DOI: 10.1002/ejoc.200500539

Synthesis and Electronic Properties of 3-Acceptor-Substituted and 3,7-Bisacceptor-Substituted Phenothiazines

Markus Sailer,[a] Michael Nonnenmacher,[a] Thomas Oeser,[a][‡] and Thomas J. J. Müller*[a]

Keywords: Catalysis / Cyclic voltammetry / Fluorescence / Heterocycles / Substituent effects

3-Acceptor-substituted and 3,7-bisacceptor-substituted phenothiazines can be synthesized in moderate to excellent yields through Suzuki cross-coupling reactions between phenothiazin-3-yl pinacolyl boronates or phenothiazin-3,7-diyl bis(pinacolyl boronates) and electron-deficient (hetero)aryl halides. The electronic properties of (hetero)aryl-substituted *N*-methyl phenothiazines (UV/Vis absorption, fluorescence, redox potentials) can be correlated with the computed energies of the frontier molecular orbitals. Nitro-substituted derivatives reveal electronically amphoteric behavior, displaying both reversible oxidations and reversible reductions. X-ray structure analysis of the phenothiazinyl *p*-(2,5-dinitro)phenylene-bridged dyad **13** revealed donor–acceptor interactions between the molecules. Pyridyl and pyrimidyl derivatives fluoresce with quantum yields (Φ_f) of up to 49 % and can be regarded as redox-active fluorophores.

Introduction

Donor–acceptor (Do–Acc) or push-pull substitution is a fundamental heuristic concept in the design of functional π-electron systems[1] that has been well studied theoretically[2] and now allows reliable prediction of functional chromophores for basic research in future molecular electronics and for technical applications as high-performance dyes.[3] Additionally, functional π-electron systems with Acc–Do and Acc–Do–Acc topologies based upon reversible heterocyclic redox units displaying electronic bi- or multistability (e.g., neutral-radical ion, or even several stable oxidation states) are highly intriguing as electrochemically addressable switches (native-doped; ON-OFF),[4] low bandgap polymers,[5] and as functional units and building blocks in single-molecule-based molecular electronics.[6] In particular, phenothiazines,[7] a pharmaceutically important class of heterocycles (known as pharmacophores in sedatives, tranquilizers, antiepilectics, antituberculotics, antipyretics, antitumor agents, bactericides, and parasiticides)[8] possess low and highly reversible first oxidation potentials[7,9] with a pronounced propensity to form stable radical cations. Interestingly, this peculiar property is also responsible for their physiological activities[10] and phenothiazines have moreover also been found to be able to cleave DNA upon UV irradiation.[11] As a consequence the favorable electronic properties of phenothiazines have given rise to applications as electrophore probes in supramolecular assemblies[12] for PET (**p**hoto-induced **e**lectron **t**ransfer) and sensor studies, and as electron donor components – in electrically conducting charge-transfer composites,[13] polymers,[14] and donor–acceptor arrangements,[15] for example – in materials science investigations. We therefore became interested in electronic effects on phenothiazine oxidation potentials, and also in absorption and emission behavior upon remote 3-mono- and 3,7-bisacceptor substitution. We have recently reported on the syntheses and electronic properties of 3-mono- and 3,7-dialkynylated phenothiazines **1** and **2** (Scheme 1),[16] and on initial approaches to directly linked biphenothiazinyls **3** and terphenothiazinyls **4** as part of our program to establish a bottom-up approach to redox-active nanometer-scale molecular wires.[17] Most remarkably, these di- and trimers display intense intramolecular electronic communication, as shown by cyclic voltammetry. Here we wish to report the syntheses and electronic properties (cyclic voltammetry, absorption and emission spectroscopy, together with DFT calculations) of 3-mono- (Acc–phenothiazine) and 3,7-bisacceptor-substituted phenothiazines (Acc–phenothiazine–Acc).

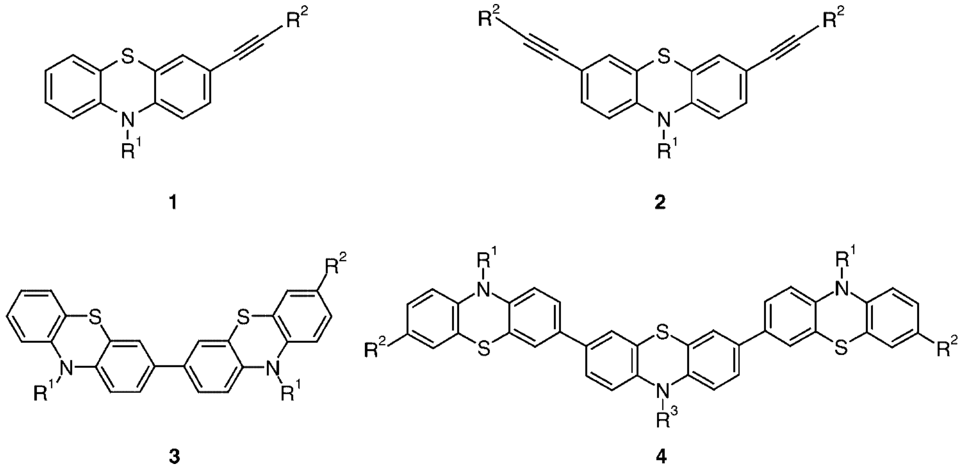
Syntheses and Structures of 3-(Hetero)aryl and 3,7-Di(hetero)aryl Phenothiazines

We have recently established a facile and general route to 3-mono- and 3,7-diarylated phenothiazines, symmetrical and unsymmetrical diphenothiazines, and symmetrical terphenothiazines, based upon Suzuki arylations with 3-mono- and 3,7-diborylated phenothiazines as organometallic building blocks.[17] This straightforward strategy is well suited as a route to a wide selection of C-arylated phenothiazines for explaining remote electronic substituent effects on the phenothiazine cores' oxidation potentials. The 3-

---

[a] Organisch-Chemisches Institut der Ruprecht-Karls-Universität Heidelberg,
Im Neuenheimer Feld 270, 69120 Heidelberg
E-mail: Thomas_J.J.Mueller@urz.uni-heidelberg.de

[‡] X-ray structure analysis of compound **13**.



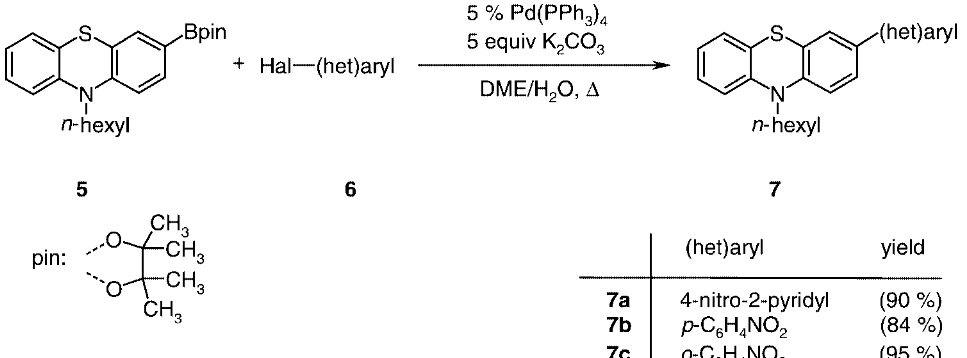
Scheme 1.

(hetero)arylated phenothiazines **7** were thus isolated in good to excellent yields – either as a red-violet solid (**7a**) or as yellow to orange-red oils (**7b**–**7g**) – upon subjection of pinacolyl 10-hexyl-10*H*-phenothiazin-3-yl boronate (**5**) and (hetero)aryl halides **6** to the presence of catalytic amounts of $Pd(PPh_3)_4$ and excess potassium carbonate in boiling mixtures of dimethoxyethane (DME) and water (Scheme 2).

Furthermore, bis(pinacolyl) 10-hexyl-10*H*-phenothiazine-3,7-diyl bisboronate (**8**) and a range of electronically diverse (hetero)aryl halides **6** (2.5 equiv. each) were heated in boiling mixtures of DME and water in the presence of catalytic amounts of $Pd(PPh_3)_4$ and excess potassium carbonate to furnish 3,7-di(hetero)aryl phenothiazines **9** in good to excellent yields, either as yellow to orange-red solids (**9a**–**f**, **9i**–**k**) or as resins (**9g**, **9h**) (Scheme 3).

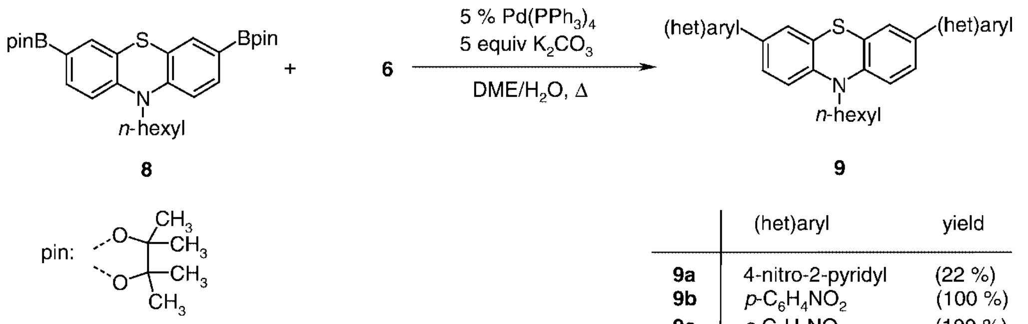
The dumbbell-shaped diphenothiazines **12** and **13**, expanded by nitro-substituted electron-deficient phenylene bridges, were likewise obtained in moderate yields as red to dark red solids upon Suzuki coupling of **5** (2 equiv.) and 1,4-dibromo-2-nitrobenzene (**10**) or 1,4-dibromo-2,5-dinitrobenzene (**11**) (Scheme 4).

The spectroscopic/spectrometric (^1H and ^{13}C NMR, IR, MS) and combustion analytical data unambiguously support the structural assignments of the Acc–phenothiazine (**7**), Acc–phenothiazine–Acc/Do–phenothiazine–Do (**9**), and phenothiazine–Acc–phenothiazine (**12** and **13**) systems. As a consequence of the C_S symmetry of the 3,7-disubstituted phenothiazines **9** and the bridged system **13** the appearance of a single set of resonances for the magnetically and chemically equivalent inner phenothiazinyl cores (**9**) and the terminal phenothiazinyl fragments (**13**) in the proton and the carbon NMR spectra confirms the highly symmetric solution structures of these dumbbell-shaped entities. Most characteristically for all *N*-hexyl-substituted phenothiazines the amino methylene protons appear as triplets between $\delta = 3.9$ and $\delta = 4.1$ ppm with vicinal coupling constants of 7.0–7.4 Hz. For the aromatic phenothiazinyl proton resonances, well resolved coupling patterns of the signals are found in some cases between $\delta = 6.9$ and $\delta = 8.3$ ppm. Another typical spectroscopic characteristic of the (hetero)aryl-substituted and bridged phenothiazines is found in the mass spectra. Not only is the molecular peak,



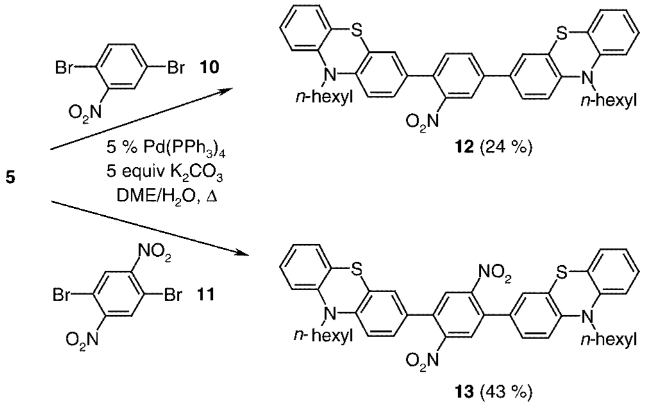
	(het)aryl	yield
7a	4-nitro-2-pyridyl	(90 %)
7b	*p*-$C_6H_4NO_2$	(84 %)
7c	*o*-$C_6H_4NO_2$	(95 %)
7d	*m*-$C_6H_4NO_2$	(94 %)
7e	2-pyrimidyl	(65 %)
7f	4-pyridyl	(96 %)
7g	2-pyridyl	(99 %)

Scheme 2. 3-Monoacceptor-substituted phenothiazines (Acc–phenothiazine) **7** obtained by Suzuki coupling.



