Charge Injection on Extended π-Electron-Systems
An *in situ* ESR/UV-Vis-NIR spectroelectrochemical study

P. Rapta[‡], L. Dunsch[‡], N. Schulte[#] and A.-D. Schlüter[#]

[‡] Institut für Festkörper- und Werkstofforschung Dresden

Helmholtzstrasse 20
D - 01069 Dresden
e-mail: L.Dunsch@ifw-dresden.de
P.Rapta@ifw-dresden.de

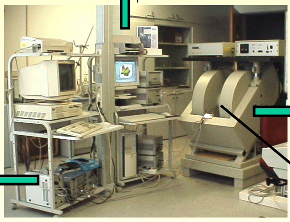
[#] Freie Universität Berlin

Takustrasse 3
D - 14195 Berlin
e-mail: niels@chemie.fu-berlin.de

In situ ESR/UV-Vis-NIR Cyclovoltammetry

- *in situ* multi-spectroelectrochemical technique enables the study of electrochemical reactions employing various spectroscopic techniques at the same experimental conditions
- NIR region is the most useful and informative for reduced and oxidized extended π-systems
- paramagnetic intermediates and charge transfer complexes absorb usually in NIR region
- both paramagnetic and diamagnetic species can be unambiguously determined using characteristic patterns of ESR signals and characteristic bands in Vis and NIR regions

EXPERIMENTAL



UV-Vis-NIR spectra were recorded on a diode array UV-Vis-NIR spectrometer system from J&M (Germany).

The *in situ* ESR/UV-Vis-NIR spectrocyclovoltammetric measurements were carried out using a home made program driving a potentiostat (HEKA Electronic, Germany) by means of AD-DA plug-in boards (ACAO and ACJr, Strawberrysoft, Sunnyvale, CA) simultaneously triggering an ESR spectrometer as well as a diode array UV-Vis-NIR spectrometer [1-3].

ESR spectra were recorded on an ESR 300D X-Band spectrometer (Bruker, Germany)

Laminated platin-mesh electrode inserted in the ESR flat cell, positioned in the center of the ESR cavity, was employed in the spectroelectrochemical experiments. Redox cycling of the investigated compounds with simultaneous EPR and UV-Vis-NIR measurements was carried out in 0.1 $TBAPF_6$ in dichloromethane, acetonitrile:toluene (1:1) or in 0.1M $TBABF_4$ in dichlorbenzene. The reference consisted of a silver wire coated with silver chloride.

AIM

⇒ structure dependence of charge injection in perfect π-conjugated double-stranded (ladder) oligomers and polymers

⇒ what kind of spin states are generated if additional charges are transferred to the ladder structures?

RESULTS

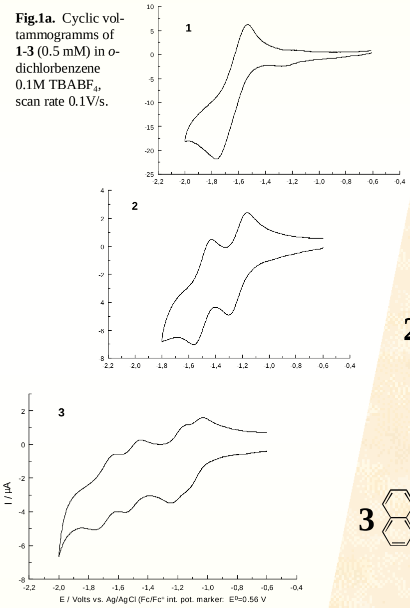
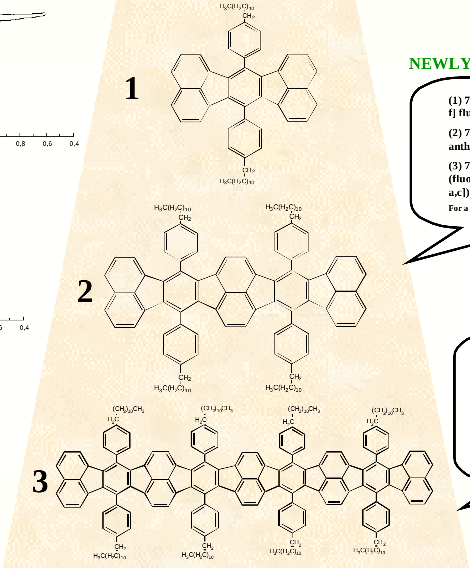


Fig.1a. Cyclic voltammogramms of **1-3** (0.5 mM) in *o*-dichlorbenzene 0.1M $TBABF_4$, scan rate 0.1V/s.



