Modular Synthesis and Electronic and Hole-Transport Properties of Monodisperse Oligophenothiazines

Thomas J. J. Müller,[*1] *Adam W. Franz,*[1] *Christa S. Barkschat (née Kämer),*[1] *Markus Sailer,*[1] *Klaus Meerholz,*[2] *David Müller,*[2] *Alexander Colsmann,*[3] *Uli Lemmer*[3]

Summary: Monodisperse oligophenothiazines are rapidly synthesized in good yields by use of Suzuki arylation. These well defined oligomers reveal both highly fluorescence and low oxidation potentials. As a consequence of intense electronic coupling as supported by cyclic voltammetry a selected trimer shows hole-transport properties in a hole-conductor-only set-up of a diode with relatively low on-set voltage.

Keywords: C–C coupling; charge transfer; cyclic voltammetry; fluorescence; heterocycles; oligomerization

Introduction

Conjugated polymers have received much scientific and technological research interest due to their potential in diverse applications such as transistors,[1] photovoltaic devices,[2] nonlinear optical devices,[3] and polymer light-emitting diodes (PLEDs).[4,5] In particular, PLEDs fabricated from conjugated polymers[6,7] have become increasingly important due to their favorable properties for the design of flat panel displays, such as good processability, low operating voltages, fast response times, and facile color tunability over the full visible range. However, profound understanding of structure-property relationships requires shorter, well-defined units.[8] Monodisperse oligomers with extended π-electron delocalization are molecularly well-defined entities with a fundamental importance for the understanding of the molecular to polymer transition. Besides answering questions about the effective conjugation lengths and reliable electronic structure-property relationships[9] well-defined conjugated oligomers are key constituents in molecular electronics.[10]

Among numerous π-systems suitable for repetitive syntheses of well-defined oligomers[11] electron-rich entities are of peculiar interest due to their ease of oxidation. In particular, reversibly oxidizable heterocyclic redox systems can be very promising for the design of suitable hole-transport materials for molecule based OLED and OFET (organic field effect transistors) devices and for switchable molecular wires for future molecular electronics. Most prominently, oligothiophenes[12] and oligopyrroles[13] have been well established in the past, yet, thiophene or pyrrole do form stable radical cations upon oxidation. More favorable are polycyclic heterocycles and, although 3,6-linked[14] and 2,7-linked di- and tricarbazoles[15] have been synthesized and studied the corresponding oligophenothiazines have remained unexplored prior to our contributions.[16] In particular, phenothiazine derivatives have become electrophore probes in supramolecular

[1] Lehrstuhl für Organische Chemie, Institut für Organische Chemie und Makromolekulare Chemie, Heinrich-Heine-Universität Düsseldorf, Universitätsstr. 1, D-40225 Düsseldorf, Germany
Fax: (+49) 0211 81 14324;
E-mail: ThomasJJ.Mueller@uni-duesseldorf.de
[2] Department für Chemie, Universität zu Köln, Luxemburgerstr. 116, D-50939 Köln, Germany
[3] Lichttechnisches Institut, Universität Karlsruhe (TH), Kaiserstr. 12, D-76128 Karlsruhe

assemblies[17] for PET (photo-induced electron transfer), and as electron donor components in material scientific investigations such as electrically conducting charge-transfer composites,[18] polymers,[19] and donor-acceptor arrangements [20,21] due to their pronounced propensity to form stable radical cations possess low and highly reversible first oxidation potentials.[22]

Oligophenothiazines by Rapid Toolkit Synthesis

Just recently, we have reported a versatile construction kit of brominated and borylated phenothiazines that can be easily prepared from *N*-hexyl phenothiazine (**1**) by a sequence of bromination, bromolithium exchange-borylation, and Suzuki coupling.[16a] With this toolbox set of various brominated and borylated phenothiazine derivatives at hand subsequent Suzuki arylation of the building blocks gives soluble, monodisperse and structurally well-defined oligophenothiazines **2**–**7** ranging from dimer to heptamer in a highly convergent fashion and decent to excellent overall yields (Scheme 1).[23]

