

# Ferrocenyl oligophenothiazines as organic–organometallic hybrid electrophores – Synthesis, structure, and electronic properties

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## Abstract

Oligomeric ferrocene–phenothiazine systems, a novel class of organometallic–organic hybrid electrophores, are easily accessible by Suzuki coupling of iodo ferrocenes and phenothiazinyl and diphenothiazinyl pinacolyl boronates. The triad and the pentad with 1,1'-disubstitution on ferrocene adopt preferentially an eclipsed orientation as a consequence of partial intramolecular  $\pi$ -stacking. In cyclic voltammetry the central ferrocenyl unit acts as an electronic communicator between phenothiazinyl side chains.

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## 1. Introduction

For the rapidly developing field of molecular electronics [1] new syntheses and structures of novel molecule based conjugated organic and organometallic materials have gained considerable interest in recent years. Among organometallic compounds  $\sigma$ -complexed and metallocene based building blocks have been playing a key role in the search for organic–inorganic structures as novel magnetic, semiconductor, ceramics and redox catalyst materials [2]. Besides, nonlinear optical chromophores on the basis of organometallic functional units have also considerably enriched the field [3]. Metallocene type structures in general and ferrocenyl units in particular are of fundamental interest as novel organic–organometallic hybrid materials [4]. As a consequence of the robustness of ferrocene, its facile “organic” transformability, and its propensity to form a stable 17 electron specimen, i.e. the ferrocenium ion, ferrocene has become an attractive and important functional unit in molecular systems with extended  $\pi$ -electron conjugation for the development of conjugated ferrocenyl oligomers [5] and polymers

[6]. In combination with other redox active moieties, such as coordinated transition metals [7], an intense electronic communication between the redox centers can be observed, setting the stage for the concept of ferrocene-based molecular wires [8]. Hence, dyads [9] and polymers [10] consisting of ferrocene and organic redox systems, such as porphyrins, dithiafulvenes, or tetrathiafulvenes have been synthesized. All these motifs have lower or similar oxidation potentials, however, directly linked redox systems with a slightly higher oxidation potential have not been considered so far. Therefore, the question of electronic communication through ferrocene as an electronic communicator arises.

Recently, we have communicated syntheses and electronic properties of coupled and decoupled oligophenothiazines [11] as part of our program to establish a bottom-up approach to redox active nanometer-sized molecular wires [12]. Here, we wish to report our synthetic approaches to ferrocenyl oligophenothiazines, their electronic properties according to cyclic voltammetry, and first preliminary computational studies on their electronic structures.

## 2. Results and discussion

Recently, we have transposed Suzuki cross-coupling reactions to halo and borylated phenothiazines as an expeditious

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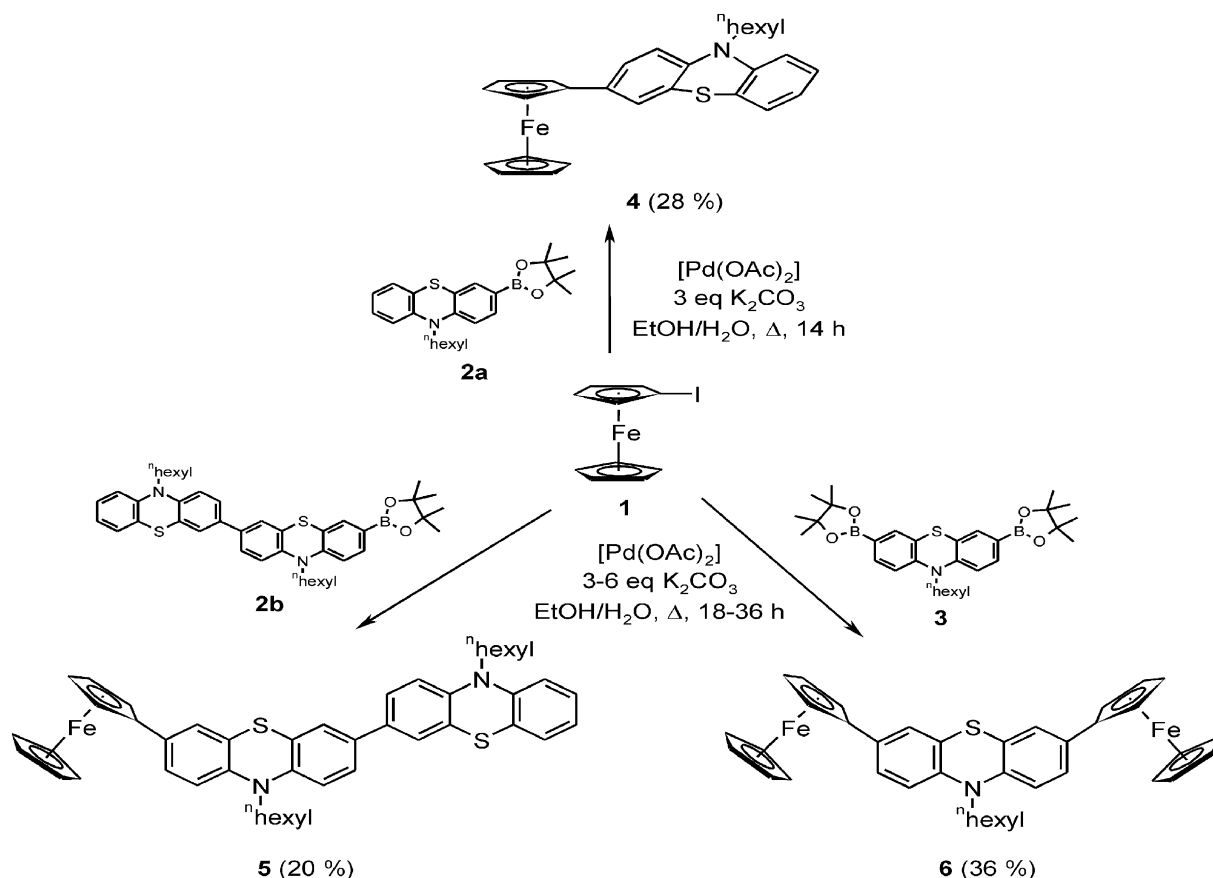
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route to oligophenothiazines with extended  $\pi$ -electron conjugation. With borylated phenothiazines in hand the Suzuki coupling with iodo ferrocenes appeared to be the arylation method of choice [13]. Therefore, upon reacting iodo ferrocene (**1**) and the pinacolyl phenothiazin-3-yl and biphenothiazinyl boronates **2**, or the bis(pinacolyl) phenothiazin-3,7-diyl bisboronate **3** under modified Suzuki conditions [14] in ethanol/water for 18 h the ferrocenyl-phenothiazine dyad, Fc-PT, (**4**) and the triads Fc-PT-PT (**5**) and Fc-PT-Fc (**6**) were obtained as orange-red resins (**4**: 28%; **5**: 20%) and as an orange powder (**6**: 36%) (Scheme 1). Surprisingly, in comparison to couplings with 1,1'-diiodo ferrocene (vide infra), prolonged heating under standard conditions with  $\text{Pd}(\text{PPh}_3)_4$  as a catalyst did not lead to the formation of the expected coupling products.

