Computational electrochemistry study of derivatives of anthraquinone and phenanthraquinone analogues: the substitution effect†

Zhen Wang, Anyang Li, Jingzheng Ren and Gaohong Zhai

The substituent effect on fused heteroaromatic anthraquinone and phenanthraquinone are investigated by density functional calculations to determine some guidelines for designing potential cathode materials for rechargeable Li-ion batteries. The calculated redox potentials of the quinone derivatives change monotonically with increasing number of substitutions. Full substitution with electron-withdrawing groups brings the highest redox potential; however, mono-substitution results in the largest mass energy density. Carbonyl groups are the most favorable active Li-binding sites; moreover, intramolecular lithium bonds can be formed between Li atoms and electronegative atoms from the substituent groups. The lithium bonds increase the redox potential by improving the thermodynamic stabilization of the lithiation derivatives. Furthermore, the calculation of nucleus-independent chemical shift indicates that the derivatives with Li-bound carbonyl groups are more stable than the bare derivatives.

1. Introduction

Driven by the requirement of sustainable development, the research focus has shifted from conventional inorganic electrode materials based on the lithium metal oxides to organic electrode materials in the past decades. Organic conjugated carbonyl compounds such as quinone, anhydride, oxo-carbon salt, Li-carboxylate salt and diimide dilithium salt are considered to be promising candidates as electrode materials because of their excellent electrochemical redox characteristics. Among them, quinone and its derivatives attract considerable attention due to their superior electron transfer properties, stability, lower cost for electricity storage, and the ability to tune their electronic properties by making modifications to the structure and substituents. For example, the incorporation of heteroaromatic structures is recommended to improve electrical conductivity, and the redox potential can be increased via chemical substitutions. The large number of candidate quinone derivatives poses a challenge for the identification of optimal redox couples.

Experimental searching is extremely time-consuming and expensive. A reliable computational method could be viable alternative approach for rapid screening with minimal investment. Several previous computational studies have examined the redox properties of quinone derivatives and provide some understanding of electrochemical windows at the molecular level. Assary and co-workers investigated the influence of functional groups on the redox windows of anthraquinone derivatives and aromatic nitrogen-containing quinones. They found a relationship between the computed lowest unoccupied molecular orbital (LUMO) energy and the redox potential used to screen reduction windows of novel molecules. Hernández-Burgos et al. studied the heteroatom and substituent effects in carbonyl-based organic molecules and identified the most promising candidate materials for electrical energy storage. Er et al. predicted the redox potentials and solvation free energies of quinone derivatives using high-throughput computational screening with the aim of designing quinone molecules for use in organic-based aqueous flow batteries. Very recently, Kim et al. reported the Li-binding thermodynamics and redox potentials of quinone derivatives. Most of these works are based on density functional theory (DFT), which has proven a robust and useful method for the design of new molecules capable of participating in redox processes.

Anthraquinone and phenanthraquinone and their derivatives are environmentally friendly and possess fast reaction kinetics, which are required in organic cathode materials. However, their redox potentials are lower than the potentials of conventional inorganic electrode materials. As recommended...
by previous studies, the addition of substituent groups could be an attractive strategy to increase the potentials of these molecules. In this work, we focus on the effects of substituent groups on fused heteroaromatic anthraquinone- and phenantraquinone-bearing thiophene, furan and pyridine rings (i.e., anthraquinone analogues benzo[1,2-b:4,5-b']dithiophene-4,8-dione (BDTD), benzo[furano-4,8-dione (BFFD), and pyrido[3,4-g]isoquinoline-5,10-dione (PID) and phenantraquinone analogues benzo[1,2-b:4,5-b']dithiophene-4,5-quinone (BDTQ), benzo[1,2-b:4,5-b']difuran-4,5-dione (BFD), and benzo[2,1-b:3,4-b']dithiophene-4,5-dione (TQ), 1,10-phenanthroline-5,6-dione (PhenQ)) which are illustrated in Fig. 1. The effects of the incorporated functional groups on the redox potentials of the quinone derivative couples are investigated for single substitution to full substitution. The Li-binding sites were better than that obtained using B3LYP (see Fig. S2†) containing both anthraquinone and phenantraquinone analogues investigated in this paper. It is clear that the linear correlation between the calculated and experimental values is excellent, confirming the validity of our calculations. The linear regression coefficients of determination ($R^2$) obtained using other functionals are also close to one, but none were better than that obtained using B3LYP (see Fig. S2†). In the discussion below, the linear fit shown in Fig. 2 is used to predict the formal potentials.