	(het)aryl	yield
9a	4-nitro-2-pyridyl	(22 %)
9b	p-$C_6H_4NO_2$	(100 %)
9c	o-$C_6H_4NO_2$	(100 %)
9d	m-$C_6H_4NO_2$	(70 %)
9e	2-pyrimidyl	(76 %)
9f	4-pyridyl	(76 %)
9g	2-pyridyl	(87 %)
9h	3-pyridyl	(98 %)
9i	p-$C_6H_4OCH_3$	(72 %)
9j	p-$C_6H_4N(CH_3)_2$	(22 %)
9k	2,4-$(NO_2)C_6H_3$	(100 %)

Scheme 3. 3,7-Di(hetero)aryl-substituted phenothiazines (Acc–phenothiazine–Acc and Do–phenothiazine–Do) **9** obtained by Suzuki coupling.



Scheme 4. Dumbbell-shaped nitrophenylene-bridged diphenothiazines (phenothiazine–Acc–phenothiazine) **12** and **13**.

representing a radical cation, present for all compounds, but in most cases it is also accompanied by the basis peak. The fragmentation occurs through the expected α-cleavage of the *n*-hexyl substituent. In addition, an X-ray crystal structure analysis of the dumbbell-shaped diphenothiazine **13**[18] (Figure 1) clearly shows the characteristic butterfly conformation[7] of the phenothiazine moieties, with torsion angles of 151.3(3)° (C12–N1–C14–C5), –154.7(3)° (C14–N1–C12–C4), –151.3(2)° (C11–S1–C13–C8), and 148.6(2)° (C13–S1–C11–C1), and the torsion with respect to the 2,5-dinitrophenylene bridge, with an interplanar angle of 49.3(3)° (plane C17A–C15–C16 vs. plane C1–C2–C3). The bond lengths of the phenothiazinyl moieties and the aryl bridge also lie within the expected margins. Furthermore, the *N*-hexyl substituents adopt a pseudoequatorial arrangement with only a slight deviation from coplanarity, of

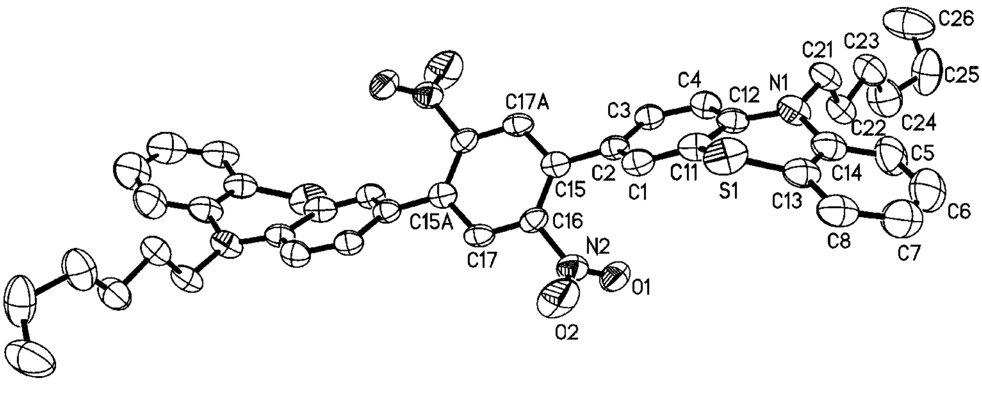


Figure 1. ORTEP plots of the dumbbell-shaped diphenothiazine **13** (side-on view, hydrogen atoms and second disorder positions have been omitted for clarity). Selected bond lengths [Å] and angles [°]: C2–C15: 1.478(4), C16–N2: 1.480(4), N2–O1: 1.215(3), N2–O2: 1.206(3), N1–C12: 1.404(4), C11–S1: 1.760(3), N1–C21: 1.472(4), ∢ plane C17A–C15–C16/plane C1–C2–C3: 49.3(3)°, ∢ plane O2–N2–O1/plane C17–C16–C15: 59.8(4)°, C12–N1–C14–C5: 151.3(3)°, C14–N1–C12–C4: –154.7(3)°, C11–S1–C13–C8: –151.3(2)°, C13–S1–C11–C1: 148.6(2)°, C21–N1–C12–C4: 6.1(4)°, C21–N1–C14–C5: –9.4(4)°.

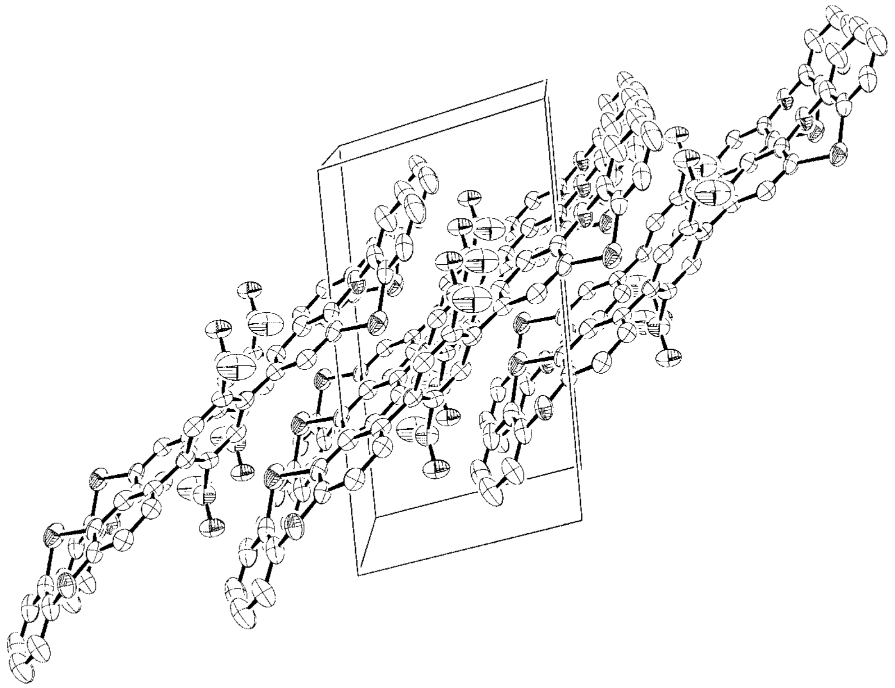


Figure 2. Crystal packing of the dumbbell-shaped diphenothiazine **13** (hydrogen atoms and hexyl groups have been omitted for clarity; perspective view along the *a*-axis).

6.1(4)° (C21–N1–C12–C4) and –9.4(4)° (C21–N1–C14–C5). In the crystal packing the phenothiazine–Acc–phenothiazine entities are arranged through donor–acceptor interactions between the stacks (i.e., phenothiazine donor fragments are positioned with the sulfur atoms in edge-on proximity of 3.9 Å over and under the centroid of the dinitrophenylene acceptor moiety; Figure 2).

Electronic Structures and Properties of (Hetero)aryl-Substituted and Bridged Phenothiazines

The electronic structures and properties of (hetero)aryl-substituted and bridged phenothiazines have been investigated by experimental (absorption and emission spectra, cyclic voltammetry) and computational (DFT calculations on the ethyl-substituted derivatives)[19] methods (Table 1).

Optical spectroscopy (UV/Vis and fluorescence spectra) reveals that only systems without nitro substitution display considerable fluorescence, with emission of blue to blue-green light and remarkable Stokes shifts ($\Delta\tilde{\nu}$ = 6800–11400 cm^{-1}). The longest-wavelength absorption maxima correlate reasonably well (with the exception of 2-nitrophenyl-substituted derivatives **7c** and **9c**) with the calculated HOMO–LUMO gaps $\Delta_{\text{HOMO–LUMO}}$ ($\lambda_{\text{max,abs.}}$ [cm^{-1}] – $\Delta_{\text{HOMO–LUMO}}$ [eV]; r^2 = 0.954), indicating that the major contribution of this transition arises from the charge-transfer character, from the phenothiazine-centered HOMOs to the acceptor-centered LUMOs (Figure 3). Interestingly, among the fluorescent pyridyl and pyrimidyl derivatives in the 3-monosubstituted systems **7e**–**g** the emission maxima correlate only with the LUMO energies ($\lambda_{\text{max,em.}}$ [cm^{-1}] – LUMO [eV]; r^2 = 0.981), but not with the HOMO–LUMO gap (excitation energy; r^2 = 0.414) nor with the HOMO (oxidation potential; r^2 = 0.003). On the other hand the emission maxima of the corresponding 3,7-disubstituted systems **9e**–**g** correlate only poorly with the LUMO energies ($\lambda_{\text{max,em.}}$ [cm^{-1}] – LUMO [eV]; r^2 = 0.768). This can be interpreted as meaning that for the less symmetrical monosubstituted systems **7e**–**g** the structure of the excited S_1 state responsible for fluorescence behavior is largely characterized by an increase in dipole moment with respect to the ground state.[20] Hence, the emission behavior can be very sensitive to solvent polarity. Another issue of fluorescence efficiency, as reflected in the determined fluorescence quantum yields (Φ_f),[21] represents the conformational coplanarity of the substituents. 2-Pyridyl- (**7g** and **9g**) and 2-pyrimidyl-substituted (**7e** and **9e**) phenothiazines fluoresce with significant higher quantum yields (Φ_f = 21–49%) than the 4- or 3-substituted representatives **7f**, **9f**, and **9h** (Φ_f = 3–6%). As a consequence of the coplanar arrangement of the 2-pyrimidyl substituents with the phenothiazine cores (**7e** and **9e**) the longest-wavelength electronic transitions from HOMO to LUMO possess significant charge-transfer character (Figure 4) and become more efficient both for absorption and spontaneous emission.

Electrochemical data for the (hetero)aryl monosubstituted (**7**), disubstituted (**9**), and bridged (**12** and **13**) phenothiazines were obtained by cyclic voltammetry in the anodic (up to +1.5 V) and cathodic regions (up to –2.0 V). The measurements reveal that for the monoacceptor-substituted (**7**) and bisacceptor-substituted phenothiazines (**9a**–**h**, **9k**),

Table 1. Absorption and emission spectra, cyclic voltammetry, and DFT calculations for the ethyl-substituted derivatives.

Compound	Absorption[a] $\lambda_{\text{max,abs.}}$ [nm] (ε)	Emission[b] $\lambda_{\text{max,em.}}$ [nm] (Φ_f)	Stokes shift $\Delta\bar{\nu}$ [cm^{-1}]	$E_{1/2}$[c] [mV]	HOMO[d] [eV]	LUMO[d] [eV]	$\Delta_{\text{HOMO–LUMO}}$ [eV]
7a	258 (24400), 308 (14200), 442 (9900)	–	–	790; –1100	–5.380	–2.604	2.776
7b[e]	257 (23900), 295 (15100), 409 (8000)	–	–	770; –1110	–5.357	–2.366	2.991
7c	262 (32700), 280 (12200), 304 (7700)	–	–	746; –1290	–5.166	–2.187	2.979
7d	238 (22500), 268 (25500), 312 (8700)	–	–	750; –1210	–5.293	–2.352	2.941
7e	246 (20100), 274 (25600), 290 (19500), **362** (6900)	**509** (38%)	8000	734	–5.047	–1.299	3.748
7f	244 (19800), 272 (25900), 292 (15700), **318** (7200)	**499** (6%)	11400	766	–5.226	–1.159	4.067
7 g	240 (16600), 270 (25200), 288 (13900), **328** (7100)	**490** (21%)	10100	700	–5.030	–1.079	3.951
9a	256 (31000), 312 (30900), 454 (23900), 576 (1800)	–	–	870; –1121	–5.566	–2.831	2.735
9b	256 (23900), 296 (26700), 418 (14600)	–	–	810; –1160[f]	–5.509	–2.540	2.969
9c	266 (31000), 354 (4400), 370 (3600)	–	–	790; –1300[f]	–5.140	–2.256	2.884
9d	282 (45900), 332 (9800)	–	–	800; –1200[f]	–5.386	–2.462	2.924
9e	242 (24900), 292 (48100), 360 (28400), **366** (28400)	**511**(49%)	7800	760	–4.956	–1.453	3.503
9f	236 (26700), 286 (35800), **366** (9500)	**497** (3%)	7200	810	–5.279	–1.427	3.852
9g	250 (20500), 288 (39500), **368** (10800)	**492** (24%)	6800	700; 1410	–4.927	–1.238	3.689
9h	280 (37000), **336** (10000)	**477** (5%)	8800	760	–5.148	–1.203	3.945
9i	250 (27800), 280 (64700), 334 (14600)	–	–	600; 1230	–4.748	–0.673	4.075
9j	250 (23400), 302 (52300), 342 (24900)	–	–	560; 830	–4.470	–0.469	4.001
9k	257 (45900), 296 (15600), 444 (10400)	–	–	900; –980[f]	–	–	–
12	243 (13900), 267 (17900), 365 (5700)	–	–	750; –1280	–	–	–
13	242 (46000), 266 (6400), 316 (20900), 428 (5000)	–	–	800	–	–	–
10-hexylphenothiazine	256 (33000), 311 (5100)	–	–	728	–4.702	–1.723	2.979
nitrobenzene	258 (qual.)[26]	–	–	–1147	–7.102	–3.822	3.280