However, upon reacting 1,1'-diiodo ferrocene (**7**) and the pinacolyl phenothiazin-3-yl and biphenothiazinyl boronates **2**, under standard Suzuki conditions in DME/water at 80 °C with  $\text{Pd}(\text{PPh}_3)_4$  as a catalyst for 18 h the triad PT-Fc-PT (**8**) and the pentad PT-PT-Fc-PT-PT (**9**) were obtained in reasonable yields as orange solids (see Scheme 2).

The structures of the Fc-PT oligomers **4–6**, **8**, and **9** are unambiguously supported by spectroscopic and combustion analytical data. Expectedly, the molecular symmetry of the 3,7-diferrocenyl substituted phenothiazine **6** and

the 1,1'-disubstituted ferrocenes **8** and **9** are reflected by the appearance of a single set of signals for the corresponding substituents in the proton and carbon NMR spectra. At high field the hexyl chain protons can be readily identified, in particular, the triplets for the methylene groups adjacent to the phenothiazinyl nitrogen atom are detected at  $\delta$  3.7 to 4.0 with vicinal coupling constants of 6.9 to 7.3 Hz. For the systems **4–6** the characteristic signals of the unsubstituted Cp ring are found at  $\delta$  4.03 to 4.05 as sharp singlets. The monosubstitution is reflected by the appearance of two sets of pseudo triplets at  $\delta$  4.3 and 4.6 to 4.7 with vicinal coupling constants of 1.8 Hz. Likewise the 1,1'-substitution of ferrocene is supported by the appearance of two sets of pseudo triplets at  $\delta$  4.1 to 4.3 and 4.3 to 4.5. The aromatic proton resonances of the phenothiazines are detected between  $\delta$  6.6 and 7.5, in a few cases yet well resolved, and can be unambiguously assigned to the ring positions by incremental calculations. Besides the hexyl carbon resonances in the  $^{13}\text{C}$  NMR spectra the most characteristic signals stem from the Cp carbon nuclei that appear in a small window between  $\delta$  66.0 to 75.7 and can be identified by the DEPT experiments as methine and quaternary carbon resonances. The aromatic resonances of the phenothiazine methine and quaternary nuclei are not specific and are found in the expected region between  $\delta$  115.1 and 147.5. FAB and MALDI-TOF mass spectrometry shows for all



Scheme 1. Synthesis of the Fc-PT dyad **4** and the triads Fc-PT-PT (**5**) and Fc-PT-Fc (**6**).



( $\Delta E [(C_2\text{-syn}) - (C_2\text{-anti})] = -10.2$  kcal/mol) the DFT computations reveal that the  $C_2\text{-syn}$  conformation is only stabilized by 1 kcal/mol in the gas phase. This energy difference is of a comparable magnitude as the rotational barrier of the Cp rings [18]. In the unit cell the molecules of **8** (Fig. 2) show an *anti* parallel stacking with an intermolecular stack-to-stack distance of 20.4 Å, i.e. the length of the b-axis, where the ferrocenyl Cp rings are with an edge-to-plane distance of 3.9 Å in close proximity to the inner benzo rings of the next neighbor. Furthermore, the hexyl chains are directed into the interstack space.

For all Fc-PT oligomers electrochemical data of reversible oxidation processes can be readily obtained in the anodic region by cyclic voltammetry (Table 1, Figs. 3–7). Most distinctly, the difference in the first oxidations between monosubstituted ferrocenes **4–6**, and the 1,1'-disubstituted ferrocenes **8** and **9** becomes apparent. An ad hoc assignment suggests that in all cases this first oxidation event occurs on the ferrocenyl core (ferrocene:  $E_0^{0/+1} = 450$  mV [19]).

Although 10-hexyl-10*H*-phenothiazine is an electron-rich heteroaromatic system (in agreement with correlation studies the Hammett–Taft parameter of *N*-hexyl phenothiazine can be estimated to  $\sigma_P = -0.70$ ) and displays a first oxidation potential of  $E_0^{0/+1} = +730$  mV, ferrocene possesses with  $E_0^{0/+1} = +450$  mV a considerably lower oxidation potential. This view is also supported by DFT calculations [20] on the dyad **4** (facilitated by substituting "hexyl by ethyl) where the orbital coefficients in HOMO and HOMO-1 are predominantly ferrocene centered and HOMO-2 is phenothiazine centered to a large extent (Fig. 8).

Differences in the first oxidations of monosubstituted ferrocenes **4–6** and the 1,1'-disubstituted ferrocenes **8** and **9** can be attributed to stereoelectronic aspects. As a consequence of a significant torsion of the phenothiazinyl moiety from coplanarity with the Cp ring in monosubstituted ferrocenes (as calculated for the Fc-PT dyad **4**) the  $\pi$ -orbital overlap is decreased and therefore ferrocene experiences a balanced combination of the positive mesomeric and the negative inductive effects of the heteroaromatic substituent to a considerable extent. Hence, the ferrocene centered oxidations of the monosubstituted ferrocenes **4–6** appears in a