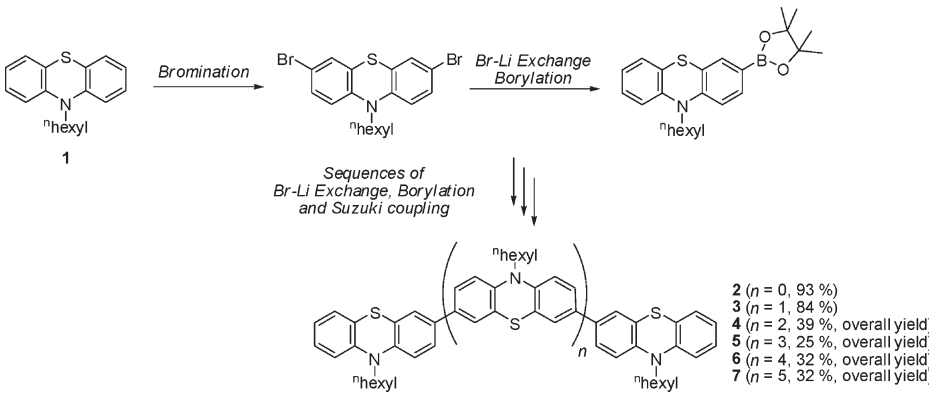
The molecular weights at the peak maximum M_p, obtained by GPC (gel permeation chromatography), and the actual molecular weights of the oligomer series, obtained by mass spectrometry, give an excellent correlation. Expectedly, GPC underestimates the molecular weights by 28% (polystyrene standard) and 10% (poly(*para*-phenylene) standard), respectively. A QM/MM conformational analysis for the complete series reveals that the obvious butterfly-shaped phenothiazine structure multiplies and significantly reduces the hydrodynamic volume of the oligomers.

Intramolecular Electronically Communicating Phenothiazinyl Units

Most interestingly, all oligophenothiazines display significant intramolecular electronic interactions.[16a,c,d,f,i,j] Indeed with exception of the monomer all oligophenothiazines are highly blue to blue-green fluorescent with remarkable Stokes shifts ($\Delta\tilde{\nu}$ 6000–6500 cm^{-1}) and increasing quantum yields ($\Phi_f = 10$–77%) with increasing number of phenothiazine units (Figure 1).

These substantial Stokes shifts can be attributed to significant geometrical changes upon excitation from a highly non-planar ground-state to a largely planarized excited state.[24] In the consanguineous series of the oligomers **1**–**7** the effective conjugation length for the emission maxima is already reached with the hexamer at an emission maximum of 482 nm.

The electrochemical behavior of the oligophenothiazines of the lower oligomers **1**–**4** reveals at low concentration clearly



Scheme 1.
Toolkit synthesis of oligophenothiazines.

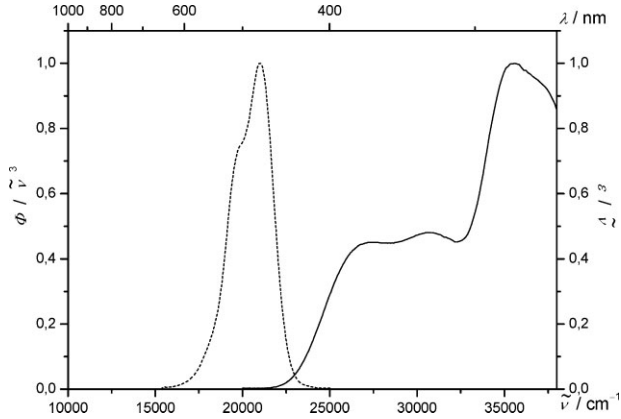


Figure 1.
Normalized absorption (solid line) and emission (dotted line) spectra of trimer **3** (recorded in CH_2Cl_2, $T = 298$ K).

separated, well-resolved one-electron oxidation events with Nernstian behaviour corresponding to the number of phenothiazine units (Figure 2).[16a,j] As a consequence of an intense intramolecular electronic coupling the first oxidation affects the subsequent electron transfer and delocalization of the generated radical cations is apparently favored. For the higher oligomers **5**–**7** multi-sweep experiments

