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**Synthesis and electronic properties of some
new phenothiazine derivatives designed as
building blocks for functional materials**

Ph.D. Thesis

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1. Introduction

1.1. Generalities

Functional organic molecules are the key components for future nanosized functional materials.¹ Functional materials cover a wide range of molecular systems from self assembled monolayers to molecular machines. Self assembled monolayers are complex systems formed by adsorption of an organic compound on a metal, oxide or semiconductor surface. They exhibit interesting properties like hydrophilicity, hydrophobicity, redox activity or photoactivity and can be used in molecular recognition, catalysis or biological membrane simulation.² Molecular machines are nanosystems which can perform motion at molecular level as a response to external stimuli (radiation, pH or potential variation).³ One monography⁴ and several reviews⁵ have been dedicated to molecular machines, some of the most recently reported being the molecular rotors, valves or elevators.

1.2. Phenothiazine: structure and properties

Phenothiazines belong to an important class of heterocyclic compounds known for their pharmaceutical properties. Phenothiazine core is the active component in sedatives, tranquilizers, antituberculotics or bactericides.⁶ Phenothiazines are electron donor compounds with a low oxidation potential and they can form easily radical-cations.⁷

Lately phenothiazine has become very popular in material science or in biochemistry as marker for proteins and DNA.⁸ Phenothiazine is found as the redox active unit in donor-acceptor

¹ (a) C. Joachim, J. K. Gimzewski, A. Aviram *Nature* **2000**, *408*, 541. (b) S. R. Forrest *Nature* **2004**, *428*, 911.

² (a) S. Shampah, O. Lev *Adv. Mater.* **1997**, *9*, 410. (b) J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides *Chem. Rev.* **2005**, *105*, 1103.

³ (a) A. Archut, F. Vögtle, L. De Cola, G. C. Azzellini, V. Balzani, P. S. Ramanujam, R. H. Berg *Chem. Eur. J.* **1998**, *4*, 699. (b) V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddart *Angew. Chem. Int. Ed.* **2000**, *39*, 3348.

⁴ V. Balzani, A. Credi, M. Venturi *Molecular Devices and Machines – A Journey into the Nano World*, Wiley-VCH, Weinheim, **2003**.

⁵ W. R. Browne, B. L. Feringa *Nature Nanotechnology* **2006**, *1*, 25.

⁶ (a) F. Mietzsch *Angew. Chem.* **1954**, *66*, 363. (b) C. Bodea, I. Silberg *Adv. Heterocycl. Chem.* **1968**, *9*, 321.

⁷ (a) L. A. Tinker, A. J. Bard *J. Am. Chem. Soc.* **1979**, *101*, 2316. (b) Y. Ida *Bull. Chem. Soc. Jpn.* **1971**, *44*, 663.

⁸ (a) N. Nakadan, S.-I. Imabayashi, M. Watanabe *Langmuir* **2004**, *20*, 8786. (b) C. Wagner, H.-A. Wagenknecht *Chem. Eur. J.* **2005**, *22*, 1871.

systems,⁹ oligophenothiazines,¹⁰ fluorophores¹¹ but also in ligands used for functionalizing different surfaces.¹²

2. Phenothiazine derivatives designed for surface functionalization

2.1. Introduction

The surfaces formed by chemisorption of sulphur compounds (thiols, thioethers, thiocyanates, disulfides) on gold, are among the most studied functionalized surfaces.¹³ These so called self assembled monolayers can present redox activity, photosensitivity or catalytic properties depending of the adsorbed molecules on the surface.¹⁴

Fujihara et al reported redox active gold nanoparticles with phenothiazine units¹⁵ and recently Franz et al.¹⁶ reported redox active monolayers with phenothiazine units.

⁹ (a) N. Bucci, T. J. J. Müller *Tetrahedron Lett.* **2006**, *47*, 8323.

¹⁰ M. Sailer, A. W. Franz, T. J. J. Müller *Chem. Eur. J.* **2008**, *14*, 2602.

¹¹ M. Hauck, J. Schönhaber, A. J. Zuccherro, K. I. Hardcastle, T. J. J. Müller, U. H. F. Bunz *J. Org. Chem.* **2007**, *72*, 6714.

¹² (a) A. W. Franz, Z. Zhou, R. Turdean, A. Wagener, B. Sarkar, M. Hartmann, S. Ernst, W. R. Thiel, T. J. J. Müller *Eur. J. Org. Chem.* **2009**, 3895. (b) C. S. Barkschat, S. Stoycheva, M. Himmelhaus, T. J. J. Müller *Chem. Mater.* **2010**, *22*, 52.

¹³ (a) R. G. Nuzzo, D. L. Allara *J. Am. Chem. Soc.* **1983**, *105*, 4481. (b) A. Ulman *Chem. Rev.* **1996**, *96*, 1533. (c) R. A. Gropeanu, M. L. Tintas, C. Pilon, M. Morin, L. Breau, R. Turdean, I. Grosu *J. Heterocycl. Chem.* **2007**, *44*, 521.

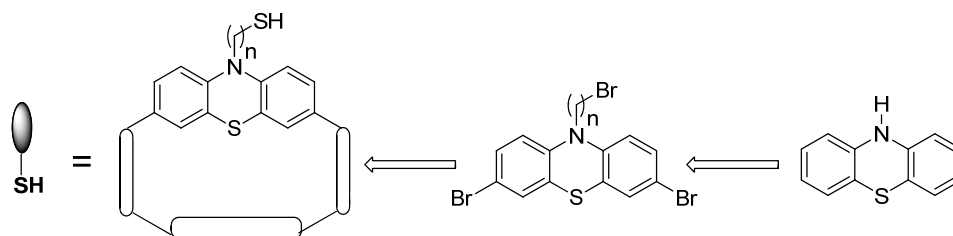
¹⁴ (a) M. Tamura, H. Fujihara *J. Am. Chem. Soc.* **2003**, *125*, 15742. (b) N. O. Fischer, R. Paulini, U. Dreschsler, V. M. Rotello *Chem. Commun.* **2004**, 2866.

¹⁵ T. Goto, H. Fujihara *J. Mat. Science* **2004**, 2171.

¹⁶ A. W. Franz, S. Stoycheva, M. Himmelhaus, T. J. J. Müller *Beilstein J. Org. Chem.* **2010**, *6*, 1.

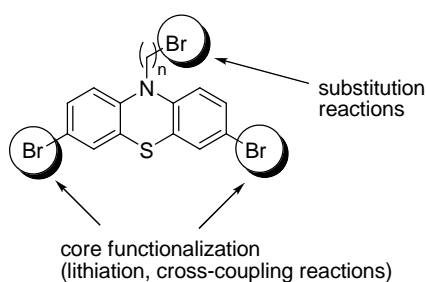
2.2. Results and discussions

Our goal was to synthesise some new complex derivatives like macrocycles to be used as ligands in experiments of sulphur mediated chemisorbtion on gold (Scheme 4).



Scheme 4

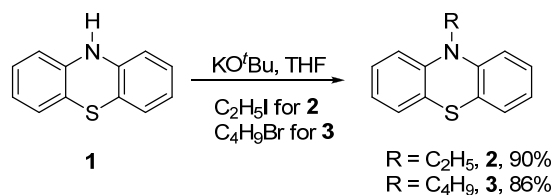
The key intermediate in the synthesis is the tribromurated phenothiazine derivative. This can be functionalized at the alkyl branch by substitution reactions with sulphur containing groups and also can be core functionalized by lithiation or coupling reactions (Scheme 5).



Scheme 5

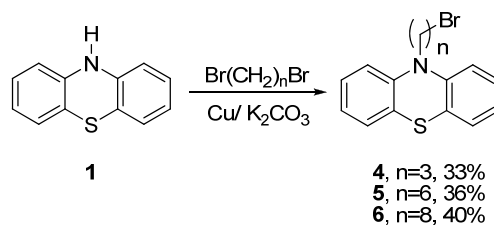
Alkyl derivatives **2** and **3** were obtained by deprotonation of 10H-phenothiazine **1** with potassium *tert*-butylate in tetrahydrofuran¹⁷ followed by alkylation with iodoethane or buthylbromide, respectively (Scheme 6).

¹⁷ (a) J. Cymerman-Craig, W. P. Rogers, G. P. Warwick *Aust. J. Chem.* **1955**, *8*, 252.



Scheme 6

This procedure proved inefficient in order to obtain bromoalkylated phenothiazine derivatives, so another method adapted from the literature was chosen.¹⁸ Heating 10*H*-phenothiazine with dibromoalkanes in the presence of potassium carbonate and copper powder, furnished the desired compounds **4-6** in moderate yields (Scheme 7).



Scheme 7

The structure of the compounds was confirmed by NMR spectroscopy. In figure 1 the ¹H NMR spectrum of derivative **4** is depicted. In the aliphatic region, two characteristic triplet signals appear: one at 4.04 ppm corresponding to the protons in the methylene group linked to the nitrogen atom and one at 3.60 ppm corresponding to the protons in the methylene group linked to the bromine atom.

