CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200701341

Synthesis and Electronic Properties of Monodisperse Oligophenothiazines

Markus Sailer, Adam W. Franz, and Thomas J. J. Müller*[a]

Dedicated to Professor Dr. Herbert Mayr on the occasion of his 60th birthday

Abstract: Starting from *N*-hexylphenothiazine, a versatile construction kit of brominated and borylated phenothiazines can be easily prepared by a sequence of bromination, bromo–lithium exchange/borylation, and Suzuki coupling. Subsequent Suzuki arylation of the building blocks gives soluble, monodisperse, and structurally well defined oligophenothiazines in good yields. The molecular weights at the peak maximum (M_p), obtained by GPC (*g*el *p*ermeation *c*hromatography), and the actual molecular weights of the oligomer series, obtained by mass spectrometry, show excellent correlation. 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. The electronic properties (absorption and emission spectroscopy and cyclic voltammetry) give reasonable correlations with the chain length. With regard to the emission maxima, the effective conjugation length is already reached with the hexamer. Oligophenothiazines are highly fluorescent, with high fluorescence quantum yields, and are simultaneously highly electroactive, with low oxidation potentials.

Keywords: C–C coupling · cyclic voltammetry · fluorescence · heterocycles · oligomerization

Introduction

In the past decades conjugated polymers have attracted much scientific and technological research interest, due to their potential uses as semiconductors and electroactive materials in diverse applications such as transistors,[1] photovoltaic devices,[2] nonlinear optical devices,[3] and polymer light-emitting diodes (PLEDs).[4,5] In particular, the search for PLEDs fabricated from conjugated polymers[6,7] has intensified tremendously because of their favorable properties for the design of flat panel displays, such as good processability, low operating voltages, fast response times, and ease of color tunability over the full visible range. Still, for a more profound understanding of structure/property relationships, shorter, well defined units would be helpful.[8] Therefore, monodisperse oligomers with extended π-electron delocalization, which are molecularly well defined entities, can be of fundamental importance for the understanding of the transition of properties upon going from small molecules to polymers. For instance, questions about the effective conjugation lengths and about reliable electronic structure/property relationships can be tackled and answered.[9] Likewise, well defined conjugated oligomers are key elements 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 not only for the design of suitable hole-transport materials for molecule-based OLED and OFET (*o*rganic *f*ield *e*ffect *t*ransistor) devices but also for switchable molecular wires for future molecular electronics. Most prominently, oligothiophenes[12] and oligopyrroles[13] have become well established in the past. However, polycyclic heterocycles tend to give more stable radical cations than thiophene or pyrrole systems upon oxidation. Whereas 3,6-linked[14] and 2,7-linked di- and tricarbazoles[15] have been synthesized and studied, the corresponding oligophenothiazines have so far remained unexplored.

Phenothiazine derivatives[16] possess low and highly reversible first oxidation potentials[16,17] with pronounced propensities to form stable radical cations. As a consequence, the favorable electronic properties of phenothiazines have led to applications as electrophore probes in supramolecular assemblies[18] for PET (*p*hotoinduced *e*lectron *t*ransfer) and

[a] Dr. M. Sailer, Dipl.-Chem. A. W. Franz, Prof. Dr. T. J. J. Müller
Institut für Organische Chemie und Makromolekulare Chemie
Heinrich-Heine-Universität Düsseldorf
Universitätsstrasse 1 (26.43.00), 40225 Düsseldorf (Germany)
Fax: (+49) 211-81-14324
E-mail: ThomasJJ.Mueller@uni-duesseldorf.de

sensor studies, and also as electron donor components in materials science investigations, such as electrically conducting charge-transfer composites,[19] polymers,[20] and donor–acceptor arrangements.[21]

Therefore, in continuation of our program to synthesize and study bi- and terphenothiazines with alkynyl,[22] alkenyl,[23] aryl,[24] and organometallic[25] bridges and to explore their applications to PET systems,[26] we also became interested in higher oligomers of phenothiazine as low molecular weight representatives of polyphenothiazines. Here we report the synthesis of a homologous series of oligophenothiazines, together with correlation of their actual molecular weights and gel permeation chromatography, computed structures, and first electronic properties (cyclic voltammetry, absorption and emission spectroscopy).

Results and Discussion

Synthesis of the oligophenothiazine construction kit: In recent years we have adapted Suzuki cross-coupling reactions to halogenated and borylated phenothiazines as an expeditious route to phenothiazines with extended π-electron conjugation.[24] With borylated phenothiazines to hand, the Suzuki coupling appears to be the arylation method of choice. Inspired by the synthesis of well defined oligofluorenes[27] we next set out to develop a toolbox of phenothiazine derivatives suitable for a selective synthesis of well defined, monodisperse oligophenothiazines.

Starting from 10*H*-phenothiazine and 3-bromo-10*H*-phenothiazine, a whole library of brominated and borylated oligophenothiazines can be created in a few straightforward synthetic steps (Scheme 1). For the sake of solubility of higher members of a consanguineous series, *n*-hexyl groups were introduced onto the deprotonated phenothiazine nitrogen atoms by nucleophilic substitution with 1-bromohexane to give the *N*-hexylphenothiazines **1** and **2** in excellent yields. Upon bromination, **1** was readily converted into the 3,7-dibromo derivative **3**, whereas bromophenothiazine **2** was transformed into the boronate **4** by a one-pot sequence of bromo–lithium exchange, electrophilic trapping with trimethyl borate, and transesterification with pinacol.[24a]

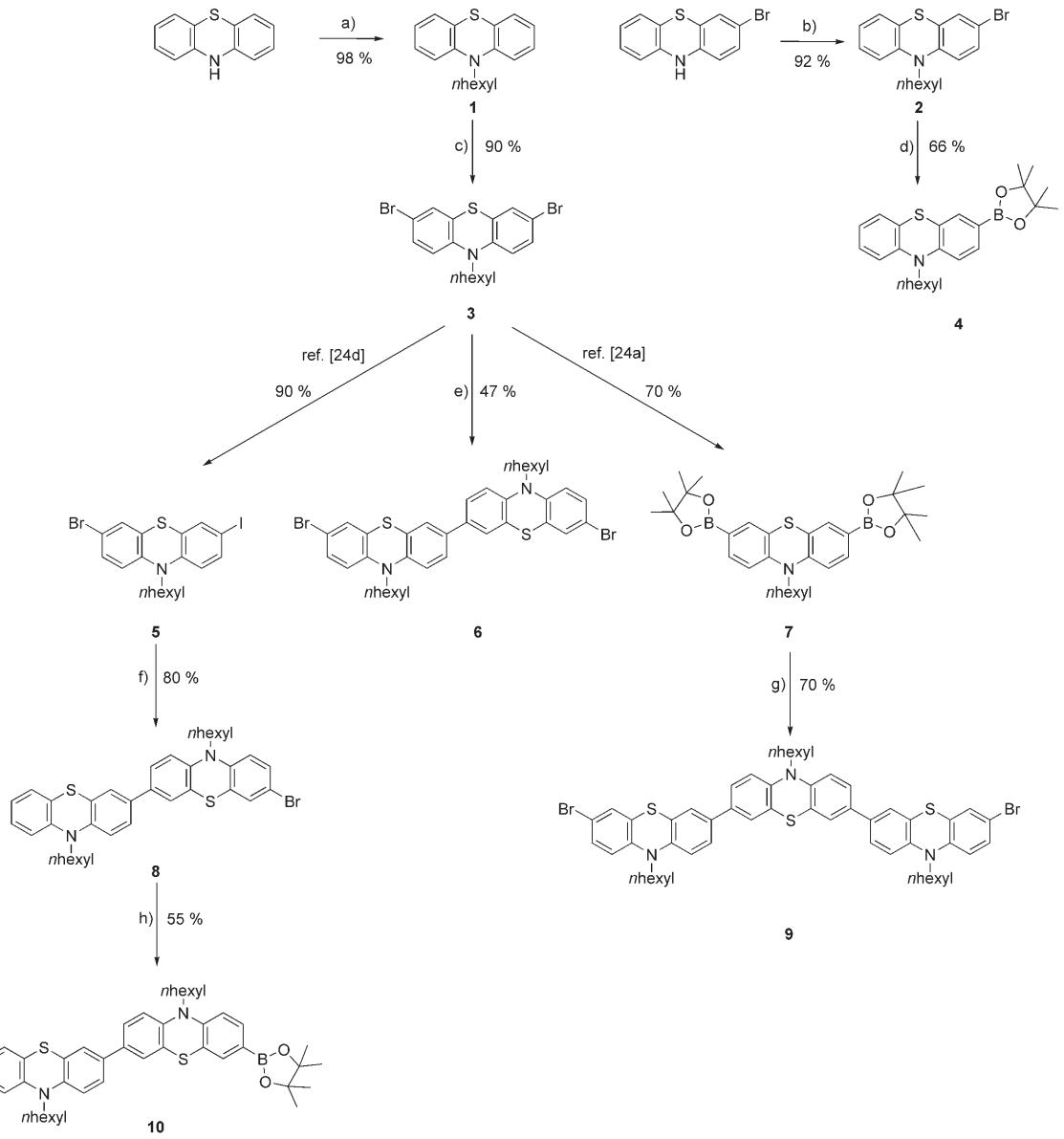
3,7-Dibromo-10-hexyl-10*H*-phenothiazine (**3**) is a quite unique and versatile starting compound that can be transformed by selective monobromine–lithium exchange and subsequent trapping with an equimolar amount of iodine into the unsymmetrical bromoiodophenothiazine **5**,[24d] or by subsequent transmetalation with copper(I) cyanide and oxidative coupling upon gentle air oxidation at low temperature[28] to furnish the symmetrical dibrominated diphenothiazine **6**. Double bromine–lithium exchange on **3**, followed by electrophilic trapping with trimethyl borate and transesterification with pinacol, gave rise to the formation of the symmetrical bisboronate **7**.[24a]

Suzuki coupling of the unsymmetrical bromoiodophenothiazine **5** with boronate **4** gave straightforward access to the monobrominated diphenothiazine **8**, whereas coupling with the bisboronate **7** furnished the symmetrical bisbrominated terphenothiazine **9** in good yield. Finally, upon subjection of the bromodiphenothiazine **8** to the sequence of bromine–lithium exchange, electrophilic trapping with trimethyl borate, and transesterification with pinacol, the diphenothiazine boronate **10** can be obtained in decent yield. All compounds have been fully characterized by spectroscopic and analytical methods. With this expanded set of brominated and borylated building blocks to hand, the stage for the synthesis of a homologous series of oligophenothiazines had now been set.

Synthesis of oligophenothiazines: A standard Suzuki protocol originally developed for phenothiazine acceptor systems[24e] was successfully adapted for the synthesis of oligophenothiazines ranging from diphenothiazine to heptaphenothiazine (Scheme 2). Treatment of the boronates **4** and **10** with the monobrominated phenothiazine **2** and the dibrominated phenothiazines **3**, **6**, and **9** in the presence of potassium carbonate in dioxane/water or DME/water, together with catalytic amounts of palladium(0) tetrakis(triphenylphosphane), for 18 to 48 h gave rise to the selective formation of the oligophenothiazines **11**–**16** in good to excellent yields. The symmetrical molecular structures of the oligophenothiazines are in agreement with the NMR spectroscopic data (^{1}H, ^{13}C, and DEPT NMR experiments) and were unambiguously supported by mass spectrometry (FAB, MALDI-TOF), as well as by IR and UV/Vis spectroscopy and combustion analyses.

