:** Formal analysis. **Hongtao Zhang:** Supervision, Writing - review & editing, Supervision. **Yanfeng Ma:** Formal analysis, Supervision. **Chenxi Li:** Supervision, Writing - review & editing. **Yongsheng Chen:** Conceptualization, Validation, Formal analysis, Data curation, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2021.106055.

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