[a] Recorded in CH_2Cl_2. [b] Recorded in $CHCl_3$ with 7-(diethylamino)-4-methylchromen-2-one (coumarin 1; $\Phi f = 0.73$)[21] as a standard. [c] Recorded in CH_2Cl_2. [d] Calculated for the ethyl-substituted derivative. [e] Recorded in $CHCl_3$. [f] Reversible two-electron reduction.

and also for the acceptor-bridged diphenothiazines (**12** and **13**), the first reversible phenothiazine-centered oxidation potential can be fine-tuned with a suitable acceptor substituent in an $E_0^{0/+1}$ range between 700 and 900 mV. Both bisdonor-substituted derivatives **9i** and **9j** display considerably lower oxidation potentials and are found at $E_0^{0/+1}$ = 600 and 560 mV. In addition, in the nitro-substituted derivatives, reversible reductions in the nitro(hetero)aryl fragment occur at potentials between $E_0^{0/-1}$ = –980 to –1111 mV (**3a**, **3b**) and $E_0^{0/-2}$ = –980 to –1300 mV (**9a–d**, **9k**, **12**), respectively.

Closer inspection of the electrochemical behavior of the nitrophenyl-substituted phenothiazines **7b–d** and **9b–d** shows that the reversible one-electron oxidations at $E_0^{0/+1}$ = 746–810 mV are anodically shifted relative to that of *N*-hexyl phenothiazine ($E_0^{0/+1}$ = 728 mV) as a consequence of the electron-withdrawing substituents (Figure 5, Figure 6, and Figure 7). Similarly, the reductions of the nitrophenyl

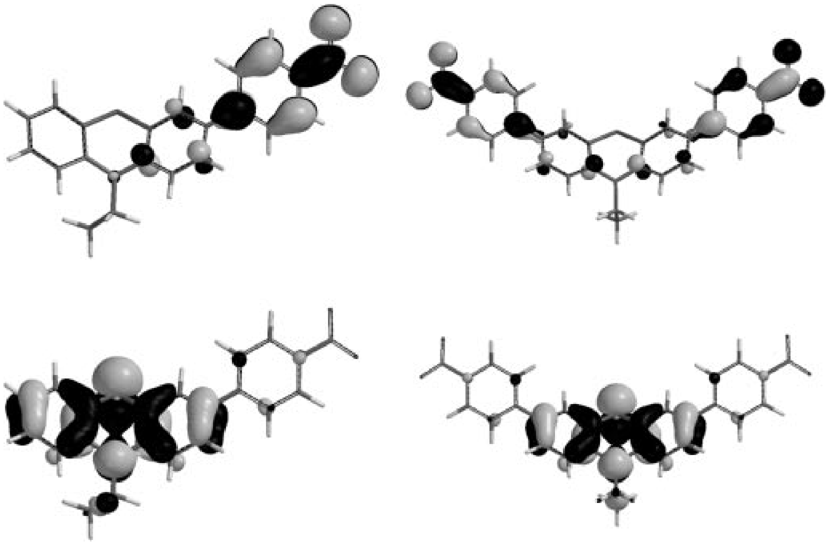


Figure 3. LUMOs (top) and HOMOs (bottom) of **7b** (left) and **9b** (right).

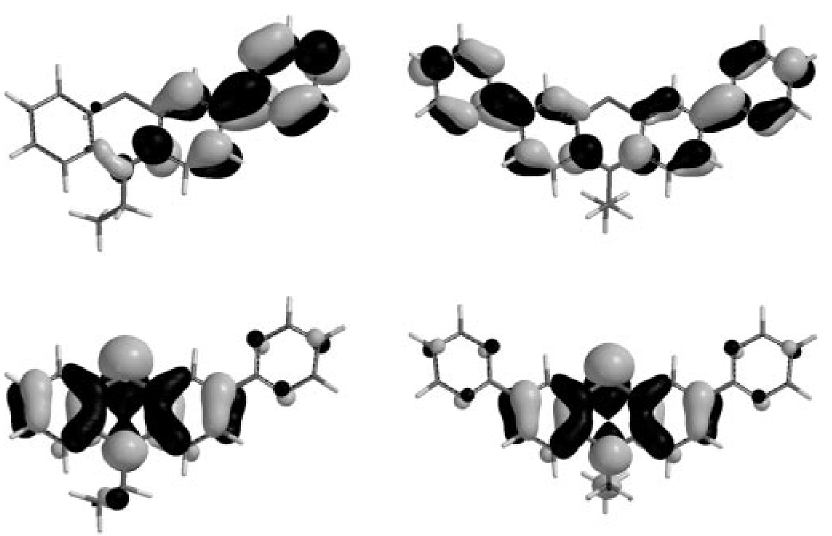


Figure 4. LUMOs (top) and HOMOs (bottom) of **7e** (left) and **9e** (right).

moieties experience the electron-releasing nature of the phenothiazinyl core and the reversible reduction waves are shifted cathodically. In comparison to nitrobenzene ($E_0^{0/-1}$ = –1147 mV) this radical anion formation is impeded by the donor character of phenothiazine. These systems can therefore be identified as electrochemically amphoteric push-pull chromophores that can reversibly accept or donate electrons at relatively low voltages. For applications in OLEDs (**o**rganic **l**ight-**e**mitting **d**iodes),[22] OFETs (**o**rganic **f**ield-**e**ffect **t**ransistors),[23] or molecular rectifiers[6] as functional hole and electron transport molecules this is a rather favorable property. In addition, however, the fluorescent representatives (**7e**, **7g**, **9e**, and **9g**) could serve as redox-switchable emitters in OLED devices.

For establishing semiquantitative structure–electronic property relationships it became apparent that the oxidation potentials $E_0^{0/+1}$ of 3-(hetero)aryl-substituted (**7**) and 3,7-di(hetero)aryl-substituted *N*-hexyl phenothiazines (**9**) correlate reasonably well with the corresponding HOMO energies calculated at the DFT level of theory[19] (r^2 = 0.869). With the exception of the *ortho*-nitrophenyl-substituted systems **7b** and **9b** the calculated LUMO energies also correlate excellently with the reversible one-electron reduction potentials ($E_0^{0/-1}$) of 3-substituted derivatives **7** (r^2 = 0.999) and the reversible two-electron reduction potentials ($E_0^{0/-2}$) of 3,7-disubstituted systems **9** (r^2 = 0.948). As already shown for alkynyl-substituted phenothiazines,[16c] the best correlation (r^2 = 0.940) of the electrochemical data and the Hammett substitution parameters can be established between $E_0^{0/+1}$and σ_P, indicating that the electronic communication between the remote substituent and the phenothiazine electrophore is transmitted through resonance and field effects. Rational design of tailor-made (hetero)aryl-substituted phenothiazine electrophores with fine-

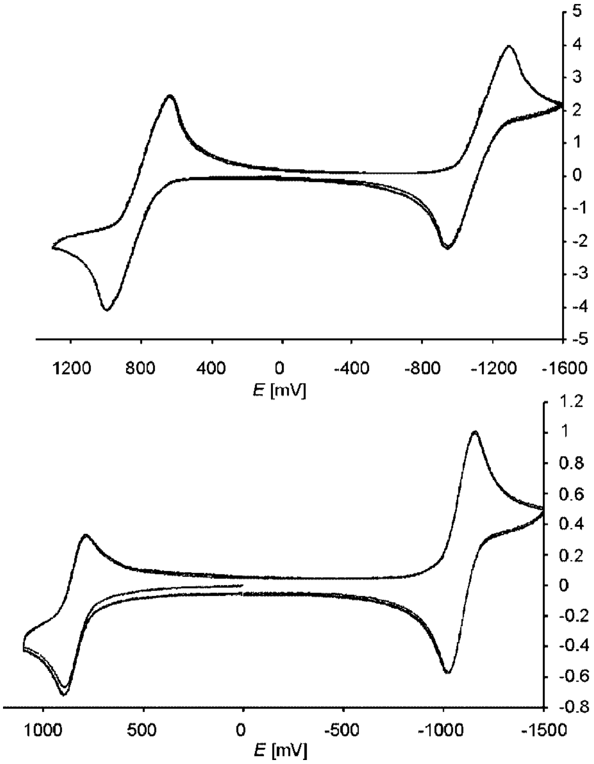


Figure 5. Cyclic voltammograms of **7a** (top) and **9a** (bottom) in CH_2Cl_2: T = 293 K, electrolyte = NBu_4PF_6 (0.1 M in CH_2Cl_2), v = 100 $mV s^{-1}$, Pt as a working electrode, Ag/AgCl as a reference electrode, and Pt as a counter-electrode (determined vs. ferrocene, $E_0^{0/+1}$= +450 mV).

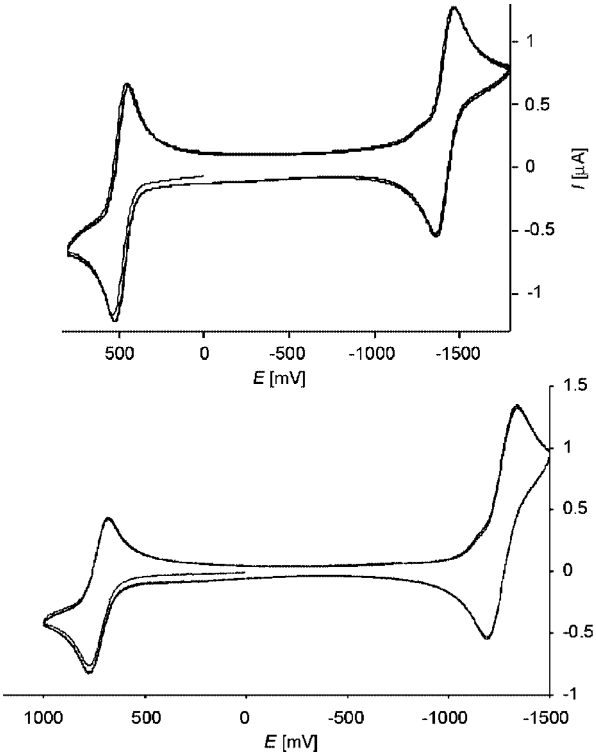


Figure 6. Cyclic voltammograms of **7b** (top) and **9b** (bottom) in CH_2Cl_2: T = 293 K, electrolyte = NBu_4PF_6 (0.1 M in CH_2Cl_2), v = 100 $mV s^{-1}$, Pt as a working electrode, Ag/AgCl as a reference electrode, and Pt as a counter-electrode (determined vs. ferrocene, $E_0^{0/+1}$= +450 mV).

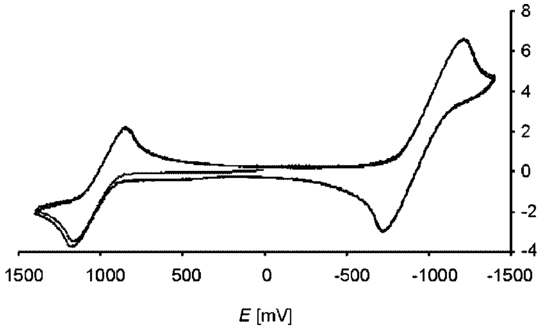


Figure 7. Cyclic voltammogram of **9k** in CH_2Cl_2: T = 293 K, electrolyte = NBu_4PF_6 (0.1 M in CH_2Cl_2), v = 100 $mV s^{-1}$, Pt as a working electrode, Ag/AgCl as a reference electrode, and Pt as a counter-electrode (determined vs. ferrocene, $E_0^{0/+1}$= +450 mV).

tunable oxidation potentials can therefore now predictably be founded on this correlation of experimentally measured and computationally calculated electronic properties.

