Molecular Design of Phenanthrenequinone Derivatives as Organic Cathode Materials

Liu-Bin Zhao,* Shu-Ting Gao, Rongxing He, Wei Shen, and Ming Li[a]

Conjugated carbonyl compounds have become the most promising type of organic electrode materials for rechargeable Li-ion batteries because only they can achieve simultaneously high energy density, high cycling stability, and high power density. In this work, we have performed first-principles density functional theory (DFT) calculations to explore the fundamental rules of how the electronic structure and redox properties of a typical conjugated carbonyl compound, phenanthrenequinone (PQ), are modified by adjusting the heteroaromatic building blocks. Such a molecular design strategy allows for the improvement in discharge potential while the specific capacity remains nearly unchanged. The correlation between the electronic structures and redox properties for the designed PQ derivatives is systematically discussed. It is demonstrated that the discharge potential of the PQ derivatives depends strongly on the frontier orbital levels, the electric potential, and the Li-bonding configurations. The electrostatic potential (ESP) maps show visible displays of molecular electric structures and can be applied to understand how the redox properties of the PQ derivatives are modified by the heteroaromatic building blocks.

Introduction

Rechargeable Li-ion batteries (LIB) with high energy density and power density are considered the most promising electron energy storage devices for the world’s ever growing demand for energy.[1] LIBs are widely used in portable electronics,[2] electronic vehicles,[3] and smart grids.[4] Organic redox compounds composed of naturally abundant chemical elements (C, H, N, O, and S) should be ideal electrode materials in the view of sustainable development.[5] Compared with inorganic materials, the redox potential of organic electrodes can be agiley tuned through molecular design and can be used as either cathodes or anodes.[6] Many organic cathode materials have been proposed so far including conductive polymers, organosulfide, thioether, nitroxy radical compounds, and conjugated carbonyl compounds.[6,7] Organic carbonyl compounds have attracted the most attention because only they can achieve simultaneously high energy density, high cycling stability, and high power density.[7,8]

Although organic carbonyls are considered as the most promising type of organic electrode materials, the intrinsic low working potential comparable to those of state-to-the-art inorganic electrode materials still remains a primary obstacle to achieving high energy electrode materials. A series of studies have been carried out to explore high energy density organic carbonyl materials. Dunn and co-workers systematically studied a family of naphthalene-diimide-based materials.[9] By changing the aryl substituents from electron-donating groups (–NMe2) to electron-withdrawing groups (–F and –CN), the discharge potentials of these materials varied from 2.3 to 2.9 V (vs. Li/Li+), demonstrating the good voltage tunability of organic carbonyls. Yokoji et al. reported that benzoquinones modified with perfluoroalkyl groups exhibit reduction potentials higher than 3 V (vs. Li/Li+).[10] Park, Kang et al. proposed a high-energy organic cathode using a tetrachloro substituted quinone with a high discharge voltage of 2.72 V vs. Na/Na+.[11] Jang and co-workers studied the Li-binding thermodynamics and redox potentials of functionalized anthraquinone (AQ) derivatives.[12,13] They found that the redox properties of the AQ derivatives can be improved by modifying their chemical structures with electron-withdrawing carboxyl groups. These studies highlight the potential for carbonyl compounds to be improved through the use of electron-withdrawing functional-group substitution. However, the increase in molecular weight considerably reduces the specific capacities and results in overall low energy densities.[13]

An alternative strategy to improve the redox potential of organic carbonyls is substitution of the benzene ring with other heterocyclic compounds. For instance, by introducing two pyridine rings into AQ, the first discharge potential could be raised by 0.44 V (2.71 V vs. Li/Li+), but the theoretical capacity barely dropped from 257 to 255 mAhg−1.[14] Similarly, changing the conjugated backbone of phenanthrenequinone (PQ) from biphenyl to bithiophe and to bipyrindine increases the average discharge potential from 2.61 to 2.68 and to 2.74 V (vs. Li/Li+), respectively.[15] In our recent theoretical study on a series of AQ derivatives, we demonstrated that both thermodynamic and kinetic properties of AQ could be significantly modified by in
Introducing heteroaromatic building blocks. Shimizu et al. showed that nitrogen atoms \( \beta \) to the carbonyl group of ketones could effectively stabilize the reduced form through the chelate effect, thus increasing the reduction potential.

