Electronic Supplementary Material (ESI) for Energy & Environmental Science.

# Supporting Information

## A Quinone Based Oligomeric Lithium Salt for Superior Li–Organic Battery

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**Purification of $Li_2$PDHBQS**

There are two approaches to purify $Li_2$PDHBQS. The first one is much easier by using ethanol as solvent. In a typical process, as-prepared $Li_2$PDHBQS (0.40 g) was completely dissolved in 40 mL ethanol by adding 5 M HCl solution (as less as possible). 5 M LiOH solution was added into the clear solution drop by drop until precipitate generated, meanwhile the pH value of the solution indicated by a test paper turned to approx. 7. The mixture was centrifuged and washed with ethanol until the solution is colorless. The product was dried at 80 °C in air, obtaining a solid with deeper color than the crude product. A typical yield of this process is 88%.

The second approach of purification contains two separated steps, involving poly(2,5-dihydroxy-*p*-benzoquinonyl sulfide) (PDHBQS) as an intermediate product. In a typical process, as-prepared $Li_2$PDHBQS (0.50 g) was added into 20 mL 5 M HCl solution and the mixture was stirred at room temperature for 2 days. The mixture was then centrifuged and washed with 5 M HCl solution for twice. After drying at 80 °C in air, we can obtain PDHBQS as product with a dark brown color and a yield of 54%. In order to retrieve $Li_2$PDHBQS, PDHBQS (0.20 g) was added into 20 mL 5 M LiOH solution and the mixture was stirred at room temperature for 2 days. The mixture was then centrifuged and washed with ethanol until the pH value of the solution indicated by a test paper turned to approx. 7. The product was dried at 80 °C in air, obtaining a coral solid with yield closed to 100%.

As a lithium salt, $Li_2$PDHBQS is soluble in water (solubility is 2–3 mg $mL^{-1}$) but absolutely insoluble in ethanol. After stirring in 5 M HCl solution for 2 days, most enolate anions were protonated into hydroxyls, producing an oligomer called PDHBQS. During this process, NMP and low molecular weight oligomers were washed off. In contrast to $Li_2$PDHBQS, PDHBQS is soluble in ethanol, slightly soluble in water and absolutely insoluble in 5 M HCl solution. Thus in order to retrieve $Li_2$PDHBQS, PDHBQS can be either stirred in 5 M LiOH solution for 2 days or dissolved in ethanol and precipitated by adding LiOH.

## Synthesis and characterization of $Li_2CL$

Dilithium chloranilate ($Li_2CL$) was synthesized by a simple acid–base reaction similar to the literature[27]. In a typical process, CLA (0.418 g, 0.002 mol) and $LiOH \bullet H_2O$ (0.168 g, 0.004 mol) were dissolved in 20 mL $H_2O$. After evaporating excess $H_2O$, the product was dried at 230 °C under vacuum to stoichiometrically get anhydrous $Li_2CL$. However, the anhydrous $Li_2CL$ strongly tend to absorb moisture when stored in air atmosphere, and the stable phase is usually $Li_2C_6O_4Cl_2 \bullet H_2O$ with a brown color, which can be confirmed by different characterization methods including FTIR, EA and XRD.

*$Li_2CL$ ($Li_2C_6O_4Cl_2 \bullet H_2O$).* $^1H$ NMR (500MHz, $D_2O$): $\delta$=4.63 ppm ($H_2O$). $^{13}C$ NMR (500MHz, $D_2O$): $\delta$=106.6 ppm (C—Cl), $\delta$=174.3 ppm (conjugated C=O and $C—O^-$). FTIR (KBr pellets): $\nu$=3434, 1630, 1549, 1520, 1389, 1024, 848, 746, 599, 581, 499 $cm^{-1}$. HRMS calculated for $[Li_3C_6O_4Cl_2 \bullet H_2O]^+$: m/z=244.976; found: m/z=244.938. EA calculated for $Li_2C_6O_4Cl_2 \bullet H_2O$: C 30.17%, H 0.84%, O 33.49%, Cl 29.68%; found: C 30.21%, H 0.95%, O 30.62 %, Cl 27.41%.