¹⁸ W. Huang, M. Helvenston, J. L. Casson, R. Wang, J.-F. Bardeau, Y. Lee, M. S. Johal, B. I. Swanson, J. M. Robinson, D. Li *Langmuir* **1999**, *15*, 6510.

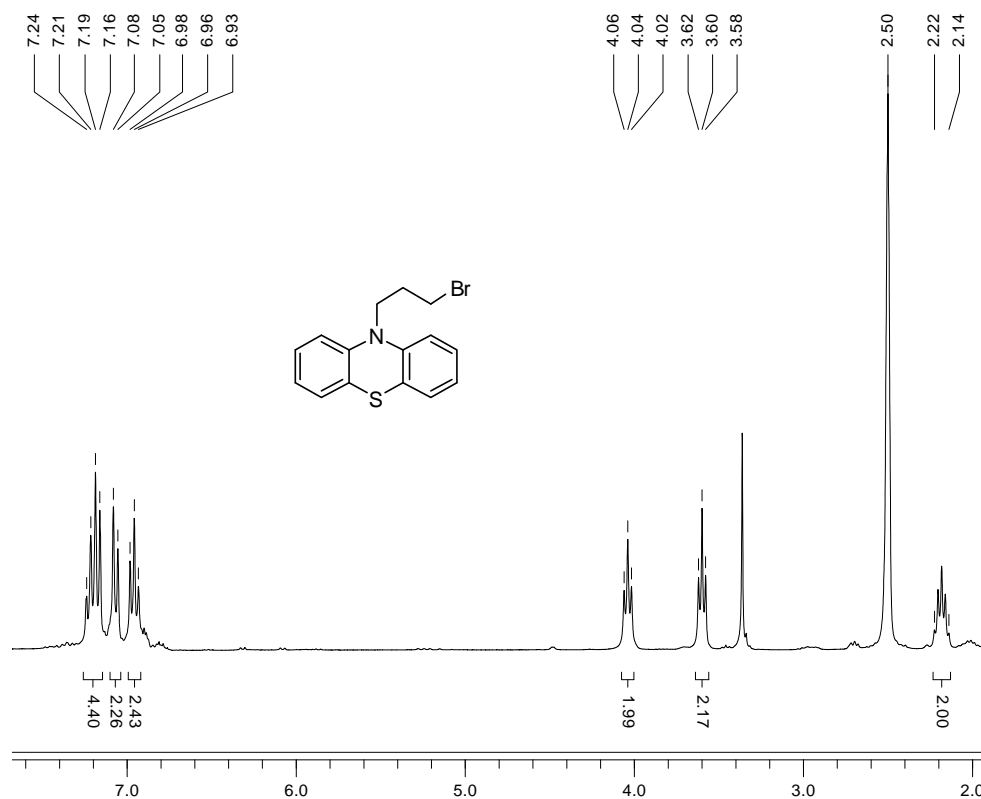
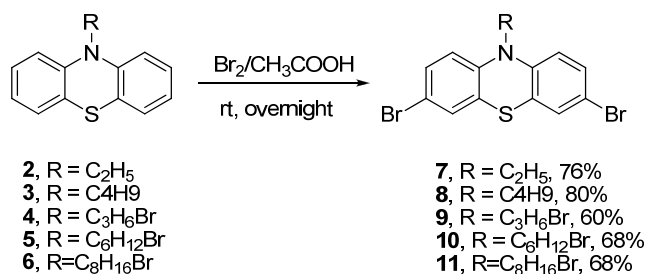


Figure 1 ¹H-NMR spectrum of **4** (DMSO-*d*₆, 300 MHz, rt).

The compounds **2-6** were subjected to a bromination reaction with bromine in glacial acetic acid to yield the phenothiazine derivatives **7-11** in good yields (Scheme 8).¹⁹



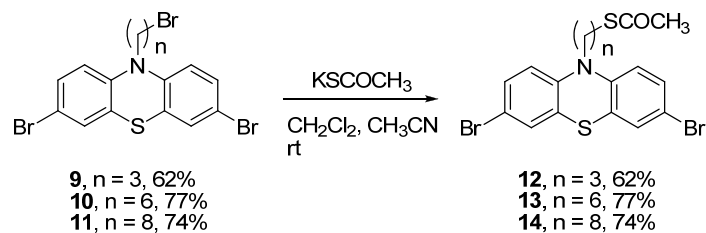
Scheme 8

Compounds **9-11** were treated with potassium tioacetate following a procedure described in the literature²⁰ to build up the phenothiazine thioacetates **12-14** in good yields (Scheme 9).²¹

¹⁹ H. Chiou, P. Reeves, E. R. Biehl *J. Het. Chem.* **1976**, *13*, 77.

²⁰ T. Tsukatani, H. Fujihara *Langmuir* **2005**, *21*, 12093.

²¹ R. Turdean, E. Bogdan, A. Terec, A. Petran, L. Vlase, I. Turcu, I. Grosu *Cent. Eur. J. Chem.* **2009**, *7*, 111.



Scheme 9

The structure of these thioacetates was confirmed by NMR spectroscopy. The differences between the spectra of the brominated derivatives used as starting material and those of the thioacetates is the singlet signal corresponding to the methyl group in thioacetyl and the shielding of the protons in the methylenic group attached to the sulphur atom (Figure 4).

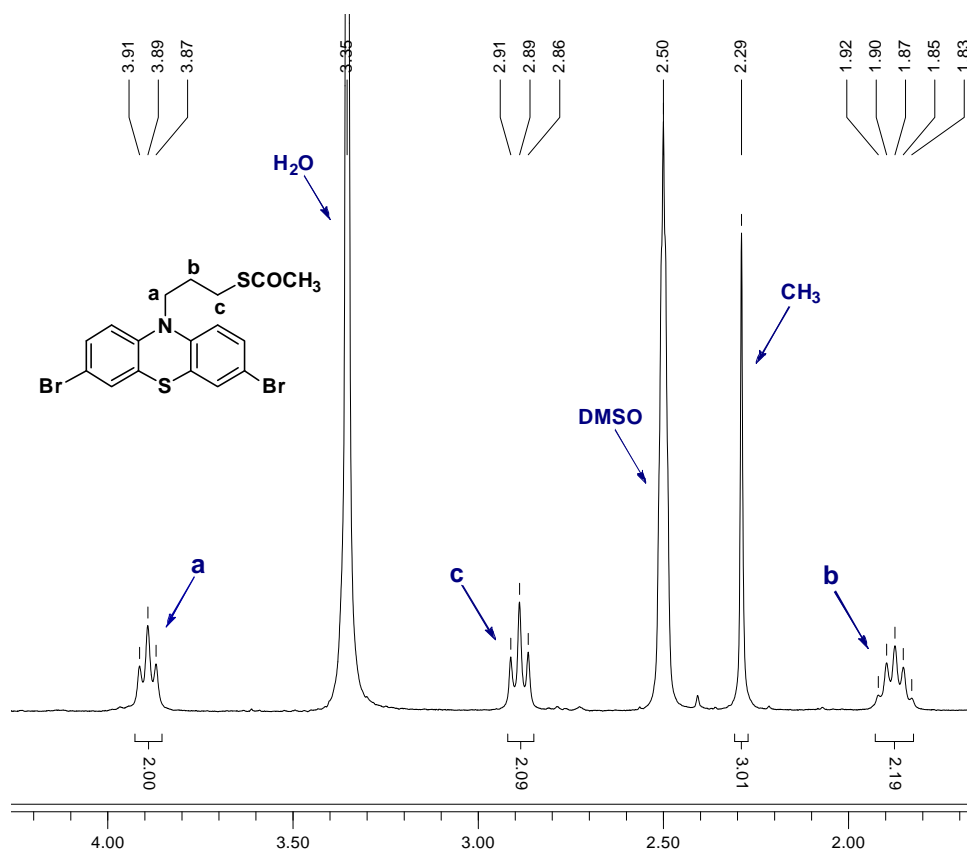
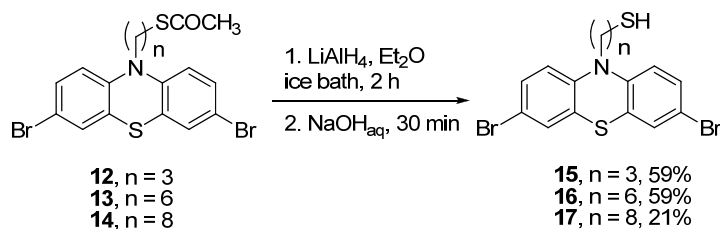


Figure 4 ¹H-NMR spectrum of **12** (DMSO-*d*₆, 300 MHz, rt).