Actual molecular weight and GPC M_p—conformational analysis: The correlation of the actual molecular weights of

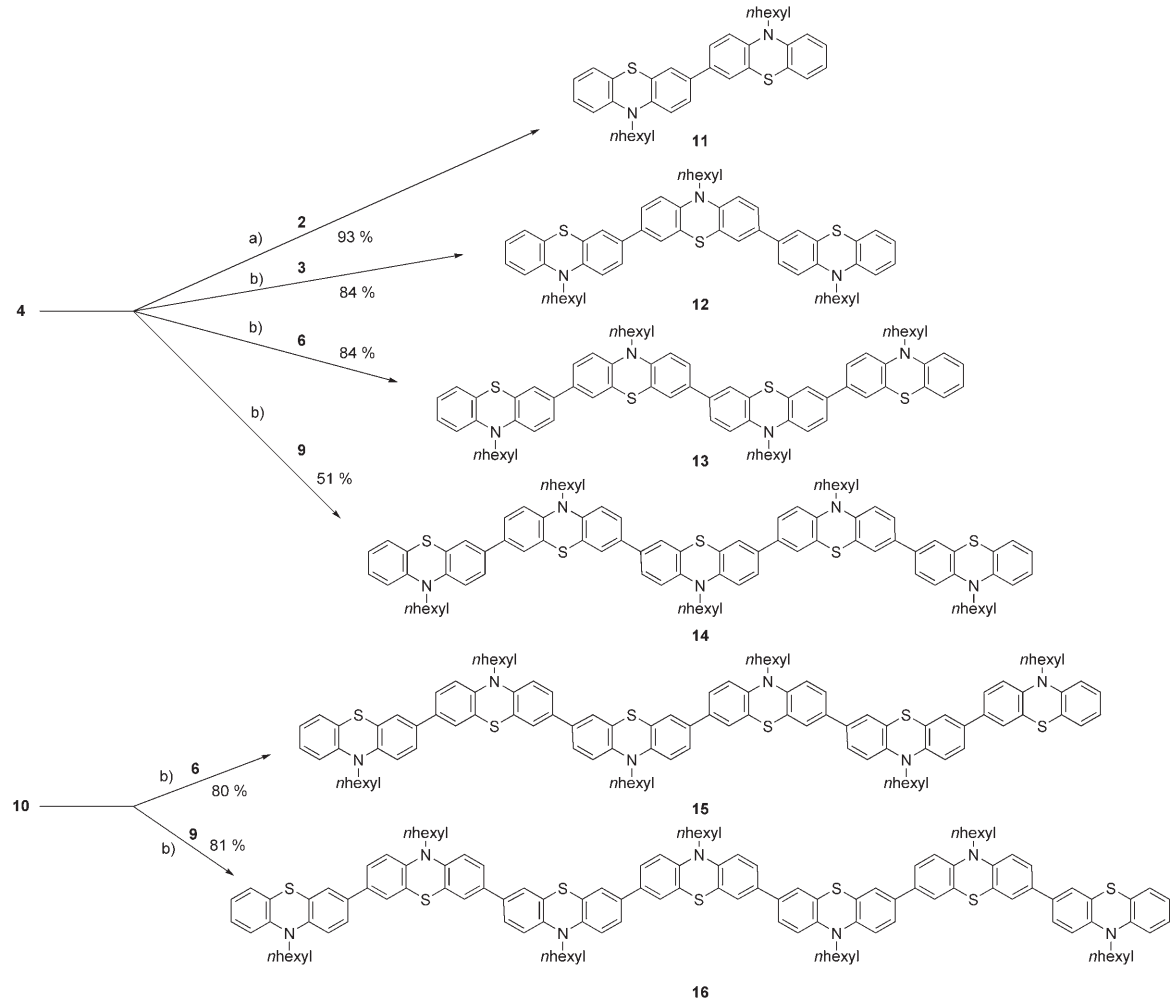
Abstract in German: *Ausgehend von* N-*Hexylphenothiazin kann leicht ein vielseitiger Baukasten aus bromierten und borylierten Phenothiazinen über eine Sequenz aus Bromierung, Bromo–Lithium-Austausch/Borylierung und Suzuki Kupplung hergestellt werden. Die nachfolgende Suzuki-Arylierung der Bausteine führt in guten Ausbeuten zu löslichen, monodispersen und strukturtreuen Oligophenothiazinen. Die Molekulargewichte beim Peakmaximum (M_p), die aus GPC (Gelpermeationschromatographie) erhalten werden und die tatsächlichen Molekulargewichte der Oligomeren, erhalten durch Massenspektrometrie, ergeben eine exzellente Korrelation. Die QM/MM-Konformationsanalyse der gesamten Serie zeigt, das der Effekt der Schmetterlingsstruktur der Phenothiazine sich vervielfältigt und so das hydrodynamische Volumen der Oligomere deutlich verkleinert. Die elektronischen Eigenschaften der Oligomere (Absorptions- und Emissionsspektroskopie und Cyclovoltammetrie) korrelieren mit der Kettenlänge. Im Falle der Emissionsmaxima wird die effektive Konjugationslänge bereits mit dem Hexamer erreicht. Oligophenothiazine fluoreszieren mit hohen Fluoreszenzquantenausbeuten und erweisen sich gleichzeitig wegen ihrer niedrigen Oxidationspotenziale als äußerst elektroaktiv.*



Scheme 1. Synthesis of the oligophenothiazine toolbox: a) KO*t*Bu, 1-bromohexane, THF, 66 °C, 3 h; b) KO*t*Bu, THF, −78 °C, 2 h, 1-bromohexane, room temperature 12 h; c) HOAc, Br_2, room temperature, 19 h at room temperature; d) *n*BuLi, THF, −78 °C, 15 min, then: $B(OMe)_3$, 15 min, then: pinacol, THF, HOAc, room temperature; e) *n*BuLi, THF, −78 °C, 15 min, then: CuCN, TMEDA, 10 min, air, 1 h; f) **4**, K_2CO_3, DME/H_2O (2:1), 4 mol % $[Pd(PPh_3)_4]$, 18 h, 85 °C; g) **5**, K_2CO_3, DME/H_2O (3:1), 5 mol % $[Pd(PPh_3)_4]$, 18 h, 95 °C; h) *n*BuLi, THF, −78 °C, 15 min, then: $B(OMe)_3$, 15 min, then: pinacol, THF, HOAc, room temperature.

the homologous series of oligophenothiazines **12**–**16**, as determined by mass spectrometry, with relative molecular weights was studied by gel permeation chromatography (GPC) in THF with polystyrene and poly(*p*-phenylene) standards (Table 1). The molecular weight at the peak maximum (M_p), obtained by GPC along with M_n and M_w, was used for establishing correlations with the molecular masses. Linear regression of the actual molecular weights M plotted against M_p of polystyrene and poly(*p*-phenylene) standards reveals that GPC traces with the poly(*p*-phenylene) standard ($M = 0.9001\ M_p + 190.54$ [g mol^{-1}]; $r^2 = 0.9998$) gives a better correlation with the actual molecular weights (Figure 1) than with the polystyrene standard ($M = 0.7218\ M_p + 332.41$ [g mol^{-1}]; $r^2 = 0.9984$). Expectedly, GPC underestimates the molecular weights by 28 % (polystyrene standard) and 10 % (poly(*p*-phenylene) standard). However, the deviation from poly(*p*-phenylene) can be attributed to significant conformational divergence from a rigid rod-like structure (as assumed from the poly(*p*-phenylene) data) with effects on the hydrodynamic volume.

QM/MM calculations[29] on the oligomers **11**–**16** were therefore carried out by optimization of the truncated 10-ethyl-10*H*-phenothiazine at a high level of theory by application of the B3LYP/6-31+G(d,p) functional, followed by



Scheme 2. Synthesis of oligophenothiazines: a) 5 mol% $[Pd(PPh_3)_4]$, K_2CO_3, 1,4-dioxane/H_2O 2:1, 90°C, 2 d; b) 5 mol% $[Pd(PPh_3)_4]$, K_2CO_3, DME/H_2O 2:1, 85°C, 18 h.

Table 1. GPC data (polystyrene and poly(*p*-phenylene) as standards—eluent: THF; flow rate: 1.0 mL min^{-1}; T=30°C) and molecular masses (determined by MALDI-TOF) of *N*-hexylphenothiazine oligomers.

	Polystyrene standard [g mol^{-1}]			Poly(*p*-phenylene) standard [g mol^{-1}]			Molecular mass [g mol^{-1}]
	M_n	M_w	M_p	M_n	M_w	M_p	
12	676.6	703.3	740.8	685.3	705.8	740.1	846.3
13	1038.9	1065.0	1086.4	996.0	1015.1	1034.2	1127.7
14	1392.7	1430.6	1467.3	1287.0	1313.7	1345.0	1409.1
15	1789.8	1833.1	1867.2	1602.2	1631.7	1660.3	1690.6
16	2261.1	2390.5	2296.6	1967.9	2053.2	1989.6	1972.0

minimization of the linked and frozen phenothiazine units with respect to their mutual dihedral torsion by application of the MM2 force field, giving rise to the lowest-energy conformers in the gas phase (Figure 2).

These minimized structures not only explain the GPC results and the significant deviation from perfect rigid-rod behavior as expected for many conjugated oligomers, but also explain an increasing tendency of higher oligophenothiazines to bend and to form sigmoid and helical conformers. In comparison with molecule lengths estimated from the intramolecular distances of the unsubstituted terminal 3- and 7-positions (Figure 3), in a linear zigzag arrangement of the phenothiazine cores the butterfly structure[16] of the phenothiazine units causes a pronounced curvature and leads to considerably reduced molecular dimensions (Table 2). Furthermore, an interphenothiazine dihedral torsion of about 35° suggests that coplanarity and mutual overlap of the π orbitals in the pristine states of oligo- and polyphenothiazines should reduce the conjugation pathway to a few units. Hence, the effective conjugation length should be reached rather quickly and the most distinctive electronic effects can be expected in the range of the lower oligophenothiazines.

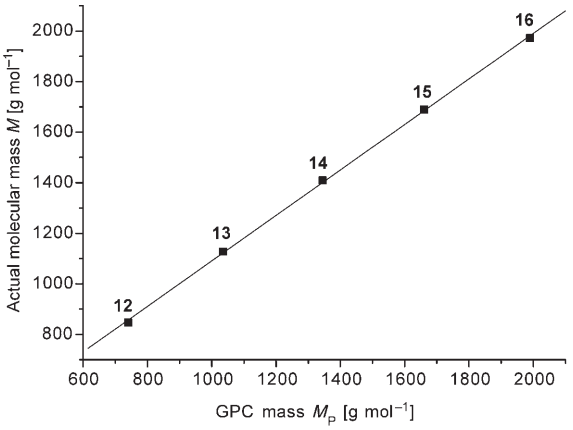


Figure 1. Correlation and linear fit of the molecular mass (determined by MALDI-TOF) and GPC M_p (poly(*p*-phenylene) as a standard) ($M = 0.90008\ M_p + 190.54245$ [g mol^{-1}] ($r^2 = 0.99979$)).

Electronic properties: The electronic properties of the homologous series of oligophenothiazines **1** and **11**–**16** were investigated by absorption and emission spectroscopy and by cyclic voltammetry (Table 3). In CH_2Cl_2 solution the longest-wavelength absorption band—except in the case of **1** ($\lambda_{max,abs} = 312$ nm)—is a distinct shoulder that shifts from 350 nm for the dimer **11** to 374 nm for the heptamer **16**. According to TDDFT calculations on phenothiazine oligomers[30] this band represents a HOMO–LUMO transition with π–π* character. The longest-wavelength bands (in wavenumbers) of all members of the series correlate reasonably well with the reciprocal numbers of phenothiazine units ($\lambda_{max,abs} = 6227.6\ 1/n + 25\,682$ [cm^{-1}] ($r^2 = 0.991$)), from which a maximal wavelength for a polymer with infinite chain length of 25 682 cm^{-1} (389 nm) can be estimated. The extinction of the oligophenothiazines is plotted vs. the number of phenothiazine units in a log–log plot in Figure 4. The extinction per phenothiazine unit increases superlinearly with the length of the conjugated system as a consequence of the increase in the oscillator strength with the length of the conjugated system [Eq. (1)]. A linear regression in the log–log plot gives a slope of 1.46:

$$\varepsilon \approx n^{\alpha} \text{ with } \alpha = 1.46 \quad (1)$$

where ε represents the extinction coefficient of an oligomer with n phenothiazine units. According to the literature, power laws with values for α of about 1.16 to 1.3 have been described.[11b,31,32] Two effects are responsible for this superlinear increase. The number of phenothiazine units per molecule expands both the chromophore and the extinction per unit.

Fluorescence spectroscopy reveals that, with exception of the monomer **1**, in which the fluorescence quantum yield is below 1%, all members of the series **11**–**16** fluoresce with blue to blue–green light and remarkable Stokes shifts, defined as the difference between the energies of the absorption and emission maximum ($\Delta\tilde{\delta} = 6000$–$6500$ cm^{-1}), together with moderate to large quantum yields ($\Phi_f = 10$–77%). These substantial Stokes shifts can be attributed to significant geometrical changes occurring upon excitation from a highly nonplanar ground state to a largely planarized excited state.[30] The Stokes shifts decrease with the sizes of the conjugated systems. Interestingly, for the series of dimer **11** to pentamer **14** the emission maxima correlate well with the reciprocal chain lengths, and the effective conjugation length is reached at 482 nm with six phenothiazine cores and remains constant for the heptamer (Figure 5).