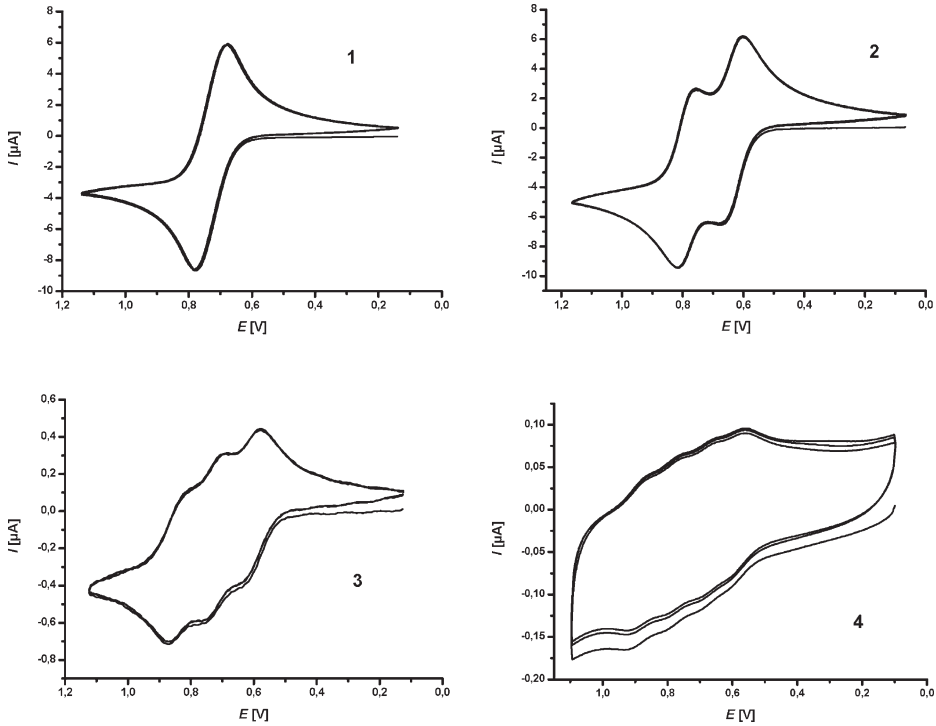


Figure 2.
Cyclic voltammograms of the monomer to tetramer **1**-**4** in CH_2Cl_2; $T = 293$ K; $c_o = 10^{-5}$ M; electrolyte: 0.05 M NBu_4PF_6 (CH_2Cl_2); $v = 100$ mV/s (**1**, **2**, and **3**), $v = 250$ mV/s (**4**); Pt as a working electrode, Ag/AgCl as a reference electrode, and Pt as a counter electrode (determined vs. ferrocene, $E_o^{0/+1} = +450$ mV).

reveal adsorption effects of electroactive specimen on the electrode surface causing a steady growth of the current intensity which can be attributed to electrocrystallization.

A comparison of four symmetrical trimers **3** and **8–10** with electronically variable substitution pattern at the terminal 3- and 7-position and with or without hexyl substituent at the nitrogen atom discloses an insight where the first oxidation in the trimers is located (Figure 3).

Since all symmetrical trimers display a similar shape of the cyclic voltammograms with three distinct reversible oxidation waves the initial oxidation can be attributed to the central phenothiazinyl unit, which is found for the reference trimer **3** at $E_0^{0/+1} = 602\,\text{mV}$. For the centrally unsubstituted trimer **8** this oxidation is shifted cathodically ($E_0^{0/+1} = 509\,\text{mV}$) as a consequence of the lower oxidation potential of 10 *H*-phenothiazine ($E_0^{0/+1} = 658\,\text{mV}$) in

