1	Phenothiazine-Based	Copolymer	with	Redox	Functional	Backbones	for	Organic	Battery
2	Cathode Materials								

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22 ABSTRACT

23 Organic battery materials are receiving increasing attention owing to their elemental abundance, environmental sustainability, and structural diversity. Challenges including the solubility in 24 25 electrolytes, moderate redox potentials and inactive molecular fragments prevent organic materials 26 from being ideal cathodes for practical implementation. Although polymerization, salification and 27 alike are effective in lowering the solubility in electrolytes, they unavoidably bring additional 28 inactive fragments into the molecular structures, resulting in the sacrifice of theoretical 29 galvanometric capacity compared with the pristine molecule. In this study, we use two redox-30 active fragments to construct an insoluble copolymer as a cathode material for organic batteries. 31 The copolymer avoids the use of unnecessary molecular weight while maintaining high specific 32 capacity and cycling stability. We find that a twisted geometry between the two redox-active 33 fragments leads to a cross-conjugation effect that further consolidates the low stability of 34 individual fragment and enhances the flexibility of copolymer chains by forming mesopores that accelerate ion diffusion. The copolymer shows a high capacity of 142.5 mAh g⁻¹ with 35 energy/power density of 577 Wh kg⁻¹/1685 W kg⁻¹ and a decent capacity retention of 87% after 36 37 500 cycles. Our strategy demonstrates the feasibility of designing organic battery materials that 38 are qualified for taking solubility, capacity, and stability into consideration.

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40 KEYWORDS

41 Organic batteries, p-type materials, molecular design, polymeric materials, multi-electron redox
42 reactive

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45 **1. Introduction**

46 The continuously growing production of lithium-ion batteries (LIBs) has imposed great challenges 47 on the limited supply of unsustainable natural resources and the associated cost on battery recycling and environmental impact^{1,2,3}. It is therefore urgent to develop alternative battery 48 49 materials, particularly cathode materials, that are more sustainable and environmental-friendly at 50 affordable cost. Redox-active organic materials have attracted increasing attention in batteries 51 because of their intrinsic features such as sustainability, structural diversity and adjustability of electrochemical characteristics^{4,5,6,7,8}. More importantly, redox-active organic materials avoid the 52 53 kinetic limitation derived from the (de)intercalation mechanism that is widely adopted by 54 conventional inorganic counterparts, thus being suitable electrode candidates across various battery chemistries and charge carriers^{9,10,11}. However, the dissolution of organic materials is 55 crucial as it is responsible for the continuous capacity loss or igniting side reactions^{12,13}, known as 56 57 the "shuttle effect". The most widely used strategies so far to reduce the dissolution are salification^{14,15,16} and polymerization^{17,18,19,20,21,22}. Suga et al. have synthesized a bipolar redox-58 59 active polymer poly((nitronylnitroxylstyrene) and successfully applied it in a pole less battery¹⁷. 60 Xiang et al. have designed new ferrocene-containing poly(fluorenylethynylene) derivatives. This oligomer showed a low solubility in propylene carbonate and impressive cyclic stability¹⁸. Acker 61 62 et al. demonstrated that phenothiazine copolymers as organic cathodes exhibited long-term cycling stability and ultra-high rate capability¹⁹. It is worth noting that redox inactive fragments are 63 64 unavoidably brought into the structure of the organic molecules through salification and polymerization. For instance, in the case of polymerization, redox inactive fragments function as 65 66 either the backbones of the polymers while redox-active centers locating on the side chains (Figure 67 1A and Table S1) or the linkers to bridge redox-active centers (Figure 1B and Table S1). As redox

68 inactive fragments do not contribute to ion storage, the reduced dissolution is achieved at the cost 69 of specific capacities²³. Bearing in mind that low molecular weights and a high amount of redox 70 active centers are essential to achieve high capacities of organic materials, reduced dissolution and 71 a high specific capacity of an organic molecule could be obtained simultaneously when all 72 molecular fragments/monomers are redox-active and have low molecular weights (Figure 1C).

