



Isoindole-4,7-dione Polymers As Candidates For Organic Lithium Ion Battery Cathodes

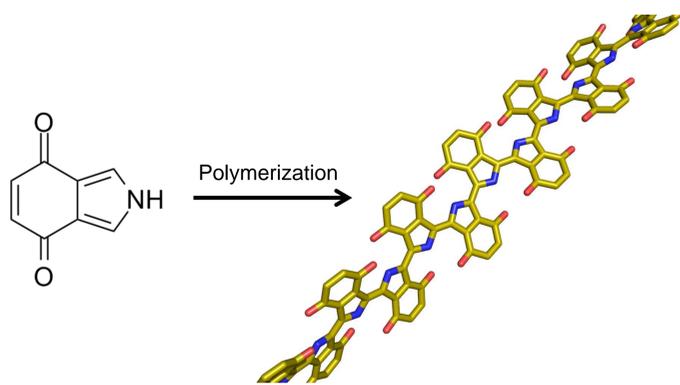


Figure 1. Polymerization of isoindole-4,7-dione.

Results & Discussion

A method based on **DFT calculations** has previously been used to **predict redox potentials** of a series of IIDs using the Boltzmann equation to account for the possible protonation and redox reactions.¹ The predictions fit very well to the behavior of the compounds synthesized here (figure 2) with a **mean absolute deviation of 38 mV**.^{1,2}

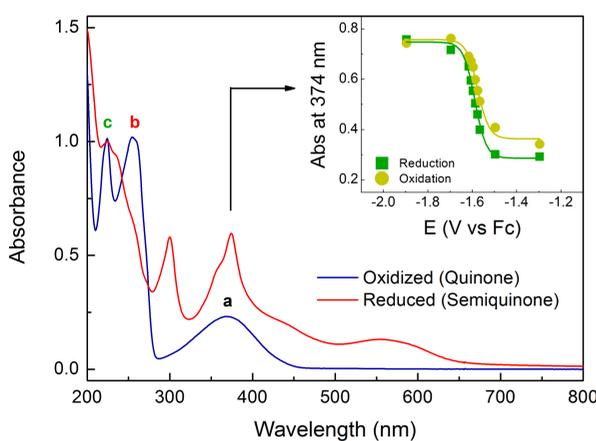


Figure 3. UV/vis spectra of compound **3** in MeCN. The three bands of the oxidized species are marked a-c. The absorbance at all wavelengths upon in situ reduction and oxidation followed the Nernst equation (inset graph).

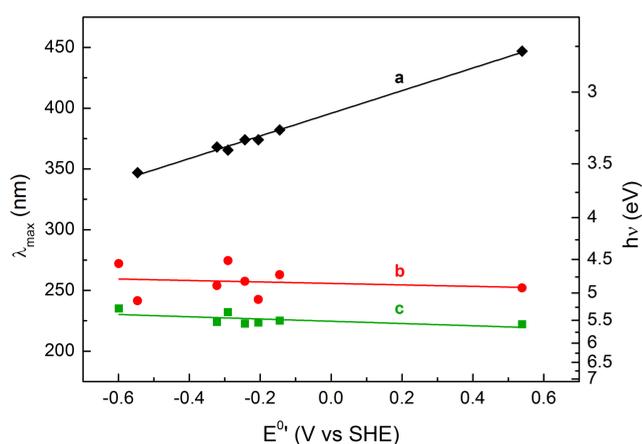


Figure 4. Position of the absorption bands a-c in the IID series **1-8** vs the reduction potential. Right y-axis is energy scale.

Introduction

Isoindole-4,7-diones (IIDs) are bifunctional molecules with a pyrrole and a *p*-benzoquinone ring and can be polymerized (figure 1) to function as cathode materials in lithium ion batteries (LIBs). The pyrrole units form a conducting polymer backbone, while the quinone moieties can be redox cycled between the quinone, semiquinone and hydroquinone states. Such organic matter based cathodes are expected to be **cheaper**, more **environmentally friendly** and have **higher specific energies** and **higher specific capacities** than inorganic lithium intercalation compounds.

A computational strategy was devised to assess the usefulness of a series of IID derivatives (**1-8**) as active materials in LIB cathodes. Some of these compounds (**1-5**) were synthesized for comparison with the calculations, and were studied with electrochemical and spectroscopic techniques.