## Elemental analysis of $Li_2PDHBQS$

The measured C, H, O, S, N, Cl and Li content in $Li_2PDHBQS$ is respectively 34.5%, 2.5%, 41.4%, 9.3%, 0.16%, 1.7% and 6.4% (total value is 96.0%). The residual Cl content is greatly reduced from theoretical value of 33.9% in CLA, indicating almost all Cl atoms are substituted. Unfortunately, the measured S content in $Li_2PDHBQS$ is too low and thus obtained C/S molar ratio is approx. 11:1, far away from the theoretical value of 6:1. The contradiction between low residual Cl content and low substituting S content puzzled us for a long time. Finally we found the high Li content in $Li_2PDHBQS$ brought huge error in the elemental analysis of C, S and O through a combustion method, due to the formation of $Li_2SO_4$ and/or $Li_2CO_3$ in combustion process.

**Table S1** Characteristic IR band assignments of the four samples. All characteristic peaks of CLA are well assigned according to the literature.[39] The suffix follow the wavenumber (cm$^{-1}$) means the strength and shape of the peak: s, strong; m, medium; w, weak; vw, very weak; br, broad.

| Vibration Type | CLA | $Li_2CL$ | PDHBQS | $Li_2$PDHBQS |
|---|---|---|---|---|
| O—H of $H_2O$, stretching | | 3434s,br | 3443s,br | 3412m,br |
| O—H, stretching | 3237s | | | |
| O—H of $H_2O$, bending | | 1630w | | 1649w |
| C=O, stretching | 1665s | 1549s | 1650s | |
| C=C, stretching | 1633s | 1520s | 1609s | 1527s |
| C—O, stretching | 1371s | 1389w | 1361m | 1390w |
| O—H, bending | 1286–1271s,br | | 1292–1235m,br | 1281w, 1230w |
| C—C, stretching | 984s | | 974w | |
| C—Cl, stretching | 856m | 848w | | |
| C=O, wagging | 753m | 746w | | |
| O—H, torsion | 693m | | | |
| C—Cl, wagging | 572m | 581w | | |
| Ar—S, stretching | | | | 1120vw |

**Table S2** Energy level data calculated by DFT method with B3LYP exchange-correlation functional.

| Molecule | $C_6H_4O_4$ | $LiC_6H_4O_4$ | $Li_2C_6H_4O_4$ | $Li_2C_6H_2O_4$ | $Li_3C_6H_2O_4$ | $Li_4C_6H_2O_4$ |
|---|---|---|---|---|---|---|
| LUMO (eV) | -3.4368 | -2.0517 | -1.4395 | -2.2749 | -1.6898 | -1.0095 |
| HOMO (eV) | -7.0614 | -4.1144 | -3.0477 | -5.3797 | -3.5484 | -2.5198 |

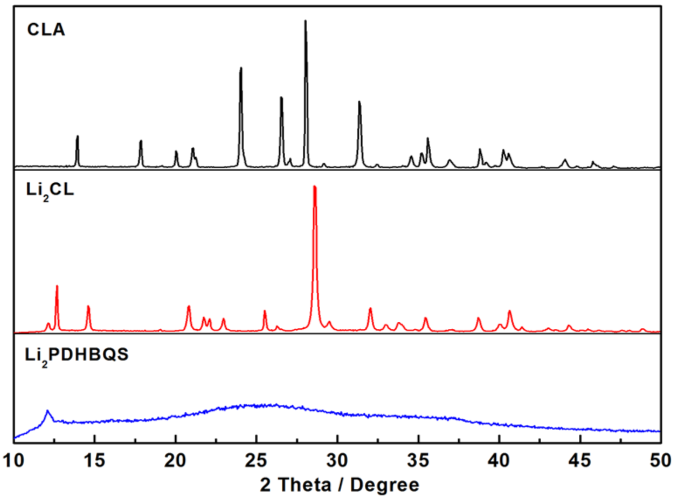

**Fig. S1** XRD patterns of CLA, $Li_2CL$ and $Li_2PDHBQS$. Both CLA and $Li_2CL$ ($Li_2C_6O_4Cl_2$•$H_2O$) exist in crystalline phase but $Li_2PDHBQS$ exists in amorphous phase although it is also a lithium salt.