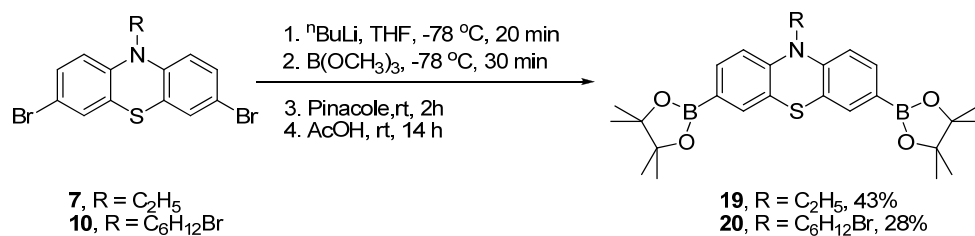
Thioacetates **12-14** are reduced to the corresponding thiols **15-17** with lithium aluminium hydride in dry diethyl ether, following a procedure earlier reported in the literature with other substrates²² (Scheme 10).



Scheme 10

The structure of these thiols is supported by proton and carbon NMR spectroscopy. In the ¹H NMR spectra of the thiols the singlet corresponding to methyl protons disappears instead the signal corresponding to the mercapto protons appear at different chemical shifts.

The dibrominated derivatives **7** and **9** were subjected to a double Br-Li exchange with ⁿBuLi at low temperatures, followed by addition of trimethyl borate and in situ transesterification with pinacole²³ to yield the pinacolyl boronic esters of phenothiazine **19** and **20** (Scheme 12).

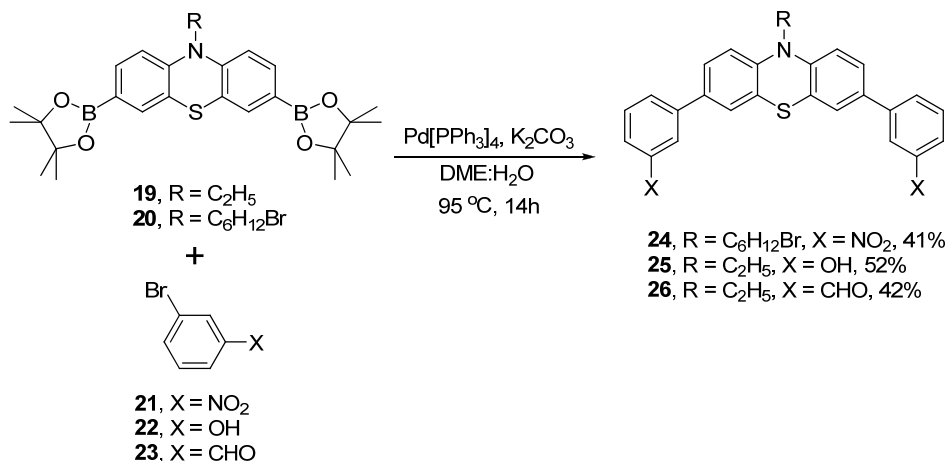


Scheme 12

The pinacolyl boronic esters **19** and **20** were used in Suzuki cross-coupling reactions with different halogenated aryl derivatives to afford the compounds **24-26** (Scheme 14).

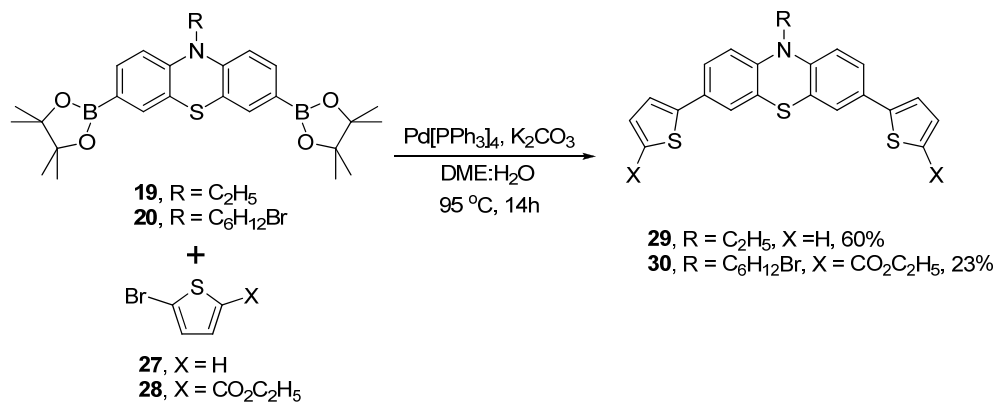
²² S.-L. Tseng, T.-K. Yang *Tetrahedron: Asymmetry* **2004**, *15*, 3375.

²³ C. Krämer, T. J. Zimmermann, M. Sailer, T. J. J. Müller *Synthesis* **2002**, *9*, 1163.



Scheme 14

The reactions take place in standard conditions for Suzuki cross-coupling reactions: a mixture of dimethoxyethane and water as the solvent, potassium carbonate as a base and the catalyst tetrakis[triphenylphosphine]palladium.²⁴ Subjecting the boronic esters **19** and **20** to a Suzuki cross-coupling reaction with thiophene derivatives, new thienyl substituted phenothiazines were obtained (Scheme 15).



Scheme 15

These derivatives can be subjected to macrocyclization reactions, followed by terminal bromine substitution with sulphur containing groups to ensure the chemisorption of the compounds on gold surfaces.

²⁴ (a) N. Miyaura, A. Suzuki *Chem. Rev.* **1995**, *95*, 2457. (b) M. Sailer, R.-A. Gropeanu, T. J. J. Müller *J. Org. Chem.* **2003**, *68*, 7509. (b)

2.3. Conclusions

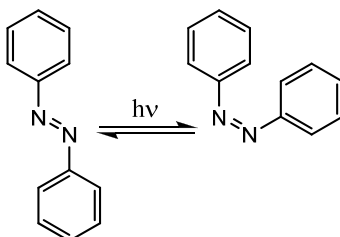
New phenothiazine derivatives with terminal thioacetate and thiol groups have been synthesized, their structure being supported by NMR spectroscopy. These derivatives have been used as ligands in experiments of chemisorption on gold surfaces, and the measurements performed on the resulting surfaces proved the formation of self assembled monolayers.

Several (hetero)aryl phenothiazine derivatives have been obtained and they can be used as precursors for more complex structures such as macrocycles.

3. Photoswitchable phenothiazine derivatives

3.1. Introduction

Cis-trans photoisomerisation of azobenzene is a form of light-induced molecular motion, azobenzene being able to switch by irradiation at different wavelengths from an extended *trans* configuration to a more sterically hindered *cis* form (Scheme 1).²⁵



Scheme 1

The azobenzene is considered the prototype of molecular switches and is present as the photoactive driving group in molecules like azacrownethers²⁶ or the more recent reported molecular tweezers.²⁷

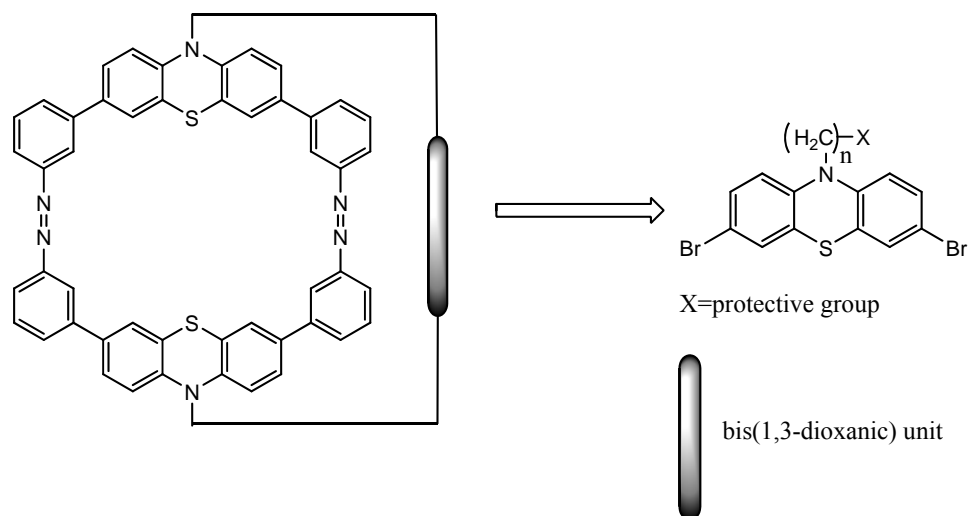
²⁵ (a) G. S. Kumar, D. C. Neckers *Chem. Rev.* **1989**, *89*, 1915. (b) T. Ishikawa, T. Noro, T. Shoda *J. Chem. Phys.* **2001**, *115*, 7503.

²⁶ S. Shinkai, M. Ishibara, K. Ueda, O. Manabe *J. Chem. Soc. Perkin Trans.* **1985**, *2*, 511.

²⁷ K. Kinbara, T. Muraoka, T. Aida *Org. Biomol. Chem.* **2008**, *6*, 1871.