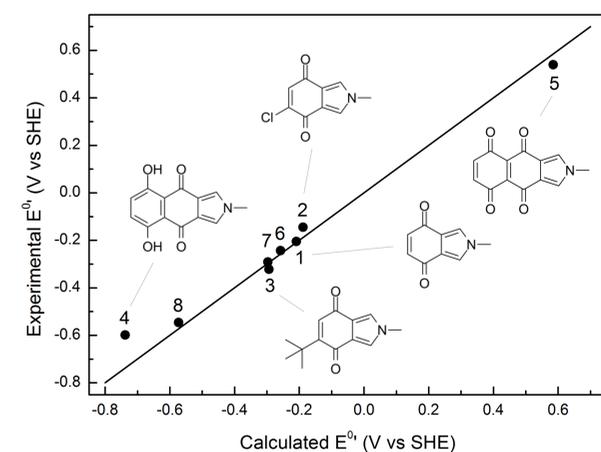


Figure 2. Comparison between calculated¹ and experimentally observed^{1,2} redox potentials (in aqueous solution buffered at pH 7.0).

The UV/vis spectra of the IIDs show three absorption bands (**a**, **b** and **c** in figures 3-5). The spectra could be followed during *in situ* reduction and oxidation and the absorbances followed the Nernst equation.

Transition **a** has a very high correlation with the redox potential ($r^2 = 0.99$, figure 4), while transitions **b** and **c** have little or no dependence on the redox potential. The LUMO has a high electron density on the quinone ring (figure 5) and its energy therefore varies when the quinone ring is substituted. Hence the large variation in reduction potential, which depends on the LUMO energy. The HOMO, however, has no electron density on the substituted quinone positions, and the HOMO energy is therefore rather constant. The transition energy for **a** will consequently be closely correlated with the reduction potential.

The possibility to polymerize IIDs was previously assessed using DFT calculations with promising results.¹ Polymerization of **1-5** could however not be accomplished with electrochemical oxidation methods used in this work. Attempts to copolymerize IIDs with pyrrole also failed. One problem could be steric hindrance due to the N-methyl group. The high potentials needed for oxidation of the pyrrole ring could also be a problem if the formed polymer is overoxidized immediately.

Conclusions

Four new IID derivatives were synthesized, namely 5-chloro-2-methyl-isoindole-4,7-dione (**2**), 5-(*t*-butyl)-2-methyl-isoindole-4,7-dione (**3**), 5,8-dihydroxy-2-methyl-benzo[*f*]isoindole-4,9-dione (**4**) and 2-methyl-benzo[*f*]isoindole-4,5,8,9-tetraone (**5**), demonstrating the versatility of the reaction. The redox behavior of **2-5** was consistent with computational predictions (the mean absolute deviation of the redox potentials was 38 mV for **1-8**).

The one-electron redox transition between the quinone and semiquinone states could be followed spectroscopically *in situ*. One of the observed absorption bands had a very high correlation with the redox potential, while the others do not, which can be explained with the molecular orbitals involved.

IID polymers are promising candidates for organic LIB cathodes but a working polymerization route needs to be developed.

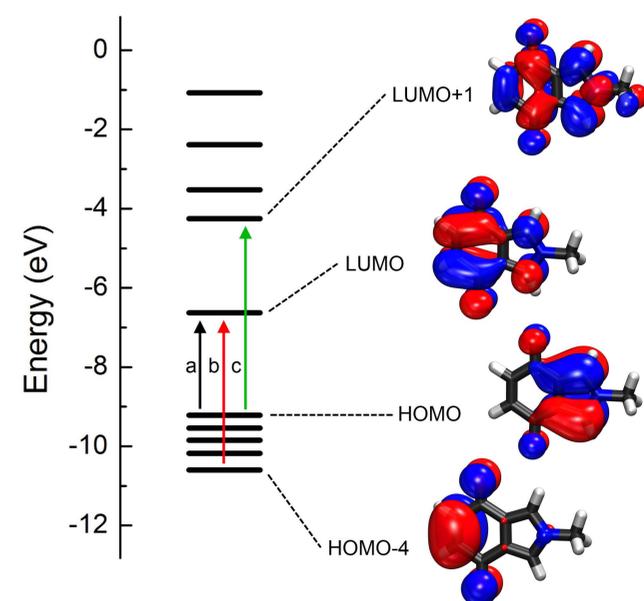


Figure 5. Energy diagram of compound **1** with molecular orbitals involved in transitions a-c.

References

1. Karlsson, C.; Jämstorp, E.; Strømme, M.; Sjödin, M. *J. Phys. Chem. C* **2012**, *116*, 3793-3801.
2. a) Schubert-Zsilavecz, M.; Likussar, W.; Gusterhuber, D.; Michelitsch, A. *Monatsh. Chem.* **1991**, *122*, 383-387. b) Schubert-Zsilavecz, M.; Schramm, H. W. *Liebigs Ann. Chem.* **1991**, 973.