The electrochemical behavior of the oligophenothiazines is most peculiar and clearly reveals a significant difference between the lower oligomers **1** and **11**–**13** and the higher oligomers **13**–**16** (Table 3). Interestingly, the first three representatives of the homologous series display separated, well resolved one-electron oxidation events corresponding to the number of phenothiazine units (Figure 6). As a consequence of intramolecular electronic coupling the first oxidation affects the subsequent electron transfer, and delocalization of the generated radical cations is apparently favored. For tetramer **13** the fourfold separation of the anodic oxidations can only be observed at low concentration. Upon a dropwise tenfold increase of the concentration not only does the appearance of the cyclic voltammogram change from four reversible one-electron oxidations to broad oxidation and reduction waves (Figure 7), but also, in multi-sweep experiments, adsorption effects of electroactive specimen on the electrode surface cause a steady growth in the current intensity that can be attributed to electrocrystallization.

Similar behavior in multisweep experiments is found for the higher oligomers **13**–**16**, with which adsorption on the electrode leads to a growth in the peak currents in the oxidative and reductive regions (Figure 8). Hence, two oxidation and two reduction waves can be identified (Table 3), with the average of lower potentials (oxidation and reduction wave) seeming to represent the oxidation to the state of a radical cation. Self-organization of radical cations in condensed phase has frequently been observed and can also be regarded as an important intermolecular interaction for model studies of a charge-transport phenomenon in positively doped conducting polymers.[34]

Furthermore, the first reversible oxidation potentials ($E^{0/+1}$) of the monomer to tetramer (**1**, **11**–**13**) correlate well with the reciprocal chain length ($E^{0/+1} = 184.06(1/n) + 545.38$; $r^2 = 0.9974$) (Figure 9). The adsorption tendency of the higher oligomers **13**–**16** at increased concentrations also manifests in a linear correlation with the reciprocal chain length ($E^{0/+1} = 726.05(1/n) + 434.14$; $r^2 = 0.9916$), but with a steeper slope, indicating that the polymer would stack and be oxidizable at a potential 100 mV lower than that of the free chain. The ease of oxidation with increasing chain length concurrently favors self-organization of the generated radical cations in the sense of stacking, which, in turn, increases the charge transport through the layer.

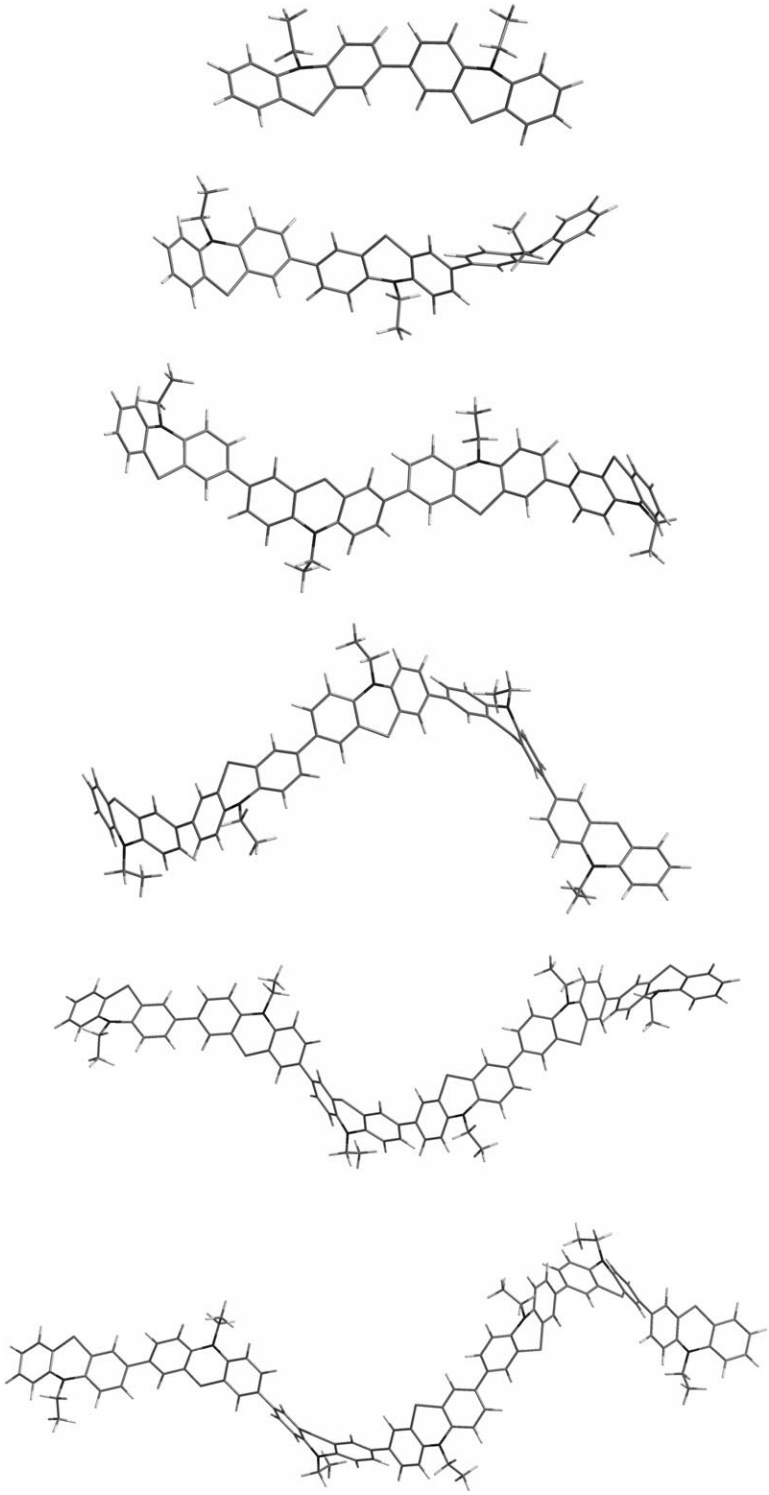


Figure 2. Energy-optimized conformers (QM/MM approach with B3LYP/6-31+G(d,p) for the 10-ethyl-10*H*-phenothiazine core and MM2 for minimizing the dihedral torsion) of the oligophenothiazines **11**–**16**.

Conclusion

In conclusion, we have developed a simple construction kit approach to soluble, monodisperse, and structurally well defined oligophenothiazines in good yields by use of Suzuki arylation. The molecular weight at the peak maximum (M_p), obtained from GPC, and the actual molecular weights of the oligomer series, obtained by mass spectrometry, correlate very well and give a valuable estimation for masses of related higher polymers. The peculiar deviation from the rigid rod behavior of the oligomers with respect to the model and standard poly(*p*-phenylene) and estimated molecular lengths can be interpreted by a QM/MM conformational analysis for the complete series. The obvious inherent butterfly-shaped conformation of the phenothiazine structure multiplies and enhances helical and sigmoid oligomer conformations, concomitantly reducing the hydrodynamic volume of the oligomers. The electronic properties were investigated by absorption and emission spectroscopy and cyclic voltammetry. Correlations with chain length were readily established, and for the emission the effective conjugation length is already reached in the hexamer. Moreover, it is worth mentioning that oligophenothiazines are both highly fluorescent with high fluorescence quantum yields and electroactive with low oxidation potentials. Therefore, their use as hole transporters and emitters in molecular electronic devices seems to be quite advantageous. Further studies directed towards polyphenothiazines, self-organization on surfaces and in porous materials, and tailor-made oligophenothiazine-based chromo-, fluoro-, and electrophores are currently underway.

Experimental Section

General considerations: Reagents, catalysts, and solvents were purchased reagent grade and used without further purification. THF and 1,4-dioxane were dried and distilled by standard procedures.[35] Column chromatography: silica gel 60, mesh 70–230. TLC: silica gel plates. ^{1}H and

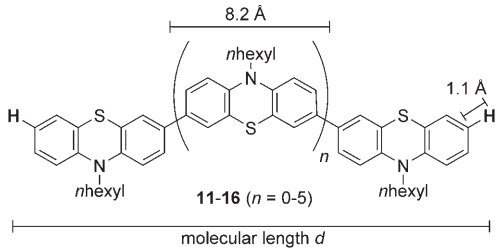


Figure 3. Model for measuring molecular lengths.

Table 2. Estimated and computed molecular dimensions according to the model in Figure 3.

Oligophenothiazine	Estimated molecular length [Å]	Computed molecular length [Å]
11	17.5	17.6
12	25.7	26.3
13	33.9	30.2
14	42.1	33.8
15	50.3	44.5
16	58.3	49.6

Table 3. UV/Vis, fluorescence, and oxidation potentials of oligophenothiazines (recorded in CH_2Cl_2, $T=298$ K; bold values: absorption and emission maxima used for determining the Stokes shift).

Compound	Absorption[a] $\lambda_{max,abs}$ [nm] (ε)	$\Delta_{HOMO-LUMO}$ [eV]	Emission[b] $\lambda_{max,em}$ [nm] (Φ_f/%)	Stokes shift[d] $\Delta\tilde{\nu}$ [cm^{-1}]	$E_{1/2}$[e] [mV]
1	258 (30900), **312** (4900)	3.977	**444** (–)	9600	728
11	268 (47800), 282 (40000), 322 (18600), **350** (14300, sh)	3.545	**454** (10)[c]	6500	642, 788
12	268 (62900, sh), 279 (63500), 324 (26300), **364** (21400, sh)	3.409	**471** (15)[c]	6200	606, 727, 861
13	286 (79700), 326 (33000), **366** (sh, 30200)	3.407	**476** (77)	6300	589, 686, 789, 896[f] 722 (514), 901 (773)[g,h]
14	264 (94900), 284 (132300), 322 (57500, sh), **371** (43100, sh)	3.360	**479** (68)	6100	604 (545), 1079 (828)[g,h]
15	282 (155500), 322 (74400), **373** (67600, sh)	3.343	**482** (75)	6100	587 (523), 1126 (861)[g,h]
16	284 (217800), 330 (88200, sh), **374** (83000, sh)	3.334	**482** (62)	6000	575 (505), 1111 (868)[g,h]

[a] Recorded in CH_2Cl_2. [b] Recorded in CH_2Cl_2 at $c=10^{-7}$ M with 7-diethylamino-4-methylchromen-2-one ($\Phi_f=0.73$)[33] as a standard. [c] Recorded in $CHCl_3$ at $c=10^{-7}$ M with perylene ($\Phi_f=1.00$) as a standard. [d] $\Delta\tilde{\nu}=\lambda_{max,abs}-\lambda_{max,em}$ [cm^{-1}]. [e] Recorded in CH_2Cl_2. [f] Recorded at a concentration of 10^{-5} M. [g] Single scan, recorded at a concentration of 10^{-4} M. [h] Oxidation waves; reduction waves in parentheses. Recorded at a concentration of 10^{-5} M.

^{13}C NMR spectra: CD_2Cl_2, $CDCl_3$, and [D_6]acetone (locked to Me_4Si). The assignments of quaternary C, CH, CH_2, and CH_3 were made by use of DEPT spectra. Elemental analyses were carried out in the Microanalytical Laboratories of the Organisch-Chemisches Institut, Ruprecht-Karls-Universität, Heidelberg, Germany and in the Microanalytical Laboratories of the Institut für Pharmazeutische Chemie, Heinrich-Heine-Universität, Düsseldorf, Germany.