Theoretical calculations were employed to understand the relationship between molecular electronic structures and their electrochemical property. Aspuru-Guzik and co-workers employed a high-throughput computational screening approach to investigate the quantitative structure–property relationship of 1710 quinone derivatives with the aim of identifying promising candidates for all-quinone redox flow batteries. Park et al. studied the thermodynamic and electrochemical redox property of a set of ketone derivatives by using first-principles density functional theory (DFT). It was concluded that the thermodynamic stabilities rely on the distribution of carbonyl groups and the redox potentials increase with the increasing number of carbonyl groups. Zhou and co-workers examined the correlation the electron delocalization (aromaticity) and the lithiation voltage of carbonyl-containing polycyclic aromatic hydrocarbons by Clar’s aromatic sextet theory. Bachman et al. showed that the LUMO energy can be applied as a descriptor to access the reduction potential of AQ derivatives without performing detailed free-energy calculations for neutral and reduced electronic states. Yu studied the binding energy and work function of organic electrode materials adsorbed on conducting substrates by using dispersion-corrected DFT. Abruna and co-workers carried out a nuclear independent chemical-shift calculation to study the aromaticity and stability of organic molecules as cathode materials.

Tomerini et al. studied the relationship between spin density with redox potential and stability in a series of N-substituted pentalenedione derivatives. Manzhos and co-workers presented a systematically study of the effects of p-doping and n-doping in small molecules with and without redox centers on the voltage and capacity of organic electrode materials. Liu et al. revealed the multiple redox reactions between self-polymerized dopamine and electrolyte ions are revealed by combining electrochemical measurement with DFT calculation.

Previous theoretical studies had shown that the redox properties of conjugated carbonyl compounds depend strongly on their electronic structures. In this work, we have performed first-principles DFT calculations to explore the fundamental rules that how the electronic structure and redox property of a typical conjugated carbonyl compound PQ is adjusted by the heteroaromatic building blocks. By comparing the redox property of a set of functionalized PQ derivatives, we show that incorporation of heteroaromatic building blocks seems to be a better molecular design strategy, which allows the improvement of discharge potential while the specific capacity remains nearly unchanged. Then, the structure–property correlations among the designed PQ derivatives are discussed. It is demonstrated that the discharge potential of the PQ derivatives depends strongly on the frontier orbital levels, the electric potential, and the Li-bonding configurations. The most interesting finding in this study is that the electrostatic potential (ESP) maps give visible displays to show how the electronic structures and redox properties of the PQ derivatives are tuned by the heteroaromatic building blocks.

Results and Discussion

Electrochemical performance of the cathode materials

The designed PQ derivatives are shown in Figure 1. Two alternative molecular design strategies are employed to explore high electrochemical performance electrode materials. For the first strategy, the two side benzene rings are replaced by six-membered (series A and B) or five-membered (series C and D) heterocycles. For the second strategy, electron-withdrawing inductive (series E) or conjugative (series F) functional groups are incorporated to PQ. In our recent theoretical study on AQ derivatives, we demonstrated that the electronic structures of conjugated carbonyl compounds could be significantly modified by hetero-atom substitution. Jang and co-workers found that the redox properties of the AQ derivatives can be improved by modifying their chemical structures with electron-withdrawing carboxyl groups.