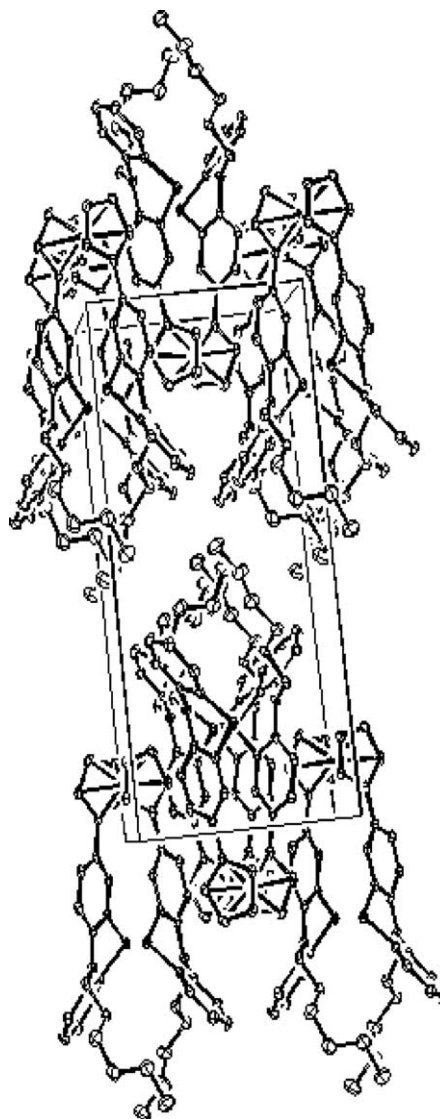


Fig. 2. Crystal packing of **8** (hydrogen atoms are omitted for clarity).

region similar to ferrocene. However, upon imposing partial  $\pi$ -stacking as in the case of the 1,1'-disubstituted ferrocenes **8** and **9** the induced coplanarity improves the  $\pi$ -orbital overlap and the orbital mixing and, therefore, causes to a cathodic shift of the first ferrocene centered

Table 1  
Oxidation potentials [mV] of the Fc-PT oligomers (recorded in  $\text{CH}_2\text{Cl}_2$  at 293 K)<sup>a</sup>

Fc-PT oligomer	First oxidation	Second oxidation	Third oxidation	Fourth oxidation
<b>4</b>	$E_0^{0/+1} = +450$	$E_0^{+1/+2} = +820$		
<b>5</b>	$E_0^{0/+1} = +440$	$E_0^{+1/+2} = +690$	$E_0^{+2/+3} = +870$	
<b>6</b>	$E_0^{0/+2} = +450$	$E_0^{+2/+3} = +920$		
<b>8</b>	$E_0^{0/+1} = +390$	$E_0^{+1/+2} = +740$	$E_0^{+2/+3} = +920$	
<b>9</b>	$E_0^{0/+1} = +390$	$E_0^{+1/+3} = +660$	$E_0^{+3/+4} = +860$	$E_0^{+4/+5} = +980$
Ferrocene	$E_0^{0/+1} = +450$			
10-Hexyl-10 <i>H</i> -phenothiazine	$E_0^{0/+1} = +730$			

<sup>a</sup> 0.1 M  $\text{NBu}_4\text{PF}_6$  as supporting electrolyte, Pt as a working electrode,  $\text{Ag}/\text{AgCl}$  as a reference electrode, and Pt as a counter electrode; all cyclic voltammograms were calibrated against 1,10-diphenyl anthracene,  $E_0^{0/+1} = +1210$  mV, that was determined relative to ferrocene/ferrocenium  $E_0^{0/+1} = 450$  mV [19].

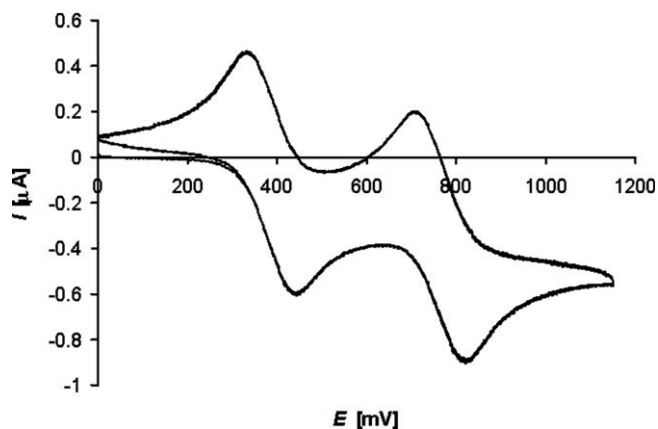


Fig. 3. Cyclic voltammogram of **4** in  $\text{CH}_2\text{Cl}_2$ ;  $T = 293 \text{ K}$ ; electrolyte:  $0.1 \text{ M NBu}_4\text{PF}_6 (\text{CH}_2\text{Cl}_2)$ ;  $\nu = 50 \text{ mV/s}$ ; Pt as a working electrode, Ag/AgCl as a reference electrode, and Pt as a counter electrode (vs. 9,10-diphenyl anthracene,  $E_0^{0/+1} = +1210 \text{ mV}$ ).

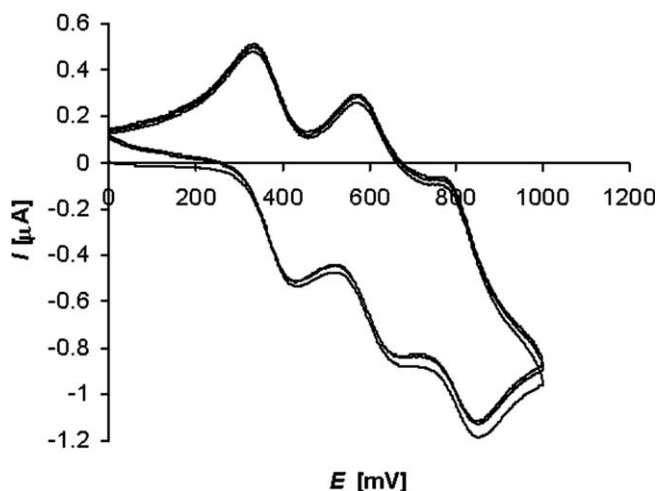


Fig. 4. Cyclic voltammogram of **5** in  $\text{CH}_2\text{Cl}_2$ ;  $T = 293 \text{ K}$ ; electrolyte:  $0.1 \text{ M NBu}_4\text{PF}_6 (\text{CH}_2\text{Cl}_2)$ ;  $\nu = 100 \text{ mV/s}$ ; Pt as a working electrode, Ag/AgCl as a reference electrode, and Pt as a counter electrode (vs. 9,10-diphenyl anthracene,  $E_0^{0/+1} = +1210 \text{ mV}$ ).

oxidations to lower potentials. This qualitative picture is also supported by DFT calculations [17] on the  $C_2$ -*syn*- and  $C_2$ -*anti*-conformations of triad **8** (vide supra). As reflected by the orbital coefficients and the orbital mixing the electron density in the highest occupied frontier orbitals are predominantly ferrocene centered for the thermodynamically more stable  $C_2$ -*syn*-conformation of **8** (Table 2, Fig. 9), whereas for the  $C_2$ -*anti*-conformer of **8** a dominance of electron density in the phenothiazinyl substituents can be found. However, the electronic stabilization of  $C_2$ -*syn*-**8** over  $C_2$ -*anti*-**8** can be attributed to a positive secondary orbital interference (through space) in the HOMO-1 of  $C_2$ -*syn*-**8** (Fig. 9 center).