73 To this end, copolymerization using rigid redox-active centers represents a promising way to 74 obtain a low solubility and a high capacity. This minimizes the inactive molecular fragments in 75 the copolymer and hence maximizes its capacity. In addition, using two different rigid redox-active 76 centers copolymerized with "ABABA" form, the adjacent rigid redox-active centers may form 77 cross-conjugation (A to A, B to B), further enhancing the charge delocalization between molecular 78 fragments and ensuring the stability of the redox intermediates during charge/discharge. The break 79 of aromatic conjugation between A and B would lead to the formation of localized conjugation 80 that is beneficial to decrease the interaction between the backbone chains, which facilitates the diffusion of charge carriers²⁴. Previous work has demonstrated hexatomic heterocyclic-ring 81 molecules, such as dihydrophenazine^{25,26,27}, phenothiazine^{19,28}, and carbazole^{29,30}, are excellent 82 83 redox active molecules with stable structures and polymerization has been reported predominantly 84 through linking the molecules to side chains or redox inactive fragments. There has be a recent 85 attempt of polymerization using two redox active molecules, 5,10-dihydrophenazine and 3,7dibromo-10*H*-phenothiazine³¹, but the lack of control on the polymerization, presumably due to 86 the different reactivity of the NH groups in the two molecules, resulted in an unstable resonance 87 structure, where the two redox-active fragments are not adjacent to each other, and thus a quick 88 89 capacity decay of the copolymer.

90 In this work, we used the carbon-nitrogen coupling polymerization reaction between two 91 hexatomic heterocyclic-ring redox-active fragments 4-(3,7-dibromo-10H-phenothiazin-10-yl) 92 benzonitrile (denoted as PTZ) and dihydrophenazine (denoted as PZ) to synthesize a copolymer 93 p-PTPZ. The two redox active fragments were adjacent to each other and a high theoretical 94 capacity was enabled by the three redox sites in each repeating consisting of the two fragments 95 (Figure 1D). Our geometry optimization also indicated that p-PTPZ has a cross conjugated 96 structure, which further ensures a stable molecular structure and fast ion diffusion in and out of 97 the copolymer. It is also worth noting that p-PTPZ has a porous spatial geometry formed by the 98 voids of the copolymer chains. The geometry can accelerate ion diffusion since the copolymer 99 chains are sufficiently flexible to connect redox units in an angled configuration, forming the porous geometry^{19,24,32}. p-PTPZ demonstrated impressive electrochemical performance, delivering 100 101 a high reversible capacity of 142.5 mAh g⁻¹ and high discharge voltages of 4.11, 3.82 and 3.10 V 102 as well as a good cycling stability. This work may shed a light into the design of organic battery 103 materials to simultaneously achieve multi-electron battery chemistry and favorable molecular 104 geometries.

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106 2. Results & Discussion

107 We first carried out Density Functional Theory (DFT) simulations to confirm the feasibility of 108 designing p-PTPZ from the perspectives of geometry and redox activity. The optimized geometry 109 of PTPZ (the repeating unit of p-PTPZ) showed a dihedral angle of 87° between the two aromatic 110 ring planes of PTZ and PZ (Figure 1E). The geometry suggests that PZ and PTZ could form cross-111 conjugation in the molecular structure of p-PTPZ. Calculations of the HOMO/LOMO of PTPZ 112 (Figure S1) in comparison with various molecules confirm that π -electron localization in the 113 HOMO/LUMO remains the same in PZ and PTZ. This can increase the charge delocalization of 114 PZ and PTZ individually during multi-step redox reactions and hence prompt the stability of redox 115 intermediates. The frontier molecular orbital populations of PTPZ (Figure S2) clearly indicated 116 that only π electrons participate in the redox reactions and no bond rearrangement can be observed 117 in the molecules at four valence states, which further demonstrates the molecular stability of p-118 PTPZ. Furthermore, the nearly vertical-cross configuration caused by the dihedral angle of 87° 119 between the PZ and PTZ planes can form structural porosity of p-PTPZ, which in turn accelerates 120 ion diffusion during redox reactions. The structural optimization of p-PTPZ showed a semicircular 121 arrangement of the oligomer chain (Figure S3), and the interaction energies between two chains 122 were calculated to be weaker than the interaction energy between a chain and PF_6^- (Figure S4). 123 The comparison suggests that the interaction between the p-PTPZ chains is not an impediment to 124 the PF_6^- diffusion into/out of the chains, providing a favorable kinetics of the occurring redox 125 relations. The porosity of p-PTPZ is visualized in three directions (Figure 1D), showing a nearly 126 circular configuration and large pores that could serve as ion diffusion channels. Therefore, our 127 simulation results proved the molecular stability and porous geometry of p-PTPZ and both features 128 favor p-PTPZ to be an organic cathode with stable redox activity and fast ion diffusion kinetics.