Conclusions

In conclusion, we have been able to show that phenothiazines with broad patterns of electronically diverse conjugated substituents can be readily synthesized by application of Suzuki arylation to borylated phenothiazinyl derivatives and halo (hetero)arenes. Both electronic spectra (UV/Vis and fluorescene) and cyclic voltammetry reveal a strong influence of the remote substituents on the oxidation potential of the phenothiazinyl moiety. These data can be reasonably well interpreted by correlation with computationally determined energies of the frontier orbitals. These novel functionalized oligomers are therefore excellent candidates as redox-addressable functional chromophores and fluorophores. Further studies directed towards higher oligomer and polymer syntheses, as well as investigation of their electronic structures and photophysical behavior, are currently underway.

Experimental Section

All reactions were carried out in flame-dried Schlenk flasks under argon. Reagents, catalysts, and ligands were purchased as reagent grade and were used without further purification. Solvents were dried and distilled by standard procedures.[24] Pinacolyl 10-hexyl-10*H*-phenothiazin-3-yl boronate (**5**) and bis(pinacolyl) 10-hexyl-10*H*-phenothiazin-3,7-diyl bisboronate (**8**) were prepared by our previously published procedure.[17c] Column chromatography: silica gel 60, mesh 70–230. TLC: silica gel plates. Melting points: uncorrected values. ^1H and ^{13}C NMR spectra: [D$_6$]acetone or CD_2Cl_2 (locked to Me_4Si). The assignments of quaternary C, CH, CH_2 and CH_3 were made with the aid of DEPT spectra. Elemental analyses were carried out in the Microanalytical Laboratories of the Organisch-Chemisches Institut, Ruprecht-Karls-Universität, Heidelberg, 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 $mV s^{-1}$. 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).[25]

X-ray Structure Determination of Compound 13: Suitable crystals were mounted on a Hampton Research Cryo Loop and transferred to a Bruker Smart CCD 1 K diffractometer. The structure was solved by direct methods and refined anisotropically on F^2 (SHELXTL V5.10, and SADABS V2.03 for absorption correction, G. M. Sheldrick, University of Göttingen (Germany), and Bruker Analytical X-ray Division, Madison, Wisconsin (USA), 1997 and 2001). Hydrogen atoms were calculated according to stereochemical aspects and refined constrained. The molecule lies upon a crystallographic center of inversion and the outer two carbon atoms were found to be disordered (54%:46%). The data from the X-ray structure analysis of **13** are summarized in Table 2.

Table 2. Crystal data and structure refinements for **13**.

Compound	**13**
Empirical formula	$C_{42}H_{42}N_4O_4S_2$
Formula weight	730.92
Temperature [K]	200(2) K
Wavelength [Å]	0.71073 Å
Crystal system	triclinic
Space group	$P\bar{1}$
Z	1
Unit cell dimensions	a = 8.2259(6) Å, α = 102.287(2)° b = 8.5093(7) Å, β = 92.685(2)° c = 14.060(1) Å, γ = 106.805(2)°
Volume [Å^3]	914.4(1)
Density (calculated) [g cm^{-3}]	1.33
Absorption coefficient [mm^{-1}]	0.19
Crystal size (mm^3)	0.34 × 0.26 × 0.08
Theta range for data collection [°]	1.5 to 22.8
Index ranges	$-8 \le h \le 8$ $-9 \le k \le 9$ $-15 \le l \le 15$
Reflections collected	6503
Independent reflections	2455 [R(int.) = 0.050]
Observed reflections	1653 [$I > 2\sigma(I)$]
Absorption correction	semiempirical from equivalents
Max. and min. transmission	0.98 and 0.94
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	2455/10/254
Goodness-of-fit on F^2	1.02
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.048, wR_2 = 0.110
Largest diff. peak/hole [e·Å^{-3}]	0.23/–0.26

Suzuki Coupling between Pinacolyl 10-Hexylphenothiazin-3-yl Boronate (5) and (Hetero)aryl Halides 6 (General Procedure): A mixture of **5** (1.0 equiv.), the (hetero)aryl halide **6** (1.2–1.5 equiv.), potassium carbonate (4–5 equiv.), and a palladium tetrakis(triphenylphosphane) catalyst (0.05 equiv.) was dissolved in a mixture of degassed 1,2-dimethoxyethane and water (2:1, 0.05 M) and the reaction mixture was then stirred at 90 °C (oil bath) for 18 h (see Table 3 for experimental details). After cooling to room temp. the reaction mixture was diluted with ethyl acetate (80 mL). The organic phase was washed with water and brine, the aqueous layer was extracted with ethyl acetate, and the combined organic phases were finally dried with magnesium sulfate. The solvents were evaporated in vacuo and the residue was chromatographed on silica gel to furnish the pure 3-(hetero)arylated phenothiazine **7**, either as a red-violet solid (**7a**) or as a yellow to orange-red oil (**7b**–**g**).

10-Hexyl-3-(5-nitropyridin-2-yl)-10*H*-phenothiazine (7a): This compound was prepared as described in the GP; after chromatography on silica gel (acetone/hexane, 1:3), **7a** (364 mg, 90%) was isolated as a violet solid. R_f (acetone/hexane, 1:5) = 0.39. ^1H NMR ([D$_6$]acetone, 300 MHz): δ = 0.86 (m, 3 H), 1.32 (m, 4 H), 1.49 (m, 2 H), 1.83 (m, 2 H), 4.03 (t, J = 7.0 Hz, 2 H), 6.96–7.25 (m, 5 H), 8.01–8.18 (m, 3 H), 8.57 (dd, J = 2.9, 9.2 Hz, 1 H), 9.38 (m, 1 H) ppm. ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 14.2 (CH_3), 23.2 (CH_2), 27.1 (CH_2), 27.5 (CH_2), 32.1 (CH_2), 48.1 (CH_2), 116.6 (CH), 117.0 (CH), 120.0 (CH), 123.9 (CH), 124.6 ($C_{quat.}$), 125.8 ($C_{quat.}$), 127.0 (CH), 128.1 (CH), 128.1 (CH), 128.5 (CH), 132.0 ($C_{quat.}$), 133.0 (CH), 143.7 ($C_{quat.}$), 145.2 ($C_{quat.}$), 145.2 ($C_{quat.}$), 145.8 (CH), 148.6 ($C_{quat.}$), 161.5 ($C_{quat.}$) ppm. IR (KBr): $\tilde{\nu}$ = 2930, 2855, 1638, 1595, 1569, 1515, 1457, 1410, 1344, 1271, 1252, 1117, 822, 768, 743 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 258 nm (24400), 308 (14200), 442 (9900). MS (70 eV, CI): m/z (%) = 406.2 (100) [M]$^+$. $C_{23}H_{23}N_3O_2S$ (405.5): calcd. C 68.12, H 5.72, N 10.36, S 7.91; found C 68.13, H 5.78, N 10.13, S 7.89.

10-Hexyl-3-(4-nitrophenyl)-10*H*-phenothiazine (7b): This compound was prepared as described in the GP; after chromatography on silica gel (pentane/diethyl ether, 4:1) **7b** (170 mg, 84%) was isolated as a red, viscous oil. R_f (diethyl ether/pentane, 1:4) = 0.64. ^1H NMR ([D$_6$]acetone, 300 MHz): δ = 0.84 (m, 3 H), 1.27–1.32 (m, 4 H), 1.46 (m, 2 H), 1.80 (m, 2 H), 3.97 (t, J = 7.1 Hz, 2 H), 6.95 (t, J = 6.6 Hz, 1 H), 7.03–7.23 (m, 4 H), 7.52 (d, J = 2.0 Hz, 1 H), 7.59 (dd, J = 2.2, 8.5 Hz, 1 H), 7.88 (d, J = 8.7 Hz, 2 H), 8.25 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 14.2 (CH_3), 23.2 (CH_2), 27.1 (CH_2), 27.4 (CH_2), 32.1 (CH_2), 47.9 (CH_2), 116.8 (CH), 116.9 (CH), 123.6 (CH), 124.7 ($C_{quat.}$), 124.8 (CH), 126.2 ($C_{quat.}$), 126.5 (CH), 127.4 (CH), 127.8 (CH), 128.0 (CH), 128.5 (CH), 133.2 ($C_{quat.}$), 145.5 ($C_{quat.}$), 146.9 ($C_{quat.}$), 147.0 ($C_{quat.}$), 147.6 ($C_{quat.}$) ppm. IR (KBr): $\tilde{\nu}$ = 3066, 2956, 2927, 2854, 1678, 1595, 1576, 1514, 1485, 1464, 1339, 1288, 1253, 1187, 1121, 1082, 1048, 888, 874, 854, 816, 755 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 257 nm (23900), 295 (15100), 409 (8000). MS (70 eV, EI): m/z (%) = 384 (25), 383 [M]$^+$ (95), 312 (31), 299 (31), 298 (100), 280 (12). HRMS ($C_{24}H_{24}N_2O_2S$): calcd. 404.1558; found 404.1580.

10-Hexyl-3-(2-nitrophenyl)-10*H*-phenothiazine (7c): This compound was prepared as described in the GP; after chromatography on sil-

Table 3. Experimental details for the syntheses of 3-(hetero)arylated phenothiazines **7**.

Entry	Phenothiazine-3-monoboron esters **5**	(Hetero)aryl halide **6**	3-(Hetero)aryl-*N*-hexylphenothiazines **7** (yield)
1	409 mg (1.00 mmol)	244 mg (1.20 mmol) of 2-bromo-3-nitropyridine (**6a**)	364 mg (90%) of **7a**
2[a,b]	205 mg (0.50 mmol)	298 mg (0.82 mmol) of 1-iodo-4-nitrobenzene (**6b**)	170 mg (84%) of **7b**
3	740 mg (1.80 mmol)	505 mg (2.50 mmol) of 1-bromo-2-nitrobenzene (**6c**)	689 mg (95%) of **7c**
4	819 mg (2.00 mmol)	697 mg (2.80 mmol) of 1-iodo-3-nitrobenzene (**6d**)	758 mg (94%) of **7d**
5[c]	141 mg (0.34 mmol)	68 mg (0.43 mmol) of 2-bromopyrimidine (**6e**)	80 mg (65%) of **7e**
6	819 mg (2.00 mmol)	544 mg (2.80 mmol) of 4-bromopyridinium hydrochloride (**6f**)	690 mg (96%) of **7f**
7	819 mg (2.00 mmol)	442 mg (2.80 mmol) of 2-bromopyridine (**6g**)	710 mg (99%) of **7g**

[a] In 1,4-dioxane/water, 2.5:1. [b] Reaction time of 48 h. [c] Reaction time of 72 h.

ica gel (acetone/hexane, 1:10), **7c** (689 mg, 95%) was isolated as a red oil. R_f (acetone/hexane, 1:5) = 0.34. ^{1}H NMR ([D$_6$]acetone, 300 MHz): δ = 0.86 (m, 3 H), 1.32 (m, 4 H), 1.49 (m, 2 H), 1.82 (tt, J = 6.6, 6.6 Hz, 2 H), 3.98 (t, J = 7.0 Hz, 2 H), 6.96 (dt, J = 1.1, 7.4 Hz, 1 H), 7.05–7.25 (m, 6 H), 7.59 (m, 2 H), 7.73 (dt, J = 1.5, 7.7 Hz, 1 H), 7.90 (dd, J = 1.1, 8.09 Hz, 1 H) ppm. ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 14.2 (CH_3), 23.3 (CH_2), 27.2 (CH_2), 27.5 (CH_2), 32.2 (CH_2), 47.9 (CH_2), 116.6 (1C, CH), 116.8 (CH), 123.6 (CH), 124.8 (CH), 124.8 ($C_{quat.}$), 125.8 ($C_{quat.}$), 127.3 (CH), 128.0 (CH), 128.1 (CH), 128.5 (CH), 129.3 (CH), 132.4 ($C_{quat.}$), 132.6 (CH), 133.3 (CH), 135.5 ($C_{quat.}$), 145.8 ($C_{quat.}$), 146.5 ($C_{quat.}$) ppm. IR (KBr): $\tilde{\nu}$ = 3062, 2955, 2927, 2855, 1605, 1575, 1525, 1458, 1397, 1356, 1250, 1194, 1163, 1136, 1106, 889, 854, 819, 781, 751, 709 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 262 nm (32700), 280 (12200), 304 (7700). MS (70 eV, FAB): m/z (%) = 404.1 (100) [M]$^+$, 319.0 [$M - C_6H_{13}$]$^+$ (9). $C_{24}H_{24}N_2O_2S$ (404.5): calcd. C 71.26, H 5.98, N 6.92, S 7.93; found C 70.87, H 5.95, N 6.68, S 7.68.