Electrochemistry: Cyclic voltammetry experiments (EG & G potentiostatic instrumentation) were performed under argon in dry and degassed CH_2Cl_2 at room temperature and at scan rates of 100, 250, 500, and 1000 mVs^{-1}. The electrolyte was Bu_4NPF_6 (0.025 M). The working electrode was a 1 mm platinum disk, the counter electrode was a platinum wire, and the reference electrode was a Ag/AgCl electrode. The potentials were corrected to the internal standard of Fc/Fc^+ in CH_2Cl_2 ($E_0^{0/+1}=450$ mV).[36]

Fluorescence spectra: Fluorescence measurements (Perkin–Elmer LS-55) were performed in dry and degassed CH_2Cl_2 at room temperature. To avoid reabsorption and re-emission effects the concentrations were kept strictly below 1 μM. The solutions were irradiated at approximately 10 nm less in energy than the longest-wavelength absorption maximum or shoulder. We estimated the quantum yields of our compounds by comparison with the known quantum yields of perylene ($\Phi_f=1.00$) or 7-diethylamino-4-methylchromen-2-one, coumarine 1 ($\Phi_f=0.73$).[33] According to Eq. (2) the fluorescence emission (I_i) of standards R and samples S at five different optical densities OD_I—that is, concentrations—were determined and corrected for the refractive index (n_i) of the corresponding solutions i. The presented quantum yields (Q) were obtained in each case by averaging of five measurements, yielding a corresponding standard deviation $<0.1\,\%$.[37]

$$Q_S = Q_R \frac{I_S}{I_R}\frac{OD_R}{OD_S}\frac{n_S^2}{n_R^2} \qquad (2)$$

10-Hexyl-10*H*-phenothiazine (PT-hex) (1):[38] In an oven-dried Schlenk flask (500 mL), 10*H*-phenothiazine (15.0 g, 75.3 mmol) and potassium *tert*-butoxide (9.36 g, 83.4 mmol) were dissolved in dry THF (150 mL). After the system had been stirred for 1 h, 1-bromohexane (24.8 g, 150 mmol) was added by syringe. The color of the reaction mixture changed from brown to yellow, and the solution was stirred at 66 °C for 3 h. After cooling to room temperature, the crude product was filtrated through a short plug of silica gel, and the solvent was removed under reduced pressure. The residual brown oil was chromatographed on silica gel (hexane) to give **1** (21.0 g, 98 %) as a light yellow oil. ^{1}H NMR (300 MHz, [D_6]acetone, 300 K): $\delta=7.18$ (ddd, $J=8.2$, 7.3, 1.6 Hz, 2H), 7.15–7.11 (m, 2H), 7.00 (dd, $J=8.2$, 0.9 Hz, 2H), 6.92 (dt, $J=7.4$, 1.2 Hz, 2H), 3.92 (t, $J=6.9$ Hz, 2H), 1.82–1.72 (m, 2H), 1.49–1.39 (m, 2H), 1.31–1.25 (m, 4H), 0.87–0.82 ppm (m, 3H); ^{13}C NMR (75 MHz, [D_6]acetone, 300 K): $\delta=$ 146.4 (C_{quat}), 128.3 (CH), 128.1 (CH), 125.7 (C_{quat}), 123.3 (CH), 116.7 (CH), 47.8 (CH_2), 32.2 (CH_2), 27.6 (CH_2), 27.2 (CH_2), 23.3 (CH_2), 14.3 ppm (CH_3); IR (neat): $\tilde{\nu}=3063$, 2954, 2927, 2855, 2580, 1923, 1885, 1770, 1679, 1594, 1571, 1485, 1457, 1443, 1369, 1333, 1285, 1250, 1238, 1195, 1140, 1127, 1105, 1039, 749, 728 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 312 nm (4900), 258 nm (30900 $mol^{-1}dm^3cm^{-1}$); EI MS (70 eV): m/z (%): 284 (21), 283 $[M]^+$ (100), 212 $[M-C_5H_{11}]^+$ (67), 199 (16), 198 $[M-C_6H_{13}]^+$ (73); elemental analysis calcd (%) for $C_{18}H_{21}NS$ (283.4): C 76.27, H 7.47, N 4.94, S 11.32; found: C 76.03, H 7.45, N 5.01, S 11.19.

3-Bromo-10-hexyl-10*H*-phenothiazine (2):[39] In an oven-dried Schlenk flask (500 mL), potassium *tert*-butoxide (4.50 g, 40.0 mmol) was suspended in dry THF (150 mL) and the suspension was cooled to −78 °C (acetone/dry ice bath). Then, 3-bromo-10*H*-phenothiazine (10.0 g, 35.9 mmol) dissolved in dry THF (50 mL) was slowly added dropwise to the reaction mixture. After the system had been stirred at −78 °C for 2 h, 1-bromohexane (6.60 g, 40.0 mmol) was added. The cooling bath was removed and the reaction mixture was stirred for 12 h at room temperature. The mixture was filtered through a short column of silica gel, and the solvent was removed under reduced pressure. The residual brown oil

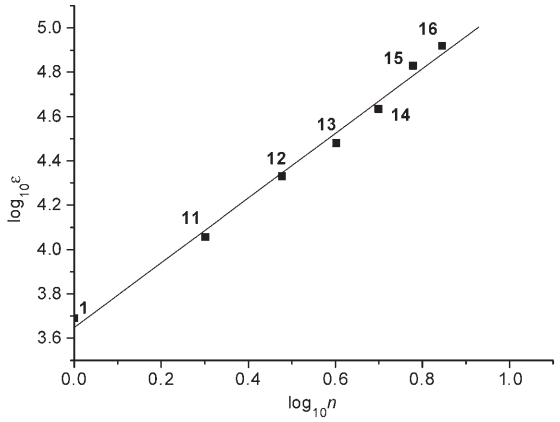


Figure 4. Correlation and linear fit of the extinction coefficient (ε) and phenothiazine units n ($\log_{10}\varepsilon = 1.4588 \log_{10} n + 3.6486$ ($r^2 = 0.9914$)).

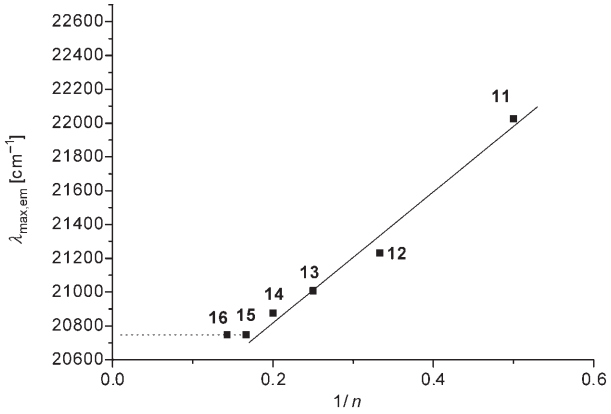


Figure 5. Correlation of the emission maxima $\lambda_{max,em}$ and phenothiazine units n for **11**–**14** (solid line: $\lambda_{max,em} = 3876\ 1/n + 20042$ ($r^2 = 0.980$); dotted line: effective conjugation length at 482 nm).

was chromatographed on silica gel (hexane) to give **2** (12.0 g, 92%) as a light yellow oil. ^{1}H NMR (300 MHz, [D$_6$]acetone, 300 K): $\delta = 7.32$ (dd, $J = 8.6$, 2.3 Hz, 1H), 7.27 (d, $J = 2.3$ Hz, 1H), 7.21 (ddd, $J = 8.2$, 7.3, 1.6 Hz, 1H), 7.14 (ddd, $J = 7.6$, 1.6, 0.3 Hz, 1H), 7.03 (dd, $J = 8.2$, 1.1 Hz, 1H), 6.98–6.93 (m, 2H), 3.92 (t, $J = 6.9$ Hz, 2H), 1.81–1.71 (m, 2H), 1.49–1.39 (m, 2H), 1.31–1.25 (m, 4H), 0.86–0.82 ppm (m, 3H); ^{13}C NMR (75 MHz, [D$_6$]acetone, 300 K): $\delta = 146.0$ (C$_{quat}$), 145.8 (C$_{quat}$), 131.0 (CH), 130.1 (CH), 128.7 (CH), 128.2 (CH), 127.0 (C$_{quat}$), 124.8 (C$_{quat}$), 123.7 (CH), 118.2 (CH), 117.0 (CH), 114.8 (C$_{quat}$), 48.0 (CH$_2$), 32.2 (CH$_2$), 27.5 (CH$_2$), 27.2 (CH$_2$), 23.3 (CH$_2$), 14.3 ppm (CH$_3$); IR (neat): $\tilde{\nu} = 3060$, 2954, 2927, 2855, 1588, 1484, 1457, 1392, 1331, 1271, 1250, 806, 748 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 314 nm (5200), 262 (35100 mol^{-1} dm^3 cm^{-1}); EI MS (70 eV): m/z (%): 363 [^{81}Br–M]$^+$ (100), 361 [^{79}Br–M]$^+$ (85), 292 [^{81}Br–M–C$_5$H$_{11}$]$^+$ (56), 290 [^{79}Br–M–C$_5$H$_{11}$]$^+$ (49), 278 [^{81}Br–M–C$_6$H$_{13}$]$^+$ (77), 276 [^{79}Br–M–C$_6$H$_{13}$]$^+$ (67), 260 (14), 258 (13), 197 [M–Br–C$_6$H$_{13}$]$^+$ (17), 196 (14); elemental analysis calcd (%) for C$_{18}$H$_{20}$BrNS (362.3): C 59.67, H 5.56, N 3.87, S 8.85, Br 22.05; found: C 59.41, H 5.60, N 3.85, S 9.06, Br 21.87.

3,7-Dibromo-10-hexyl-10*H*-phenothiazine (3): In a two-necked flask with a dropping funnel under a nitrogen atmosphere, compound **1** (73.4 g, 259 mmol) was dissolved in acetic acid (95.0 mL). Bromine (13.3 mL, 259 mmol) was added dropwise to the solution, whereupon it slightly warmed and its color turned dark red. After the system had been stirred for 1 h at room temperature, another portion of bromine (13.3 mL, 259 mmol) was added to the reaction mixture and the color turned dark green. The solution was stirred for 18 h at room temperature, and then a saturated aqueous solution of sodium sulfite (70 mL) and diethyl ether (100 mL) were added to the mixture and the system was stirred for 2 h. The organic phase was separated, and the aqueous layer was extracted several times with diethyl ether. The combined organic layers were dried with magnesium sulfate, and the solvents were removed under reduced pressure. The residue was chromatographed on silica gel (isohexane/acetone 10:1) to give **3** (102.6 g, 90%) as a yellow oil, which crystallized within a week. Compound **3** is sensitive towards light and oxygen, and after exposure the color of **3** turns green. M.p. 58 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): $\delta = 7.27$–7.21 (m, 4H), 6.68 (d, $J = 8.1$ Hz, 2H), 3.75 (t, $J = 7.0$ Hz, 2H), 1.41 (m, 2H), 1.75 (m, 2H), 1.31–1.27 (m, 4H), 0.88 ppm (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): $\delta = 144.1$ (C$_{quat}$), 130.1 (CH), 129.7 (CH), 126.4 (C$_{quat}$), 116.6 (CH), 114.7 (C$_{quat}$), 47.6 (CH$_2$), 31.3 (CH$_2$), 26.6 (CH$_2$), 26.5 (CH$_2$), 22.5 (CH$_2$), 13.9 (CH$_3$); MS (FAB$^+$): m/z (%): 441 [M]$^+$ (100), 356 [M–C$_6$H$_{13}$]$^+$ (15).

10-Hexyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10*H*-phenothiazine (4): Compound **2** (14.4 g, 41.2 mmol) was dissolved in dry THF (230 mL) under argon, and the solution was cooled to −78 °C (acetone/dry ice bath). A solution of *n*-butyllithium in hexanes (2.5 M, 25.0 mL, 61.8 mmol) was then slowly added to the reaction mixture, whereupon its color turned brown. After the system had been stirred for 15 min at −78 °C, trimethyl borate (6.9 mL, 61.8 mmol) was added dropwise to the mixture, and stirring was continued for another 15 min. The solution was then allowed to warm to room temperature, and stirring was continued for 1 h. A solution of pinacol (7.41 g, 61.8 mmol; dried over 4 Å mol sieves) in THF (50 mL) was added dropwise to the reaction mixture, and the stirring was continued for 2 h. Acetic acid (2.4 mL, 41.2 mmol) was then added, and the color changed to light orange and the solution became viscous. After 14 h of stirring, a saturated solution of sodium sulfite (100 mL) was added and the mixture was extracted several times with diethyl ether. The combined organic layers were dried with magnesium sulfate and the solvents were removed under reduced pressure. The residue was chromatographed on silica gel (isohexane/acetone 10:1) to give **4** (7.71 g, 66%) as a yellow, viscous resin. ^{1}H NMR (200 MHz, $CDCl_3$, 300 K): $\delta = 7.59$ (m, 2H), 7.12 (m, 2H), 6.88 (m, 3H), 3.82 (t, $J = 7.2$ Hz, 2H), 1.79 (m, $J = 7.1$ Hz, 2H), 1.42 (m, 2H), 1.33 (m, 16H), 0.87 ppm (t, $J = 6.6$, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): $\delta = 147.5$ (C$_{quat}$), 144.4 (C$_{quat}$), 133.9 (CH), 133.6 (CH), 127.2 (CH), 126.7 (CH), 124.7 (C$_{quat}$), 123.8 (C$_{quat}$), 122.4 (CH), 115.4 (CH), 114.6 (CH), 83.5 (C$_{quat}$), 47.4 (CH$_2$), 31.2 (CH$_2$), 26.6 (CH$_2$), 26.3 (CH$_2$), 24.6 (CH$_3$), 22.3 (CH$_2$), 13.8 ppm (CH$_3$); IR (KBr): $\tilde{\nu} = 2976$, 2956, 2928, 2857, 1600, 1576, 1466, 1355, 1264, 1144, 1108, 964, 860, 748, 673 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 318 nm (63200), 264 (380600), 244 nm (143200 mol^{-1} dm^3 cm^{-1}); EI MS (70 eV): m/z (%): 409 [M]$^+$ (100), 324 [M–C$_6$H$_{13}$]$^+$ (34); elemental analysis calcd (%) for C$_{24}$H$_{23}$BNO$_2$S (409.4): C 70.41, H 7.88, N 3.42, S 7.83; found: C 70.64, H 7.81, N 3.56, S 7.86.