Figure 1. Comparison between previously designed polymer cathode materials and p-PTPZ in this work: (A) polymers with redox-active fragments locating on the side chains; (B) polymers with redox-active fragments and linkers; (C) polymers with all redox molecular fragments. (D) Schematic of p-PTPZ and redox process. (E) Geometry structures of PTPZ. (F) Optimized interaction configuration of p-PTPZ oligomers shown from x, y, and z directions.

135 With the simulation results established, we next seek to demonstrate the stability of p-PTPZ in 136 electrolytes. p-PTPZ was synthesized via a palladium catalyst coupling polymerization due to the 137 ease of controlling alternative monomers and incorporating redox active units directly into the 138 backbone of the copolymer. As shown in Figure 2A, 4-(3,7-dibromo-10H-phenothiazin-10-139 yl)benzonitrile (5) was synthesized through two steps of reactions, including the Buchwald-140 Hartwig coupling reaction of 10H-phenothiazine (1) and 4-bromobenzonitrile (2), and the 141 bromination by N-bromosuccineiunide (4). The as-synthesized 4-(3,7-dibrom -10H-142 phenothiazin-10-yl)benzonitrile (5) then reacted with 5,10-dihydrophenazine (6) to form p-PTPZ. 143 The molecular weight of p-PTPZ was determined by matrix assisted laser desorption ionization

144 time-of-flight mass spectrometry (MALDI-TOF MS) (Figure 2B and Figure S5). According to the 145 comparison between the results and simulations, the as-synthesized p-PTPZ, after being purified 146 by washing with organic solvents and vacuum heating, is mostly composed of 4 repeating units. 147 UV-Vis absorption spectra (Figure 2C and Figure S6) were measured to verify the solubility of p-148 PTPZ in the electrolyte such as ethylene carbonate/diethyl carbonate (EC:DEC = 1:1, vol%) in 149 comparison with the PTPZ-OMe (see "Expanded experimental procedures" in Supplementary 150 Materials for its synthesis and characterization). Characteristic absorption peaks were found in the case of PTPZ-OMe even at a low concentration of 10⁻⁵ M. On the contrary, neglectable absorption 151 152 peaks can be observed in the case of p-PTPZ even after being soaked in the electrolyte for one 153 week, revealing that p-PTPZ showed an extremely low solubility and long-term high stability in 154 the carbonate electrolyte. Having previously recognized that salification is an available way to against the dissolution of active material in electrolytes^{12,14,33}, the solubility can be weakened with 155 156 the increase of oxidation state due to the active materials can be regarded as compound ion salt in 157 oxidized form^{34,35,36}. The low solubility of p-PTPZ can be further supported by the calculation of 158 its solvation free energy. As shown in Figure 2D, the solvation free energy decreased rapidly at a 159 low degree of polymerization and gradually stabilized towards a higher degree of polymerization. 160 This suggests that a degree of 4 can ensure the stability of p-PTPZ suppress the dissolution into 161 the applied electrolyte, which agrees with the UV-vis results. The as-synthesized p-PTPZ exhibited 162 a granular morphology (Figure S7) with a particle size ranging from several to tens of micrometers. 163 X-ray diffraction (XRD) pattern of p-PTPZ (Figure S8) showed one broad diffraction peak in the 164 wide-angle region and no obvious diffraction peak in the small-angle region. The results suggested that there were weak π - π stacking intercalations³⁷ but no ordered or strong aggregation between 165 166 copolymer backbones. The amorphous nature of p-PTPZ may be beneficial for ion diffusion

between copolymer chains³⁸. It is worth emphasizing that p-PTPZ has superior thermal stability. No decomposition was observed up to 270°C in air and 350°C in N₂ (Figure S9) according to the thermogravimetric analysis (TGA), and no evident melting or glass transition occurred in the temperature range of 0-250°C according to the differential scanning calorimeter (DSC) analysis (Figure S10). In summary, p-PTPZ possesses the characteristics of low solubility in organic electrolytes and high thermal stability, both of which are desirable for the application as a LIB cathode material.