Systemic theoretical calculations were carried out to compare the electrochemical performance of the PQ derivatives modified by heterocycle substitution (series A to D) and by
functional-group incorporation. The first and second lithiation potentials, average reduction potentials, theoretical capacities, and energy densities of 40 PQ derivatives are computed (see Table S1 in the Supporting Information). Molecules with the best redox properties are selected and compared with PQ as shown in Figure 2. The computed average reduction potentials of the PQ derivatives at the PCM/B3LYP/6-311 + G(d,p) level match well with experimental results (see Figure S1). Among all the designed molecules, D05 exhibits the highest energy density of 841 Wh kg⁻¹ with simultaneously high reduction potential (3.02 V vs. Li/Li⁺) and high specific capacity (297 mAh g⁻¹). This value is 32% higher than PQ and can be comparable to those of state-of-the-art inorganic electrode materials. However, the computed energy densities of series E and F molecules are lower than PQ, although their reduction potentials are increased. The highest energy density of the functional-group incorporated PQs is only 580 Wh kg⁻¹ (F06). From the computed electrochemical properties of 40 PQ derivatives, we conclude that heterocyclic substitution is a better molecular design strategy than functional-group incorporation, which gives a balance between increasing working potential and maintaining specific capacity.

Electronic effects of the heterocyclic aromatic compounds

Owing to the electron-withdrawing or electron-donating electronic effect of heteroatoms, heteroaromatic compounds exhibit significantly different properties relative to benzene, such as ionization potentials and excitation energies. Figure 3 compares the HOMO and LUMO levels of benzene and 13 heterocyclic compounds. For six-membered heterocyclic compounds, the electron-withdrawing effect of the N atom lowers the electron density of the aromatic ring and leads to a decrease of LUMO energy. The computed LUMO level of pyridine is 0.66 eV lower than that of benzene. We also notice the electron-withdrawing effect of nitrogen atom can be accumulative. The LUMO energy shifts for pyridazine (1.16 eV), pyrimidine (1.38 eV), and pyrazine (1.42 eV) are about twice as much as that for pyridine. For five-membered heterocyclic compounds, the LUMO levels of pyrrole and furan are higher than that of benzene because of the electron-donating effect of sp³-hybridized N and O atoms. However, the LUMO level of thiophene is unchanged (series A and B) or slightly increase (series C and D except for S-containing molecules). On the contrary, the capacities of series E and F molecules dramatically decreased owing to the substitution of H atoms by an electron-withdrawing heavy functional group. For –NO₂-, –COOH-, and –CN-modified PQ, the theoretical capacity decreases from 255 to 178, 179, and 205 mAh g⁻¹, respectively.

The energy density of an electrode is defined as a product of the average charge/discharge potential and the specific capacity. Among all the designed molecules, D05 exhibits the highest energy density of 841 Wh kg⁻¹ with simultaneously high reduction potential (3.02 V vs. Li/Li⁺) and high specific capacity (297 mAh g⁻¹). This value is 32% higher than PQ and can be comparable to those of state-of-the-art inorganic electrode materials. However, the computed energy densities of series E and F molecules are lower than PQ, although their reduction potentials are increased. The highest energy density of the functional-group incorporated PQs is only 580 Wh kg⁻¹ (F06). From the computed electrochemical properties of 40 PQ derivatives, we conclude that heterocyclic substitution is a better molecular design strategy than functional-group incorporation, which gives a balance between increasing working potential and maintaining specific capacity.

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slightly lower than that of benzene. A possible reason is that the d–p hybridization of the S atom weakens the conjugative effect. Replacement of a C–H fragment in pyrrole, furan, and thiophene to a sp³-hybridized N atom leads to a further decrease of LUMO energy. The LUMO level of furan is 0.21 eV lower than that of benzene and the LUMO level of isoxazole is 0.50 eV higher than that of benzene. The variation trend for HOMO levels is quite similar to the LUMO levels. Figure 3 demonstrates how the frontier orbital levels of benzene can be significantly tuned by heteroatom substitution.

The ESP map can present a visible display of molecular polarity and helps us to understand how the electronic structure of aromatic rings is adjusted by the substituted heteroatoms. Figure 4 compares the ESP map of benzene with 13 other heterocyclic compounds. The ESP map of benzene is centrosymmetric. Positive charges are distributed along the edge while negative charges are localized in the center of aromatic ring. As the C–H fragment is replaced by a N atom in six-membered heterocyclic compounds, the most prominent and visible change is the decrease of electron density at the center of aromatic ring because of the electron-withdrawing effect of sp³-hybridized N atoms. The sp³-hybridized N atom with strong electron-donating effect, by contrast, increases the electron density at ring center as seen from the ESP map of pyrrole. Further substitution of C–H fragment in pyrrole to N atom can lower the electron density at ring center, resulting in the ESP values at the center of imidazole and pyrazole to be more positive than that of benzene. Such a trend can be also be found in the ESP map of furan and thiophene.