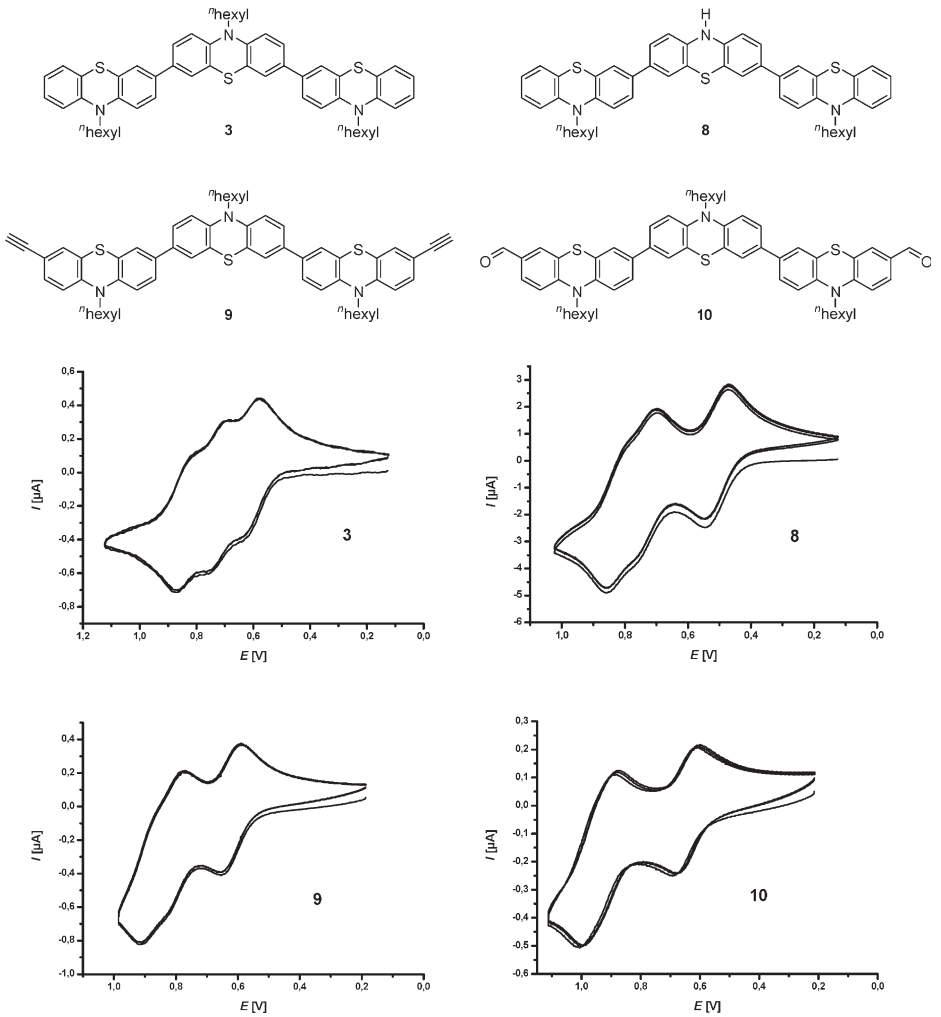


Figure 3.
Cyclic voltammograms of the trimers **3** and **8–10** in CH_2Cl_2; $T = 293\,\text{K}$; $c_o = 10^{-5}\,M$; electrolyte: 0.05 *M* NBu_4PF_6 (CH_2Cl_2); $v = 100\,\text{mV/s}$ (**3**, **9**, and **10**), $v = 250\,\text{mV/s}$ (**8**); Pt as a working electrode, Ag/AgCl as a reference electrode, and Pt as a counter electrode (determined vs. ferrocene, $E_0^{0/+1} = +450\,\text{mV}$).

comparison to *N*-hexyl phenothiazine (**1**) ($E_0^{0/+1} = 728\,\text{mV}$).

Interestingly, the first oxidations of the trimers **9** ($E_0^{0/+1} = 622\,\text{mV}$) and **10** ($E_0^{0/+1} = 646\,\text{mV}$) bearing electron withdrawing ethynyl or formyl substituents at the remote termini of the phenothiazinyl units are shifted anodically. Therefore, upon substitution at various positions of the trimers the electrochemical profile can be fine-tuned without changing the basic electrochemical feature with four reversibly accessible redox states, i.e. neutral, cation, dication, and trication, in the anodic region. This multistate stability makes trimers interesting candidates for electron rich materials with adjustable work function.

Hole-Transport Property of a Phenothiazinyl Trimer

In principle, molecular electron-rich π-systems are of particular interest as hole-transport materials for OLED[25] and OFET applications.[26] Therefore, as a model the trimer **3** was first qualitatively studied in a hole-conductor-only set-up of a diode and the current density-voltage (*i-V*) plot was recorded (Figure 4).