The second oxidations are expectedly phenothiazine centered, however, they do not all appear around the potential of 10-hexyl-10*H*-phenothiazine which has been chosen as the reference system. Interestingly, the simulta-

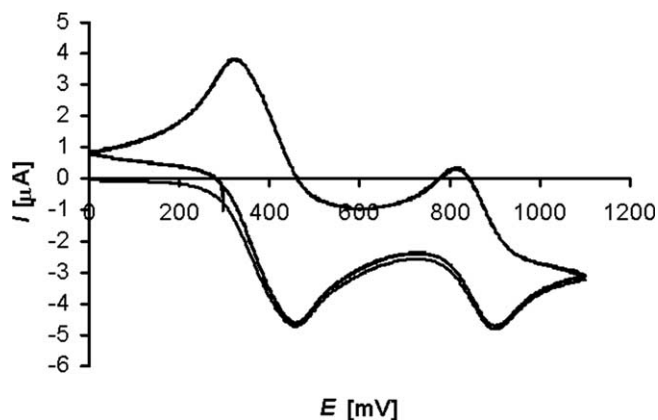


Fig. 5. Cyclic voltammogram of **6** in  $\text{CH}_2\text{Cl}_2$ ;  $T = 293 \text{ K}$ ; electrolyte:  $0.1 \text{ M NBu}_4\text{PF}_6 (\text{CH}_2\text{Cl}_2)$ ;  $\nu = 100 \text{ mV/s}$ ; Pt as a working electrode, Ag/AgCl as a reference electrode, and Pt as a counter electrode (vs. 9,10-diphenyl anthracene,  $E_0^{0/+1} = +1210 \text{ mV}$ ).

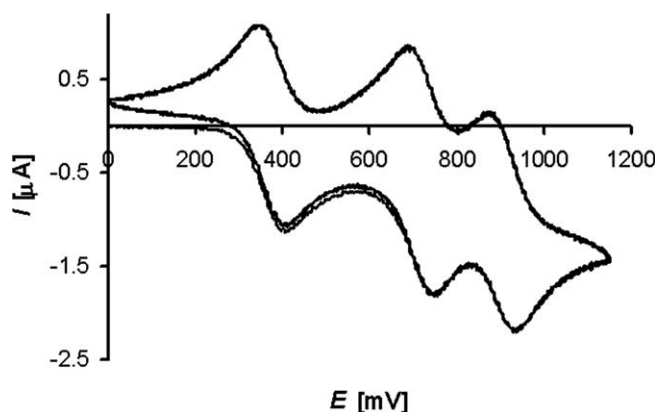


Fig. 6. Cyclic voltammogram of **8** in  $\text{CH}_2\text{Cl}_2$ ;  $T = 293 \text{ K}$ ; electrolyte:  $0.1 \text{ M NBu}_4\text{PF}_6 (\text{CH}_2\text{Cl}_2)$ ;  $\nu = 100 \text{ mV/s}$ ; Pt as a working electrode, Ag/AgCl as a reference electrode, and Pt as a counter electrode (vs. 9,10-diphenyl anthracene,  $E_0^{0/+1} = +1210 \text{ mV}$ ).

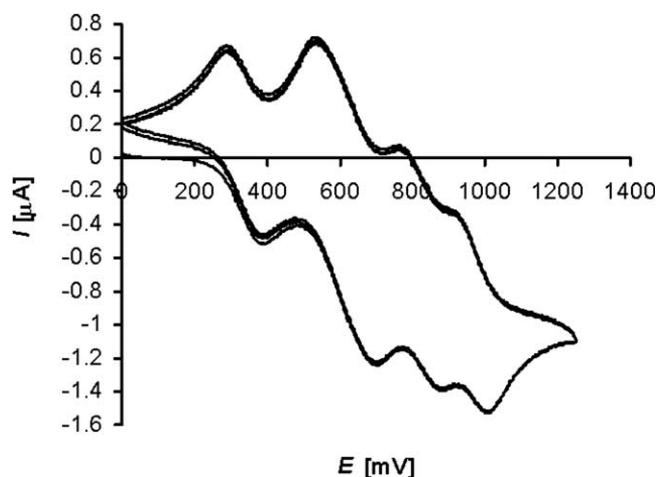


Fig. 7. Cyclic voltammogram of **9** in  $\text{CH}_2\text{Cl}_2$ ;  $T = 293 \text{ K}$ ; electrolyte:  $0.1 \text{ M NBu}_4\text{PF}_6 (\text{CH}_2\text{Cl}_2)$ ;  $\nu = 50 \text{ mV/s}$ ; Pt as a working electrode, Ag/AgCl as a reference electrode, and Pt as a counter electrode (vs. 9,10-diphenyl anthracene,  $E_0^{0/+1} = +1210 \text{ mV}$ ).



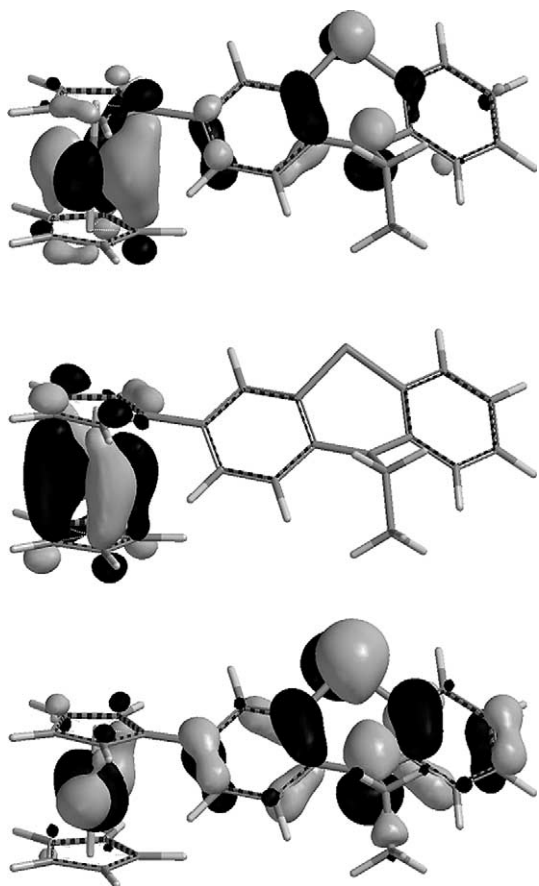


Fig. 8. HOMO (top,  $-4.523$  eV), HOMO-1 (middle,  $-4.610$  eV), and HOMO-2 (bottom,  $-4.770$  eV) of the dyad **4** (DFT calculations).