In addition, the aromaticities of these derivatives were evaluated by NICS.35,36 The NICS values were calculated using the gauge-independent atomic method at the B3LYP/6-31+G(d,p) level with the same solvent parameters based on the

$$
\Delta G = \Delta G_{gas} + \Delta G_{sol}(MLi_2) - \Delta G_{sol}(M) - 2\Delta G_{sol}(Li^+) - 2\Delta G_{sol}(M) - 2\Delta G_{sol}(Li^+)
$$

Thus $\Delta G = \Delta G_{gas} + \Delta G_{sol}(MLi_2) - \Delta G_{sol}(M) - 2\Delta G_{sol}(Li^+) - 2\Delta G_{sol}(M) - 2\Delta G_{sol}(Li^+)$, where $\Delta G_{gas}$ is the reaction Gibbs free energy in the gas phase. The gas-phase geometries of each species were optimized at the B3LYP/6-31+G(d,p) level,25,26 and the Gibbs energies were calculated at $T = 298.15$ K and $P = 1$ atm. Based on the optimized gas-phase geometries, single-point energy calculations were performed using the SMD model27 to obtain the solvation free energy of each species, $\Delta G_{sol}$. The SMD model was employed using dimethylsulfoxide as the solvent with the dielectric constant ($\varepsilon = 46.7$) fit to model the bulk solvent effect of a ethylene carbonate-dimethyl carbonate (EC-DMC) mixture ($\varepsilon = 85.1$ and $3.1$, respectively), which is typically employed as the electrolyte solvent.14 This is an effective approximation for computing the free energies of redox-active species in solution. In addition, the energy of electrons $\Delta G_{sol}(e^-)$ was approximated as zero. All calculations were carried out using the Gaussian 09 software.28

With respect to the reference potential of Li/Li', the calculated redox potential $E_{cal}$ is shifted by 1.24 ($E_{cal} = E - 1.24$) since the standard hydrogen electrode (SHE) is $-4.28$ V versus vacuum and Li/Li' is $-3.04$ V versus SHE. The $ab initio$ $E_{cal}$ might agree quantitatively with the experimental value; however, the two are not directly equivalent9,31 due to cell resistance in measurements or a lack of a better description of the electrolyte solvent in calculations. In addition to B3LYP, other functionals such as B98,29 PBEPBE,30 BHHandHLYP,31 mPW1PW91,12 oB97XD13 and M06 34 are used to check the accuracy of the calculations. Fig. 2 compares the calculated values using B3LYP to the experimental redox potentials of 12 molecules (see Fig. S1†) containing both anthraquinone and phenantraquinone analogues investigated in this paper. The linear regression coefficient of determination ($R^2$) obtained using other functionals are also close to one, but none were better than that obtained using B3LYP (see Fig. S2†). In the discussion below, the linear fit shown in Fig. 2 is used to predict the formal potentials.

2. Computational details

The reduction of a quinone was treated as a single-step, two-electron, two-Li⁺ process as suggested by Er et al.4 The redox potential was calculated by the Nernst equation $E = -\Delta G/nF$, where $n = 2$ is the number of electrons transferred and $F$ is the Faraday constant. Similar to in recent studies,16,24 the Gibbs free energy $\Delta G$ of a species $M$ was computed by a thermodynamic cycle:

$$
\begin{align*}
M_{gas} + 2e_{gas}^- + 2Li_{gas}^+ \rightarrow & \\
MLi_2_{gas} \downarrow \Delta G_{sol}(M) \downarrow \Delta G_{sol}(e^-) \downarrow \Delta G_{sol}(Li^+) \downarrow \Delta G_{sol}(MLi_2)_{sol} \downarrow & \\
2e_{sol}^- + 2Li_{sol}^+ + \frac{\Delta G}{M_{sol}} \rightarrow MLi_2_{sol} & (1)
\end{align*}
$$