10-Hexyl-3-(3-nitrophenyl)-10*H*-phenothiazine (7d): This compound was prepared as described in the GP; after chromatography on silica gel (acetone/hexane, 1:15), **7d** (758 mg, 94%) was isolated as a red oil. R_f (acetone/hexane, 1:5) = 0.63. ^{1}H NMR ([D$_6$]acetone, 300 MHz): δ = 0.86 (m, 3 H), 1.32 (m, 4 H), 1.49 (m, 2 H), 1.82 (tt, J = 6.9, 6.9 Hz, 2 H), 4.00 (t, J = 7.1 Hz, 2 H), 6.97 (dt, J = 1.1, 7.5 Hz, 1 H), 7.06 (d, J = 7.4 Hz, 1 H), 7.13–7.22 (m, 3 H), 7.55 (d, J = 2.2 Hz, 1 H), 7.61 (dd, J = 2.2, 8.5 Hz, 1 H), 7.72 (t, J = 8.0 Hz, 1 H), 8.08 (dt, J = 1.1, 8.0 Hz, 1 H), 8.17 (dt, J = 1.4, 6.8 Hz, 1 H), 8.44 (t, J = 2.0 Hz, 1 H) ppm. ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 14.1 (CH_3), 23.1 (CH_2), 26.0 (CH_2), 27.4 (CH_2), 32.0 (CH_2), 47.8 (CH_2), 116.7 (CH), 116.9 (CH), 121.4 (CH), 122.2 (CH), 123.5 (CH), 124.8 ($C_{quat.}$), 126.2 ($C_{quat.}$), 126.3 (CH), 127.0 (CH), 128.0 (CH), 128.3 (CH), 130.9 (CH), 133.1 (CH), 133.3 ($C_{quat.}$), 142.2 ($C_{quat.}$), 145.6 ($C_{quat.}$), 146.5 ($C_{quat.}$), 149.7 ($C_{quat.}$) ppm. IR (KBr): $\tilde{\nu}$ = 2954, 2928, 2855, 1601, 1577, 1527, 1505, 1458, 1444, 1393, 1347, 1251, 878, 803, 742, 704, 685 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 238 nm (22500), 268 (25500), 312 (8700). MS (70 eV, FAB): m/z (%) = 404.1 (100) [M]$^+$, 319.0 [$M - C_6H_{13}$]$^+$ (11). $C_{24}H_{24}N_2O_2S \times 0.3\,H_2O$ (404.5 + 6.0): calcd. C 70.22, H 6.06, N 6.82; found C 70.11, H 5.85, N 6.91.

10-Hexyl-3-(pyrimidin-2-yl)-10*H*-phenothiazine (7e): This compound was prepared as described in the GP; after chromatography on silica gel (acetone/hexane, 1:3), **7e** (80 mg, 65%) was isolated as a greenish oil. R_f (acetone/hexane, 1:5) = 0.58. ^{1}H NMR ([D$_6$]acetone, 300 MHz): δ = 0.85 (m, 3 H), 1.31 (m, 4 H), 1.48 (m, 2 H), 1.82 (tt, J = 6.6, 6.6 Hz, 2 H), 4.01 (t, J = 7.0 Hz, 2 H), 6.96 (dt, J = 1.1, 7.7 Hz, 1 H), 7.04–7.24 (m, 3 H), 7.24–7.31 (m, 2 H), 8.22 (d, J = 1.8 Hz, 1 H), 8.31 (dd, J = 2.2, 8.5 Hz, 1 H), 8.80 (m, 2 H) ppm. ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 14.2 (CH_3), 23.3 (CH_2), 27.1 (CH_2), 27.5 (CH_2), 32.2 (CH_2), 48.0 (CH_2), 116.3 (CH), 116.9 (CH), 119.9 (CH), 123.7 (CH), 125.0 ($C_{quat.}$), 125.2 ($C_{quat.}$), 127.4 (CH), 128.1 (CH), 128.4 (CH), 128.4 (CH), 133.0 ($C_{quat.}$), 145.5 ($C_{quat.}$), 148.5 ($C_{quat.}$), 158.2 (CH), 164.2 ($C_{quat.}$) ppm. IR (KBr): $\tilde{\nu}$ = 3060, 2954, 2928, 2855, 1600, 1567, 1546, 1470, 1444, 1416, 1397, 1332, 1280, 1249, 1149, 799, 747, 701 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 246 nm (20100), 274 (25600), 290 (19500), 362 (6900). MS (70 eV, FAB): m/z (%) = 361.1 (100) [M]$^+$, 276.0 [$M - C_6H_{13}$]$^+$ (20). $C_{22}H_{23}N_3S$ (361.5): calcd. C 73.09, H 6.41, N 11.62; found C 73.41, H 6.41, N 11.43.

10-Hexyl-3-(pyridin-4-yl)-10*H*-phenothiazine (7f): This compound was prepared as described in the GP; after chromatography on silica gel (acetone/hexane, 1:3), **7f** (690 mg, 96%) was isolated as an orange oil. R_f (acetone/hexane, 1:5) = 0.27. ^{1}H NMR ([D$_6$]acetone, 300 MHz): δ = 0.85 (m, 3 H), 1.30 (m, 4 H), 1.47 (m, 2 H), 1.81 (tt, J = 7.0, 7.0 Hz, 2 H), 3.98 (t, J = 7.4 Hz, 2 H), 6.96 (dt, J = 1.1, 7.4 Hz, 1 H), 7.05 (dd, J = 1.1, 8.5 Hz, 1 H), 7.11–7.24 (m, 3 H), 7.55 (d, J = 1.8 Hz, 1 H), 7.59–7.64 (m, 3 H), 8.58 (dd, J = 1.8, 4.8 Hz, 2 H) ppm. ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 14.1 (CH_3), 23.1 (CH_2), 27.0 (CH_2), 27.3 (CH_2), 32.0 (CH_2), 47.8 (CH_2), 116.7 (CH), 116.8 (CH), 121.2 (CH), 123.5 (CH), 124.7 ($C_{quat.}$), 126.0 ($C_{quat.}$), 126.2 (CH), 126.8 (CH), 128.0 (CH), 128.3 (CH), 132.6 ($C_{quat.}$), 145.5 ($C_{quat.}$), 147.0 ($C_{quat.}$), 147.1 ($C_{quat.}$), 151.1 (CH) ppm. IR (KBr): $\tilde{\nu}$ = 3062, 3028, 2954, 2928, 2855, 1596, 1576, 1509, 1486, 1463, 1444, 1418, 1395, 1365, 1336, 1294, 1270, 1252, 1221, 1137, 707, 749 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 244 nm (19800), 272 (25900), 292 (15700), 318 (7200). MS (70 eV, FAB): m/z (%) = 360.1 (100) [M]$^+$, 289.0 [$M - C_5H_{11}$]$^+$ (14), 276.0 [$M - C_6H_{13}$]$^+$ (24). $C_{23}H_{24}N_2S$ (360.5): calcd. C 76.63, H 6.71, N 7.77, S 8.89; found C 76.36, H 6.70, N 7.72, S 8.76.

10-Hexyl-3-(pyridin-2-yl)-10*H*-phenothiazine (7g): This compound was prepared as described in the GP; after chromatography on silica gel (acetone/hexane, 1:3), **7g** (710 mg, 99%) was isolated as a brown oil. R_f (acetone/hexane, 1:5) = 0.30. ^{1}H NMR ([D$_6$]acetone, 300 MHz): δ = 0.85 (m, 3 H), 1.30 (m, 4 H), 1.47 (m, 2 H), 1.81 (tt, J = 7.4, 7.4 Hz, 2 H), 3.98 (t, J = 7.0 Hz, 2 H), 6.95 (dt, J = 1.5, 7.4 Hz, 1 H), 7.02–7.27 (m, 5 H), 7.76–7.87 (m, 2 H), 7.92–7.97 (m, 2 H), 8.60–8.62 (m, 1 H) ppm. ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 14.2 (CH_3), 23.2 (CH_2), 27.1 (CH_2), 27.5 (CH_2), 32.1 (CH_2), 47.9 (CH_2), 116.5 (CH), 116.7 (CH), 120.0 (CH), 122.6 (CH), 123.4 (CH), 125.0 ($C_{quat.}$), 125.6 ($C_{quat.}$), 126.0 (CH), 126.7 (CH), 128.0 (CH), 128.3 (CH), 134.4 ($C_{quat.}$), 137.6 (CH), 145.7 ($C_{quat.}$), 146.9 ($C_{quat.}$), 150.4 (CH), 156.5 ($C_{quat.}$) ppm. IR (KBr): $\tilde{\nu}$ = 3092, 3059, 2954, 2928, 2855, 1600, 1585, 1560, 1458, 1432, 1361, 1333, 1301, 1288, 1251, 1106, 779, 747 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 240 nm (16600), 270 (25200), 288 (13900), 328 (7100). MS (70 eV, FAB): m/z (%) = 360.1 (100) [M]$^+$, 289.0 [$M - C_5H_{11}$]$^+$ (20), 276.0 [$M - C_6H_{13}$]$^+$ (31). $C_{23}H_{24}N_2S \times 0.3\,H_2O$ (360.5 + 6.0): calcd. C 75.37, H 6.78, N 7.64; found C 75.78, H 6.65, N 7.65.

Suzuki Coupling of Bis(pinacolyl) 10-Hexylphenothiazin-3,7-diyl Bis(boronate) (8) with (Hetero)aryl Halides 6. General Procedure: A mixture of **8** (1.0 equiv.), the (hetero)aryl halide **6** (2.5 equiv.), potassium carbonate (4–5 equiv.), and a palladium tetrakis(triphenylphosphane) catalyst (0.05 equiv.) was dissolved in a mixture of degassed 1,2-dimethoxyethane and water (2:1, 0.05 M) and the reaction mixture was then stirred at 90 °C (oil bath) for 18 h (see Table 4 for experimental details). After cooling to room temp. the reaction mixture was diluted with ethyl acetate (80 mL). The organic phase was washed with water and brine, the aqueous layer was extracted with ethyl acetate, and the combined organic phases were finally dried with magnesium sulfate. The solvents were evaporated in vacuo and the residue was chromatographed on silica gel to furnish the pure 3,7-di(hetero)arylated phenothiazines **9** as yellow to orange-red solids or resins. Further purification could be achieved in some cases by recrystallization.

10-Hexyl-3,7-bis(5-nitropyridin-2-yl)-10*H*-phenothiazine (9a): This compound was prepared as described in the GP; after chromatography on silica gel (acetone/hexane, 1:5), **9a** (118 mg, 22%) was isolated as a dark red powder. R_f (acetone/hexane, 1:5) = 0.18. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 0.82 (m, 3 H), 1.27 (m, 4 H), 1.42 (m, 2 H), 1.73 (m, 2 H), 3.98 (t, J = 6.2 Hz, 2 H), 7.20 (d, J = 8.8 Hz, 2 H), 8.01 (d, J = 2.0 Hz, 2 H), 8.08 (d, J = 8.6 Hz, 2 H), 8.22 (d, J = 8.9 Hz, 2 H), 8.58 (dd, J = 2.6, 8.8 Hz, 2 H), 9.37 (d, J = 2.5 Hz, 2 H) ppm. ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 13.8 (CH_3), 23.1 (CH_2), 22.1 (CH_2), 25.7 (CH_2), 26.1 (CH_2), 46.9 (CH_2), 116.3 (CH), 119.9 (CH), 123.2 ($C_{quat.}$), 126.0 (CH), 127.5

Table 4. Experimental details of the syntheses of 3,7-di(hetero)arylated phenothiazines **9**.