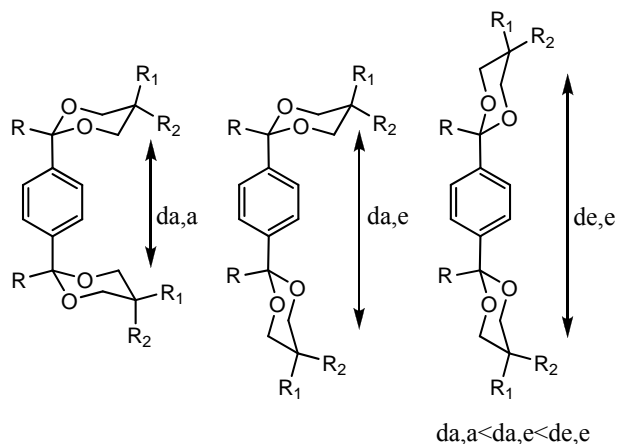
3.2. Results and discussion

Our goal is the synthesis of a new azobenzenic cyclic dimer with phenothiazine units which is able to perform molecular motion similar to an everyday hinge based on the *cis-trans* isomerisation of azobenzene. The two phenothiazine units are linked to the azobenzenic units by C-C atoms in the position 3 and 7 of the phenothiazine core and through the nitrogen atom to a dioxanic unit (Scheme 5).



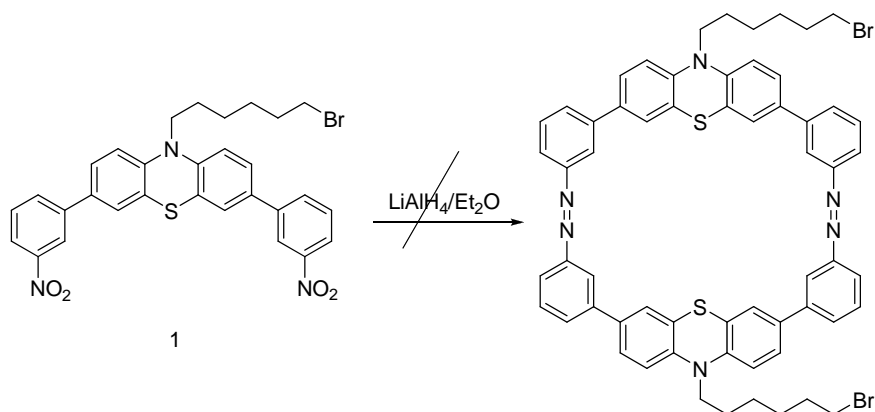
Scheme 5

These structure due do the presence of the two azobenzenic units, can switch from an “open” form when both azobenzenic units are *trans*, to a “closed” form when both azobenzenic units are *cis*. This motion can be transfered to the dioxanic bridge which can undergo conformational changes. Such a dioxanic bridge is the 1,4-bis(1,3-dioxane-2-yl)benzene, which can switch from the axial-axial conformer when the central benzenic unit is axial oriented towards the dioxanic units, to the equatorial-equatorial conformer when the benzenic ring adopts an equatorial orientation towards both dioxanic units. In the case of axial-axial conformer the distance between the two terminal dioxanic units is smaller than in the case of equatorial-equatorial conformer (Scheme 6).



Scheme 6

The building block of this structure is the cyclic azobenzenic dimer. One attempt to synthesize these building block was by following a method adapted from the literature.²⁸ This involved the reduction of dinitro phenothiazine derivative **1** with lithium aluminium hydride in dry diethylether at ultradilution. The mass spectrum of the crude product revealed a complex mixture of compounds hard to identify from which the expected cyclic dimer was missing (Scheme 7).



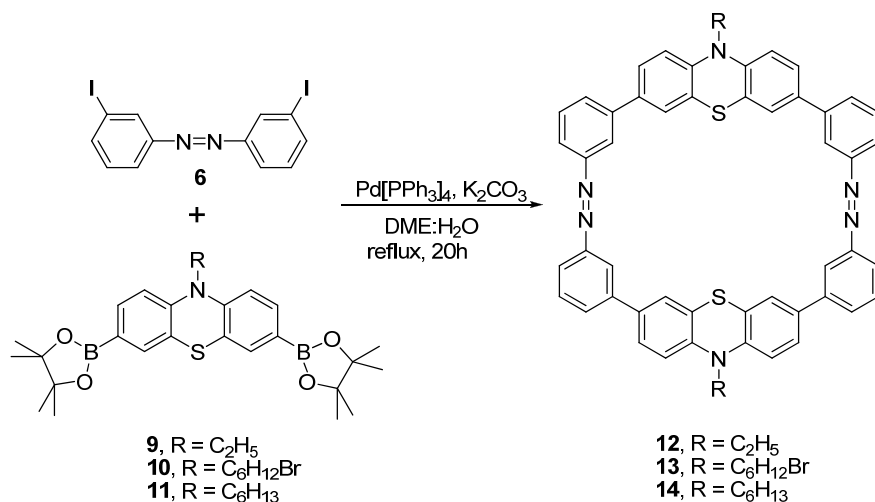
Scheme 7

The strategy was modified and another attempt was made by palladium catalyzed Suzuki cross-coupling macrocyclization,²⁹ between the boronic ester of phenothiazine and

²⁸ N. Tamaoki, M. Wada *J. Am. Chem. Soc.* **2006**, *128*, 6284.

²⁹ K. Memminger, T. Oeser, T. J. J. Müller *Org. Lett.* **2008**, *10*, 2797.

diiodoazobenzene at ultradilution in the presence of potassium carbonate as the base (Scheme 12).



Scheme 12

The mass spectra of the crude products reveals the corresponding peaks for the compounds **12-14**. In figure 2 the mass spectrum of ethyl derivative **12** is depicted.

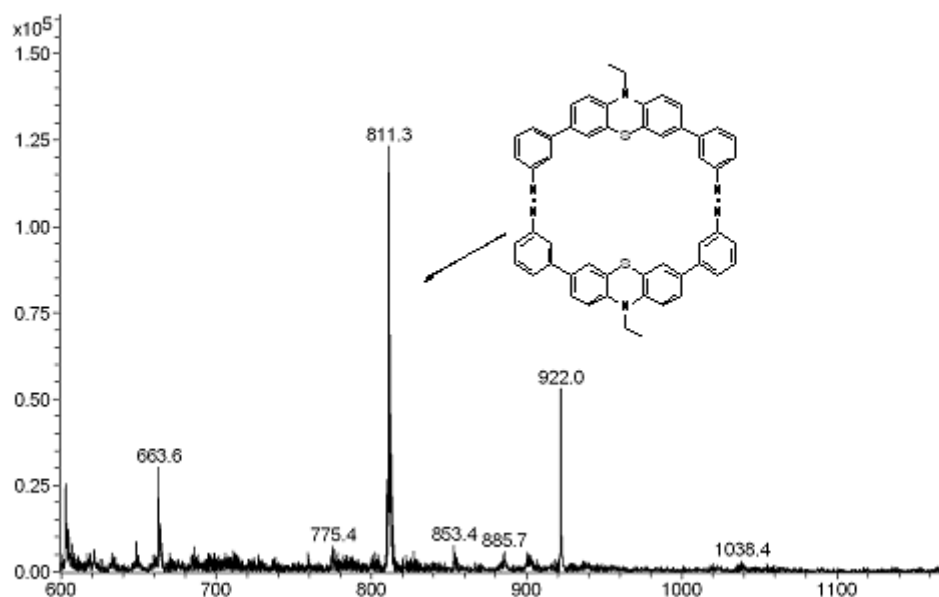


Figure 2 APCI+ mass spectrum of **12**.

The repeated attempts to purify the derivatives **12-14**, to perform other measurements to support their structure, failed. After purification the cyclic dimer **13**, can be further functionalized by substitution reactions with thioacetate or the phenothiazine units can be linked by dioxanic units due to the presence of bromine atoms susceptible of substitution reactions.

3.3. Conclusions

Suzuki cross-coupling intermolecular macrocyclization furnished the desired cyclic azobenzene dimers, but the repeated attempts to purify them in sufficient quantities to perform other analysis to support their structures failed. The cyclic dimer with bromohexyl unit can be linked by a dioxanic bridge to study the transfer of molecular motion provided by the *cis-trans* isomerisation of azobenzene to the dioxanic units.

4. Aromatic and heteroaromatic bridged diphenothiazines

4.1. Introduction

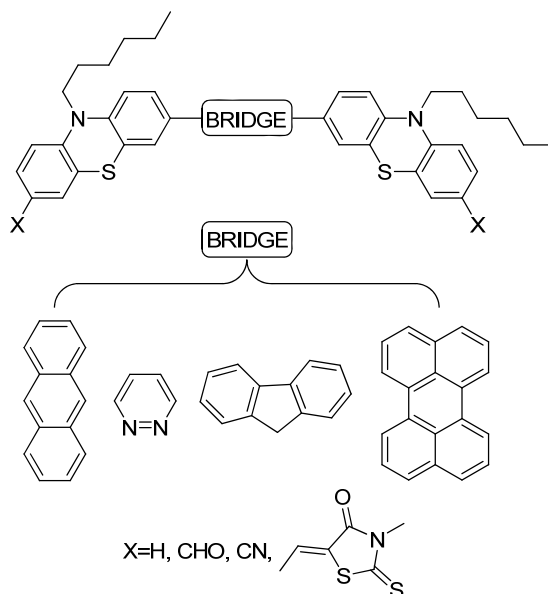
Recently a new series of diphenothiazine bridged by (hetero)aromatic units C-C ligated,³⁰ or N-C ligated were reported.³¹ These derivatives exhibit interesting electronic properties like high quantum yields, large Stokes Shifts and electronic communication between the phenothiazine units in the molecule.