Table 2  
Calculated DFT energies [eV] of the occupied frontier orbitals of  $C_2$ -*syn*-**8** and  $C_2$ -*anti*-**8**

	$C_2$ - <i>syn</i> - <b>8</b>	$C_2$ - <i>anti</i> - <b>8</b>
HOMO	$-4.006^a$	$-4.057^b$
HOMO-1	$-4.214^b$	$-4.181^b$
HOMO-2	$-4.338^a$	$-4.232^a$

<sup>a</sup> Ferrocene centered.

<sup>b</sup> Phenothiazine centered.

neous two-electron oxidation of the ferrocenyl moieties in compound **6** clearly support that these two metallocene centers are electronically decoupled. As a consequence of the adjacent ferrocenium substituent or substituents the oxidation of the phenothiazinyl moieties in the compounds **4** and **6** are considerably shifted anodically indicating a strong electronic communication between ferrocene and phenothiazine in the state of the monocation. However, in the case of the 1,1'-disubstituted ferrocene **8** this anodic shift is rather small. Again, the dominance of eclipsed conformational orientation of the phenothiazinyl substituents as a consequence of intramolecular  $\pi$ -stacking appears to be responsible for an enhanced stabilization of the positive charge of the ferrocenium ion and, hence, the second oxidation is facilitated in comparison to the monosubstituted

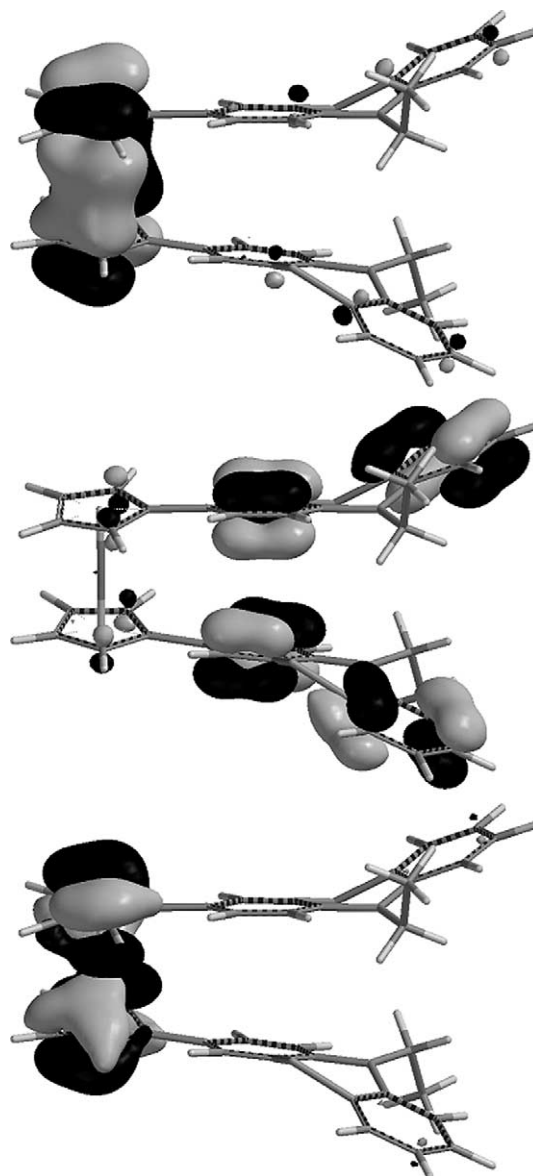


Fig. 9. HOMO (top), HOMO-1 (middle), and HOMO-2 (bottom) of the  $C_2$ -*syn*-triad **8** (DFT calculations).

representatives **4** and **6**. Here, conformational aspects also support the electronic communication in the state of the monocation. Puzzling at first sight, however, is the pronounced cathodic shift of the second oxidations in the biphenothiazinyl substituted systems **5** and **9**. For compound **9** this oxidation event even occurs as a simultaneous two-electron transfer indicating an electronic decoupling of these two phenothiazinyl moieties. Therefore, in the systems **5** and **9** the second oxidation does not occur in proximity to the ferrocenium system but at the remote terminal phenothiazine substituent where the adjacent inner phenothiazines can donate electron density to the ferrocenium and the terminal phenothiazinyl radical cations. Finally and most interestingly, the third and fourth oxidations in the triads **5** and **8** and in the pentad **9** are again phenothiazine centered and occur for the systems **8** and **9**

as coupled one-electron transfer events as a consequence of an intense electronic coupling through the ferrocenium center and favored by an intramolecular  $\pi$ -stacking conformation.

### 3. Conclusion

Oligomeric ferrocene–phenothiazine systems can be synthesized by Suzuki coupling of iodo ferrocenes and phenothiazinyl and diphenothiazinyl pinacolyl boronates. Structurally, these organometallic–organic hybrid electrophores with 1,1'-disubstitution on ferrocene adopt preferentially an eclipsed orientation as a consequence of partial intramolecular  $\pi$ -stacking. In cyclic voltammetry an intense electronic communication is observed if ferrocene adopts the central part of the oligomers and hence, the ferrocenyl moiety can be considered as an electronic communicator between the electronically active phenothiazine side chains. Future studies will address the materials properties of Fc–PT systems as novel hole transport materials and electrochemical switches as well as the implementation of the functional PT–Fc–PT unit into cyclic topologies like cyclophans to study intramolecular electron transfer behavior.

### 4. Experimental

All reactions were carried out in flame-dried Schlenk flasks under argon by using septum and syringe techniques. Reagents, catalysts, ligands and solvents were purchased reagent grade and used without further purification. Solvents were dried and distilled according to standard procedures [21]. Pinacolyl 10-hexyl-10*H*-phenothiazin-3-yl boronate (**2a**) and bis(pinacolyl) 10-hexyl-10*H*-phenothiazin-3,7-diyl bisboronate (**3**) were prepared by our previously published procedure [12c]. 10,10'-Dihexyl-7-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-10*H*, 10'*H*-[3,3']-biphenothiazinyl (**2b**) was synthesized analogously. Iodo ferrocene (**1**) was synthesized by sequential electrophilic trapping (1 equiv of water, then 1 equiv of iodine) and 1,1'-diiodo ferrocene (**7**) was synthesized from 1,1'-bis(tributylstannyl)ferrocene according to literature [22]. Column chromatography: silica gel 60, mesh 230–400. TLC: silica gel plates. Melting points: uncorrected values. <sup>1</sup>H and <sup>13</sup>C NMR spectra: [D<sub>6</sub>] acetone or CD<sub>2</sub>Cl<sub>2</sub> (locked to Me<sub>4</sub>Si). Using DEPT spectra has made the assignments of quaternary C, CH, CH<sub>2</sub> and CH<sub>3</sub>. Elemental analyses were carried out in the Microanalytical Laboratories of the Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg.