Correlation between electronic structure and redox properties

The LUMO level of a molecule is usually used to evaluate its reduction potential. Liang et al. demonstrated that the measured average working potential of PQ, A04, and C05 showed a nice linear fit with the computed LUMO level. They further predicted that electron-deficient building blocks, such as bithiazole, biokaxaozo, and bipyrimidine, were expected to induce even lower LUMO levels and promote discharge potentials. Because the frontier orbital levels of benzene can be adjusted by heteroaromatic building blocks, it is of interest how the LUMO level of PQ changes with heterocycle substitution. Computation results show that electron-withdrawing rings lead to a decrease of LUMO level, whereas electron-donating rings result in an increase of LUMO level. The LUMO level of PQ is −3.6 eV. Substitution of two side rings of PQ with electron-withdrawing pyridine rings decrease the LUMO level to about −3.9 eV, whereas electron-donating pyrrole rings increase the LUMO level to about −3.1 eV. Among the designed molecules, the computed LUMO levels range from −3.11 (C02 with two pyrrole rings) to −4.49 eV (B03 with two pyridazine rings). The electronic effect of aromatic heterocyclic compounds on the frontier orbital level agrees with that of substituted functional groups.

The change of electronic structures through heterocycles substitution will certainly further influence the redox properties of PQ derivatives. As seen from Figure 5a, the computed average reduction potential of PQ analogues increases linearly with the decreasing of their LUMO level. The correlation coefficient \( R^2 \) is 0.987. B03 with the lowest LUMO level (−4.49 eV) gives the highest reduction potential (3.15 V vs. Li/Li⁺), whereas C02 with the highest LUMO level (−3.11 eV) exhibits the lowest reduction potential (2.22 V vs. Li/Li⁺). Although the LUMO plots of various PQ analogues are quite similar in general, still delicate difference can be found. Figure 6 compares LUMO plots of PQ, B03, C02, and D05. Comparison of PQ and B03 shows the electron distribution in B03 is more delocalized. Such a difference can also be found between C02 and D05. As seen in Figure 6, the differences in MO plots of PQ derivatives exist, but are very slight. It is seemed that MO plots are not the best...
way to display how the electronic structures of PQ are modified by the heteroaromatic building blocks.

After two electron reduction, the LUMO of PQ becomes the HOMO of PQ-Li₂ as seen in Figure 6. The HOMO level of PQ-Li₂ reflects not only the electron affinity but also the bonding energy of the Li-ion with the carbonyl group. In our recent study, it was illustrated that the HOMO energy of AQ-Li₂ is a better indicator to evaluate the reduction potential of AQ derivatives because both the electron transfer factor and the Li-ion transfer factor are included. Figure 5b shows an excellent linear correlation between the computed reduction potential and HOMO energy of AQ-Li₂ derivatives. The HOMO energy seems to be quite sensitive to the extent of electron delocalization. As seen in Figure 6, the HOMO electron distribution of B03-Li₂ and D05-Li₂ is obviously more delocalized than that of PQ-Li₂ and C02-Li₂. Here all the PQ-Li₂ derivatives are assumed to have similar configuration, in which two Li atoms are bonding to the bridge sites of two carbonyl groups.