Entry	Phenothiazine-3,7-bis(boron ester) **8**	(Hetero)aryl halide **6**	3,7-Di(hetero)aryl-*N*-hexylphenothiazines **9** (yield)
1	535 mg (1.00 mmol)	508 mg (2.50 mmol) of **6a**	118 mg (22%) of **9a**
2	1.07 g (2.00 mmol)	1.25 g (5.00 mmol) of **6b**	1.06 g (100%) of **9b**
3	1.07 g (2.00 mmol)	1.01 g (5.00 mmol) of **6c**	1.06 g (100%) of **9c**
4	1.07 g (2.00 mmol)	1.25 g (5.00 mmol) of **6d**	741 mg (70%) of **9d**
5	482 mg (0.90 mmol)	346 mg (2.18 mmol) of **6e**	302 mg (76%) of **9e**
6	1.07 g (2.00 mmol)	0.97 g (5.00 mmol) of **6f**	668 mg (76%) of **9f**
7	1.07 g (2.00 mmol)	0.79 g (5.00 mmol) of **6g**	763 mg (87%) of **9g**
8	1.07 g (2.00 mmol)	0.79 g (5.00 mmol) of 3-bromopyridine (**6h**)	861 mg (98%) of **9h**
9	1.07 g (2.00 mmol)	440 mg (5.00 mmol) of 4-bromoanisole (**6i**)	715 mg (72%) of **9i**
10	535 mg (1.00 mmol)	618 mg (2.50 mmol) of 4-iodo-*N*,*N*-dimethylaniline (**6j**)	114 mg (22%) of **9j**
11	1.07 g (2.00 mmol)	1.47 g (5.0 mmol) of 1-iodo-2,4-dinitrobenzene (**6k**)	1.23 mg (100%) of **9k**

(CH), 131.1 ($C_{quat.}$), 132.5 (CH), 142.6 ($C_{quat.}$), 144.9 (CH), 145.9 ($C_{quat.}$), 159.7 ($C_{quat.}$) ppm. IR (KBr): $\tilde{\nu}$ = 2927, 2855, 1595, 1570, 1516, 1489, 1455, 1409, 1342, 1270, 1190, 1149, 1117, 1013, 854, 817, 768 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 256 nm (31000), 312 (30900), 454 (23900), 576 (1800). MS (70 eV, FAB): *m/z* = 527.0 (100) $[M]^+$, 442.0 $[M - C_6H_{13}]^+$ (13). $C_{28}H_{25}N_5O_4S \times 0.5$ acetone (527.6 + 29.1): calcd. C 63.65, H 5.07, N 12.58; found C 63.86, H 5.01, N 12.77.

10-Hexyl-3,7-bis(4-nitrophenyl)-10*H*-phenothiazine (9b): This compound was prepared as described in the GP; after chromatography on silica gel (acetone/hexane, 1:10), **9b** (1.06 g, 100%) was isolated as a red powder. R_f (acetone/hexane, 1:5) = 0.24. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.90 (m, 3 H), 1.35 (m, 4 H), 1.47 (m, 2 H), 1.86 (m, 2 H), 3.92 (t, *J* = 7.2 Hz, 2 H), 6.96 (d, *J* = 8.4 Hz, 2 H), 7.39–7.47 (m, 4 H), 7.97 (m, 8 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.4 (CH_3), 23.0 (CH_2), 27.0 (CH_2), 27.1 (CH_2), 31.8 (CH_2), 48.2 (CH_2), 116.2 (CH), 124.6 (CH), 125.2 ($C_{quat.}$), 126.4 (CH), 126.9 (CH), 127.2 (CH), 133.5 ($C_{quat.}$), 145.6 ($C_{quat.}$), 146.5 ($C_{quat.}$), 147.2 ($C_{quat.}$) ppm. IR (KBr): $\tilde{\nu}$ = 3077, 2954, 2929, 2855, 1710, 1595, 1583, 1513, 1529, 1467, 1492, 1422, 1391, 1338, 1285, 1266, 1188, 1110, 853, 815, 754, 696 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 256 nm (23900), 296 (26700), 418 (14600). MS (70 eV, FAB): *m/z* (%) = 525.4 (100) $[M]^+$, 440.3 $[M - C_6H_{13}]^+$ (11). $C_{30}H_{27}N_3O_4S$ (525.6): calcd. C 68.55, H 5.18, N 7.99, S 6.10; found C 68.27, H 5.26, N 7.80, S 6.08.

10-Hexyl-3,7-bis(2-nitrophenyl)-10*H*-phenothiazine (9c): This compound was prepared as described in the GP; after chromatography on silica gel (acetone/hexane, 1:10), **9c** (1.06 g, 100%) was isolated as red flakes. R_f (acetone/hexane, 1:5) = 0.19. ^{1}H NMR ([D_6]acetone, 300 MHz): δ = 0.88 (m, 3 H), 1.34 (m, 4 H), 1.52 (m, 2 H), 1.86 (tt, *J* = 7.4, 7.4 Hz, 2 H), 4.03 (t, *J* = 6.99 Hz, 2 H), 7.12–7.21 (m, 6 H), 7.56–7.64 (m, 4 H), 7.75 (dt, *J* = 1.5, 7.7 Hz, 2 H), 7.91 (dd, *J* = 0.7, 8.1 Hz, 2 H) ppm. ^{13}C NMR ([D_6]acetone, 75 MHz): δ = 14.3 (CH_3), 23.3 (CH_2), 27.2 (CH_2), 27.5 (CH_2), 32.2 (CH_2), 48.1 (CH_2), 116.8 (CH), 124.8 (CH), 125.2 ($C_{quat.}$), 127.4 (CH), 128.2 (CH), 129.4 (CH), 132.7 (CH), 132.7 ($C_{quat.}$), 133.4 (CH), 135.4 ($C_{quat.}$), 145.9 ($C_{quat.}$), 150.3 ($C_{quat.}$) ppm. IR (KBr): $\tilde{\nu}$ = 2954, 2928, 2855, 1607, 1525, 1491, 1462, 1398, 1358, 1249, 1160, 1110, 855, 819, 780, 752, 703 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 266 nm (31000), 354 (4400), 370 (3600). MS (70 eV, FAB): *m/z* (%) = 525.1 (100) $[M]^+$, 440.0 $[M - C_6H_{13}]^+$ (11). $C_{30}H_{27}N_3O_4S$ (525.6): calcd. C 68.55, H 5.18, N 7.99, S 6.10; found C 68.42, H 5.42, N 7.68, S 5.99.

10-Hexyl-3,7-bis(3-nitrophenyl)-10*H*-phenothiazine (9d): This compound was prepared as described in the GP; after chromatography on silica gel (acetone/hexane, 1:10), **9d** (741 mg, 70%) was isolated as fine orange needles. R_f (acetone/hexane, 1:5) = 0.27. ^{1}H NMR ([D_6]acetone, 300 MHz): δ = 0.88 (m, 3 H), 1.33 (m, 4 H), 1.53 (m, 2 H), 1.86 (m, 2 H), 4.07 (t, *J* = 7.0 Hz, 2 H), 7.2 (d, *J* = 8.5 Hz, 2 H), 7.59–7.76 (m, 6 H), 8.15 (dd, *J* = 4.3, 8.5 Hz, 4 H), 8.46 (d, *J* = 1.8 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.2 (CH_3), 23.3 (CH_2), 27.0 (CH_2), 27.1 (CH_2), 32.2 (CH_2), 48.1 (CH_2), 117.1 (CH), 121.6 (CH), 122.4 (CH), 125.8 ($C_{quat.}$), 126.4 (CH), 127.3 (CH), 131.1 (CH), 133.3 (CH), 133.8 ($C_{quat.}$), 142.3 ($C_{quat.}$), 146.0 ($C_{quat.}$), 149.9 ($C_{quat.}$) ppm. IR (KBr): $\tilde{\nu}$ = 3028, 2952, 2927, 2855, 1606, 1588, 1490, 1464, 1424, 1388, 1359, 1248, 1190, 1116, 1018, 800, 711 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 282 nm (45900), 352 (9800). MS (70 eV, CI): *m/z* = 526.2 (100) $[M]^+$. $C_{30}H_{27}N_3O_4S$ (525.6): calcd. C 68.55, H 5.18, N 7.99, S 6.10; found C 68.42, H 5.26, N 8.02, S 6.11.

10-Hexyl-3,7-bis(pyrimidin-2-yl)-10*H*-phenothiazine (9e): This compound was prepared as described in the GP; after chromatography on silica gel (acetone/hexane, 1:5), **9e** (302 mg, 76%) was isolated as greenish flakes. R_f (acetone/hexane, 1:5) = 0.30. ^{1}H NMR ([D_6]acetone, 300 MHz): δ = 0.85 (m, 3 H), 1.32 (m, 4 H),1.50 (m, 2 H), 1.86 (m, 2 H), 4.06 (t, *J* = 7.0 Hz, 2 H), 7.15 (d, *J* = 8.8 Hz, 2 H), 7.31 (t, *J* = 4.8 Hz, 2 H), 8.24–8.33 (m, 4 H), 8.81 (d, *J* = 4.8 Hz, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.1 (CH_3), 23.1 (CH_2), 26.9 (CH_2), 27.3 (CH_2), 32.0 (CH_2), 48.2 (CH_2), 116.4 (CH), 119.8 (CH), 124.6 ($C_{quat.}$), 127.3 (CH), 128.4 (CH), 133.2 ($C_{quat.}$), 147.4 ($C_{quat.}$), 158.1 (CH), 163.9 ($C_{quat.}$) ppm. IR (KBr): $\tilde{\nu}$ = 2955, 2928, 1637, 1607, 1566, 1550, 1480, 1413, 1396, 1356, 1330, 1289, 1248, 1193, 1147, 1221, 798, 643 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 242 nm (24900), 292 (48100), 360 (28400), 366 (28400). MS (70 eV, FAB): *m/z* = 439.1 (100) $[M]^+$, 354.0 $[M - C_6H_{13}]^+$ (22). $C_{26}H_{25}N_5S$ (439.6): calcd. C 71.04, H 5.73, N 15.93, S 7.26; found C 70.93, H 5.77, N 15.56, S 7.39.

10-Hexyl-3,7-bis(pyridin-4-yl)-10*H*-phenothiazine (9f): This compound was prepared as described in the GP; after chromatography on silica gel (acetone/hexane, 1:10), **9f** (668 mg, 76%) was isolated as a yellow green, fluffy solid. R_f (acetone/hexane, 1:5) = 0.11. ^{1}H NMR ([D_6]acetone, 300 MHz): δ = 0.87 (m, 3 H), 1.33 (m, 4 H), 1.52 (m, 2 H), 1.86 (m, 2 H), 4.06 (t, *J* = 7.0 Hz, 2 H), 7.19 (d, *J* = 8.5 Hz, 2 H), 7.59–7.68 (m, 8 H), 8.60 (dd, *J* = 1.5, 4.4 Hz, 4 H) ppm. ^{13}C NMR ([D_6]acetone, 75 MHz): δ = 14.2 (CH_3), 23.3 (CH_2), 27.1 (CH_2), 27.4 (CH_2), 32.1 (CH_2), 48.1 (CH_2), 117.1 (CH), 121.4 (CH), 125.6 ($C_{quat.}$), 126.2 (CH), 127.1 (CH), 133.1 ($C_{quat.}$), 146.4 ($C_{quat.}$), 147.1 ($C_{quat.}$), 151.2 (CH) ppm. IR (KBr): $\tilde{\nu}$ = 2954, 2926, 2854, 1596, 1467, 1419, 1397, 1360, 1340, 1291, 1250, 1221, 1191, 808, 691 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 236 nm (26700), 286 (35800), 366 (9500). MS (70 eV, FAB): *m/z* (%) = 438.1 (100) $[M]^+$, 353.0 $[M - C_6H_{13}]^+$ (33). $C_{28}H_{27}N_3S$ (437.6): calcd. C 76.85, H 6.22, N 9.60; found C 76.42, H 6.34, N 9.22.