4.2. Results and discussions

Our goal was the synthesis of some new similar diphenothiazine derivatives bridged by (hetero)aromatics and the investigation of their electronic properties (Scheme 3).

³⁰ C. S. Krämer, K. Zeitler, T. J. J. Müller *Tetrahedron Lett.* **2001**, 42, 8619.

³¹ A. W. Franz, L. N. Popa, F. Rominger, T. J. J. Müller *Org. Biomol. Chem.* **2009**, 7, 469.



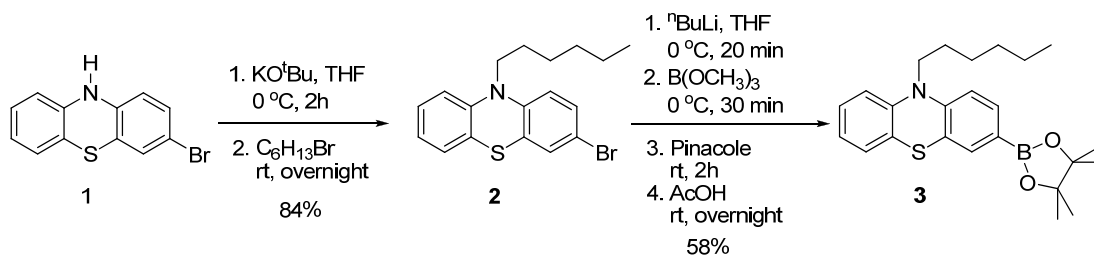
Scheme 3

These derivatives can be obtained by Suzuki cross-coupling reactions between the boronic ester of phenothiazine and the heteroaromatic halogenated derivatives.

4.2.1. Synthesis of the (hetero)aromatic bridged diphenothiazines

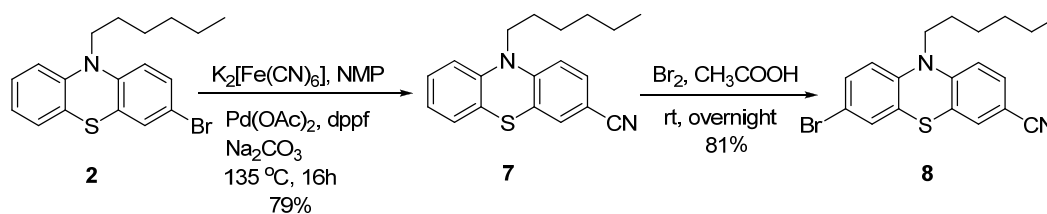
To obtain the target diphenothiazines a series of starting materials have been synthesised to be used in the final coupling reactions.

The boronic ester of phenothiazine **3** was obtained by subjecting the brominated derivative **2** to a Br-Li exchange with ⁿBu-Li followed by addition of trimethylborate and transesterification with pinacol.²³ The brominated derivative **2** was obtained by deprotonation of 3-bromo-10*H*-phenothiazine **1** with potassium tert-butyrate,¹⁷ followed by alkylation with hexyl bromide (Scheme 5).



Scheme 5

Another derivative useful in the cross-coupling reactions is the cyanoderivative **8** obtained starting from the monobrominated phenothiazine derivative **2**. The first step is the synthesis of derivative **7** from 3-bromo-10-hexyl-10*H*-phenothiazine **2**, via palladium catalyzed Beller³² cyanation, in *N*-methylpyrrolidine in the presence of sodium carbonate. The second step is the bromination of **7** with bromine in glacial acetic acid¹⁹ at room temperature to afford the cyanobrominated derivative **8** (Scheme 8).

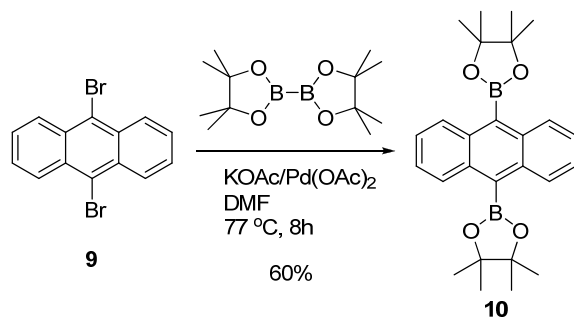


Scheme 8

Two pinacolyl boronic esters were synthesized for Suzuki cross coupling reactions. Pinacolyl boronic ester of anthracene **10** was synthesised by Miyaura coupling of 9,10-dibromoanthracene **9** with bispinacolatodiboron in the presence of palladium acetate as the catalyst³³ (Scheme 10).

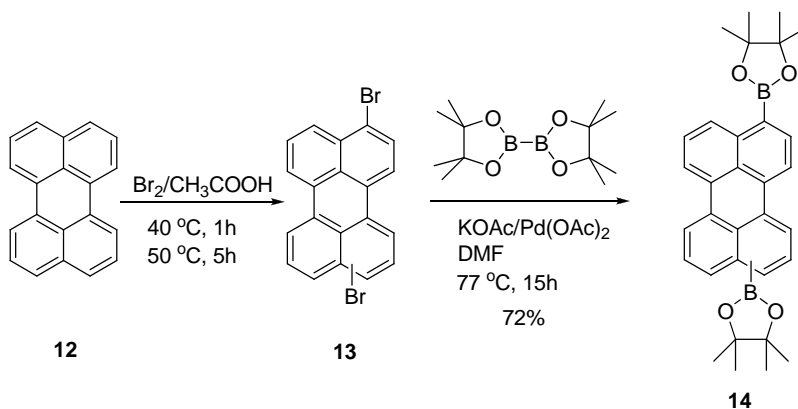
³² (a) T. Schareina, A. Zapf, M. Beller *Chem. Commun.* **2004**, 1388. (b) A. W. Franz, L. N. Popa, T. J. J. Müller *Tetrahedron Lett.* **2008**, 49, 3300.

³³ Y. Zhu, A. R. Rabindranath, T. Beyerlein, B. Tieke *Macromolecules* **2007**, 6981.



Scheme 10

To synthesize the bisboronic perylene derivative **14**, first was obtained the dibrominated derivative **13** by bromination of perylene **12** with bromine in glacial acetic acid. The reaction afforded an inseparable mixture of isomers (3,9 si 3,10-dibromoperylene)³⁴, which was further reacted to the pinacolyl boronic ester following the same procedure described in the case of anthracene³³ (Scheme 11).

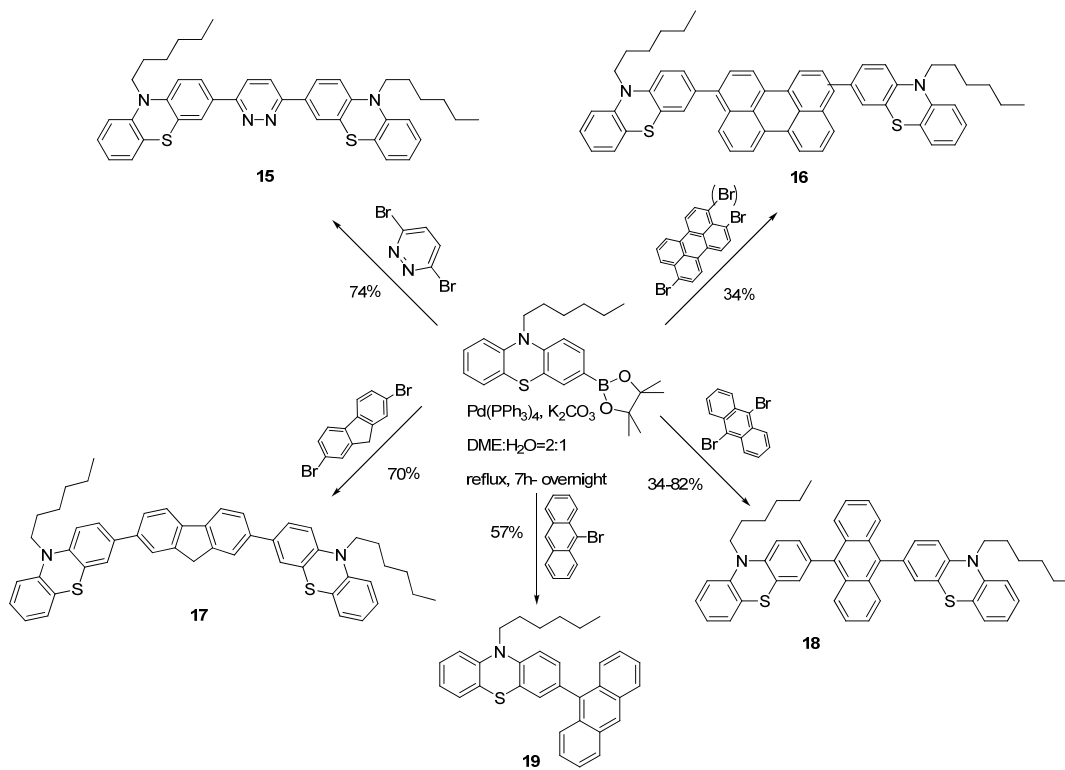


Scheme 11

The pinacolyl boronic ester of phenothiazine **3** was subjected to Suzuki coupling reactions using the standard conditions,²⁴ with different (hetero)aromatic halogenated derivatives to yield diphenothiazines **15-18** and monoderivative **19** in good yields³⁵ (Scheme 12).