Thus $\Delta G = \Delta G_{gas} + \Delta G_{sol}(MLi_2) - \Delta G_{sol}(M) - 2\Delta G_{sol}(Li^+) - 2\Delta G_{sol}(M) - 2\Delta G_{sol}(Li^+)$, where $\Delta G_{gas}$ is the reaction Gibbs free energy in the gas phase. The gas-phase geometries of each species were optimized at the B3LYP/6-31+G(d,p) level,25,26 and the Gibbs energies were calculated at $T = 298.15$ K and $P = 1$ atm. Based on the optimized gas-phase geometries, single-point energy calculations were performed using the SMD model27 to obtain the solvation free energy of each species, $\Delta G_{sol}$. The SMD model was employed using dimethylsulfoxide as the solvent with the dielectric constant ($\varepsilon = 46.7$) fit to model the bulk solvent effect of a ethylene carbonate-dimethyl carbonate (EC-DMC) mixture ($\varepsilon = 85.1$ and $3.1$, respectively), which is typically employed as the electrolyte solvent.14 This is an effective approximation for computing the free energies of redox-active species in solution. In addition, the energy of electrons $\Delta G_{sol}(e^-)$ was approximated as zero. All calculations were carried out using the Gaussian 09 software.28

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In addition, the aromaticities of these derivatives were evaluated by NICS.35,36 The NICS values were calculated using the gauge-independent atomic method at the B3LYP/6-31+G(d,p) level with the same solvent parameters based on the
optimized structures. The NICS values 1 Å above the center of ring place (NICS(1)), are recommended as good measures of π effects. A more negative NICS value corresponds to a higher aromatic character of the molecule, while a positive NICS value corresponds to antiaromaticity.

3. Results and discussion

3.1 Substituent effects on the redox potential and energy density

The redox potentials ($E_{\text{cal}}$) of BDTD with typical electron-withdrawing substituent CN and electron-donating substituent NH$_2$ are listed in Table 1. It is clear that when the substituent is CN, all the nine derivatives increase the $E_{\text{cal}}$ of the pure parent BDTD. However, the functionalization of BDTD with NH$_2$ shows the opposite effect, regardless of the number or site of the substituent. During the reduction process, a lower-energy LUMO could lead to a higher redox potential since electrons prefer to fill in the orbital with lowest energy. In general, electron-withdrawing groups (EWGs) are supposed to decrease the energy of the LUMO, whereas electron-donating groups (EDGs) increase it.$^{16,23}$ As shown in Table 1, the LUMO energies continue to decline with increasing number of electron-withdrawing groups (CN groups). Consequently, the corresponding redox potential grows. For mono-substitutions, the LUMO energies decrease by 0.4 to 0.5 eV, and the values of $E_{\text{cal}}$ increase by 0.2 to 0.3 V. The potential growth of the four di-substitutions derivatives are over 0.5 V to be 3.0 V or greater. When three H atoms are replaced by CN, the LUMO energies are reduced by more than 1.0 eV, and the potentials reach 3.2 to 3.3 V. In the last row of Table 1, the full CN-substituted derivative has the highest $E_{\text{cal}}$ (3.460 V) and the lowest LUMO energy ($-5.05$ eV). On the other hand, increasing the number of electron-donating groups (NH$_2$) tends to increase the LUMO energies and lower the redox potentials.

To verify the effect of substitution on redox potential, more functional groups (CH$_3$, PO$_2$H$_2$, F, COOH, SO$_2$H and NO$_2$) were investigated at the same calculation level. The $E_{\text{cal}}$ values of BFFD derivatives incorporating all eight substituents were also calculated for comparison. The horizontal red and blue lines in Fig. 3 indicate the calculated redox potentials $E_{\text{cal}}$ of unsubstituted BDTD and BFFD. The mean values of $E_{\text{cal}}$ for all possible single, double, triple and quadruple substitutions for each of the functional groups are indicated. As shown in Fig. 3, the EDGs such as NH$_2$ and CH$_3$ are expected to decrease the redox potentials with the values below the lines, while the EWGs, such as PO$_2$H$_2$, F, COOH, SO$_2$H, NO$_2$ and CN, are effective in promoting the $E_{\text{cal}}$. Confirming the trend discussed above, $E_{\text{cal}}$ changes monotonically with increasing number of substitutions. This is in accordance with previous works.$^{1,26}$

It should be noted that the redox potentials of monosubstituted derivatives of BFFD with all the functional groups are larger than those of BDTD derivatives. Comparing these molecules with molecules containing sulfur as the heteroatom (BDTD derivatives), the oxygen-containing molecules have lower LUMO energy levels, corresponding to higher redox potentials. However, the multi-substituted derivatives do not follow this rule. For di-, tri- and tetra-substituted molecules with F and CN, the calculated potentials of BFFD derivatives are lower than those of BDTD derivatives. More substituents bring complex structures and different Li atom binding effects, which is discussed in the next part of this section.