#### 4.1. X-ray structure determination of compound **8**

C<sub>46</sub>H<sub>48</sub>FeN<sub>2</sub>S<sub>2</sub>, red crystal (irregular), dimensions 0.28 × 0.20 × 0.08 mm<sup>3</sup>, crystal system monoclinic, space group *P*2<sub>1</sub>, *Z* = 2, *a* = 10.062(1) Å, *b* = 9.164(1) Å, *c* = 20.395(3) Å,  $\alpha$  = 90.0°,  $\beta$  = 98.858(2)°,  $\gamma$  = 90.0°,

*V* = 1858.3(4) Å<sup>3</sup>,  $\rho$  = 1.338 g/cm<sup>3</sup>, *T* = 100(2) K,  $\theta_{\max}$  = 28.34°, radiation Mo K $\alpha$ ,  $\lambda$  = 0.71073 Å, 0.3° omega-scans with CCD area detector, covering a whole sphere in reciprocal space, 18107 reflections measured, 8920 unique (*R*<sub>(int)</sub> = 0.0322), 8323 observed (*I* > 2 $\sigma$ (*I*)), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS [23] based on the Laue symmetry of the reciprocal space,  $\mu$  = 0.55 mm<sup>-1</sup>, *T*<sub>min</sub> = 0.86, *T*<sub>max</sub> = 0.96, structure solved by direct methods and refined against *F*<sup>2</sup> with a full-matrix least-squares algorithm using the SHELXTL (6.12) software package [24], 550 parameters refined, hydrogen atoms of the aliphatic side chains were treated using appropriate riding models, all other hydrogen atoms were refined isotropically, Flack absolute structure parameter 0.035(11), goodness of fit 1.08 for observed reflections, final residual values *R*<sub>1</sub>(*F*) = 0.039,  $\omega R$ (*F*<sup>2</sup>) = 0.089 for observed reflections, residual electron density from -0.41 to 0.56 eÅ<sup>-3</sup>. CCDC - #285004 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or on the web www: www.ccdc.cam.ac.uk/conts/retrieving.html.

#### 4.2. 10-Hexyl-10*H*-phenothiazin-3-yl ferrocene (**4**)

In a 50 mL two-necked round bottom flask 0.50 g (1.60 mmol) of iodo ferrocene (**1**), 0.66 g (1.61 mmol) of pinacolyl 10-hexyl-10*H*-phenothiazin-3-yl boronate (**2a**), 0.66 g (4.78 mmol) of potassium carbonate were dissolved in a degassed (with argon) mixture of 21 mL of ethanol and 2 mL of water. Then 11 mg (0.05 mmol) of Pd(OAc)<sub>2</sub> were added and the reaction mixture was heated under argon to 80 °C (oil bath) for 14 h. After cooling to room temp. a saturated aqueous solution of sodium sulfite was added and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried with anhydrous magnesium sulfate and the solvents were removed in vacuo. The residue was chromatographed on silica gel (hexane/acetone 30:1) to give 207 mg (28%) of **4** as red resin. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.87–0.92 (m, 3H), 1.27–1.36 (m, 4 H), 1.41–1.50 (m, 2H), 1.78–1.88 (m, 2H), 3.85 (t, *J* = 7.0 Hz, 2H), 4.05 (s, 5H), 4.28 (t, *J* = 1.8 Hz, 2H), 4.56 (t, *J* = 1.8 Hz, 2H), 6.77–6.95 (m, 2H), 7.14–7.19 (m, 2H), 7.24–7.27 (m, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  14.0 (CH<sub>3</sub>), 22.6 (CH<sub>2</sub>), 26.7 (CH<sub>2</sub>), 26.9 (CH<sub>2</sub>), 31.5 (CH<sub>2</sub>), 47.5 (CH<sub>2</sub>), 66.0 (CH), 66.6 (CH), 69.5 (CH), 69.5 (C<sub>quat.</sub>), 115.1 (CH), 115.2 (CH), 122.2 (CH), 124.5 (C<sub>quat.</sub>), 124.6 (C<sub>quat.</sub>), 124.8 (CH), 125.0 (CH), 127.2 (CH), 127.4 (CH), 133.4 (C<sub>quat.</sub>), 143.3 (C<sub>quat.</sub>), 145.2 (C<sub>quat.</sub>). MS (FAB+), *m/z* (%) = 467.2 (M<sup>+</sup>, 100), 382.0 (M<sup>+</sup> - C<sub>6</sub>H<sub>13</sub>, 15). IR (KBr),  $\tilde{\nu}$  = 3092, 3060, 2954, 2928, 2855, 1603, 1578, 1514, 1474, 1448, 1267, 1249, 1106, 818, 750 cm<sup>-1</sup>. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  ( $\epsilon$ ) 262 nm (29100). Anal. Calc. for C<sub>28</sub>H<sub>29</sub>FeNS (467.8): C, 71.94; H, 6.25; N, 3.00; S, 6.86. Found: C, 71.65; H, 6.28; N, 3.02; S, 6.73%.