³⁴ P. Schlichting, U. Rohr, K. Müllen *Liebigs Ann./Recueil* **1997**, 395.

³⁵ M. Hauck, R. Turdean, K. Memminger, J. Schönhaber, F. Rominger, T. J. J. Müller *J. Org. Chem.* **2010**, 75, 8591.



Scheme 12

The structure of these diphenothiazines is supported by ¹H and ¹³C NMR, UV-Vis, IR and mass spectra and correct combustion analysis.

In the case of derivative **16**, the ¹H NMR doesn't show different sets of signals for the possible two isomers as opposed to the dibrominated perylene derivative used as starting material.

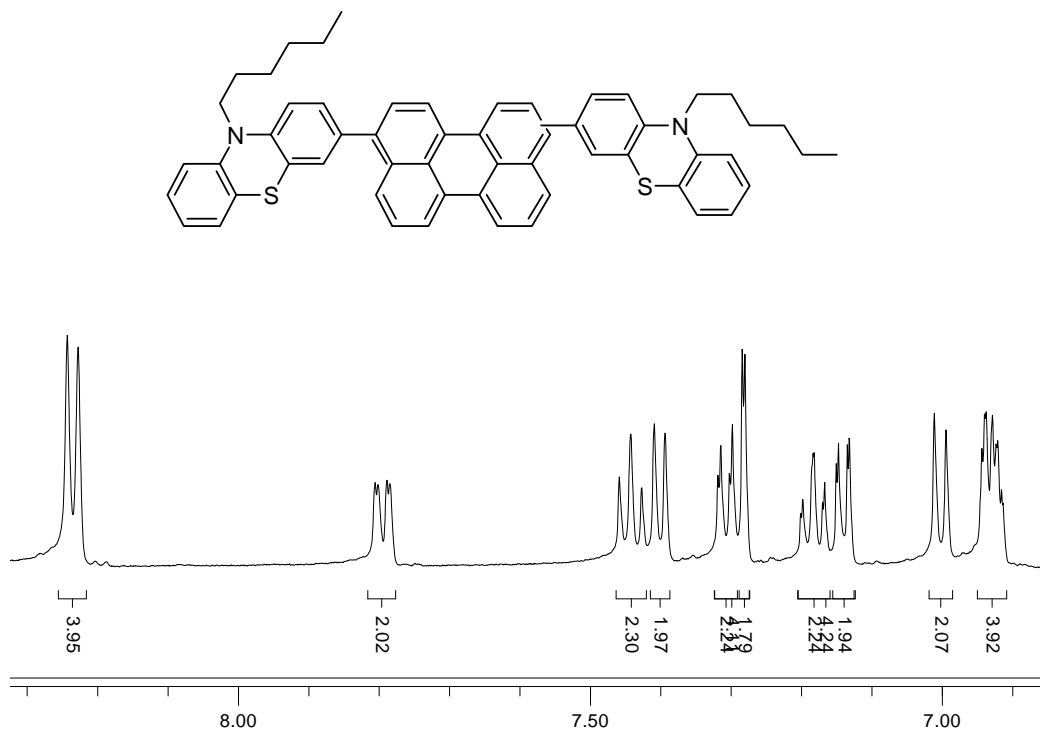
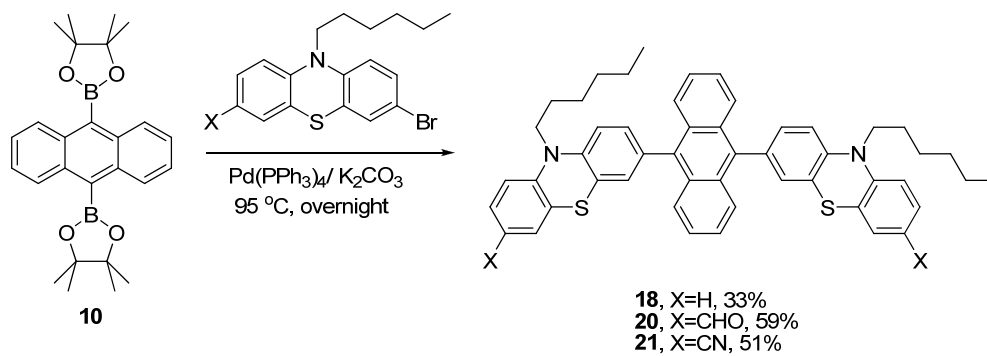


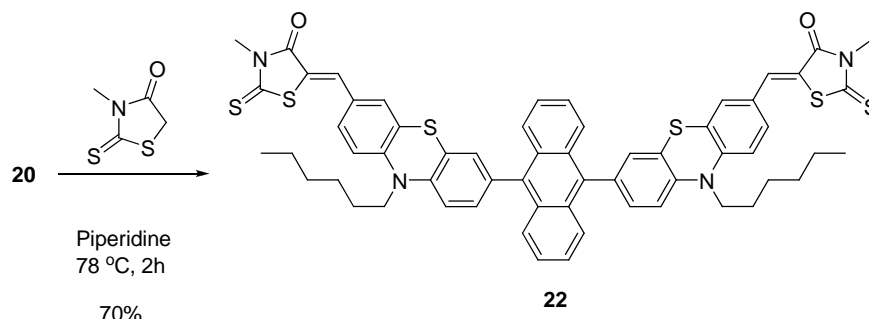
Figure 2 ¹H-NMR of **16** recorded in CH₂Cl₂, rt.

A new series of diphenothiazines bridged by anthracene units were synthesized by Suzuki cross-coupling between the pinacolyl boronic ester of anthracene and different halogenated phenothiazine derivatives (Scheme 13).



Scheme 13

Dialdehyde **20** was subjected to a new derivatization with cu rhodanine³⁶ in piperidine to furnish the derivative **22** (Scheme 14).



Scheme 14

In the mass spectrum of the compound **22** is observed the peak corresponding to the mass of the compound, but no ¹H NMR was recorded due to the very poor solubility of this compound.

4.2.2. Electronic properties of the (hetero)aromatic bridged diphenothiazines

The electronic properties of the diphenothiazine derivatives were investigated using absorption and emission spectroscopy and cyclic voltammetry.

The UV-Vis spectra of these derivatives show broad bands of absorption from 345 nm to 468 nm. They are fluorescent with yellow to orange emission and they exhibit broad emission bands in a range from 488 nm to 579 nm (Figure 3).

³⁶ S. S. Park, Y. S. Won, Y. C. Choi, J. H. Kim *Energy Fuels* **2009**, *23*, 3732.

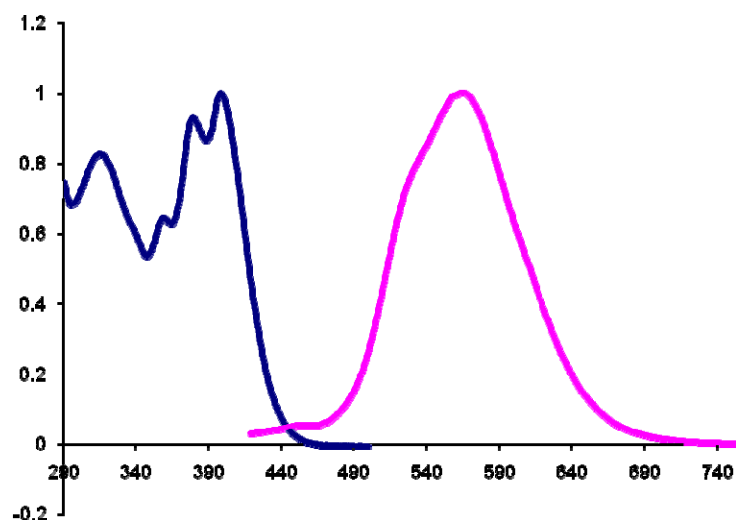


Figure 3 Absorption and emission spectra of **18** recorded in CH_2Cl_2 at room temperature.