Although the redox property of the PQ derivatives exhibits a linear correlation with their frontier orbital energies, the influence of the heterocyclic substitution on the electronic structure of PQ can be hardly represented directly from the MO plots. In this case, we are looking towards a more visual way to display the change of electronic structures among different PQ derivatives. The discharge potential of quinone molecules reflects the ability in accepting an electron to the molecules containing highly polar carbonyl groups. ESP gives a visible display of molecular polarity and can help us to understand how the electronic structure of PQ derivatives is modified by the substituted heterocyclic rings. In a recent study on the redox property of AQ derivatives, we find that the discharge potentials of quinones are quite sensitive to the electric potential in the quinone ring. Here, a more quantitative correlation between the reduction potential and electric potential value is performed in Figure 7. In case that the two side rings of PQ are replaced by various heterocyclic compounds, the electron-density distribution in the central ring is strongly influenced by the introduced heterocycles at two sides. Electron-donating heterocycles, such as pyrrole, push electrons to the central ring and increase the electric potential. On the other hand, electron-withdrawing heterocycles, such as pyridine, pull electrons back toward the side rings and lower the electric potential. The change of electric potential at the central ring directly correlates to the difficulty for electron attachment, which is expected for predicting the reduction potential. A well linear correlation between the calculated reduction potential and average ESP value of six carbon atoms in the central ring is illustrated in Figure 7. It is found that the reduction potential of the first Li transfer (E₁, PQ to PQ-Li) and second Li transfer (E₂, PQ-Li to PQ-Li₂) can be estimated from the ESP in PQ and PQ-Li, respectively.

ESP mapped on the isosurface (0.001 au) of electron density for PQ and PQ-Li derivatives are plotted in Figure 8. The reduction potential of the selected five molecules increases gradually from the left to right side. The most significant difference among their ESP maps is the electronic cloud density in the central ring. Figure 8. Comparison of ESP map of PQ, PQ-Li, and their heterocyclic derivatives. The blue color represents a positive electronic potential, whereas the red color represents a negative electronic potential.
central ring. As discussed above in Figure 4, the electric potential of benzene and heterocyclic compounds increase in the order of pyrrole < benzene < pyridine < isoxazole < pyridazine. Pyrrole containing a sp² N atom shows the strongest electron-donating effect, whereas pyridazine containing two sp² N atoms exhibits the strongest electron-withdrawing effect. In the case where the two side rings of PQ are replaced by heterocycles, the electron affinity is influenced by the heterocycles through the conjugative electronic effect. The ESP value and reduction potential of five molecules increase in the same order as the electronic effect of heterocyclic compounds, C01 < PQ < A03 < D05 < B03. In our recent study on AQ derivatives, the isoxazole- and pyridazine-substituted AQ also exhibit the highest discharge potential among all the designed molecules.\(^{[13]}\)

It is noted from Figure 7 that the reduction potential of the second Li transfer is about 1.0 V smaller than that of the first Li transfer. The energy difference between the first and second lithiation for the PQ derivatives is larger than that for AQ.\(^{[15]}\) As indicated from electrochemical experiments, the discharge curve of AQ is almost flat during the whole capacity region, whereas the discharge curve of PQ shows a 0.5 V potential drop at the half capacity region.\(^{[15, 16]}\) Such a difference can be well explained from the ESP maps. ESP map of PQ-Li shows the positive charges are localized on the Li atom and the negative charges are delocalized in the PQ ring. So following by the reduction from PQ to PQ-Li, most of the electron is injected to the PQ ring. The region of the central ring is colored light blue in the ESP map of PQ, whereas it is colored light red in the ESP map of PQ-Li. The increase of electron density on the PQ increases the difficulty for the attachment of a second electron. So a decrease of reduction potential for the second Li transfer is expected.

From the above electronic structure analysis of PQ derivatives, it is concluded that conjugated carbonyl molecules can be reasonably designed to improve the electrochemical performance by introducing heterocyclic compounds with strong electron-withdrawing effect.

**Influence of Li bonding interaction**

The discharge process of PQ derivatives as a positive electrode involves two electron transfer steps and two Li-ion transfer steps. The discharge potentials of PQ derivatives are computed from the change in Gibbs free energy, which can be divided into the electron transfer part and Li-ion transfer part. In the above discussion, the discharge potentials of PQ derivatives are obtained assuming that the reduced form of all the PQ derivatives has a similar Li-bonding configuration. In this case, the difference in discharge potential rises mainly from the electron-transfer contribution. Next, the influence of Li bonding (Li-ion transfer contribution) on the redox property is discussed.