Indium tin oxide (ITO) was applied as an anode that was coated with a 40 nm layer of poly(3,4-ethylenedioxy-thiophene) (PEDOT) as a hole injector. Starting from a dilute solution of trimer **3** in dichloromethane a 100 nm layer was prepared by spin coating and a 200 nm layer of aluminium by vapor deposition as a cathode completes the set-up of the device. The layer thicknesses were determined by profilometer measurements. From the *i-V* plot the diode characteristics proofs the hole conductivity of the trimer **3** and shows an exponential increase with increasing voltage and the on-set voltage is about 4 V.

For considering the stability of thin layers of the same trimer **3**, in a second set of experiments with very similar settings the PEDOT hole injection layer was omitted. With a diode prepared at a concentration of $2.4 \cdot 10^{-5}\,\text{mol/L}$ and a spinning velocity of 5002 rpm furnishing the thin layers up to 16 measurements were performed to give an average diode characteristic (Figure 5). In comparison to the set-up with the PEDOT hole injection layer the on-set voltage is higher and appears between 8–10 V. Most remarkably, the measurements could be reproduced several times with the same sample and without noticeable depression of the diode characteristics.

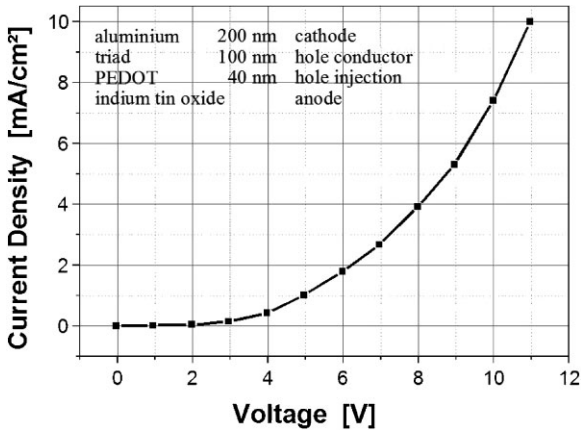


Figure 4.
i-V plot of trimer **3** in a hole-conductor-only diode set-up (anode: ITO; hole injector: 40 nm layer of PEDOT; trimer **3**: 100 nm layer by spin coating; cathode: 200 nm of aluminium, room temperature).

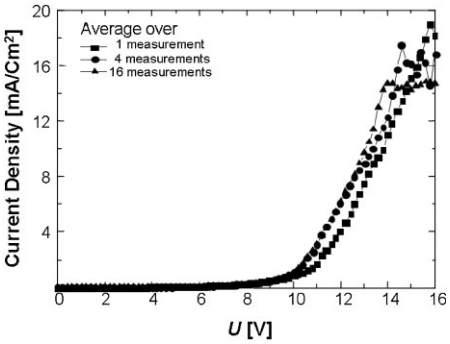


Figure 5.
i-V plot of trimer **3** in a hole-conductor-only diode set-up (anode: ITO; trimer **3**: $c_1 = 2.4 \cdot 10^{-5}$ mol/L at a spin coating velocity of 5002 rpm; cathode: 109 nm of aluminium, room temperature).

Conclusion and Outlook

In conclusion, we have developed a facile toolkit approach to soluble, monodisperse, and structurally well defined oligophenothiazines in good yields by use of Suzuki arylation. The electronic properties were investigated by absorption and emission spectroscopy and cyclic voltammetry. Interestingly, oligophenothiazines are both highly fluorescent with high fluorescence quantum yields and electroactive with low oxidation potentials. The lower oligomers display intense electronic coupling as supported by cyclic voltammetry of a selected set of trimers. In first scouting experiments the hole-transport properties were shown in a hole-conductor-only set-up of a diode and the current density-voltage (*i-V*) plots with respect to layer thickness as prepared by spin coating. Thin layers of the trimer show relatively low on-set voltages. Electronrich materials with both hole-transport and emitter properties are highly interesting for the development of multifunctional molecular electronic devices. Further studies directed towards polyphenothiazines, self organization on surfaces and in porous materials, and tailor-made oligophenothiazines based chromo-, fluoro-, and electrophores are currently underway.

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