The synthesized chromophores have large Stokes Shifts and high quantum yields calculated using as standards coumarine derivatives. Table 1 summarizes the absorption and emission spectroscopic data of derivatives **15-18** and **21**.

Compound	Absorption λ_{max} (nm)	Emission λ_{max} (nm)	Stokes shift (cm^{-1})	Quantum yield (%)
15	278, 394	521	6200	34
16	259, 468	579	4100	36
17	262, 329, 362	488	7200	60
18	258, 315, 398	572	7600	1
21	259, 327, 360, 379, 398	509	5500	14

Table 1 UV/vis, fluorescence and fluorescence quantum yields of derivatives **15-18** measured in dichloromethane at room temperature using as standards coumarin 151 ($\Phi_f=0.49$) for **15** and **17** and coumarin 153 ($\Phi_f=0.38$) for **16**, **18** and **21**.

Cyclic voltammetry was also employed to determine the electronic properties of the diphenothiazine derivatives in the electronic ground state (Figure 5).

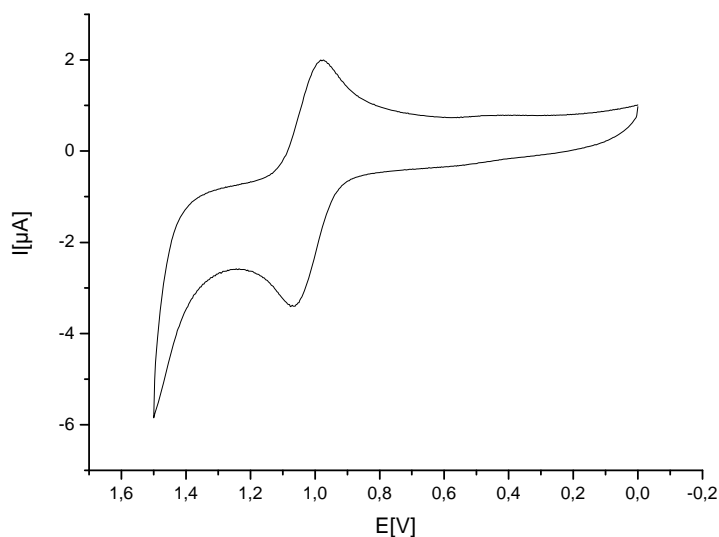


Figure 5 Cyclic voltammogram of **21** (CH_2Cl_2 , 20°C , scan rate=100 mV/s, supporting electrolyte: Bu_4NPF_6 ; Pt working electrode, Pt wire counter electrode, Ag/AgCl reference electrode).

The oxidation potentials of the unsubstituted derivatives **15-18** range from 678 mV to 764 mV. In the case of pyridazylene bridged diphenothiazine **15** the oxidation curve is anodically shifted to 764 mV, in comparison with *N*-hexyl phenothiazine potential ($E_0^{0/+1}=728$ mV). In the case of derivative **21** a greater anodic shift is observed (974 mV) due to the electronwithdrawing effect of the cyano substituent.

4.3. Conclusions

New (hetero)aromatic bridged diphenothiazines have been synthesized in good yields by Suzuki-Miyaura cross-coupling reactions. These derivatives exhibit interesting electronic properties: high quantum yields, large Stokes Shifts and various oxidation potentials.

5. Symmetrical naphthalene and perylene diimides with (oligo)phenothiazine units

5. 1. Introduction

Naphthalene diimides are an important class of organic compounds used as electron acceptor units in molecular sensors,³⁷ organic semiconductors³⁸ or in the supramolecular chemistry in rotaxanes or catenanes.³⁹

Naphthalene diimides can be synthesized in good yields by condensation of an amine with 1,4,5,8-naphthalenetetracarboxylic bisanhydride in dimethylformamide,⁴⁰ in glacial acetic acid⁴¹ or in quinoline in the presence of zinc acetate.⁴²

Perylenic diimides are electron acceptor units which can be reversibly reduced in mild conditions.⁴³ They are used as fluorescence standards,⁴⁴ in solar cells,⁴⁵ in self assembly experiments⁴⁶ and they can be easily synthesized by condensation of 3,4,9,10-perylenetetracarboxylic bisanhydride with an amine in dimethylformamide,⁴⁷ triethylamine, toluene or imidazole.⁴⁸

³⁷ S. V. Bhosale, C. H. Jani, S. J. Langford *Chem. Soc. Rev.* **2008**, *37*, 331.

³⁸ M. Takahashi, N. Nishizawa, S. Ohno, M. Kakita, N. Fujita, M. Yamashita, T. Sengoku, H. Yoda *Tetrahedron* **2009**, *65*, 2669.

³⁹ G. D. Pantos, P. Pengo, J. K. M. Sanders *Angew. Chem. Int. Ed.* **2007**, *46*, 194.

⁴⁰ Y. S. Chong, K. D. Shimizu *Synthesis* **2002**, *9*, 1239.

⁴¹ F. Würthner, S. Ahmed, C. Thalacker, T. Debaerdemaeker *Chem. Eur. J.* **2002**, *8*, 4742.

⁴² H. E. Katz, A. J. Lovinger, J. Johnson, C. Kloc, T. Siegrist, W. Li, Y.-Y. Lin, A. Dodalabapur *Nature* **2000**, *404*, 478.

⁴³ (a) H. Langhals *Heterocycles* **1995**, *40*, 477. (b) A. Arnaud, J. Bellenev, F. Boue, L. Bouteiller, G. Carot, V. Wintgens *Angew. Chem. Int. Ed.* **2004**, *43*, 1718.

⁴⁴ H. Langhals, R. Ismael, O. Yürück *Tetrahedron* **2000**, *56*, 5435.

⁴⁵ Q. Zhang, A. Cirpan, T. P. Russell, T. Emrick *Macromolecules* **2009**, *42*, 1079.

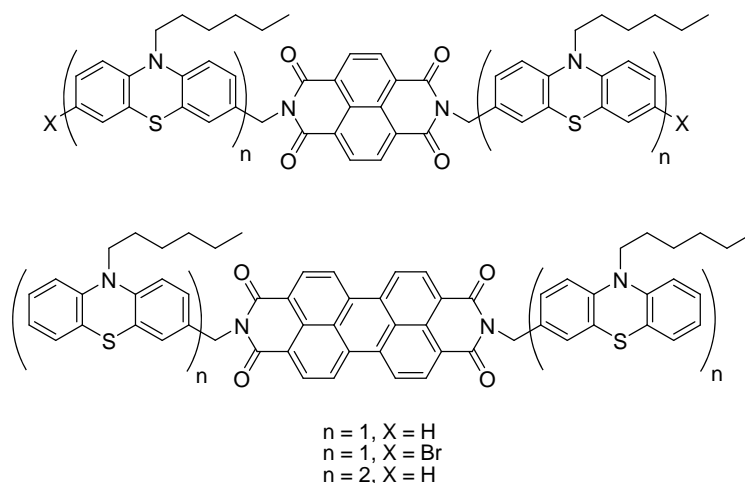
⁴⁶ W. Wang, J. J. Han, L.-S. Li, W. J. Shaw, A. D. Q. Li *Nano Lett.* **2003**, *3*, 455.

⁴⁷ J. Hou, S. Zhang, T. L. Chen, Y. Yang *Chem. Commun.* **2008**, 6034.

⁴⁸ J. Feng, Y. Zhang, C. Zhao, R. Li, W. Xu, X. Li, J. Jiang *Chem. Eur. J.* **2008**, *14*, 7000.

5.2. Results and discussion

Our goal was to synthesize new naphthalene and perylene diimides with (oligo) phenothiazine units and to investigate their electronic properties. The target compounds are showed in Scheme 3.



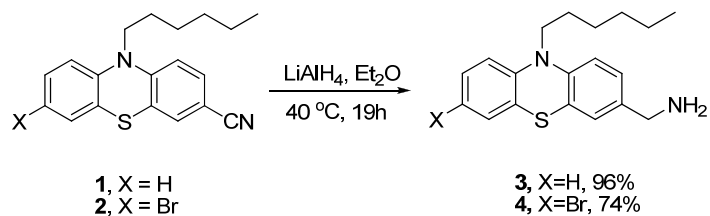
Scheme 3

The target compounds are obtained by condensation of phenothiazine amines with 1,4,5,8-naphthalenetetracarboxylic bisanhydride and 3,4,9,10-perylenetetracarboxylic bisanhydride respectively.