The redox potential is one of the parameters to improve in these organic cathode materials. Mass energy density, namely stored electrochemical energy per unit mass, is also a very important parameter when choosing the electrode material for lithium ion batteries. The calculation of mass energy density ($\rho = nFE/3.6M$) depends on molecular mass ($M$), redox potential ($E$), and the number of electrons transferred ($n$). When the H atoms are substituted by functional groups, additional mass is added to the molecule, resulting in a decrease in the mass energy density. Though the redox potential is the highest when BDTD is fully substituted with CN groups, the theoretical energy density is reduced relative to the parent BDTD (see Table 1). However, the mono-, di- and tri-substituted molecules all have larger energy densities, and the largest one is the derivative with a single C-N group substituted at a specific site. After the CN-substituted molecule, all the mono-substituted BDTD molecules with EWGs have the largest energy densities.

3.2 Effect of substituent position on the redox potential

As mentioned above, the positions of the substituted groups have significant effects on the redox potentials. Taking account of the mass energy density, we focus on the anthraquinone and phenanthraquinone analogues incorporating single EWGs. All possible substitution sites on a quinone are systematically studied. The substitution of EWGs close to the carbonyl group in anthraquinone analogues, such as 1-b, 2-b, 3-b and 3-c (seen in Fig. 4a), increase the $E_{\text{cal}}$ more effectively than substitution with remote ring hydrogen. Carbonyl groups are the most favorable active Li-binding sites.$^{9}$ Indeed, two Li atoms bind strongly at each carbonyl group of all the derivatives, as shown in Fig. S3.$^{†}$ However, when the functional groups are closed to the carbonyl group, such as in the b-type
or c-type derivates, one Li can bind with the electronegative atoms (N, O and F) of the EWGs. To provide deep insight into this feature, the binding energies and Wiberg bond orders between Li with other atoms are calculated based on the optimized geometries of the lithiation states of mono-substituted derivatives. For instance, Fig. 5 shows the stable structures and binding energies of the CN-, NO₂- and F-substituted BDTD derivatives with lithium, and some bond lengths and Wiberg bond orders are also marked. For the α-type derivatives, the negative binding energies indicate favorable binding, the carbonyl oxygen forms a chemical bond with a Li atom since the bond lengths are about 1.7 Å less than the sum of the covalent bond radii (1.94 Å), and the bond orders of the Li–O bonds are even close to 1. For the β-type derivatives, the orders of two Li–O bonds show almost no change; however, one Li–O bond deflects, and other binding sites are activated. The newly formed bonds of Li–N (or O, F), where the lone-pair electrons of the N, O and F atoms of the EWGs act as

<table>
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Table 1  The LUMO energies (LUMO), predicted redox potentials (E_cal) and mass energy densities (ρ) of BDTD with CN and NH₂.
Fig. 3 Effects of functional group substitutions on the redox potential. The horizontal red and blue lines indicate the predicted redox potentials of unsubstituted BDTD and BFFD, respectively. The symbols indicate potentials for all possible single and multi-substitutions for each of the functional groups. The 1,2,3-substitution value was obtained from the average of the isomers.

Fig. 4 Positional effects of functional group on the $E_{\text{cal}}$ for single electron-withdrawing group (NO$_2$, SO$_3$H, PO$_3$H$_2$, COOH, CN and F) substitution of (a) anthraquinone analogues and (b) phenanthraquinone analogues.
electron donors, could be considered as intramolecular lithium bonds (ILBs),\(^\text{39}\) which are similar to the intramolecular hydrogen bonds in hydroquinone derivatives\(^\text{40}\) but much stronger. As shown in Fig. 5, the Wiberg bond orders of the ILBs are about 0.5, while the hydrogen bond orders mostly are less than 0.1.\(^\text{40}\) Moreover, the bond lengths of the ILBs are only slightly larger than the distance between Li and carbonyl oxygen, and six- or seven-membered cyclic structures are formed with bridging Li atoms. Accordingly, the binding energies are more negative as a result of electronic delocalization in the more stable quasi-ring. Therefore, the presence of the intramolecular lithium bonds makes the molecules more difficult to oxidize, which enhances the redox potential.

