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Final Report

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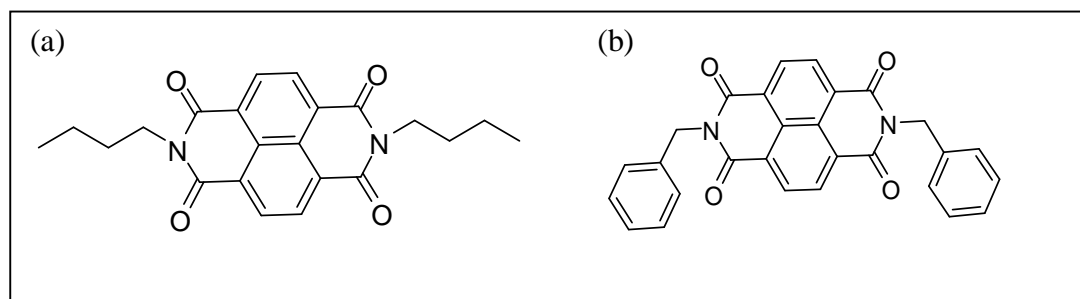
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This is the final report on exchange grant of Beatriz Meana-Esteban at Department of Physical Chemistry, Linz Institute for Organic Solar Cells (LIOS) at the Johannes Kepler University Linz, Linz, Austria hosted by Prof. N.S. Sariciftci during the period 8-28.03.2010

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Purpose of the visit: to characterized by electrochemical and spectroelectrochemical techniques two different electron-accepting materials based on naphthalene diimide with different substituents namely, butyl-naphthalene diimide (Bu-NDI) and benzene-naphthalene diimide (Bn-NDI).

Work carried out during the visit: We have studied the electrochemical and spectroscopic properties during n-doping (electrochemical reduction) of Bu-NDI and Bn-NDI. The chemical structures of the materials are shown in Scheme 1.



Scheme 1. Chemical structures of Bu-NDI (a) and Bn-NDI (b)

The redox reactions of the different materials were studied by potential cycling in a conventional three-electrode one-compartment cell at room temperature in a glove box in nitrogen atmosphere. A Pt plate electrode was used as the working electrode, a Pt plate as the counter electrode and a Ag/AgCl wire as a quasireference electrode which was calibrated with ferrocene/ferrocinium redox couple. The redox potential of this couple was +0.35 V versus this reference electrode. All the potential data reported in this work, unless otherwise stated, are given versus this reference electrode.

Both materials were drop cast from a chlorobenzene solution onto the working electrode.

Cyclic Voltammetry (CV) was used to study the redox properties of Bu-NDI and Bn-NDI at 50 mV/s scan rate in 0.1 M TBAPF₆ in acetonitrile. The voltammograms of the Bu-NDI and Bn-NDI are shown in Figure 1. For the two compounds, two reversible reduction waves are seen. They originate from the first and the second electron reduction processes of the naphthalene diimide core. It is known that naphthalene diimides undergo two consecutive one-electron reactions in organic solvents. Furthermore, despite of the slightly shift of the reduction potentials, the redox response of the materials is rather similar, which is an evidence that redox response is due to the reduction of the naphthalene diimide skeleton.

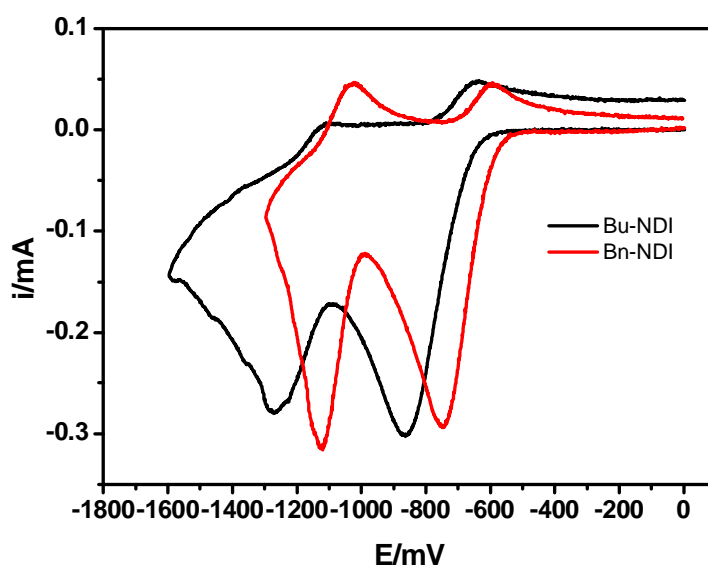


Figure 1. Redox response (n-doping) of Bu-NDI and Bn-NDI in 0.1 M TBAPF₆-ACN.

The onset potentials of the n-doping of the different materials vs the Normal Hydrogen electrode (NHE) can be used to determine the LUMO energy levels in the Fermi scale. The calculated E_{LUMO} for Bu-NDI and Bn-NDI are -4.2 and -4.3 eV respectively.

In order to get more information about the n-doping of the materials, spectroelectrochemistry of both Bu-NDI and Bn-NDI was done by recording in situ as the electrochemical reaction proceeds the FTIR-attenuated reflection (ATR) spectra. The spectroelectrochemical measurements were carried out in a small-size ATR spectroelectrochemical cell made from Teflon. The reflection element, a Ge crystal served as the working electrode together with a Pt disc and Ag/AgCl as the counter and the quasireference electrode respectively in a three-electrode electrochemical cell. For in situ FTIR-ATR experiments, the different materials were drop cast from a chlorobenzene solution onto the Ge reflection element.

The infrared spectra of both materials are obtained in situ during their reduction in 0.1 M TBAPF₆ in acetonitrile. In this way structural and electronic changes of Bu-NDI and Bn-NDI are studied as the electrochemical reaction proceeds. As the reduction reactions proceed, new infrared bands grow smoothly in the region between 2000 and 700 cm⁻¹. The spectroscopic results show, that the investigated materials can be reversibly reduced in two one-electron reduction steps. The spectral changes seen during reduction of the materials can be related to the changes in the materials in going from their neutral state to their reduced state. All the observed changes are fully reversible upon reoxidation of the materials.

Conclusions: From the experimental results, both CV and in situ FTIR-ATR, it can be said that both Bu-NDI and Bn-NDI undergo a stepwise two one-electron reduction in organic solvents giving the radical anion in the first step and then the dianion. During electrochemical reduction structure and optical properties of the two materials drastically change. A detailed characterization by different electrochemical and spectroelectrochemical methods is very useful since these charge species can be viewed as model systems for electron carriers or photoexcitation in real devices.

Projected Publication: The results briefly summarized in this report will be complemented with more experimental results which are planned for the next visit of the applicant to LIOS in April and will result in a joint manuscript.

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