Figure 2. (A) Synthetic route of p-PTPZ. (B) MALDI-TOF MS of p-PTPZ. (C) UV-vis absorption
spectra of p-PTPZ and PTPZ. (D) Solvation free energy of p-PTPZ with various degrees of
polymerization (one, two, three, four and five).

In view of the low solubility of p-PTPZ, we investigated the redox reactions of PTPZ-OMe to store Li-ions using cyclic voltammetry (CV). The measurement was carried out in comparison with N,N'-diphenyl-5,10-dihydrophenazine (DPPZ) and PTZ due to their close resemblance to the redox active units in p-PTPZ. As shown in Figure 3A, the CV profiles of PTPZ-OMe exhibited

182 three pairs of well-defined redox peaks at 3.32/3.24, 3.96/3.88 and 4.17/4.10 V, indicating three 183 steps of single electron transfer process. The small separation of the cathodic and anodic peaks in 184 each pair demonstrates the high electrochemical reversibility of the redox reactions. The peak 185 positions of PTPZ-OMe are in close proximity to those of DPPZ and PTZ, i.e., 3.28/3.22 and 186 4.04/3.98 V for the former and 3.94/3.85 V for the latter. The CV profiles of p-PTPZ (Figure 3B) 187 exhibited three pairs of redox peaks at 3.18/3.07, 3.89/3.82 and 4.18/4.08 V, which are in 188 accordance with the peaks of PTPZ-OMe, indicating a minimal change in the electrochemical 189 behavior of the redox centers after the polymerization reaction. This also proves that the nearly 190 90° angle between the molecular planes of PTZ and PZ can break the aromatic conjugation 191 between the two units, which leads to the localization of electron density at individual redox center 192 without delocalizing along the oligomer chain, contributing to stable redox reactivity over long-193 term cycling^{24,39,40}. DFT simulations (Figure S11 and Table S2) verified that the polymerization 194 reaction caused minimal change in the electronic structures and redox reactive centers of PTZ and 195 PZ, hence maintaining similar redox potentials of p-PTPZ. Furthermore, CV profiles of PTPZ were 196 recorded at the scan rates of 10-500 mV S⁻¹ (Figure S12) to calculate electron transfer rate constant (k_0) of the redox reactions. According to the Nicholson's method⁴¹, k_0 was determined to be 1.8×10^{-10} 197 ², 4.2×10^{-2} and 4.8×10^{-2} cm s⁻¹ for the redox reaction of PTPZ – $e^- \rightarrow$ PTPZ⁺, PTPZ⁺ – $e^- \rightarrow$ 198 $PTPZ^{2+}$ and $PTPZ^{2+} - e^- \rightarrow PTPZ^{3+}$, respectively (Figure S14). The three electron transfer rates 199 were relatively high and comparable to some of the best organic cathode materials^{42,43,44}, 200 201 suggesting that electron transfer was not the rate-limiting factor of the occurring redox reactions 202 and hence highlighting the importance of ion diffusion in achieving great electrochemical 203 performance of p-PTPZ (will be discussed later).



Figure 3. (A) CV profiles of DPPZ, PTZ and PTPZ-OMe in 1 M LiPF₆ solution (EC:DEC = 1:1,
vol%) with Au disk as working electrode, Pt wire as counter electrode, and Ag/AgCl as reference
electrode; (B) CV profiles of p-PTPZ in cells with p-PTPZ as the working electrode, Li as counter
electrode and reference electrode.