7,7′-Dibromo-10,10′-dihexyl-10*H*,10′*H*-3,3′-biphenothiazine (6): In an oven-dried, three-necked flask (500 mL), **3** (10.0 g, 22.7 mmol) was dissolved in dry THF (250 mL) and cooled down to −78 °C. A solution of *n*-butyllithium in hexanes (2.5 M, 9.1 mL, 22.7 mmol) was then added dropwise to the reaction mixture over 5 min. The stirring was continued for 10 min, and copper cyanide (1.01 g, 11.3 mmol) was added in small portions. After the reaction mixture had been kept for another 10 min at low temperature, TMEDA (10.1 mL, 68.0 mmol) was slowly added dropwise. The stirring was continued for another 10 min, and synthetic air was passed through the reaction mixture by syringe for 1 h. The color of the solution turned from orange to black and the cooling was removed. After the system had reached room temperature, a diluted aqueous solution of sodium sulfite was added and the mixture was extracted several times with diethyl ether. The combined organic layers were dried with magnesium sulfate and the solvents were removed under reduced pressure. The residue was chromatographed on silica gel (hexane/acetone 20:1) and recrystallized from hexane to give **6** (3.41 g, 47%) as yellow crystals. M.p. 166–175 °C; ^{1}H NMR (300 MHz, [D$_6$]acetone, 300 K): $\delta = 7.41$ (dd, $J = 8.5$, 2.2 Hz, 2H), 7.34 (d, $J = 2.1$ Hz, 2H), 7.31 (dd, $J = 8.4$, 2.2 Hz, 2H), 7.26 (d, $J = 2.2$ Hz, 2H), 7.01 (d, $J = 8.4$ Hz, 2H), 6.92 (d, $J = 8.7$ Hz, 2H), 3.89 (t, $J = 7.0$ Hz, 4H), 1.76 (m, 2H), 1.43 (m, 4H), 1.27 (m, 8H), 0.84 ppm (br t, $J = 7.0$ Hz, 6H); ^{13}C NMR (75 MHz, [D$_6$]acetone, 300 K): $\delta = 145.4$ (C$_{quat}$), 144.7 (C$_{quat}$), 135.1 (C$_{quat}$), 130.9 (CH), 130.0 (CH), 127.6

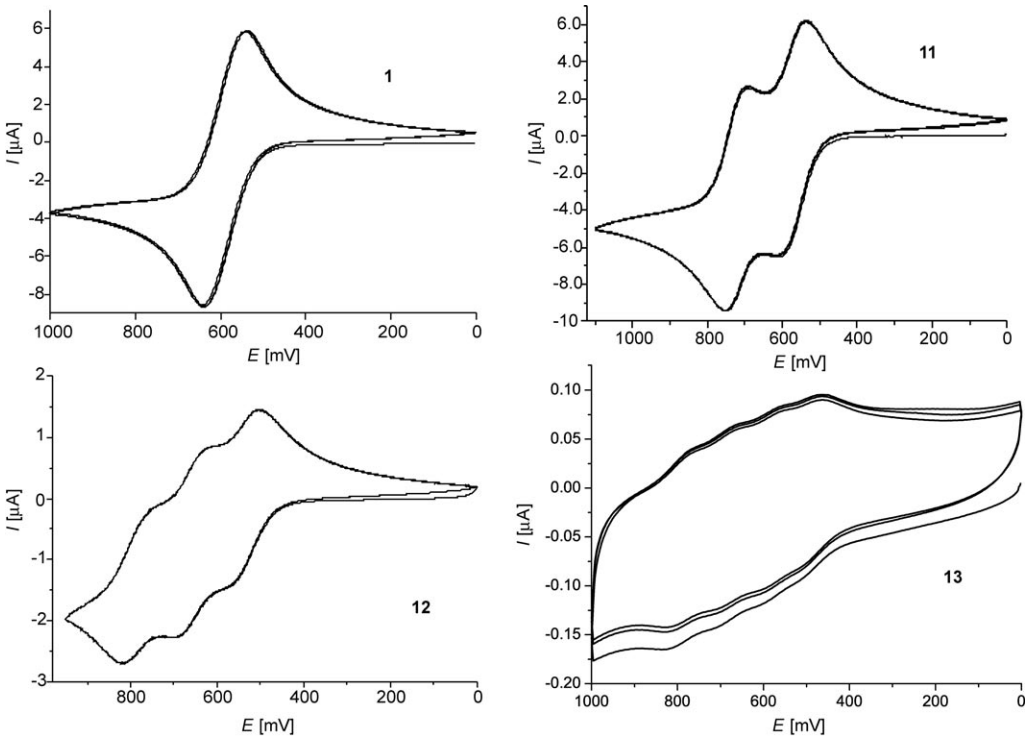


Figure 6. Cyclic voltammograms of **1** and **11**–**13** in CH_2Cl_2; $T=293$ K; $c_0=10^{-5}$ M; electrolyte: 0.05 M NBu_4PF_6 (CH_2Cl_2); $v=100$ mV s^{-1}; Pt as a working electrode, Ag/AgCl as a reference electrode, and Pt as a counter electrode (determined vs. ferrocene, $E_0^{0/+1}=+450$ mV).

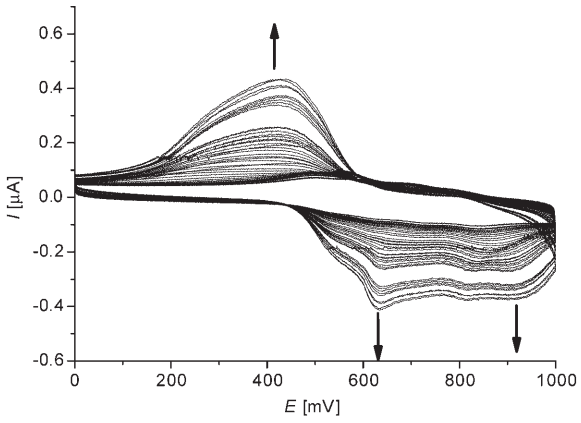


Figure 7. Multisweep experiment with tetramer **13** upon dropwise increase of concentration from 10^{-5} to 10^{-4} M (CH_2Cl_2; $T=293$ K; electrolyte: 0.05 M NBu_4PF_6 (CH_2Cl_2); $v=250$ mV s^{-1}; Pt as a working electrode, Ag/AgCl as a reference electrode, and Pt as a counter electrode (determined vs. ferrocene, $E_0^{0/+1}=+450$ mV).

(C_{quat}), 126.4 (CH), 125.6 (C_{quat}), 125.3 (CH), 118.0 (CH), 116.8 (CH), 114.8 (C_{quat}), 48.0 (CH_2), 32.1 (CH_2), 27.4 (CH_2), 27.1 (CH_2), 23.3 (CH_2), 14.3 ppm (CH_3); IR (KBr): $\tilde{\nu}=2954$, 2926, 2854, 1600, 1484, 1453, 1416, 1393, 1331, 1295, 1267, 1251, 1193, 1145, 1107, 871, 807 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 330 (2000), 270 nm (5100 mol^{-1} dm^3 cm^{-1}); MS (FAB$^+$): m/z (%): 722 $[M]^+$ (100), 638 (18) $[M-C_6H_{13}]^+$; elemental analysis calcd (%) for $C_{36}H_{38}Br_2N_2S_2$ (722.7): C 59.83, H 5.30, N 3.88; found: C 60.79, H 5.04, N 3.94.

7-Bromo-10,10′-dihexyl-10*H*-10′*H*-[3,3′]biphenothiazine (8): Compound **4** (1.52 g, 3.71 mmol), 3-iodo-7-bromo-10-hexyl-10*H*-phenothiazine (**5**,[24d] 2.19 g, 4.46 mmol), and potassium carbonate (1.54 g, 11.14 mmol) were dissolved in a mixture of DME (20 mL) and water (10 mL) and the solution was degassed with argon for 20 min. After the addition of $Pd(PPh_3)_4$ (0.17 g, 0.15 mmol) the reaction mixture was stirred for 18 h at 85 °C. After cooling down to room temperature, the solution was diluted with a saturated aqueous solution of sodium sulfite and was stirred for 15 min. The solution was diluted again with water (20 mL) and was extracted several times with dichloromethane. The combined organic layers were dried with magnesium sulfate and the solvents were removed under reduced pressure. The residue was chromatographed on silica gel (hexane/acetone 15:1) to give **8** (1.91 g, 80 %) as a yellow, glassy resin. ^{1}H NMR (300 MHz, [D$_6$]acetone, 300 K): $\delta=7.44$–7.39 (m, 2H), 7.35 (d, $J=2.2$ Hz, 2H), 7.32–7.26 (m, 2H), 7.22–7.13 (m, 2H), 7.03–6.90 (m, 5H), 3.92 (t, $J=7.0$ Hz, 2H), 3.89 (t, $J=6.8$ Hz, 2H), 1.83–1.71 (m, 4H), 1.45–1.43 (m, 4H), 1.29–1.27 (m, 8H), 0.87–0.82 ppm (m, 6H); ^{13}C NMR (75 MHz, [D$_6$]acetone, 300 K): $\delta=146.0$ (C_{quat}), 145.4 (C_{quat}), 145.3 (C_{quat}), 144.7 (C_{quat}), 135.3 (C_{quat}), 134.7 (C_{quat}), 130.9 (CH), 130.0 (CH), 128.3 (CH), 128.0 (CH), 127.6 (C_{quat}), 126.3 (CH), 126.1 (CH), 126.0 (C_{quat}), 125.6 (CH), 125.0 (C_{quat}), 123.2 (CH), 118.0 (CH), 117.0 (CH), 116.7 (CH), 116.6 (CH), 114.7 (C_{quat}), 47.9 (CH_2), 47.8 (CH_2), 32.2(CH_2), 32.1 (CH_2), 27.5 (CH_2), 27.4 (CH_2), 27.1 (CH_2), 27.1 (CH_2), 23.2(CH_2), 14.2 ppm (CH_3); IR (KBr): $\tilde{\nu}=2952$, 2925, 2853, 1600, 1575, 1457, 1250 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 362 (11800), 326 (16400), 284 (320000), 268 nm (44000 mol^{-1} dm^3 cm^{-1}); MS (FAB$^+$): m/z (%): 644 $[M]^+$ (100), 599 $[M-C_6H_{13}]^+$ (40), 474 $[M-2C_6H_{13}]^+$ (35); elemental analysis calcd (%) for $C_{36}H_{39}BrN_2S_2$ (643.8): C 67.17, H 6.11, N 4.35, S 9.96, Br 12.41; found: C 67.13, H 6.20, N 4.35, S 9.89, Br 12.23.