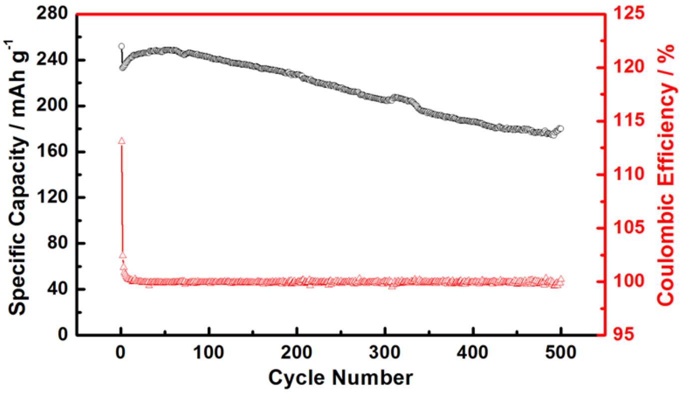

**Fig. S2** Long-term cycling profiles of $Li_2PDHBQS$ electrode without absorbed water. (1.5–3.0 V, 500 mA g$^{-1}$). The max reversible capacity is 248 mAh g$^{-1}$ and it remains 180 mAh g$^{-1}$ after 500 cycles, indicating a much poorer cycling stability than that of $Li_2PDHBQS$ with absorbed water (Figure 4c).

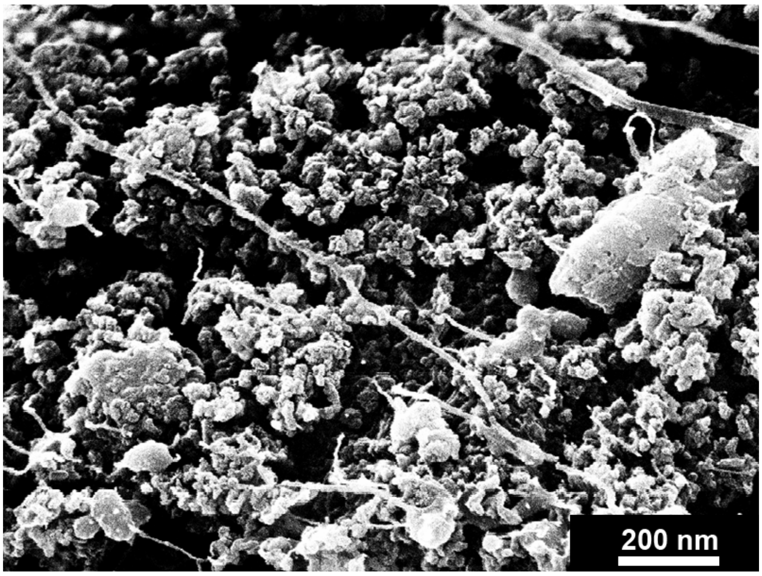

**Fig. S3** SEM image of $Li_2PDHBQS$ electrode film ($Li_2PDHBQS$: Ketjenblack carbon: PTFE=6:3:1). When grinding the mixture, water was added to promote the intimate contact between $Li_2PDHBQS$ and Ketjenblack carbon at nanoscale level benefiting from the dissolution of $Li_2PDHBQS$ in water.

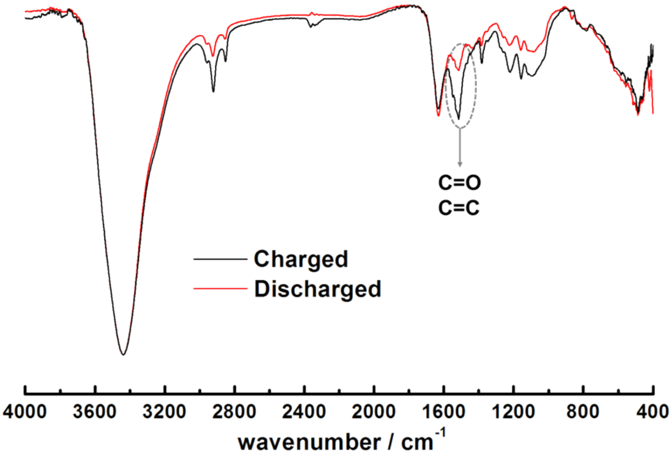

**Fig. S4** Ex-situ FTIR spectra of $Li_2PDHBQS$ electrodes. It is obvious that the characteristic peak of C=O and C=C stretching vibration at 1515 $cm^{-1}$ greatly reduces after discharging to 1.5 V.