210 We then investigated cells performance of p-PTPZ as an organic cathode via galvanostatic 211 charge and discharge at various current densities. Typical charge/discharge profiles of p-PTPZ at 1 C (168 mA g⁻¹) are shown in Figure 4A, where charge/discharge plateaus can be clearly seen at 212 4.18/4.11, 3.87/3.82 and 3.17/3.10 V during the 1st cycle. The plateau potentials agree well with 213 214 those observed in the CV profiles (Figure 3B) and the small polarization between the charge and 215 discharge plateaus suggests favorable kinetics. The cathode delivered an initial discharge capacity 216 of 142.5 mAh g⁻¹, being 84.8% of the theoretical value (168.0 mAh g⁻¹). The charge/discharge 217 plateaus remained distinguishable during the following cycles, demonstrating the structural 218 stability and excellent reversibility of p-PTPZ; as a result, 92.8% of the initial capacity (132.2 mAh 219 g⁻¹) was retained after 200 cycles. The long-term cyclability of p-PTPZ is shown in Figure 4B, 220 which demonstrates a reversible capacity of 123.3 mAh g⁻¹ delivered after 500 cycles, 221 corresponding to a decay rate as low as 0.027% per cycle. The coulombic efficiency (CE) rapidly

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222 increased to >95% after the first few cycles and remained stable between 98% and 99% after 20 223 cycles. To the best of our knowledge, the battery performance of p-PTPZ is among the top of relevant organic cathode materials when taking into consideration discharge voltage, reversible 224 capacity, cyclability and decay rate (Table S3)^{45,46,47}. Figure 4C shows the rate capability of p-225 PTPZ. It delivered reversible capacities of 156, 142, 119 and 91 mAh g⁻¹ at 0.5, 1, 2 and 5 C, 226 227 respectively. The capacity nearly fully recovered when the current rate was reduced back to 1 C. p-PTPZ delivered energy density of 574/522/438/335 Wh kg⁻¹ and power density of 228 287/522/876/1675 W kg⁻¹ at 0.5/1/2/5 C, respectively. Such performance was superior to the 229 reported organic cathode materials based on hexatomic heterocyclic-ring molecules^{19,45,47,48,49}. The 230 231 low CE in the first few cycles could be attributed to the formation of cathode-electrolyte interphase 232 (CEI) on the cathode and solid-electrolyte-interface (SEI) layer on the anode. The construction of 233 cathode-electrolyte interphase (CEI) led to an overcharge until a stable CEI formed in the initial few charge-discharge cycles^{50,51}. Simultaneously, the irreversible oxidation process in the material 234 235 also contributed to the overcharge since some Li deposited on the anode was consumed by side reactions with the electrolyte to form a solid-electrolyte-interface (SEI) layer^{52,53}. In addition, it's 236 237 inevitable that a trace amount of the active material could dissolve in the electrolyte, resulting in a 238 shuttle effect that was more obvious when the charging rate decreased.

The CV analysis on the cycled cell (Figure S15) demonstrated that all characteristic cathodic and anodic peaks maintained unchanged, indicating the good reversibility and stability of p-PTPZ. CV profiles at different current densities showed a very small peak shift with increasing the current density, indicating highly reversible redox reactions. The peak currents (i_p) of cathodic and anodic peaks were proportional to the square root of scan rates (Figure S16), and the capacity contribution from diffusion-controlled reactions was calculated to be ranging from 81.5 to 92.4% (Figure S17),

indicating the electrochemical processes in the p-PTPZ/Li cells were diffusion-controlled^{54,55}. The 245 246 electrodes after cycling were examined by scanning electron microscopy (Figure S18), which 247 revealed that the electrodes at different state-of-charge indicated a homogeneous distribution of 248 active material on their surfaces, and no sigh of active material peeling-off was observed. Diffusion coefficient (D_s) of PF_6^- (p-PTPZ is a p-type cathode) was measured using galvanostatic 249 250 intermittent titration technique (GITT). The cathode exhibited small overpotentials during 251 charge/discharge (Figure S19). As shown in Figure 4D, the diffusion coefficient was calculated to be in the order of 10^{-12} to 10^{-13} cm² s⁻¹ during PF₆⁻ intercalation (charging) and 10^{-11} to 10^{-12} cm² 252 253 s^{-1} during PF₆⁻ deintercalation (discharging). The obtained diffusion coefficient is on par with 254 conventional inorganic Li⁺-ion intercalation-type cathodes and organic materials that adopt an anion-exchange mechanism^{56,57,58}. It is attributed to the twisted copolymer backbones that improve 255 256 the flexibility of the copolymer chains and form a porous geometry to accelerates ion diffusion. 257 The chain interaction was interrupted by the almost vertical angle between the two redox 258 fragments, which lowers the activation energy of ion diffusion and enhances electrochemical 259 performance.