For the derivatives of phenanthraquinone analogues, the similar position dependence of the redox potentials is presented for TQ and PhenQ in Fig. 4b. The \(E_{\text{cal}}\) values of 6-b and 7-c are significantly larger than those of 6-a and 7-a or b, respectively. However, the position effects are not obvious when...
fused oxygen or sulfur atoms are close to the carbonyl group, such as in BDTQ and BDFD. As shown in Fig. 6, the 1Li atom locates between two carbonyl oxygen atoms, and a five-membered ring is formed by including two lithium bonds. One of the lithium bonds is a little stronger with bond order more than 0.6, and the weaker one could be affected by the 2Li atom, since the 2Li atom just binds one carbonyl oxygen in the side way. The weak position effects of BDTQ and BDFD could be explained as there is no intramolecular lithium bond formed around the substituent, due to the substituent is far from the carbonyl group. On the other hand, since the electronegativity of the O atom is larger than that of the S atom, ILBs formed between the 2Li atoms and the fused oxygen atoms of the side rings of BDFD derivatives. Although the bond order of the ILB is less than those of the other three Li–O bonds, the additional bonds lead to more stable structures, which are reflected by the more negative binding energies.

3.3 Stability studies using NICS

The substitution of EWGs adjacent to the carbonyl group could make the lithiated anthraquinone and phenanthraquinone analogues more stable, which is beneficial for the battery cycle life and safety of the battery system. In addition to structural features, aromaticity is a simple and efficient measurement of the stability of such cyclic organic molecules. In terms of the electronic nature of the molecule, aromaticity describes conjugated systems allowing for the electrons to be delocalized.
around the ring, increasing the molecule’s stability. Here, we chose NICS, which is based on magnetic properties, to determine the aromaticity. A more negative NICS value indicates greater electron shielding via a stronger ring current and corresponds to greater aromatic character. NICS values of each ring of the mono-substituted derivatives and their lithiation states are calculated. Fig. 7 shows the NICS(1) values (ppm) for three rings of BDTD and BDTQ derivatives with six EWGs as an example (more NICS(1) results are found in Table S1†). In general, the NICS values of the two rings containing heteroatoms on both sides are negative for each molecule. However, the NICS values of center rings attached to carbonyl groups are positive. When the molecules are lithiated, a negative NICS value is obtained in the center ring. This result indicates that the derivatives with Li-bound carbonyl groups are more stable than the bare derivatives, which agrees with previous studies on carbonyl-based organic molecules.8 In addition, the NICS values of the center lithiated quinone rings of b-type BDTD molecules are more negative than those of the a-type isomers. The formation of intramolecular lithium bonds could increase the stability of the lithiated quinone ring by extending the range of electron delocalization. This idea is also supported by the more negative NICS values of the BDFD derivatives compared to the BDTQ derivatives (see Table S1b†).

4. Conclusion

As cathode materials for lithium-ion batteries, anthraquinone and phenanthraquinone derivatives show similar electrochemical characteristics as other quinone compounds. The redox potential increases with increasing number of EWGs; thus, full substitution could bring the highest redox potential. Moreover, in term of the mass energy density, single substitution is the best choice. Based on the DFT calculation results of seven anthraquinone and phenanthraquinone analogues incorporating eight functional groups, we found that the substitution effects could be enhanced by the formation of ILBs between Li atoms and the electronegative atoms of the substituent group as well as intramolecular hydrogen bonds in hydroquinone derivatives. The lithium bonds increase the redox potentials by improving the thermodynamic stabilization of the lithiation derivatives. For example, when the substituent site is close to the carbonyl group, as in the b-type structure of BDTD, its redox potential is higher than that of the a-type isomer since more stable six- or seven-membered cyclic structures are formed with bridging Li atoms. To the best of our knowledge, this study is the first to systematically study the Li-binding properties between Li atoms and substituent groups. Moreover, we studied the stabilities of the systems using aromaticity, which was calculated with NICS. The NICS values of the side rings of these derivatives are always negative and undergo reversible redox processes, while the NICS values of the center rings change from positive to negative after the molecule is lithiated. The results of this study imply that EWGs have a favorable effect on the redox potentials of organic electrode materials and may be useful in establishing guidelines for designing better electrode materials.

Acknowledgements

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References