As seen from Figure 9, there is only one Li bonding configuration for PQ-Li\(_2\) in which two Li atoms coordinate to the bridge sites of two carbonyl groups out of the molecule plane (configuration A). However, different Li-bonding configurations are involved for PQ derivatives. There are two possible Li-bonding configurations for A01-Li\(_2\) [A01-Li\(_2\)(a) and A01-Li\(_2\)(b)] and A04-Li\(_2\) [A04-Li\(_2\)(a) and A04-Li\(_2\)(c)]. A01-Li\(_2\)(a) and A04-Li\(_2\)(a) have the same configuration as PQ-Li\(_2\). However, they are not the most stable configurations. In A01-Li\(_2\)(b), two Li atoms coordinate to the sideward chelate sites between the N and O atoms (configuration B). The total Li bonding energy of A01-Li\(_2\)(b) is 0.43 eV higher than that of A01-Li\(_2\)(a). In A04-Li\(_2\)(c), one Li atom coordinates to the bridge site of two carbonyl groups and the other Li atom coordinates to the bottom chelate site between the two N atoms (configuration C). The total Li-bonding energy of A04-Li\(_2\)(c) is 0.34 eV higher than that of A04-Li\(_2\)(a).

The measured average reduction potential of PQ, A01, and A04 from cyclic voltammetry is 2.52, 2.94, and 2.73 V vs. Li/Li\(^{+}\).\(^{[16]}\) The computed reduction potential of PQ matches well with experimental value. However, the calculated reduction potentials for A01 and A04 with the same Li-bonding configuration as PQ are obviously lower than experimental values. By considering the more stable Li bonding configuration, the present theoretical computation can predict the discharge voltage.

Figure 10 compares the energy of N-atom-substituted PQ-Li\(_2\) with different Li bonding configurations. The Li bonding energies in configuration B and C are much greater than in configuration A. Coordination of both N and O atoms (configuration
B) or two N atoms (configuration C) to Li stabilizes the dianion significantly. However, if the N atoms in configuration B and C are replaced by O atoms or S atoms, it is found that the coordination energies with Li are lower than that in configuration A instead (see Figure S1 and S2). If the reduced form of all the PQ derivatives contains configuration A, B03 gives the highest average reduction potential of 3.15 V. By considering different Li bonding configurations, the reduction potential of B02 with configuration B (3.22 V) and B05 with configuration C (3.16 V) exceeds that of B03. It is suggested from our calculation that the Li bonding configuration also plays an important role in determining the actual discharge potential.

Conclusions

In this work, a series of phenanthrenequinone (PQ) derivatives were rationally designed to improve the electrochemical performance of the prototypical molecule materials. By introducing heteroaromatic building blocks, the electronic structure of PQ could be significantly modified and the molecular weight was almost unchanged. In this way, promising high energy density cathode candidates were screened with simultaneously high discharge potential and high specific capacity. It was found that the electronic effect of the heteroaromatic building blocks directly influenced the redox property of the PQ derivatives. Replacing the two side rings of PQ by electron-withdrawing heteroaromatic rings lowered the electron density and improved the discharge potential. The computed reduction potential of the PQ derivatives matched well with experimental results. It was demonstrated that the discharge potential of the PQ derivatives depended strongly on the frontier orbital levels, the electric potential, and the Li bonding configuration, which could be modified by incorporation of different heteroaromatic building blocks. Especially, the ESP maps gave visible displays of the molecular electronic structures and were applied to understand how the redox properties of the PQ derivatives were modified by the heteroaromatic building blocks. In general, the present paper focuses on how to improve the redox property of PQ by electronic structure modification and how to characterize the change of electronic structure among the designed PQ derivatives. Among all the designed PQ derivatives, B02 exhibited the highest discharge voltage of 3.22 V vs. Li/Li\(^+\), 26.4\% higher than that of the prototypical molecule PQ; D05 with simultaneously large capacity density and high reduction potential gave the largest energy density of 841 Wh kg\(^{-1}\), 31.9\% larger than that of PQ. The present study shows that first-principles DFT calculations can be employed to design and characterize organic conjugated carbonyl compounds that provide promising candidates as cathode materials for electrical energy store applications.