Figure 4. Charge/discharge profiles (A) and cycling performance (B) of p-PTPZ at 1 C. (C) Rate capability of p-PTPZ. (D) Voltage-dependent chemical diffusion coefficient of PF_6^- during charge and discharge processes.

264 Our analysis of frontier orbital energy levels and electrochemical behavior as well as the 265 observed electrochemical performance suggested that nitrogen is the active centers in the redox 266 reactions of p-PTPZ, and its redox process undergoes three steps of oxidation, resulting in PTPZ⁺, $PTPZ^{2+}$ and $PTPZ^{3+}$. Therefore, we further investigated the redox reaction mechanism of p-PTPZ 267 268 via chemical state transformation analysis in to clarify the redox activity and the stability of 269 intermediates during charge/discharge processes. The electronic spin density (ESD) distribution 270 of the PTPZ unit was calculated at the valence states of 0, +1, +2 and +3 (Figure 5A). The high 271 ESD on the N atoms in the heterocycles clearly revealed that they are the redox centers of the three 272 steps of redox reactions. The schematic reaction mechanism is illustrated in Figure 5B. Two beta 273 electrons are removed from N1 (PZ unit) and N2 (PTZ unit) in the first and second steps,

274 respectively, while an alpha electron is removed from N3 (PZ unit) in the final step. It is worth 275 noting that the remaining electron on N3 could pair with the single electron on N1, resulting in the 276 conjugate affection that further stabilizes oxidation states. The aromaticity of the redox units was 277 investigated by nucleus independent chemical shift (NICS) and the change of NICS(1)zz value 278 further supports the afore-mentioned redox reactions (Figure 5C). The heterocycle containing N1 279 and N3 changes from anti-aromatic to nonaromatic upon removing an electron from N1 in the first 280 redox reaction and further changes to aromatic upon removing an electron from N3 in the last 281 redox reaction, while the heterocycle containing N2 changes from weakly anti-aromatic to 282 nonaromatic upon removing an electron from N2 in the second redox reaction. The change in 283 aromaticity agrees with that revealed by Huckel's rule and indicates that only π electrons of p-PTPZ delocalize in the three redox processes^{59,60}, which improves the structural stability of p-284 285 PTPZ. In addition, the structural distortion of PTPZ during the redox process was estimated by root mean square displacement/deviation (RMSD)⁶¹. As shown in Figure S19, the molecule 286 287 experiences a small change from PTPZ to PTPZ⁺ due to the electron conjugate affection of PZ. 288 Although the distortion becomes more obvious from $PTPZ^+$ to $PTPZ^{2+}$, the small change recovers from $PTPZ^{2+}$ to $PTPZ^{3+}$ maintaining the electron delocalization in the molecule and strengthening 289 290 its structural stability.



Figure 5. Calculated ESD distribution (A), the schematic diagram of redox reaction mechanism
(B) and calculated NICS(1)zz values in ppm (C) of PTPZ at the valence states of 0, +1, +2 and +3.

295 **3. Conclusion**

In conclusion, this study used two redox-active fragments to construct an insoluble copolymer to address the challenges of organic battery cathode materials, which includes moderate redox potentials, excess inactive molecular fragments, and the soluble nature of the materials. We employed rigid PZ and PTZ fragments to design and synthesize a p-PTPZ copolymer that exhibited limited solubility in the organic electrolyte, stable cycling performance, a high redox potential and a reversible capacity. We found that the adjacent rigid redox-active centers can form cross302 conjugation that is beneficial to decrease the interaction between the backbone chains and thus 303 decrease the energy barrier for charge carrier diffusion, as well as stabilize the redox intermediates 304 during the electrochemical processes. As a result, p-PTPZ delivered a high reversible capacity of 142.5 mAh g⁻¹ with a discharge voltage in the range of 3.1-4.11 V (vs. Li⁺/Li) for 500 cycles. We 305 306 believe the facilitation of the practical implementation of p-PTPZ requires future efforts devoted 307 to developing efficient synthetic methods and optimizing its structure to reduce the manufacture 308 cost and improve its stability against air, moisture and counter alkali metal anode. By screening 309 appropriate type and proportion of catalysts and ligands or prolonging reaction time, it is possible 310 to increase the polymerization degree of p-PTPZ, which could further improve the purity and 311 stability of the materials against air and moisture. It is also possible to construct p-PTPZ/carbon 312 composite structures in order to ensure the composite's stability against counter lithium anode and at the same time improve the conductivity of the entire electrode matrix⁶². We hope to include 313 314 these studies in our future work.