10-Hexyl-3,7-bis(pyridin-2-yl)-10*H*-phenothiazine (9g): This compound was prepared as described in the GP; after chromatography on silica gel (acetone/hexane, 1:10), **9g** (763 mg, 87%) was isolated as an amorphous yellow foam. R_f (acetone/hexane, 1:5) = 0.17. ^{1}H NMR ([D$_6$]acetone, 300 MHz): δ = 0.89 (m, 3 H), 1.32 (m, 4 H), 1.47 (m, 2 H), 1.86 (m, 2 H), 3.91 (t, J = 7.4 Hz, 2 H), 6.94 (d, J = 8.5 Hz, 2 H), 7.18 (m, 2 H), 7.64–7.74 (m, 4 H), 7.79–7.84 (m, 4 H), 8.65 (m, 2 H) ppm. ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 14.0 (CH$_3$), 22.6 (CH$_2$), 26.5 (CH$_2$), 26.7 (CH$_2$), 31.4 (CH$_2$), 47.7 (CH$_2$), 115.3 (CH), 119.6 (CH), 121.6 (CH), 124.7 (C$_{quat.}$), 125.6 (CH), 125.9 (CH), 133.7 (C$_{quat.}$), 145.4 (C$_{quat.}$), 149.5 (CH), 156.2 (C$_{quat.}$) ppm. IR (KBr): $\tilde{\nu}$ = 3092, 3059, 3002, 2953, 2927, 2922, 2851, 1652, 1638, 1606, 1586, 1458, 1430, 1395, 1288, 1249, 777, 738 cm^{-1}. UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 250 nm (20500), 288 (39500), 368 (10800). MS (70 eV, CI): m/z (%) = 437.1 (100) $[M]^+$, 352.1 $[M - C_6H_{13}]^+$ (22). $C_{28}H_{27}N_3S$ (437.6): calcd. C 76.85, H 6.22, N 9.60, S 7.33; found C 76.49, H 6.25, N 9.60, S 7.35.

10-Hexyl-3,7-bis(pyridin-3-yl)-10*H*-phenothiazine (9h): This compound was prepared as described in the GP; after chromatography on silica gel (acetone/hexane, 1:10), **9h** (861 mg, 98%) was isolated as an amorphous, yellow foam. R_f (acetone/hexane, 1:5) = 0.05. ^{1}H NMR ([D$_6$]acetone, 300 MHz): δ = 0.87 (m, 3 H), 1.33 (m, 4 H), 1.51 (m, 2 H), 1.86 (tt, J = 7.7, 7.7 Hz, 2 H), 4.04 (t, J = 7.0 Hz, 2 H), 7.17 (d, J = 8.5 Hz, 2 H), 7.42 (m, 2 H), 7.50 (d, J = 2.2 Hz, 2 H), 7.56 (dd, J = 2.2, 8.5 Hz, 2 H), 8.00 (m, 2 H), 8.53 (dd, J = 1.5, 4.8 Hz, 2 H), 8.86 (dd, J = 1.1, 2.2 Hz, 2 H) ppm. ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 14.3 (CH$_3$), 23.3 (CH$_2$), 27.2 (CH$_2$), 27.5 (CH$_2$), 32.2 (CH$_2$), 48.0 (CH$_2$), 117.1 (CH), 124.5 (CH), 125.8 (C$_{quat.}$), 126.3 (CH), 127.1 (CH), 133.1 (C$_{quat.}$), 134.2 (CH), 135.9 (C$_{quat.}$), 145.8 (C$_{quat.}$), 148.4 (CH), 149.1 (CH) ppm. IR (KBr): $\tilde{\nu}$ = 2954, 2928, 2855, 1638, 1586, 1562, 1529, 1510, 1492, 1463, 1396, 1350, 1249, 1105, 878, 802, 741, 706, 680 cm^{-1}. UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 280 nm (37000), 336 (10000). MS (70 eV, FAB): m/z (%) = 437.1 (100) $[M]^+$, 352.0 $[M - C_6H_{13}]^+$ (22). $C_{28}H_{27}N_3S$ (437.6): calcd. C 76.85, H 6.22, N 9.60; found C 76.60, H 6.30, N 8.75.

10-Hexyl-3,7-bis(4-methoxyphenyl)-10*H*-phenothiazine (9i): This compound was prepared as described in the GP; after chromatography on silica gel (acetone/hexane, 1:10), **9i** (715 mg, 72%) was isolated as a light yellow, fluffy solid. R_f (acetone/hexane, 1:5) = 0.51. ^{1}H NMR ([D$_6$]acetone, 300 MHz): δ = 0.87 (m, 3 H), 1.32 (m, 4 H), 1.49 (m, 2 H), 1.83 (tt, J = 7.4, 7.4 Hz, 2 H), 3.98 (t, J = 7.0 Hz, 2 H), 6.97–7.02 (m, 4 H), 7.07 (d, J = 8.5 Hz, 2 H), 7.38–7.45 (m, 4 H), 7.54–7.57 (m, 4 H) ppm. ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 14.1 (CH$_3$), 23.2 (CH$_2$), 27.0 (CH$_2$), 27.4 (CH$_2$), 32.1 (CH$_2$), 47.8 (CH$_2$), 55.5 (CH$_3$), 115.0 (CH), 116.6 (CH), 125.4 (C$_{quat.}$), 125.5 (CH), 126.1 (CH), 128.0 (CH), 132.9 (C$_{quat.}$), 135.8 (C$_{quat.}$), 144.6 (C$_{quat.}$), 160.0 (C$_{quat.}$) ppm. IR (KBr): $\tilde{\nu}$ = 2952, 2929, 1609, 1562, 1543, 1517, 1494, 1468, 1392, 1340, 1241, 1180, 1111, 1047, 1027, 812, 670 cm^{-1}. UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 250 nm (27800), 280 (64700), 334 (14600). MS (70 eV, FAB): m/z (%) = 495.2 (100) $[M]^+$, 424.1 $[M - C_5H_{11}]^+$ (7), 410.1 $[M - C_6H_{13}]^+$ (20). $C_{32}H_{33}NO_2S$ (437.6): calcd. C 77.54, H 6.71, N 2.83, S 6.47; found C 77.43, H 6.73, N 2.90, S 6.54.

3,7-Bis[4-(dimethylamino)phenyl]-10-hexyl-10*H*-phenothiazine (9j): This compound was prepared as described in the GP; after chromatography on silica gel (acetone/hexane, 1:12), **9j** (114 mg, 22%) was isolated as a pale green, fluffy solid. R_f (acetone/hexane, 1:5) = 0.48. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.90 (t, J = 7.0 Hz, 3 H), 1.31–1.37 (m, 4 H), 1.47 (tt, J = 7.1, 7.1 Hz, 2 H), 1.86 (tt, J = 7.0, 7.0 Hz, 2 H), 2.99 (s, 12 H), 3.87 (t, J = 7.3 Hz, 2 H), 6.79 (d, J = 8.8 Hz, 4 H), 6.88 (d, J = 8.5 Hz, 2 H), 7.31–7.34 (m, 4 H), 7.44 (d, J = 8.8 Hz, 4 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 14.0 (CH$_3$), 22.6 (CH$_2$), 26.7 (CH$_2$), 27.0 (CH$_2$), 31.5 (CH$_2$), 40.6 (CH$_3$), 47.5 (CH$_2$), 112.9 (CH), 115.3 (CH), 124,7 (C$_{quat.}$), 124.9 (CH), 125.0 (CH), 127.1 (CH), 128.3 (C$_{quat.}$), 135.5 (C$_{quat.}$), 143.4 (C$_{quat.}$), 149.8 (C$_{quat.}$) ppm. IR (KBr): $\tilde{\nu}$ = 2954, 2927, 2853, 1611, 1526, 1469, 1444, 1392, 1354, 1242, 1200, 1168, 1060, 947, 879, 808 cm^{-1}. UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 250 nm (23400), 302 (52300), 342 (24900). MS (70 eV, FAB): m/z (%) = 521.2 (100) $[M]^+$, 436.1 $[M - C_6H_{13}]^+$ (22). $C_{34}H_{39}N_3S$ (521.8): calcd. C 78.27, H 7.53, N 8.05; found C 77.92, H 7.63, N 7.77.

3,7-Bis(2,4-dinitrophenyl)-10-hexyl-10*H*-phenothiazine (9k): This compound was prepared as described in the GP; after chromatography on silica gel (acetone/hexane, 1:12), **9k** (1.23 g, 100 %) was isolated as a deep red solid. R_f (acetone/hexane, 1:5) = 0.13. ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 0.90 (m, 3 H), 1.35 (m, 4 H), 1.47 (m, 2 H), 1.85 (m, 2 H), 3.89 (t, J = 7.2 Hz, 2 H), 6.92 (d, J = 7.8 Hz, 2 H), 7.09–7.26 (m, 4 H), 7.64 (d, J = 8.6 Hz, 2 H), 8.44 (dd, J = 2.2, 8.6 Hz, 2 H), 8.67 (d, J = 2.2 Hz, 2 H) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 14.4 (CH$_3$), 23.0 (CH$_2$), 27.0 (CH$_2$), 27.0 (CH$_2$), 31.8 (CH$_2$), 48.3 (CH$_2$), 116.1 (CH), 120.3 (CH), 125.2 (C$_{quat.}$), 126.9 (CH), 127.0 (CH), 127.6 (CH), 129.9 (C$_{quat.}$), 133.2 (CH), 141.2 (C$_{quat.}$), 146.1 (C$_{quat.}$), 147.0 (C$_{quat.}$), 149.1 (C$_{quat.}$) ppm. IR (KBr): $\tilde{\nu}$ = 3080, 2952, 2928, 2857, 1602, 1585, 1538, 1526, 1491, 1463, 1416, 1391, 1345, 1274, 1252, 1149, 1080, 833, 820, 748, 726 cm^{-1}. UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 257 nm (45900), 296 (15600), 444 (10400). MS (70 eV, FAB): m/z (%) = 615.3 (100) $[M]^+$. $C_{30}H_{25}N_5O_8S$ (615.6): calcd. C 58.53, H 4.09, N 11.38, S 5.21; found C 58.66, H 4.23, N 11.10, S 5.11.

2,5-Bis(10-hexyl-10*H*-phenothiazin-3-yl)nitrobenzene (12): A mixture of **5** (614 mg, 1.50 mmol), 1,4-dibromo-2-nitrobenzene (**10**, 211 mg, 0.75 mmol), Pd(PPh$_3$)$_4$ (87 mg, 0.08 mmol), and potassium carbonate (0.67 g, 4.84 mmol) in a degassed mixture of DME (18 mL) and water (8 mL) was heated to 90 °C (oil bath) for 42 h. After cooling to room temp. the reaction mixture was diluted with ethyl acetate (80 mL). The organic phase was washed with water and brine, the aqueous layer was extracted with ethyl acetate, and the combined organic phases were finally dried with magnesium sulfate. The solvents were evaporated in vacuo and the residue was chromatographed on silica gel (acetone/hexane, 1:5) to furnish **12** (245 mg, 24%) as a red powder. R_f (acetone/hexane, 1:5) = 0.32. ^{1}H NMR ([D$_6$]acetone, 300 MHz): δ = 0.85 (t, J = 7.1 Hz, 3 H), 0.85 (t, J = 7.1 Hz, 3 H), 1.25–1.33 (m, 8 H), 1.47 (tt, J = 7.1, 7.1 Hz, 4 H), 1.80 (tt, J = 7.1, 7.1 Hz, 4 H), 3.95 (t, J = 7.0 Hz, 2 H), 3.97 (t, J = 7.0 Hz, 2 H), 6.95 (m, 2 H), 7.02–7.09 (m, 3 H), 7.12–7.24 (m, 7 H), 7.52–7.55 (m, 2 H), 7.60 (dd, J = 2.2, 8.4 Hz, 1 H), 7.92 (dd, J = 2.1, 8.3 Hz, 1 H), 8.09 (d, J = 1.8 Hz, 1 H) ppm. ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 15.2 (CH$_3$), 24.3 (CH$_2$), 28.1 (CH$_2$), 28.2 (CH$_2$), 28.5 (CH$_2$), 33.2 (CH$_2$), 48.9 (CH$_2$), 117.6 (CH), 117.8 (CH), 117,8 (CH), 118.0 (CH), 123.1 (CH), 124.6 (CH), 125.9 (C$_{quat.}$), 125.9 (C$_{quat.}$), 126.8 (C$_{quat.}$), 127.2 (CH), 127.3 (C$_{quat.}$), 127.9 (CH), 128.2 (CH), 129.0 (CH), 129.1 (CH), 131.4 (CH), 133.0 (C$_{quat.}$), 134.0 (CH), 134.0 (CH), 134.5 (C$_{quat.}$), 141.8 (C$_{quat.}$), 146,7 (C$_{quat.}$), 146.7 (C$_{quat.}$), 147.4 (C$_{quat.}$), 147.6 (C$_{quat.}$), 151.8 (C$_{quat.}$) ppm. IR (KBr): $\tilde{\nu}$ = 2954, 2927, 2855, 1932, 1629, 1602, 1577, 1529, 1514, 1460, 1361, 1340, 1250, 1194, 1136, 1107, 1041, 881, 814, 749 cm^{-1}. UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 243 nm (13900), 267 (17900), 365 (5700). MS (70 eV, FAB): m/z = 685.1 (100) $[M]^+$, 601.0 $[M - C_6H_{13}]^+$ (18). $C_{42}H_{43}N_3O_2S_2$ (686.0): calcd. C 73.54, H 6.32, N 6.13, S 9.35; found C 73.39, H 6.34, N 6.26, S 9.15.