Experimental Section

Density functional theory (DFT) calculations were carried out with the hybrid exchange-correlation functional B3LYP.\(^{[28]}\) The basis sets for C, H, N, O, and S atoms of investigated molecules were 6-311+G(d,p), including a polarization function to all the atoms and a diffuse function to C, N, O and S atoms.\(^{[29]}\) The frequency calculations were performed to obtain the thermochemical data at a pressure of 1 atm and temperature of 298.15 K. The implicit solvation models, including polarizable continuum model (PCM)\(^{[30]}\) and SMD model,\(^{[31]}\) were employed to compute the Gibbs free energies of redox molecules in solution using propylene carbonate (PC) as the solvent with a static relative permittivity of 64.9 and a dynamic relative permittivity of 2.02.\(^{[22]}\) The hybrid implicit-explicit solvation model calculations were also performed, which describes the PC molecules bonding to Li\(^+\) as explicit solvents and model the bulk as implicit solvents (see Figure S1).\(^{[32]}\) It is found that the SMD model obviously overestimates reduction potential values. The calculated results with the PCM model match quite well with experimental values, and the differences between PCM calculations and cyclic voltammetry experiments\(^{[33]}\) are less than 0.2 V. We also note that adding propylene carbonate molecules as solvents in the reaction complex (hybrid explicit-implicit solvation model) has a slight influence on the computed reduction potentials with respect to the implicit solvation model. So in the main text, all the calculation results are given with implicit PCM solvation model. All calculations including structure optimization and thermodynamic energy computation were carried out by using Gaussian 09 package\(^{[33]}\) 

The reduction potential of a redox active molecule in solution can be computed using

\[
E = - \frac{G_{{\text{PQ-Li}^n}} - nG_{\text{Li}^+} - \frac{n}{F}}{\eta F} - 1.4, 
\]

where \(n\) is the number of electrons transferred, and \(F\) is the Faraday constant. The change in energy of electrons from vacuum to solution is treated as zero, similar to what has been used by others.\(^{[20]}\) The constant 1.4 V, is included to convert the computed reduction potential with respect to a Li/Li\(^+\) reference electrode as the SHE is \(-4.44\) V vs. vacuum\(^{[34]}\) and Li/Li\(^+\) is \(-3.04\) V vs. SHE. The first Li transfer potential for PQ to PQ-Li and second Li transfer potential for PQ-Li to PQ-Li\(_2\) are noted as \(E_1\) and \(E_2\) and the two electron reduction potential for PQ to PQ-Li\(_2\) is defined as the average reduction potential (see Table S1 for details).

Theoretical specific capacities of the PQ derivatives are computed as\(^{[7]}\)

\[
C_t = \frac{n \times F}{M_w} = \frac{26801 \times n}{M_w},
\]

Where, \(C_t\) (mAh g\(^{-1}\)), \(n\) (C mol\(^{-1}\)), and \(M_w\) (g mol\(^{-1}\)) represent the theoretical specific capacity, the transferred electron number, the Faraday constant, and the molecular weight of the conjugated carbonyl compound, respectively. The theoretical energy density is estimated as the product of the computed average reduction potential and theoretical capacity.
The authors declare no conflict of interest.

**Key words:** density functional theory · electronic structure · Lithium-ion battery · molecular design · organic electrode


Visible progress: The correlation between the electronic structures and the redox properties of a series of phenanthrenequinone (PQ) derivatives is studied. The electrostatic potential maps visibly show how the electronic structures and redox properties of these derivatives are tuned through the heteroaromatic building blocks. The pyrimidine-based derivative exhibits the highest discharge voltage and the isoxazole-based derivative gives the largest energy density, which are 28.8% and 31.9% larger than that of PQ, respectively.