7-Bromo-7′-(7-bromo-10-hexyl-10*H*-phenothiazin-3-yl)-10,10′-dihexyl-10*H*,10′*H*-3,3′-biphenothiazine (9): 3-Iodo-7-bromo-10-hexyl-10*H*-phenothiazine (**5**,[24d] 3.01 g, 6.2 mmol), 10-hexyl-3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10*H*-phenothiazine (**7**,[24a] 1.50 g, 2.8 mmol), $[Pd(PPh_3)_4]$ (0.13 g, 0.12 mmol), and potassium carbonate (2.32 g, 16.8 mmol) were dissolved in a degassed mixture of DME (85 mL) and water (25 mL). The solution was stirred for 18 h at 95 °C. After cooling down to room temperature, the mixture was diluted with water (100 mL) and extracted with several portions of dichloromethane. The combined organic layers were dried with magnesium sulfate and the solvents were

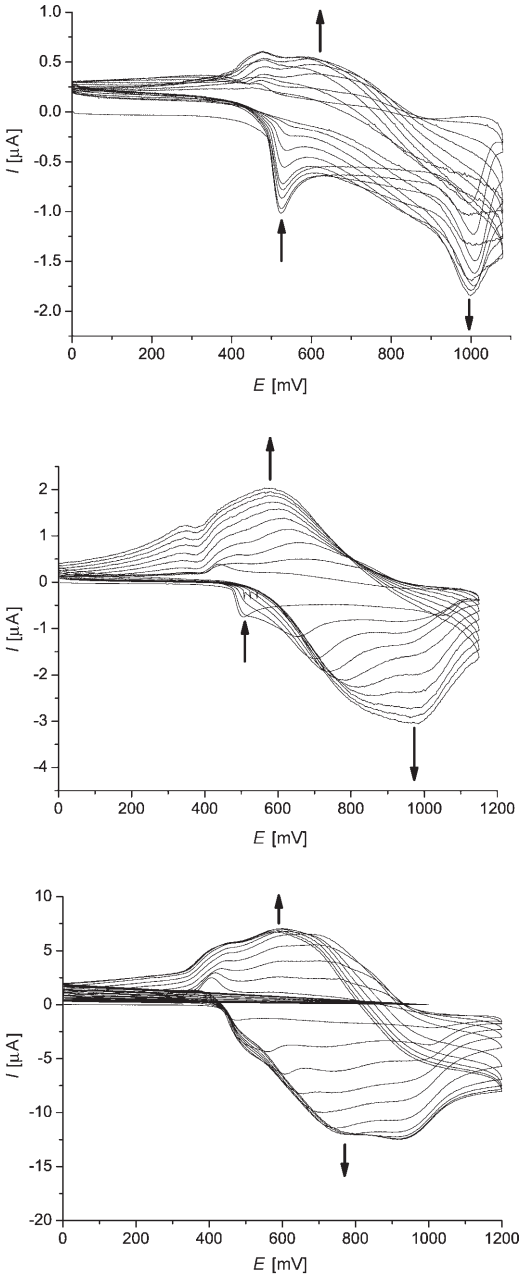


Figure 8. Multisweep experiments with **14** (top, 7 cycles), **15** (center, 10 cycles), and **16** (bottom, 10 cycles) (CH_2Cl_2; $c_0 = 10^{-4}$ M; $T = 293$ K; electrolyte: 0.05 M NBu_4PF_6 (CH_2Cl_2); $v = 250$ mV s^{-1}; Pt as a working electrode, Ag/AgCl as a reference electrode, and Pt as a counter electrode (determined vs. ferrocene, $E_0^{0/+1} = +450$ mV).

removed. The residue was chromatographed on silica gel (hexane/acetone 15:1) to give **9** (1.82 g, 70%) as a yellow, glassy resin. ^{1}H NMR (300 MHz, [D$_6$]acetone, 300 K): $\delta = 7.47$–7.42 (m, 4H), 7.38 (m, 4H), 7.32 (dd, $J = 8.8$, 2.6 Hz, 2H), 7.28 (d, $J = 2.2$ Hz, 2H), 7.07–7.03 (m, 4H), 6.95 (d, $J = 8.46$ Hz, 2H), 3.99–3.91 (m, 6H), 1.84–1.76 (m, 6H), 1.48–1.43 (m, 6H), 1.31–1.27 (m, 12H), 0.88–0.84 ppm (m, 9H); ^{13}C NMR (75 MHz, [D$_6$]acetone, 300 K): $\delta = 145.5$ (C_{quat}), 145.0 (C_{quat}), 144.7 (C_{quat}), 135.3 (C_{quat}), 134.8 (C_{quat}), 130.9 (CH), 130.0 (CH), 127.7 (C_{quat}), 126.4 (CH), 126.2, 125.6 (CH), 125.6 (CH), 125.1 (C_{quat}), 118.1 (CH), 117.0 (CH), 116.8, 114.7 (C_{quat}), 47.9 (CH_2), 32.3 (CH_2), 32.2 (CH_2), 27.5 (CH_2), 27.4 (CH_2), 27.2 (CH_2), 27.1 (CH_2), 23.3 (CH_2), 14.3 (CH_3), 14.2 ppm (CH_3); IR (KBr): $\tilde{\nu} = 2953$, 2927, 2854, 1628, 1457, 1416, 1332, 1241, 806 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 364 nm (25100), 328 (29700), 282 (66200), 270 (70000 mol^{-1} dm^3 cm^{-1}); MS (FAB$^+$): m/z (%): 1003 $[M]^+$ (100), 918 (14) $[M-C_6H_{13}]^+$; elemental analysis calcd (%) for $C_{54}H_{57}Br_2N_3S_3$ (1004.1): C 64.60, H 5.72, N 4.18, S 9.58, Br 15.92; found: C 64.67, H 5.77, N 4.21, S 9.32, Br 15.63.

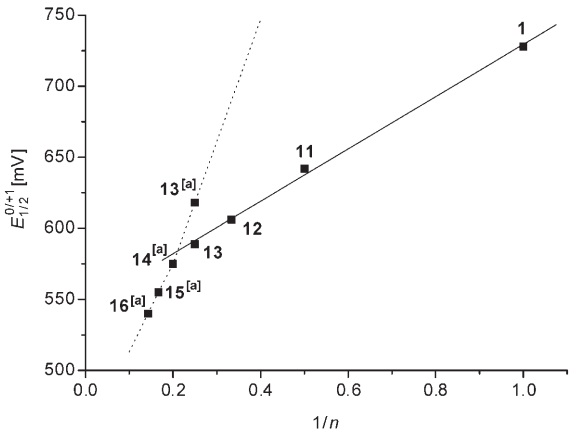


Figure 9. Correlation of $E^{0/+1}$ (Nernst behavior for **1**, **11**–**13** at $c_0 = 10^{-5}$ M; averages of oxidation and reduction waves for **13**–**16** at $c_0 = 10^{-4}$ M) and phenothiazine units n for **11**–**14** (solid line for **1**, **11**–**13**, $c_0 = 10^{-5}$ M: $E^{0/+1} = 184.06(1/n) + 545.38$; $r^2 = 0.9974$; [a] dotted line **13**–**16**, $c_0 = 10^{-4}$ M: $E^{0/+1} = 726.05(1/n) + 434.14$; $r^2 = 0.9916$).

10,10′-Dihexyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10*H*,10′*H*-3,3′-biphenothiazine (10): Under argon atmosphere, **8** (2.00 g, 3.11 mmol) was dissolved in dry THF (50 mL) and the solution was cooled down to −78 °C (acetone/dry ice bath). A solution of *n*-butyllithium in hexanes (1.6 M, 2.33 mL, 3.73 mmol) was then slowly added dropwise to the reaction mixture, whereupon the color turned brown. After the system had been stirred for 10 min at −78 °C, trimethyl borate (0.42 mL, 3.73 mmol) was added dropwise and the stirring was continued for another 15 min. The solution was then allowed to come to room temperature and stirring was continued for 2 h. Pinacol (0.44 g, 3.73 mmol) was added to the reaction mixture and the stirring was continued for 1 h. Acetic acid (0.14 mL, 2.49 mmol) was then added and the color changed to light orange and the solution became viscous. After the system had been kept for 12 h at room temperature, a saturated aqueous solution of sodium sulfite (100 mL) was added and the crude product was extracted several times with diethyl ether. The combined organic layers were dried with magnesium sulfate and the solvents were removed under reduced pressure. The residue was chromatographed on silica gel (hexane/acetone 15:1) to give **10** (1.19 g, 55%) as a light yellow, glassy resin. ^{1}H NMR (300 MHz, [D$_6$]acetone, 300 K): $\delta = 7.56$ (dd, $J = 8.1$, 1.5 Hz, 1H), 7.46 (d, $J = 1.2$ Hz, 1H), 7.44–7.40 (m, 2H), 7.37–7.32 (m, 2H), 7.22–7.13 (m, 2H), 7.05–7.00 (m, 4H), 6.96–6.91 (m, 1H), 3.96 (t, $J = 7.4$ Hz, 2H), 3.94 (t, $J = 6.9$ Hz, 2H), 1.84–1.75 (m, 4H), 1.48–1.43 (m, 4H), 1.31–1.27 (m, 20H), 0.87–0.83 ppm (m, 6H); ^{13}C NMR (75 MHz, [D$_6$]acetone, 300 K): $\delta = 149.6$ (C_{quat}), 147.0 (C_{quat}), 146.3 (C_{quat}), 145.6 (C_{quat}), 136.3 (C_{quat}), 136.2 (CH), 135.8 (C_{quat}), 135.2 (CH), 129.3 (CH), 129.0 (CH), 127.1 (CH), 127.1 (CH), 127.0 (C_{quat}), 126.8 (C_{quat}), 126.5 (CH), 126.5 (CH), 126.1 (C_{quat}), 125.1 (C_{quat}), 124.3 (CH), 118.0 (CH), 117.8, 117.6, 116.9, 48.9 (CH_2), 48.9 (CH_2), 33.2 (CH_2), 33.2 (CH_2), 28.6 (CH_2), 28.5 (CH_2), 28.2 (CH_2), 28.1 (CH_2), 26.2 (CH_2), 24.3 (CH_2), 15.3 ppm (CH_3); IR (KBr): $\tilde{\nu} = 2955$, 2928, 2855, 1604, 1584, 1462, 1354, 1144, 1108, 862, 808, 747, 672 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 358 nm (4700), 324 (7800), 278 (16900 mol^{-1} dm^3 cm^{-1}); MS (FAB$^+$): m/z (%): 690 $[M]^+$ (100), 605 (17) $[M-C_6H_{13}]^+$, 520 (8) $[M-2C_6H_{13}]^+$; elemental analysis calcd (%) for $C_{42}H_{51}BN_2O_2S_2$ (690.8): C 73.02, H 7.44, N 4.06, S 9.28; found: C 72.98, H 7.50, N 4.15, S 9.22.

10,10′-Dihexyl-10*H*,10′*H*-3,3′-biphenothiazine (PT-hex)$_2$ (11): Compound **4** (107 mg, 0.26 mmol), $[Pd(PPh_3)_4]$ (8 mg, 7 μmol), and K_2CO_3 (103 mg, 0.78 mmol) were dissolved in 1,4-dioxane (20 mL) and water (8 mL) in a

flask (50 mL). The solution was degassed with nitrogen for 10 min, and **2** (95 mg, 0.26 mmol) was added. The solution was stirred at 90 °C for 2 d. After cooling down to room temperature the reaction mixture was diluted with diethyl ether and water. The organic layer was dried with magnesium sulfate and the solvents were removed under reduced pressure. The residue was chromatographed on silica gel (pentane/diethyl ether 4:1) to give **11** (137 mg, 93 %) as a light yellow oil, which slowly crystallized. M.p. 117–119 °C; ^{1}H NMR (300 MHz, [D$_6$]acetone, 300 K): δ = 7.44 (dd, J = 8.5, 2.2 Hz, 2H), 7.38 (d, J = 1.8 Hz, 2H), 7.04 (m, 4H), 7.29–7.14 (m, 4H), 6.94 (m, 2H), 3.96 (t, J = 7.0 Hz, 4H), 1.81 (m, 4H), 1.45 (m, 4H), 1.30 (m, 8H), 0.86 ppm (m, 6H); ^{13}C NMR (75 MHz, [D$_6$]acetone, 300 K): δ = 146.1 (C$_{quat}$), 145.2 (C$_{quat}$), 134.9 (C$_{quat}$), 128.3 (CH), 128.0 (CH), 126.1 (CH), 126.0 (C$_{quat}$), 125.5 (CH), 125.2 (C$_{quat}$), 123.3 (CH), 116.8 (CH), 116.6 (CH), 47.8 (CH$_2$), 32.2 (CH$_2$), 27.6 (CH$_2$), 27.2 (CH$_2$), 23.3 (CH$_2$), 14.2 ppm (CH$_3$); IR (KBr): $\tilde{\nu}$ = 2954, 2927, 2853, 1600, 1575, 1487, 1458, 1414, 1376, 1332, 1252, 1194, 1121, 1040, 887, 874, 808, 748 cm^{-1}; UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 350 nm (14300, sh), 322 (18600), 282 (40000), 268 (47800 mol^{-1} dm^3 cm^{-1}); EI MS (70 eV): m/z (%): 566 (17), 565 (42), 564 [M]$^+$ (100), 480 (10), 479 (23), 395 (13), 394 (35); elemental analysis calcd (%) for $C_{36}H_{40}N_2S_2$ (564.8): C 76.55, H 7.14, N 4.96, S 11.35; found: C 76.68, H 7.34, N 4.67, S 11.45.