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316 **4. Experimental section**

Synthesis of p-PTPZ. Follow previous literature procedures⁶³, 5,10-dihydrophenazine (6) was 317 318 prepared and used immediately. A mixture of precursor 4-(3,7-dibromo-10H-phenothiazin-10-319 yl)benzonitrile (5) (0.458 g, 1 mmol), precursor 5,10-dihydrophenazine (6) (0.200 g, 1.1 mmol), 320 and alkali tBuONa (0.288 g, 3 mmol) in anhydrous o-xylene (20 mL) was stirred. The Pd(OAc)₂ 321 (14 mg) and ligand XPhos (57 mg) are premixed and then injected into the above mixture. Then 322 the reaction mixture under argon was stirred at 110°C for 24 h and raised the temperature to 145°C 323 for another 24 h. Before the end of reaction, 0.5 mL of bromobenzene was added into the reaction 324 system for end capping for 5 h. The solid part (crude product) was obtained by filtering the hot 325 reaction mixture, and then washing with a great deal of hot o-xylene, DCM, MeOH and H_2O . To 326 fully remove the impurities, the crude product was pestle by a mortar after drying and dispersed in DCM using ultrasonic waves for sufficiently long time, then filtered and washed with different 327 328 solvents, such as DCM, EC, and DEC. The purer product was given by repeating those procedures 329 for five times. Then Physical Vapor Deposition (PVD) instrument was used to remove small 330 molecule weight products may dissolve in electrolyte. The conditions of PVD are under vacuum 331 $(< 1 \times 10^{-3} \text{ Pa})$ at 300 °C for 10 hours. Finally, we obtained the final product as a brownish black 332 solid with big molecule weight and poor solubility in commercial electrolyte, and the yield is 81% 333 (445mg). MALDI-TOF MS: C₆₂H₃₈N₈S₂ (n=2), exact mass: 958.266, found: 957.214; C₉₃H₅₆N₁₂S₃ 334 (n=3), exact mass: 1436.391, found: 1435.295; C₁₂₄H₇₄N₁₆S₄ (n=4), exact mass: 1914.517, found: 335 1913.351; C₁₅₅H₉₂N₂₀S₅ (n=5), exact mass: 2392.642, found: 2392.377.

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337 **Electrode preparation and cell assembly.** Follow a typical electrode preparation process, the mixture of as-prepared p-PTPZ, Super P carbon (Alfa Aesar) and polyvinylidene fluoride 338 339 (Fluorochem Limited) with the weight ratio of 7:2:1 dissolved in 1-Methyl-2-pyrrolidinone 340 (SuperDry, J&K Scientific) was thoroughly stirred in a centrifugal mixer (Thinky ARE-300) for 341 30 min until a homogenous slurry formed. The slurry was then casted on flat Al foil (MTI corp) 342 with thickness of 50 µm. The Al foil with the slurry was dried in vacuum at 80 °C for 12 h. After 343 cooling to room temperature, the above-mentioned Al foil was cut into round pieces with a diameter of 10 mm. The average mass loading of each piece was ~1.5 mg cm⁻². A standard CR2032 344 345 coin cell of p-PTPZ | Li was assembled in a standard glovebox (H₂O and O₂ concentration < 1ppm). 346 The metallic Li was used as counter and reference electrodes in the coin cell, with 1.0 M LiPF_6 in 347 EC/DEC (=1/1, vol%) being the electrolyte and Celgard 2500 being the separator.

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