2,5-Bis(10-hexyl-10*H*-phenothiazin-3-yl)-1,4-dinitrobenzene (13): A mixture of **5** (818 mg, 2.00 mmol), 1,4-dibromo-2,5-dinitrobenzene (**11**, 326 mg, 1.00 mmol), Pd(PPh$_3$)$_4$ (120 mg, 0.10 mmol), and potassium carbonate (0.90 g, 6.50 mmol) in a degassed mixture of DME (25 mL) and water (12 mL) was heated to 90 °C (oil bath) for 25 h. After cooling to room temp. the reaction mixture was diluted with dichloromethane (200 mL). The organic phase was washed with water and brine, the aqueous layer was extracted with dichloromethane, and the combined organic phases were finally dried with magnesium sulfate. The solvents were evaporated in vacuo and the residue was chromatographed on silica gel (acetone/hexane, 1:10 to 1:1, and dichloromethane) to furnish **13** (315 mg, 43%) as a dark red solid. R_f (acetone/hexane, 1:5) = 0.25. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.90 (m, 6 H), 1.34 (m, 8 H), 1.45 (m, 4 H), 1.84 (m, 4 H), 3.87 (t, J = 7.4 Hz, 4 H), 6.86–6.98 (m, 6 H), 7.10–7.21 (m, 8 H), 7.81 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.0 (CH_3), 22.6 (CH_2), 26.6 (CH_2), 26.8 (CH_2), 31.4 (CH_2), 47.7 (CH_2), 115.4 (CH), 115.6 (CH), 122.9 (CH), 123.9 ($C_{quat.}$), 125.9 ($C_{quat.}$), 126.5 (CH), 126.9 (CH), 127.0 (CH), 127.5 (CH), 127.6 (CH), 128.3 ($C_{quat.}$), 134.8 ($C_{quat.}$), 144.4 ($C_{quat.}$), 146,5 ($C_{quat.}$), 150.0 ($C_{quat.}$) ppm. IR (KBr): $\tilde{\nu}$ = 2955, 2928, 2856, 1627, 1603, 1577, 1542, 1510, 1459, 1354, 1251, 1194, 1137, 1107, 885, 850, 818, 750 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 242 nm (46000), 266 (6400), 316 (20900), 428 (5000). MS (70 eV, FAB): m/z = 730.1 (100) $[M]^+$. $C_{42}H_{42}N_4O_4S_2 \times 0.5\,H_2O$ (731.0 + 9.0): calcd. C 68.17, H 5.86, N 7.57; found C 67.96, H 5.76, N 7.45.

Acknowledgments

Financial support of this work by the Deutsche Forschungsgemeinschaft (SFB, 486), the Volkswagen Foundation, the Fonds der Chemischen Industrie, the Otto-Röhm-Gedächtnis-Stiftung, and the Bayerisches Sofortprogramm "Neue Werkstoffe" is gratefully acknowledged. We cordially wish to thank Dr. Christa S. Krämer, Dipl.-Chem. Karin Memminger, and Alexandru V. Rotaru M.Sc., for analytical assistance and valuable discussions (cyclic voltammetry, fluorescence spectroscopy).

---

[1] For leading references, see, for example a) H. Meier, *Angew. Chem.* **2005**, *117*, 2536–2561; *Angew. Chem. Int. Ed.* **2005**, *44*, 2482–2506; b) M. Barzoukas, M. Blanchard-Desce, *Adv. Multi-Photon Processes Spectrosc.* **2001**, *13*, 261–337; c) R. Gompper, H. U. Wagner, *Angew. Chem.* **1988**, *100*, 1492–1511; *Angew. Chem. Int. Engl.* **1988**, *27*, 1437–1456.

[2] For reviews on theory and electronic properties of push-pull chromophores in advanced photonic applications, see, for example a) M. D. Newton, *ACS Symp. Ser.* **2003**, *844*, 196–218; b) J. J. Wolff, R. Wortmann, *J. Prakt. Chem.* **1998**, *340*, 99–111; c) J. W. Perry, S. R. Marder, F. Meyers, D. Lu, G. Chen, W. A. Goddard, J. L. Bredas, B. M. Pierce, *ACS Symp. Ser.* **1995**, *601*, 45–56; d) F. Meyers, J. L. Bredas, *Int. J. Quantum Chem.* **1992**, *42*, 1595–1614.

[3] For reviews of push-pull chromophores in advanced photonic applications, see, for example a) I. Asselberghs, K. Clays, A. Persoons, M. D. Ward, J. McCleverty, *J. Mater. Chem.* **2004**, *14*, 2831–2839; b) O. Inganas, L. S. Roman, F. Zhang, D. M. Johansson, M. R. Andersson, J. C. Hummelen, *Synth. Met.* **2001**, *121*, 1525–1528; c) A. Abbotto, L. Beverina, R. Bozio, S. Bradamante, C. Ferrante, G. A. Pagani, R. Signorini, *Adv. Mater.* **2000**, *12*, 1963–1967; d) A. K.-Y. Jen, Y. Zhang, *Plastics Engin.* **1998**, *49*, 847–894; e) M. S. Wong, C. Bosshard, F. Pan, P. Guenter, *Adv. Mater.* **1996**, *8*, 677–680; f) C. Bubeck, F. Effenberger, L. Hoeussling, D. Neher, C.-P. Niesert, H. Ringsdorf, *Adv. Mater.* **1992**, *4*, 413–416.

[4] For reviews on switchable photochromic and electron-transfer systems, see, for example a) F. M. Raymo, M. Tomasulo, *Chem. Soc. Rev.* **2005**, *34*, 327–336; b) G. Jones II, M. S. Farahat, *Adv. Electron Transfer Chem.* **1993**, *3*, 1–32.

[5] For reviews on low-bandgap polymers, see, for example a) A. Ajayaghosh, *Chem. Soc. Rev.* **2003**, *32*, 181–191; b) H. A. M. van Mullekom, J. A. J. M. Vekemans, E. E. Havinga, E. W. Meijer, *Materials Sci. Eng. R: Reports* **2001**, *R32*, 1–40; c) Y. Yamashita, M. Tomura, *J. Mater. Chem.* **1998**, *8*, 1933–1944; d) H. Segawa, N. Nakayama, F. Wu, T. Shimidzu, *Synth. Met.* **1993**, *55*, 966–971.

[6] 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. Acc. Chem. Res.* **2000**, *33*, 791–804.

[7] a) M. Sainsbury, in *Rodd's Chem. Carbon Compd.* (Ed.: M. Sainsbury), Elsevier, Amsterdam, 2nd ed., **1998**, vol. 4, pp. 575–608; b) M. Sainsbury, in *Comprehensive Heterocyclic Chemistry* (Eds.: A. R. Katritzky, C. W. Rees), Pergamon Press, Oxford, New York, Toronto, Sydney, Paris, Frankfurt, **1984**, vol. 3, p. 995.

[8] a) F. Mietzsch, *Angew. Chem.* **1954**, *66*, 363–371; b) M. Ionescu, H. Mantsch, *Adv. Heterocycl. Chem.* **1967**, *8*, 83–113; c) C. Bodea, I. Silberg, *Adv. Heterocycl. Chem.* **1968**, *9*, 321–460; d) L. Valzelli, S. Garattini, in: *Principles of Psychopharmacology* (Ed.: W. G. Clark), Academic Press, **1970**, 255–258; e) C. O. Okafor, *Heterocycles* **1977**, *7*, 391–427; f) Z. Eckstein, T. Urbanski, *Adv. Heterocycl. Chem.* **1978**, *23*, 1–53; g) J. Szabo, *Chem. Heterocycl. Compd. USSR (Engl. Trans.)* **1979**, *15*, 291–308; h) W. J. Albery, A. W. Foulds, K. J. Hall, A. R. Hillman, R. G. Edgell, A. F. Orchard, *Nature* **1979**, *282*, 793–797.

[9] R. McIntyre, H. Gerischer, *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 963–969.

[10] a) I. Forrest, F. Forrest, *Biochim. Biophys. Acta* **1958**, *29*, 441–442; b) Y. Iida, *Bull. Chem. Soc. Jpn.* **1971**, *44*, 663–667; c) J.-C. Moutet, G. Reverdy, *Nouv. J. Chim.* **1983**, *7*, 105–113.

[11] a) E. Nishiwaki, H. Nakagawa, M. Takasaki, T. Matsumoto, H. Sakurai, M. Shibuya, *Heterocycles* **1990**, *31*, 1763–1767; b) J. Decuyper, J. Piette, M. Lopez, M. P. Merville, A. Vorst, *Biochem. Pharmacol.* **1984**, *33*, 4025–4031; c) A. G. Motten, G. R. Buettner, C. F. Chignell, *Photochem. Photobiol.* **1985**, *42*, 9–15; d) H. Fujita, I. Matsuo, *Chem.-Biol. Interact.* **1988**, *66*, 27–36.

[12] 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.

[13] 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.

[14] a) F. Fungo, S. A. Jenekhe, A. J. Bard, *Chem. Mater.* **2003**, *15*, 1264–1272; b) S. A. Jenekhe, L. Lu, M. M. Alam, *Macromolecules* **2001**, *34*, 7315–7324.

[15] 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.

[16] 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.

[17] 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) T. J. Zimmermann, T. J. J. Müller, *Eur. J. Org. Chem.* **2002**, 2269–2279; d) C. S. Krämer, K. Zeitler, T. J. J. Müller, *Tetrahedron Lett.* **2001**, *42*, 8619–8624; e) T. J. Zimmermann, O. Freundel, R. Gompper, T. J. J. Müller, *Eur. J. Org. Chem.* **2000**, 3305–3312.

[18] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-278393 (for **2b**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[19] Application of B3LYP 6–31 G* density functionals as implemented in *PC Spartan Pro*, Wavefunction Inc.: Irvine, CA, **1999**.

[20] B. Valeur, *Molecular Fluorescence*, Wiley-VCH, Weinheim, **2002**.

[21] Determined with 7-(diethylamino)-4-methylchromen-2-one (coumarin 1) as a standard ($\Phi f = 0.73$), see G. Jones II, W. R. Jackson, C. Y. Choi, W. R. Bergmark, *J. Phys. Chem.* **1985**, *89*, 294–300.

[22] U. Mitschke, P. Bäuerle, *J. Mater. Chem.* **2000**, *10*, 1471–1507.

[23] For molecular solids as film transistors, see, for example a) H. E. Katz, *J. Mater. Chem.* **1997**, *7*, 369–376; b) F. Garnier, *Acc. Chem. Res.* **1999**, *32*, 209–215; c) J. Cornil, D. Beljonne, J.-P. Calbert, J.-L. Brédas, *Adv. Mater.* **2001**, *13*, 1053–1067.

[24] H. G. O. Becker, W. Berger, G. Domschke, E. Fanghänel, J. Faust, M. Fischer, F. Gentz, K. Gewald, R. Gluch, R. Mayer, K. Müller, D. Pavel, H. Schmidt, K. Schollberg, K. Schwetlick, E. Seiler, G. Zeppenfeld, *Organikum*, 20th ed., Johann Ambrosius Barth, Heidelberg, Leipzig, **1996**.

[25] P. Zanello, in: *Ferrocenes* (Eds.: A. Togni, T. Hayashi), VCH, Weinheim, New York, Basel, Cambridge, Tokyo, **1995**, 317–430.

[26] L. S. P. Mirashi, S. S. Kunte, *Spectrochim. Acta Part A* **1989**, *45*, 1147–1156.

Received: July 15, 2005