General procedure for the syntheses of odd-numbered oligophenothiazines (PT-hex)$_{2n+1}$ (GP1): A mixture of dibromo phenothiazine compound **3** or **9** (1.0 equiv), phenothiazine boronic acid ester **4** or **10** (2.2 equiv), [Pd(PPh$_3$)$_4$] (0.05 equiv), and potassium carbonate (5.0 equiv) in a degassed DME/water (2:1) mixture was stirred for 18 h at 85 °C. After cooling down to room temperature, the mixture was diluted with a diluted sodium sulfite solution and water. The mixture was extracted with several portions of dichloromethane. The combined organic layers were dried with magnesium sulfate and the solvents were removed. The residue was chromatographed on silica gel to give the pure odd-numbered oligophenothiazines **12**, **14**, or **16**.

(PT-hex)$_3$ (12): This compound was produced by GP1 from **3** and **4**, and after chromatography on silica gel (hexane/acetone 20:1), **12** (354 mg, 84 %) was isolated as a yellow resin. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, 300 K): δ = 7.34–7.31 (m, 8H), 7.19–7.12 (m, 4H), 6.94–6.88 (m, 8H), 3.86 (m, 6H), 1.80 (m, 6H), 1.45 (m, 6H), 1.32 (m, 12H), 0.89 ppm (m, 9H); ^{13}C NMR (CD$_2$Cl$_2$, 75 MHz, 300 K): δ = 145.2 (C$_{quat}$), 144.3 (C$_{quat}$), 144.1 (C$_{quat}$), 134.2 (C$_{quat}$), 134.1 (C$_{quat}$), 127.3 (CH), 125.2 (CH), 125.2 (CH), 124.9 (CH), 124.9 (CH), 124.7 (C$_{quat}$), 124.4 (C$_{quat}$), 122.4 (CH), 115.6 (CH), 115.6 (CH), 115.5 (CH), 47.6 (CH$_2$), 47.5 (CH$_2$), 31.6 (CH$_2$), 26.9 (CH$_2$), 26.7 (CH$_2$), 22.7 (CH$_2$), 13.8 ppm (CH$_3$); IR (KBr): $\tilde{\nu}$ = 2953, 2927, 2854, 1602, 1576, 1458, 1415, 1378, 1332, 1240, 1193, 1138, 1106, 874, 808, 747 cm^{-1}; UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 364 nm (21400, sh), 324 (26300), 279 (63500), 268 (62900 mol^{-1} dm^3 cm^{-1}, sh); EI-MS (70 eV): m/z (%): 848 (11), 847 (30), 846 (61), 845 [M]$^+$ (100), 761 (11), 760 (15), 590 (16), 422 (10); elemental analysis calcd (%) for $C_{54}H_{59}N_3S_3$ (846.3): C 76.64, H 7.03, N 4.96, S 11.36; found: C 76.55, H 7.33, N 4.79, S 10.78.

(PT-hex)$_5$ (14): This compound was produced by GP1 from **4** and **9**, and after chromatography on silica gel (hexane/acetone 15:1), **14** (400 mg, 51 %) was isolated as a yellow, glassy resin. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 300 K): δ = 7.32–7.29 (m, 14H), 7.26–7.09 (m, 6H), 6.91–6.86 (m, 10H), 6.71–6.68 (m, 2H), 3.85–3.75 (m, 10H), 1.86–1.73 (m, 20H), 1.53–1.41 (m, 10H), 1.27 (m, 20H), 0.90–0.85 ppm (m, 15H, CH$_3$); ^{13}C NMR (75 MHz, CD$_2$Cl$_2$, 300 K): δ = 145.2 (C$_{quat}$), 144.5 (C$_{quat}$), 144.4 (C$_{quat}$), 144.2 (C$_{quat}$), 144.1 (C$_{quat}$), 143.9 (C$_{quat}$), 134.5 (C$_{quat}$), 134.2 (C$_{quat}$), 134.1 (C$_{quat}$), 134.0 (C$_{quat}$), 130.0 (CH), 129.5 (CH), 127.4 (CH), 125.4 (CH), 125.2 (CH), 124.9 (CH), 124.7 (C$_{quat}$), 124.5 (C$_{quat}$), 124.4 (C$_{quat}$), 122.4 (CH), 116.7 (CH), 115.8 (CH), 115.7 (CH), 115.6 (CH), 115.5 (CH), 114.3 (C$_{quat}$), 47.6 (CH$_2$), 47.6 (CH$_2$), 31.6 (CH$_2$), 31.5 (CH$_2$), 29.2 (CH$_2$), 26.9 (CH$_2$), 26.8 (CH$_2$), 26.7 (CH$_2$), 26.6 (CH$_2$), 22.7 (CH$_2$), 22.7 (CH$_2$), 13.9 (CH$_3$), 13.9 ppm (CH$_3$); IR (KBr): $\tilde{\nu}$ = 2955, 2926, 2870, 2854, 1627, 1603, 1458, 1415, 1379, 1333, 1241, 873, 806, 746 cm^{-1}; UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 371 nm (43100, sh), 322 (57500), 284 (132300), 264 (94900 mol^{-1} dm^3 cm^{-1}); MS (FAB$^+$): m/z (%): 1408 [M]$^+$ (100), 1323.7 (47) [M−C$_6$H$_{13}$]$^+$, 983.3 (12) [M−2C$_6$H$_{13}$]$^+$; elemental analysis calcd (%) for $C_{72}H_{78}N_4S_4$ (1409.1): C 76.71, H 6.94, N 4.97, S 11.38; found: C 76.61, H 7.04, N 4.95, S 11.55.

(PT-hex)$_7$ (16): This compound was produced by GP1 from **10** and **9**, and after chromatography on silica gel (hexane/acetone 10:1 to dichloromethane), **16** (160 mg, 81 %) was isolated as a yellow, glassy resin. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 300 K): δ = 7.33–7.28 (m, 24H), 7.18–7.09 (m, 4H), 6.91–6.86 (m, 16H), 3.86–3.80 (m, 14H), 1.84–1.73 (m, 14H), 1.50–1.38 (m, 14H), 1.33–1.27 (m, 28H), 0.89–0.83 ppm (m, 21H); ^{13}C NMR (75 MHz, CD$_2$Cl$_2$, 300 K): δ = 145.3 (C$_{quat}$), 144.4 (C$_{quat}$), 144.1 (C$_{quat}$), 134.2 (C$_{quat}$), 127.4 (CH), 125.3 (CH), 125.2 (CH), 125.0 (CH), 124.7 (C$_{quat}$), 124.4 (C$_{quat}$), 122.4 (CH), 115.7 (CH), 115.6 (CH), 115.5 (CH), 47.7 (CH$_2$), 47.6 (CH$_2$), 31.6 (CH$_2$), 27.0 (CH$_2$), 26.9 (CH$_2$), 26.7 (CH$_2$), 22.7 (CH$_2$), 14.0 ppm (CH$_3$); IR (KBr): $\tilde{\nu}$ = 2953, 2926, 2868, 2854, 1605, 1458, 1415, 1379, 1333, 1294, 1274, 1252, 1240, 1192, 873, 806, 746 cm^{-1}; UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 374 nm (83000, sh), 330 (88200), 284 nm (217800 mol^{-1} dm^3 cm^{-1}); MS (MALDI): m/z (%): 1971 [M]$^+$ (100), 1605.0 (87) [M−C$_6$H$_{13}$]$^+$, 1519.8 (29) [M−2C$_6$H$_{13}$]$^+$, 1434.7 (12) [M−3C$_6$H$_{13}$]$^+$; elemental analysis calcd (%) for $C_{126}H_{135}N_7S_7$ (1972.0): C 76.75, H 6.90, N 4.97, S 11.38; found: C 76.67, H 6.88, N 4.89, S 11.20.

General procedure for the syntheses of even-numbered oligophenothiazines (PT-hex)$_{2n}$ (GP2): A mixture of **6** (1.0 equiv), phenothiazine boronic acid ester **4** or **10** (2.2 equiv), [Pd(PPh$_3$)$_4$] (0.05 equiv), and potassium carbonate (5.0 equiv) in a degassed DME/water (2:1) mixture was stirred for 18 h at 85 °C. After the system had cooled to room temperature, a diluted sodium sulfite solution and water were added. The mixture was extracted with several portions of dichloromethane. The combined organic layers were dried with magnesium sulfate and the solvents were removed. The residue was chromatographed on silica gel to give the pure even-numbered oligophenothiazines **13** or **15**.

(PT-hex)$_4$ (13): This compound was produced by GP2 from **4**, and after chromatography on silica gel (hexane/acetone 15:1), **13** (400 mg, 84 %) was isolated as a yellow, glassy resin. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 300 K): δ = 7.37–7.30 (m, 12H), 7.19–7.11 (m, 4H), 6.93–6.87 (m, 10H), 3.85 (t, J = 7.33 Hz, 8H), 1.87–1.75 (m, 8H), 1.50–1.39 (m, 8H), 1.35–1.28 (m, 16H), 0.90–0.85 ppm (m, 12H); ^{13}C NMR (75 MHz, CD$_2$Cl$_2$, 300 K): δ = 145.5 (C$_{quat}$), 144.7 (C$_{quat}$), 134.4 (C$_{quat}$), 127.6 (CH), 125.5 (CH), 125.2 (CH), 125.0 (C$_{quat}$), 124.7 (C$_{quat}$), 122.7 (CH), 116.0 (CH), 115.9 (CH), 115.8 (CH), 47.8 (CH$_2$), 31.7 (CH$_2$), 27.2 (CH$_2$), 27.0 (CH$_2$), 23.0 (CH$_2$), 14.1 ppm (CH$_3$); IR (KBr): $\tilde{\nu}$ = 2953, 2926, 2868, 2854, 1604, 1457, 1415, 1378, 1333, 1295, 1275, 1251, 1240, 1193, 873, 807, 747 cm^{-1}; UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 366 nm (30200, sh), 326 (33000), 286 (79700 mol^{-1} dm^3 cm^{-1}); MS (FAB$^+$): m/z (%): 1126 [M]$^+$ (100), 1042 (48) [M−C$_6$H$_{13}$]$^+$, 787.0 (43) [M−4C$_6$H$_{13}$]$^+$; elemental analysis calcd (%) for $C_{72}H_{78}N_4S_4$ (1127.7): C 76.69, H 6.97, N 4.97, S 11.37; found: C 76.39, H 6.91, N 4.87, S 11.38.

(PT-hex)$_6$ (15): This compound was produced by GP2 from **10**, and after chromatography on silica gel (hexane/acetone 15:1), **15** (229 mg, 80 %) was isolated as a yellow, glassy resin. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 300 K): δ = 7.36–7.30 (m, 18H), 7.19–7.11 (m, 6H), 6.93–6.87 (m, 12H), 3.89–3.82 (m, 12H), 1.86–1.77 (m, 12H), 1.50–1.40 (m, 12H), 1.36–1.29 (m, 24H), 0.91–0.88 ppm (m, 18H); ^{13}C NMR (75 MHz, CD$_2$Cl$_2$, 300 K): δ = 145.5 (C$_{quat}$), 144.7 (C$_{quat}$), 144.4 (C$_{quat}$), 134.5 (C$_{quat}$), 127.7 (CH), 125.6 (CH), 125.2 (CH), 125.0 (C$_{quat}$), 124.7 (C$_{quat}$), 122.7 (CH), 115.9 (CH), 115.8 (CH), 47.9 (CH$_2$), 31.9 (CH$_2$), 27.2 (CH$_2$), 27.0 (CH$_2$), 23.0 (CH$_2$), 14.2 ppm (CH$_3$); IR (KBr): $\tilde{\nu}$ = 2954, 2925, 2868, 2854, 1604, 1457, 1415, 1379, 1333, 1294, 1252, 1240, 1193, 873, 806, 746 cm^{-1}; UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 373 nm (67600, sh), 322 (74400), 282 nm (155500 mol^{-1} dm^3 cm^{-1}); MS (MALDI): m/z (%): 1689 [M]$^+$ (100), 1605 (90) [M−C$_6$H$_{13}$]$^+$, 1520 (41) [M−2C$_6$H$_{13}$]$^+$, 1435 (17) [M−3C$_6$H$_{13}$]$^+$; elemental analysis calcd (%) for $C_{108}H_{116}N_6S_6$ (1690.6): C 76.73, H 6.92, N 4.97, S 11.38; found: C: 76.47, H 7.65, N 4.60, S 10.38.