#### 4.3. 10,10'-Dihexyl-10H,10'H-[3,3']biphenothiazinyl-7-yl ferrocene (**5**)

To a solution of 0.10 g (0.32 mmol) of iodo ferrocene (**1**) in a mixture of 25 mL of ethanol and 5 mL of water was added a solution of 0.23 g (0.33 mmol) of 10,10'-dihexyl-7-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-10H, 10'H-[3,3']-biphenothiazinyl (**2b**) in 5 mL of dichloromethane. After the addition of 0.14 g (1.01 mmol) of potassium carbonate the reaction mixture was degassed with argon and then 3 mg (13  $\mu$ mol) of palladium acetate were added. The reaction mixture was heated to 80 °C (oil bath) for 18 h. After cooling to rt water was added and the organic layer was extracted with dichloromethane (3  $\times$  50 mL). The combined organic layer was dried with anhydrous magnesium sulfate and the solvents were removed in vacuo. The residue was chromatographed on silica gel (hexane) to give 47 mg (20%) of pure compound **5**.  $^1\text{H}$  NMR (300 MHz,  $d^6$ -acetone):  $\delta$  0.86 (m, 6H), 1.32 (m, 8H), 1.49 (m, 4H), 1.82 (m, 4H), 3.97 (m, 4H), 4.03 (s, 5H), 4.30 (t,  $J = 1.8$  Hz, 2H), 4.70 (t,  $J = 1.8$  Hz, 2H), 6.92–6.98 (m, 2 H), 7.02–7.09 (m, 3H), 7.14–7.23 (m, 2H), 7.32 (d,  $J = 2.2$  Hz, 1H) 7.37–7.48 (m, 5H).  $^{13}\text{C}$  NMR (75 MHz,  $d^6$ -acetone):  $\delta$  15.2 (CH<sub>3</sub>), 24.3 (CH<sub>2</sub>), 24.3 (CH<sub>2</sub>), 28.2 (CH<sub>2</sub>), 28.6 (CH<sub>2</sub>), 28.6 (CH<sub>2</sub>), 33.2 (CH<sub>2</sub>), 48.8 (CH<sub>2</sub>), 48.9 (CH<sub>2</sub>), 67.8 (CH), 70.5 (CH), 70.5 (C<sub>quat.</sub>), 71.2 (CH), 117.5 (CH), 117.6 (CH), 117.7 (C<sub>quat.</sub>), 117.8 (C<sub>quat.</sub>), 117.8 (C<sub>quat.</sub>), 124.3 (C<sub>quat.</sub>), 126.2 (CH), 126.5 (CH), 126.7 (CH), 127.0 (CH), 127.5 (C<sub>quat.</sub>), 129.0 (CH), 129.3 (C<sub>quat.</sub>), 133.2 (C<sub>quat.</sub>), 135.8 (C<sub>quat.</sub>), 136.0 (C<sub>quat.</sub>), 146.2 (C<sub>quat.</sub>), 147.5 (C<sub>quat.</sub>). MS (FAB+) 748.3 (100, M<sup>+</sup>); MS (MALDI-TOF),  $m/z$  (%) = 748.3 (72, M<sup>+</sup>), 564.3 (100, M<sup>+</sup> – ferrocene). IR (KBr),  $\tilde{\nu} = 3092$  cm<sup>-1</sup>, 3055, 3025, 2953, 2927, 2854, 1626, 1576, 1514, 1450, 1481, 1463, 1413, 1379, 1334, 1250, 1106, 874, 812, 747. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  ( $\epsilon$ ) 280 nm (43700). Anal. Calc. for C<sub>46</sub>H<sub>48</sub>FeN<sub>2</sub>S<sub>2</sub> (748.9): C, 73.78; H, 6.46; N, 3.74; S, 8.56. Found: C, 73.85; H, 6.60; N, 3.71; S, 8.62%.

#### 4.4. 3,7-Diferrocenyl-10-hexyl-10H-phenothiazine (**6**)

In a 50 mL two-necked round bottom flask 1.28 g (4.10 mmol) of iodo ferrocene (**1**), 1.00 g (1.87 mmol) of bis(pinacoyl) 10-hexyl-10H-phenothiazin-3,7-diyl bisboronate (**3**), 1.55 g (11.2 mmol) of potassium carbonate were dissolved in a degassed (with argon) mixture of 21 mL of ethanol and 2 mL of water. Then 19 mg (0.08 mmol) of Pd(OAc)<sub>2</sub> were added and the reaction mixture was heated under argon to 80 °C (oil bath) for 2.5 d. After cooling to rt water was added and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried with anhydrous magnesium sulfate and the solvents were removed in vacuo. The residue was chromatographed on silica gel (hexane/acetone 20:1) to give 436 mg (36%) of **6** as an orange powder.  $^1\text{H}$  NMR (300 MHz,  $d^6$ -acetone):  $\delta$  0.85–0.90 (m, 3H), 1.29–1.36 (m, 4H), 1.45–1.53 (m, 2H), 1.78–1.88 (m, 2H), 3.94 (t,  $J = 6.9$  Hz, 2H), 4.04 (s, 10H), 4.30 (t,  $J = 1.9$  Hz, 4H), 4.70 (t,  $J = 1.9$  Hz, 4H), 6.95 (d,

$J = 8.5$  Hz, 2H), 7.32 (d,  $J = 1.7$  Hz, 2H), 7.38 (dd,  $J = 2.1$ , 8.4 Hz, 4H).  $^{13}\text{C}$  NMR (75 MHz,  $d^6$ -acetone):  $\delta$  14.2 (CH<sub>3</sub>), 23.3 (CH<sub>2</sub>), 27.1 (CH<sub>2</sub>), 27.6 (CH<sub>2</sub>), 32.2 (CH<sub>2</sub>), 47.9 (CH<sub>2</sub>), 66.7 (CH), 69.5 (C<sub>quat.</sub>), 70.2 (CH), 116.3 (CH), 125.0 (C<sub>quat.</sub>), 125.2 (CH), 126.0 (CH), 134.3 (C<sub>quat.</sub>), 144.1 (C<sub>quat.</sub>). MS (MALDI-TOF),  $m/z$  (%) = 651.3 (M<sup>+</sup> (100)). IR (KBr),  $\tilde{\nu} = 3093$  cm<sup>-1</sup>, 3953, 2926, 2858, 1630, 1499, 1446, 1412, 1268, 1106, 816, 502. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  ( $\epsilon$ ) 268 nm (57000). Anal. Calc. for C<sub>38</sub>H<sub>37</sub>Fe<sub>2</sub>NS (651.5): C, 70.06; H, 5.72; N, 2.15. Found: C, 69.23; H, 5.62; N, 2.29%.