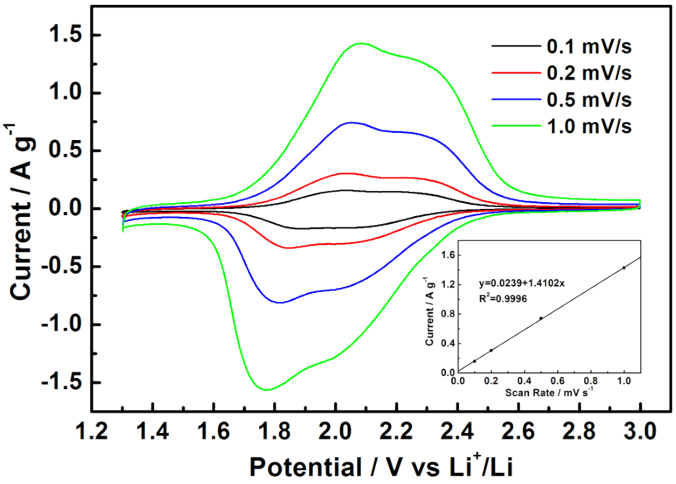

**Fig. S5** CV curves of $Li_2$PDHBQS at different scan rates (0.1, 0.2, 0.5 and 1.0 mV $s^{-1}$). The linear relation of peak (oxidation peak at 2.0–2.1 V) current vs. scan rate indicates it is a surface reaction.

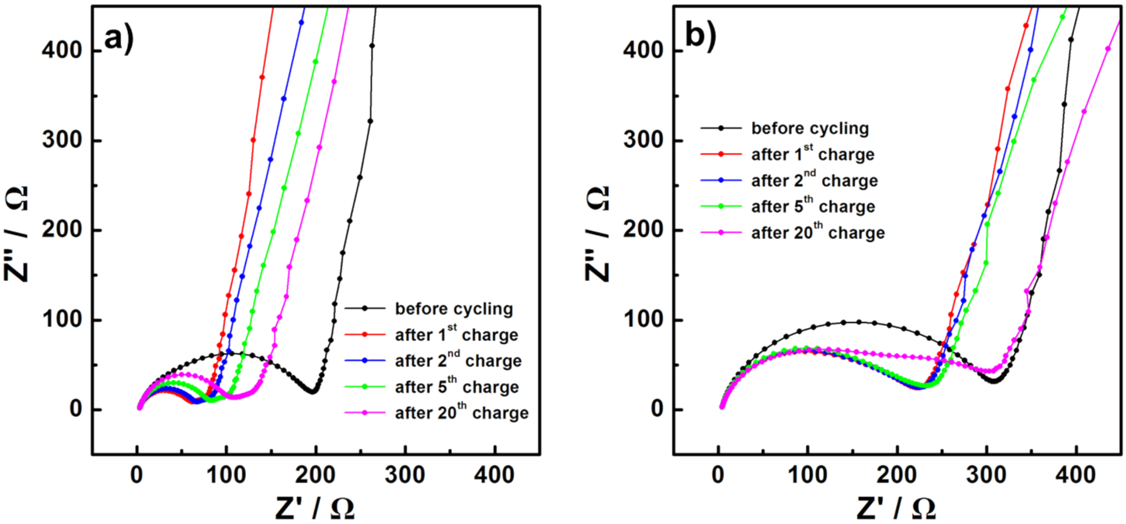

**Fig. S6** EIS profiles of $Li_2$PDHBQS electrode (a) with $H_2O$ or (b) without $H_2O$ at different status: before cycling and after 1st, 2nd, 5th and 20th charging process. The $R_{CT}$ (charge transfer resistance, approximate to the diameter of the semicircle) of electrode without absorbed water greatly increased, either before cycling or after several cycles. The $R_{CT}$ obviously reduces after 1st cycle due to the building of Li-ion transport channels and then gradually increases in the following cycles due to polarization of the electrode.