Acknowledgements

The support of this work by the Deutsche Forschungsgemeinschaft (SFB 486, support for M.S.; Graduate College 850, stipend for A.W.F.) and by the Fonds der Chemischen Industrie is gratefully acknowledged. The authors also cordially thank Radu-Adrian Gropeanu, M.Sc., for experimental assistance, Dr. A. C. Grimsdale and Professor K. Müllen for

generous support with GPC analytics, helpful interpretation, and valuable discussions, and BASF AG for the generous donation of chemicals.

[1] H. Shirringhaus, N. Tessler, R. H. Friend, *Science* **1998**, *280*, 1741–1744.
[2] J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, A. B. Holmes, *Nature* **1995**, *376*, 498–500.
[3] P. N. Prasad, D. J. Williams, *Introduction to Nonlinear Effects in Monomers and Polymers*, Wiley, New York, **1991**.
[4] a) J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, A. B. Holmes, *Nature* **1990**, *347*, 539–541; For reviews, see, for example, b) X. Gong, D. Moses, A. J. Heeger in *Organic Light-Emitting Diodes* (Eds.: K. Müllen, U. Scherf), Wiley-VCH, Weinheim, **2006**, 151–180; c) A. C. Grimsdale in *Organic Light-Emitting Diodes* (Eds.: K. Müllen, U. Scherf), Wiley-VCH, Weinheim, **2006**, 215–263.
[5] G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri, A. J. Heeger, *Nature* **1992**, *357*, 477–479.
[6] P. L. Burn, A. B. Holmes, A. Kraft, D. D. C. Bradley, A. R. Brown, R. H. Friend, R. W. Gymer, *Nature* **1992**, *356*, 47–49.
[7] A. Kraft, A. C. Grimsdale, A. B. Holmes, *Angew. Chem.* **1998**, *110*, 416–443; *Angew. Chem. Int. Ed.* **1998**, *37*, 402–428.
[8] For an excellent monograph, see *Electronic Materials: The Oligomer Approach* (Eds.: K. Müllen, G. Wegner), Wiley-VCH, Weinheim, **1998**.
[9] R. E. Martin, F. Diederich, *Angew. Chem.* **1999**, *111*, 1440–1469; *Angew. Chem. Int. Ed.* **1999**, *38*, 1350–1377.
[10] a) *An Introduction to Molecular Electronics* (Eds.: M. C. Petty, M. R. Bryce, D. Bloor), Oxford University Press, New York, **1995**; b) for molecular materials in electronic and opto-electronic devices, see for example, various authors in *Acc. Chem. Res.* **1999**, *32*, issue 3; c) R. L. Carroll, C. B. Gorman, *Angew. Chem.* **2002**, *114*, 4556–4579; *Angew. Chem. Int. Ed.* **2002**, *41*, 4378–4400; d) J. M. Tour, *Acc. Chem. Res.* **2000**, *33*, 791–804.
[11] a) For a recent review on the synthesis of uniform, non-natural oligomers, see, for example, N. Franz, G. Kreutzer, H.-A. Klok, *Synlett* **2006**, 1793–1815; b) For a systematic study on well defined oligophenylenes, see, for example, M. Remmers, B. Müller, K. Martin, H.-J. Räder, *Macromolecules* **1999**, *32*, 1073–1079; c) K. Müllen, *Pure Appl. Chem.* **1993**, *65*, 89–96.
[12] For reviews, see, for example, a) P. Bäuerle in *Electronic Materials: The Oligomer Approach* (Eds.: K. Müllen, G. Wegner), Wiley-VCH, Weinheim, **1998**, pp. 106–197; b) J. L. Segura, N. Martín, *J. Mater. Chem.* **2000**, *10*, 2403–2435; c) T. Otsubo, Y. Aso, K. Takimiya, *J. Mater. Chem.* **2002**, *12*, 2565–2575; d) E. Lukevics, P. Arsenyan, O. Pudova, *Heterocycles* **2003**, *60*, 663–687.
[13] For reviews, see, for example, a) L. Groenendaal, E. W. Meijer, J. A. J. M. Vekemans in *Electronic Materials: The Oligomer Approach* (Eds.: K. Müllen, G. Wegner), Wiley-VCH, Weinheim, **1998**, 235–272; b) P. Audebert, J.-M. Catel, V. Duchenet, L. Guyarda, P. Hapiot, G. Le Coustumer, *Synth. Met.* **1999**, *101*, 642–645.
[14] a) Z.-B. Zhang, M. Fujiki, H.-Z. Tang, M. Motonaga, K. Torimitsu, *Macromolecules* **2002**, *35*, 1988–1990; b) O. Paliulis, J. Ostrauskaite, V. Gaidelis, V. Jankauskas, P. Strohriegl, *Macromol. Chem. Phys.* **2003**, *204*, 1706–1712; c) K. Brunner, A. van Dijken, H. Börner, J. J. A. M. Bastiaansen, N. M. M. Kiggen, B. M. W. Langeveld, *J. Am. Chem. Soc.* **2004**, *126*, 6035–6042.
[15] a) M. Belletete, M. Bedard, J. Bouchard, M. Leclerc, G. Durocher, *Can. J. Chem.* **2004**, *82*, 1280–1288; b) M. Sonntag, P. Strohriegl, *Chem. Mater.* **2004**, *16*, 4736–4742.
[16] a) M. Sainsbury in *Rodd's Chem. Carbon Compd., Vol. 4* (Ed.: M. Sainsbury), Elsevier, Amsterdam, 2nd ed., **1998**, pp. 575–608; b) M. Sainsbury in *Comprehensive Heterocyclic Chemistry, Vol. 3* (Eds.: A. R. Katritzky, C. W. Rees), Pergamon Press, Oxford, **1984**, p. 995.
[17] R. McIntyre, H. Gerischer, *Ber. Bunsenges. Phys. Chem.* **1984**, *88*, 963–969.
[18] a) J. Strauss, J. Daub, *Adv. Mater.* **2002**, *14*, 1652–1655; b) R. Duesing, G. Tapolsky, T. J. Meyer, *J. Am. Chem. Soc.* **1990**, *112*, 5378–5379; c) W. E. Jones, Jr., P. Chen, T. J. Meyer, *J. Am. Chem. Soc.* **1992**, *114*, 387–388; d) A. M. Brun, A. Harriman, V. Heitz, J.-P. Sauvage, *J. Am. Chem. Soc.* **1991**, *113*, 8657–8663; e) H. D. Burrows, T. J. Kemp, M. J. Welburn, *J. Chem. Soc. Perkin Trans. 2* **1973**, 969–974; f) J.-P. Collin, S. Guillerez, J.-P. Sauvage, *J. Chem. Soc. Chem. Commun.* **1989**, 776–778.
[19] a) R. C. Wheland, J. L. Gillson, *J. Am. Chem. Soc.* **1976**, *98*, 3916–3925; b) P. Berges, J. Kudnig, G. Klar, E. Sanchez-Martinez, R. Diaz-Calleja, *Synth. Met.* **1992**, *46*, 207–219; c) A. Knorr, J. Daub, *Angew. Chem.* **1995**, *107*, 2925–2927; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2664–2666; d) H. Spreitzer, M. Scholz, G. Gescheidt, J. Daub, *Liebigs Ann.* **1996**, 2069–2077; e) H. Spreitzer, J. Daub, *Chem. Eur. J.* **1996**, *2*, 1150–1158.
[20] a) A. Higuchi, H. Inada, T. Kobata, Y. Shirota, *Adv. Mater.* **1991**, *3*, 549–550; b) S. A. Jenekhe, L. Lu, M. M. Alam, *Macromolecules* **2001**, *34*, 7315–7324; c) R. Y. Lai, X. Kong, S. A. Jenekhe, A. J. Bard, *J. Am. Chem. Soc.* **2003**, *125*, 12631–12639; d) F. Fungo, S. A. Jenekhe, A. J. Bard, *Chem. Mater.* **2003**, *15*, 1264–1272; e) X. Kong, A. P. Kulkarni, S. A. Jenekhe, *Macromolecules* **2003**, *36*, 8992–8999; f) D. H. Hwang, S. K. Kim, M. J. Park, J. H. Lee, B. W. Koo, I. N. Kang, S. H. Kim, T. Zyung, *Chem. Mater.* **2004**, *16*, 1298–1303.
[21] a) M. J. Cho, J. Y. Kim, K. Ja Youn, J. H. Kim, S. H. Lee, L. R. Dalton, D. H. Choi, *Bull. Korean Chem. Soc.* **2005**, *26*, 77–84; b) C. Petry, M. Lang, H. A. Staab, H. Bauer, *Angew. Chem.* **1993**, *105*, 1791–1795; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1711–1714.
[22] a) T. J. J. Müller, *Tetrahedron Lett.* **1999**, *40*, 6563–6566; b) C. S. Krämer, K. Zeitler, T. J. J. Müller, *Org. Lett.* **2000**, *2*, 3723–3726; c) C. S. Krämer, T. J. J. Müller, *Eur. J. Org. Chem.* **2003**, 3534–3548.
[23] M. Hauck, J. Schönhaber, A. J. Zucchero, K. I. Hardcastle, T. J. J. Müller, U. H. F. Bunz, *J. Org. Chem.* **2007**, *72*, 6714–6725.
[24] a) C. S. Krämer, T. J. Zimmermann, M. Sailer, T. J. J. Müller, *Synthesis* **2002**, 1163–1170; b) T. J. Zimmermann, T. J. J. Müller, *Synthesis* **2002**, 1157–1162; c) C. S. Krämer, K. Zeitler, T. J. J. Müller, *Tetrahedron Lett.* **2001**, *42*, 8619–8624; d) M. Sailer, R.-A. Gropeanu, T. J. J. Müller, *J. Org. Chem.* **2003**, *68*, 7509–7512; e) M. Sailer, M. Nonnenmacher, T. Oeser, T. J. J. Müller, *Eur. J. Org. Chem.* **2006**, 423–435.
[25] M. Sailer, F. Rominger, T. J. J. Müller, *J. Organomet. Chem.* **2006**, *691*, 299–308.
[26] a) N. Bucci, T. J. J. Müller, *Tetrahedron Lett.* **2006**, *47*, 8329–8332; b) N. Bucci, T. J. J. Müller, *Tetrahedron Lett.* **2006**, *47*, 8323–8327.
[27] J. Jo, C. Chi, S. Höger, G. Wegner, D. Y. Yoon, *Chem. Eur. J.* **2004**, *10*, 2681–2688.
[28] B. H. Lipshutz, K. Siegmann, E. Garcia, F. Kayser, *J. Am. Chem. Soc.* **1993**, *115*, 9276–9282.
[29] Gaussian 03 (Revision C.03), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.
[30] L. Yang, J.-K. Feng, A.-M. Ren, *J. Org. Chem.* **2005**, *70*, 5987–5996.
[31] C. Bubeck in *Electronic Materials: The Oligomer Approach* (Eds.: K. Müllen, G. Wegner), Wiley-VCH, Weinheim, **1998**, pp. 449–478.
[32] G. N. Lewis, M. Calvin, *Chem. Rev.* **1939**, *25*, 273–328.
[33] G. Jones, II, W. R. Jackson, C. Y. Choi, W. R. Bergmark, *J. Phys. Chem.* **1985**, *89*, 294–300.

[34] For a recent review on π-stacking of radical ions, see, for example, T. Nishinaga, K. Komatsu, *Org. Biomol. Chem.* **2005**, *3*, 561–569.
[35] *Organikum*, 21 st ed., H. G. O. Becker, R. Beckert, G. Domschke, E. Fanghänel, W. D. Habicher, P. Metz, D. Pavel, K. Schwetlick, Wiley-VCH, Weinheim, **2001**.
[36] P. Zanello, in *Ferrocenes* (Eds.: A. Togni, T. Hayashi), VCH, Weinheim, **1995**, pp. 317–430.
[37] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 2nd ed., Kluwer Academic/Plenum Publisher New York, **1999**, p. 52–53.
[38] D. Clarke, B. C. Gilbert, P. Hanson, C. M. Kirk, *J. Chem. Soc. Perkin Trans. 2* **1978**, 1103–1110.
[39] J. Cymerman-Craig, W. P. Rogers, G. P. Warwick, *Aust. J. Chem.* **1955**, *8*, 252–257.

Received: August 28, 2007
Published online: January 22, 2008