NEWLY SYNTHESIZED STRUCTURES

(1) 7,14di-p-dodecyl-phenylacenaphteno[1,2-f] fluoranthen

(2) 7,10,17,20 tetra-p-dodecylphenyl (bisfluorantheno[8,9-a,c])pyracylen

(3) 7,10,13,16,23,26,29,32 octa-p-dodecylphenylbis (fluorantheno[8,9-a] pyracyleno[5,6a] benzo[4,5-a,c])pyracylen

For a brief overview of the synthetic accesibility see ref. [4]

APPLICATIONS

- **n-channel semiconductors**
- **electron carriers for OLEDs**
- **electroluminiscence and photo-voltaics**

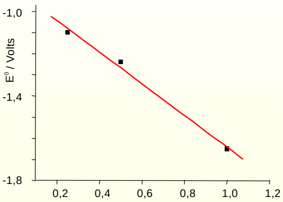


Fig.1b. E^0 for the first one-electron oxidation *vs.* 1/n for indeno-fluoranthenes **1-3**.

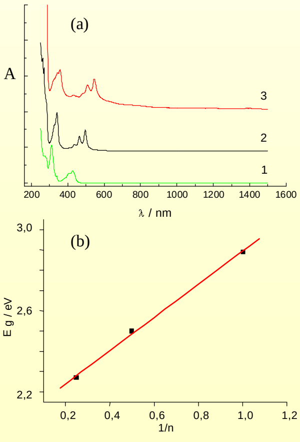


Fig.2. Optical spectra (a) and (b) optical E_g *vs.* 1/n for indeno-fluoranthene structures **1-3**.

Optical, electrochemical and ESR characteristics of indeno-fluoranthenes 1-3 in solution were investigated by cyclic voltammetry (Fig.1), UV-Vis-NIR (Fig.2) and ESR spectroscopy (Fig.3), and *in situ* spectroelectrochemical measurements (Fig.3). The spectral and redox properties of the structures are changing by the length of the chain, where as the "monomer" unit the structure 1 was considered. In the cathodic reduction of the compounds 1-3 the first reduction peak with various reversibility depends on the chain length. In the case of the structure 3 four reversible one-electron transfers on the reduction in the potential region from 0 to –1,8 V *vs.* Ag/AgCl were observed. The respective radical anions were generated electrochemically in the first reduction step and characterized by UV-Vis-NIR absorption and ESR spectroscopies.

For $1^{-\cdot}$ the optical spectrum with transition at 2.23 eV was observed with the simultaneous irreversible formation of follow up product at 1.81 eV. For $2^{-\cdot}$ the two sharp and intense absorptions at 1.86 eV and 0.94 eV were observed arising from transitions between the SOMO and LUMO, LUMO+1 orbitals. Corresponding ESR spectra indicate partial localization of the unpaired spin density in the center of the molecules. The stable dianion 2^{--} yields a simpler spectrum with transition at 1.08 eV arising from the transition between the new HOMO and LUMO orbitals of the doubly charged molecule. The optical transition was observed at 1.7 eV and very broad line in NIR region appeared simultaneously for 3 in the region of the first cyclovoltammetric double wave. However, no ESR response was found indicating that either a simultaneous transfer of two electrons occur forming spinless dianion or the presence of very broad ESR line is present.

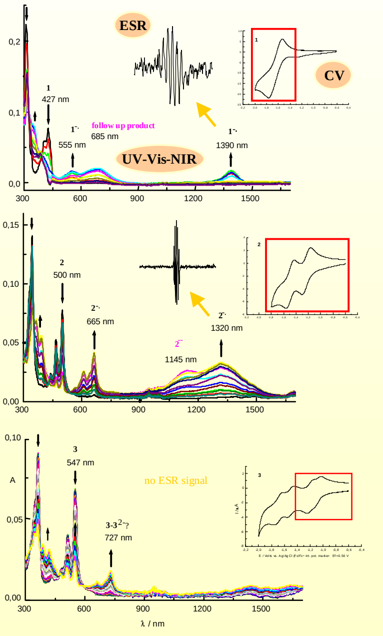


Fig.3. Cyclic voltammetry, ESR and UV-Vis-NIR responses from *in situ* spectroelectrochemical technique.

CONCLUSIONS

☞The electronic (optical gap, E_g) and electrochemical (redox potentials, E^0) characteristics well correlate with the inverse of the chain length → it was possible to obtain by extrapolation the corresponding properties of the infinite polymer chain (E_g= 2.1eV, E^0 = -0.9 V *vs.* Ag/AgCl).

☞An increase of the oligomer length greatly the formation of radical anion and allows the formation of a stable dianion of **2**. Four reversible reduction waves could be observed on the cyclic voltammetry of structure **3**.

☞The extension of the absorption spectroscopy to the NIR region opens the route for the study of dimeric charged systems.

REFERENCES

[1] A. Petr, L. Dunsch and A. Neudeck, *J. Electroanal. Chem.* **412** (1996) 153.
[2] A. Neudeck and L. Kress, *J. Electroanal. Chem.* **437** (1998) 141.
[3] P. Rapta, A. Neudeck, A. Petr and L. Dunsch, *J. Chem. Soc. Faraday Trans II*, **94** (1998) 3625.
[4] B. Schlicke, J. Frahn and A.-D. Schlüter, *J. Synth. Met.* **83** (1996) 173.

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