#### 4.5. 1,1'-Bis-(10-hexyl-10H-phenothiazin-3-yl) ferrocene (**8**)

In a 50 mL two-necked round bottom flask 464 mg (1.06 mmol) of 1,1'-diiodo ferrocene (**7**), 1.09 g (2.66 mmol) of pinacolyl 10-hexylphenothiazin-3-boronate (**2a**), 0.90 g (6.51 mmol) of potassium carbonate, and 123 mg (0.11 mmol) of Pd(PPh<sub>3</sub>)<sub>4</sub> were dissolved in a degassed mixture of 25 mL of DME and 12 mL of water. The reaction mixture was heated under argon to 90 °C (oil bath) for 18 h. The color changed from orange to black. After cooling to rt 80 mL of ethyl acetate were added and the organic layer was washed with water and brine. The aqueous layer was extracted with ethyl acetate and the combined organic layers were dried with anhydrous magnesium sulfate. The solvents were removed in vacuo and the residue was chromatographed on silica gel (hexane/acetone 25:1) to give 305 mg (38%) of **8** as a bright yellow crystalline solid.  $R_f$  (hexane/acetone 5:1) = 0.55.  $^1\text{H}$  NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  0.77–0.81 (m, 6H), 1.18–1.25 (m, 8H), 1.29–1.38 (m, 4H), 1.70 (m, 4H), 3.72 (t,  $J = 7.3$  Hz, 4H), 4.10 (dd,  $J = 1.8$  Hz, 4H), 4.30 (dd,  $J = 1.8$  Hz, 4H), 6.61 (d,  $J = 8.6$  Hz, 2H), 6.75–6.83 (m, 4H), 6.92–7.09 (m, 8H).  $^{13}\text{C}$  NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  14.2 (CH<sub>3</sub>), 23.0 (CH<sub>2</sub>), 27.1 (CH<sub>2</sub>), 27.2 (CH<sub>2</sub>), 31.9 (CH<sub>2</sub>), 47.9 (CH<sub>2</sub>), 67.7 (CH), 70.4 (CH), 70.4 (C<sub>quat.</sub>), 115.4 (CH), 115.6 (CH), 122.4 (CH), 124.5 (C<sub>quat.</sub>), 124.6 (C<sub>quat.</sub>), 124.8 (CH), 125.2, (CH), 127.5 (CH), 127.6 (CH), 132.4 (C<sub>quat.</sub>), 143.6 (C<sub>quat.</sub>), 145.5 (C<sub>quat.</sub>). MS (FAB+),  $m/z$  (%) = 748.1 (M<sup>+</sup>, 100). IR (KBr),  $\tilde{\nu} = 3060$  cm<sup>-1</sup>, 2953, 2927, 2854, 1604, 1578, 1513, 1475, 1450, 1413, 1268, 1249, 814, 748. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  ( $\epsilon$ ) 238 nm (38600), 264 (58400), 314 (19200), 452 (1200). Anal. Calc. for C<sub>46</sub>H<sub>48</sub>FeN<sub>2</sub>S<sub>2</sub> (748.9): C, 73.78; H, 6.46; N, 3.69; S, 8.45. Found: C, 73.64; H, 6.46; N, 3.80; S, 8.53%.

#### 4.6. 1,1'-Bis(10,10'-dihexyl-10H,10'H-[3,3']biphenothiazinyl-7-yl) ferrocene (**9**)

A solution of 0.10 g (0.23 mmol) of 1,1'-diiodo ferrocene (**7**), 0.35 g (0.51 mmol) of 10,10'-dihexyl-7-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-10H,10'H-[3,3']biphenothiazinyl (**2a**), and 0.19 g (1.37 mmol) of potassium carbonate in 15 mL of DME and 5 mL of water was degassed with argon for 20 min. After addition of 11 mg



(0.1 mmol) of Pd(PPh<sub>3</sub>)<sub>4</sub> the reaction mixture was heated to 85 °C (oil bath) for 20 h. Then 2 mL of THF were added and the heating was continued for 3 h. After cooling to rt water and dichloromethane were added and the aqueous phase was extracted several times with dichloromethane. The combined organic layer was dried with magnesium sulfate and the solvents were removed in vacuo. The residue was chromatographed on silica gel (hexane/acetone 15:1) to give 162 mg (54%) of pure **9** as an orange solid. <sup>1</sup>H NMR (300 MHz, d<sup>6</sup>-acetone): δ 0.85 (m, 12H), 1.28 (m, 16H), 1.42 (m, 8H), 1.78 (m, 8H), 3.82 (m, 4H), 3.91 (m, 4 H), 4.26 (t, *J* = 1.8 Hz, 4H), 4.49 (t, *J* = 1.8 Hz, 4H), 6.72 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 1.9 Hz, 2H), 6.91–7.06 (m, 10H), 7.13–7.38 (m, 12H). <sup>13</sup>C NMR (75 MHz, d<sup>6</sup>-acetone): δ 15.3 (CH<sub>3</sub>), 15.3 (CH<sub>3</sub>), 24.3 (CH<sub>2</sub>), 24.4 (CH<sub>2</sub>), 28.2 (CH<sub>2</sub>), 28.3 (CH<sub>2</sub>), 28.4 (CH<sub>2</sub>), 28.6 (CH<sub>2</sub>), 33.2 (CH<sub>2</sub>), 33.3 (CH<sub>2</sub>), 48.9 (CH<sub>2</sub>), 49.1 (CH<sub>2</sub>), 69.0 (CH), 71.1 (CH), 75.7 (CH), 116.8 (C<sub>quat.</sub>), 117.3 (CH), 117.6 (CH), 117.7 (CH), 124.3 (C<sub>quat.</sub>), 125.2 (C<sub>quat.</sub>), 125.9 (C<sub>quat.</sub>), 126.2 (CH), 126.3 (CH), 126.4 (C<sub>quat.</sub>), 126.5 (CH), 126.8 (CH), 126.8 (CH), 126.9 (CH), 127.0 (CH), 129.1 (CH), 129.3 (CH), 133.3 (C<sub>quat.</sub>), 136.0 (C<sub>quat.</sub>), 143.8 (C<sub>quat.</sub>), 144.1 (C<sub>quat.</sub>), 145.8 (C<sub>quat.</sub>), 146.1 (C<sub>quat.</sub>), 147.1 (C<sub>quat.</sub>). MS (MALDI), *m/z* (%) = 1310.3 (100, M<sup>+</sup>). IR (KBr),  $\tilde{\nu}$  = 3089 cm<sup>-1</sup>, 3062, 3027, 2953, 2927, 2854, 1604, 1577, 1517, 1481, 1463, 1414, 1378, 1334, 1241, 1193, 1107, 1032, 873, 808, 746. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  (ε) 270 nm (107500). Anal. Calc. for C<sub>82</sub>H<sub>86</sub>FeN<sub>4</sub>S<sub>4</sub> (1311.7): C, 75.09; H, 6.61; N, 4.27; S, 9.78. Found: C, 74.99; H, 6.72; N, 4.27; S, 9.58%.

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