5.2.1. Synthesis of the naphthalene and perylene diimides with (oligo)phenothiazine units

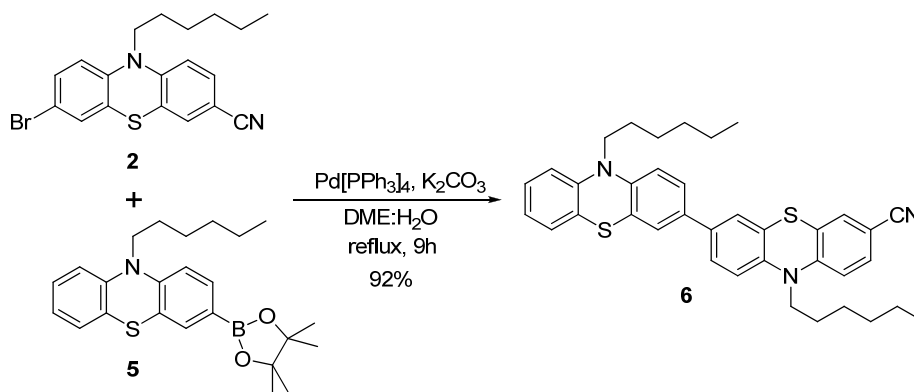
The phenothiazine amines used as starting materials in the synthesis of the diimide derivatives were obtained by reduction of cyano derivatives with lithium aluminium hydride in dry diethyl ether.⁴⁹ The amines **3** and **4** were obtained by reduction of nitrile **1** and bromonitrile **2**, the synthesis of those nitriles being described in the previous chapter (Scheme 4).

⁴⁹ A. W. Franz *Dissertation* 183.



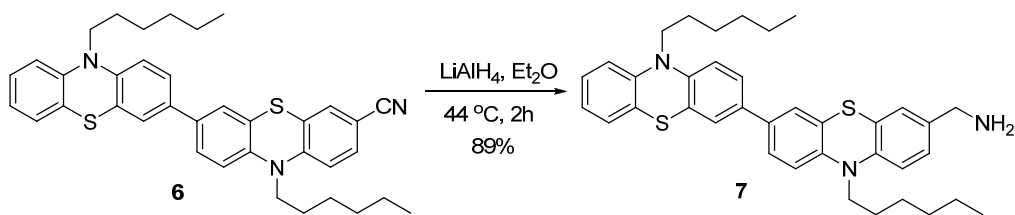
Scheme 4

Bromonitrile **2** was further used in the Suzuki²⁴ cross-coupling reaction with phenothiazine pinacolyl boronic ester **5** to obtain the diphenothiazine nitrile **6** in very good yield (Scheme 5).



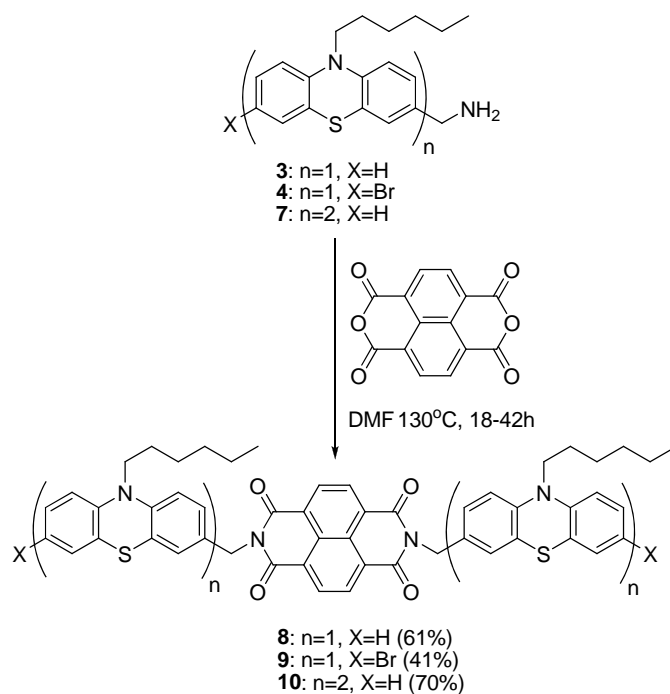
Scheme 5

Cyanoderivate **6** was reduced to the amine **7** in good yield, using the same reaction conditions presented above (Scheme 6).



Scheme 6

The amines **3**, **4** and **7** were subjected to a condensation reaction with 1,4,5,8-naphthalenetetracarboxylic bisanhydride in dimethylformamide, adapting a method described in the literature,³⁷ to afford diimides **8-10** in good yields (Scheme 7).



Scheme 7

The structure of these diimides is supported by mass, ¹H NMR, ¹³C NMR, UV-Vis and IR spectra and correct elemental analysis. In the ¹H NMR spectra the singlet signal characteristic for the protons in the methylene diimidic group appears at 5.23-5.24 ppm, while the singlet signal characteristic for the protons in the naphthalenic core appears at 8.72-8.73 ppm (Figure 1).

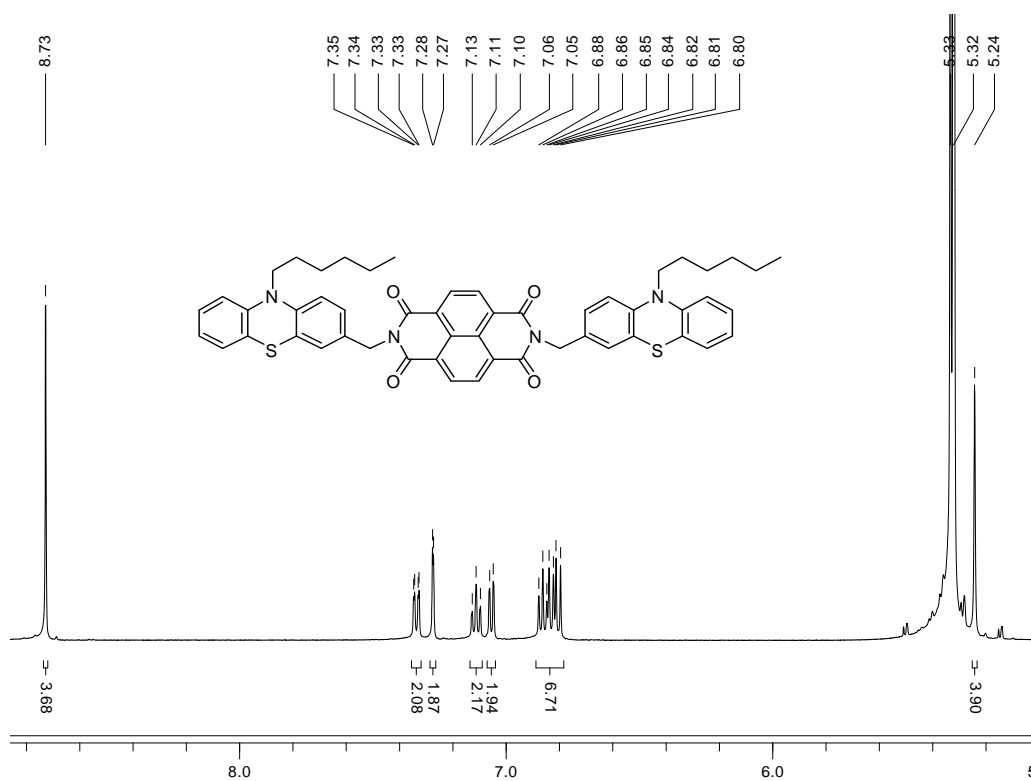
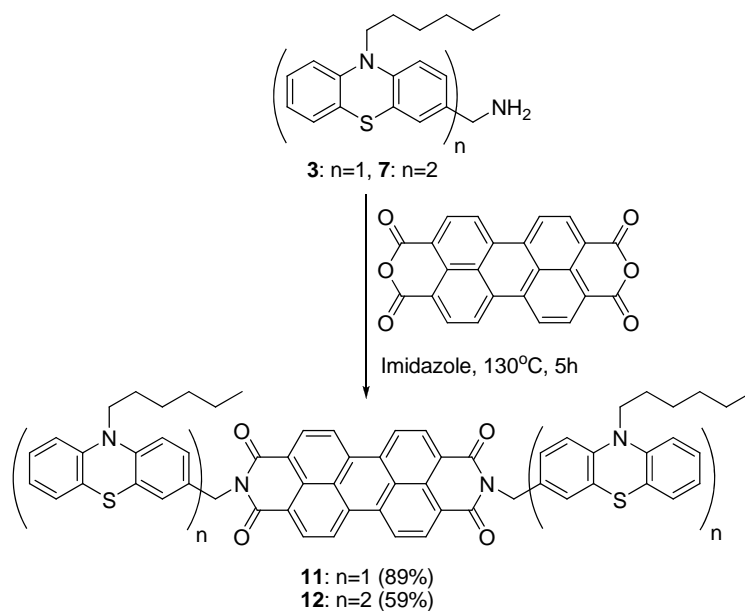


Figure 1. ¹H-NMR spectrum of **8** in CD₂Cl₂ at room temperature.

The perylene analogues were obtained by condensation of the amines **3** and **7** with 3,4,9,10-perylenetetracarboxylic bisanhydride in imidazole, adapting a procedure described previously⁴⁸ in the literature (Scheme 8).



Scheme 8

The ^1H NMR spectra exhibit the singlet signal corresponding to the protons in the methylene imidic group at 5.24 ppm and the doublet signals at 8.54-8.61 ppm corresponding to the peylenic core (Figure 3).

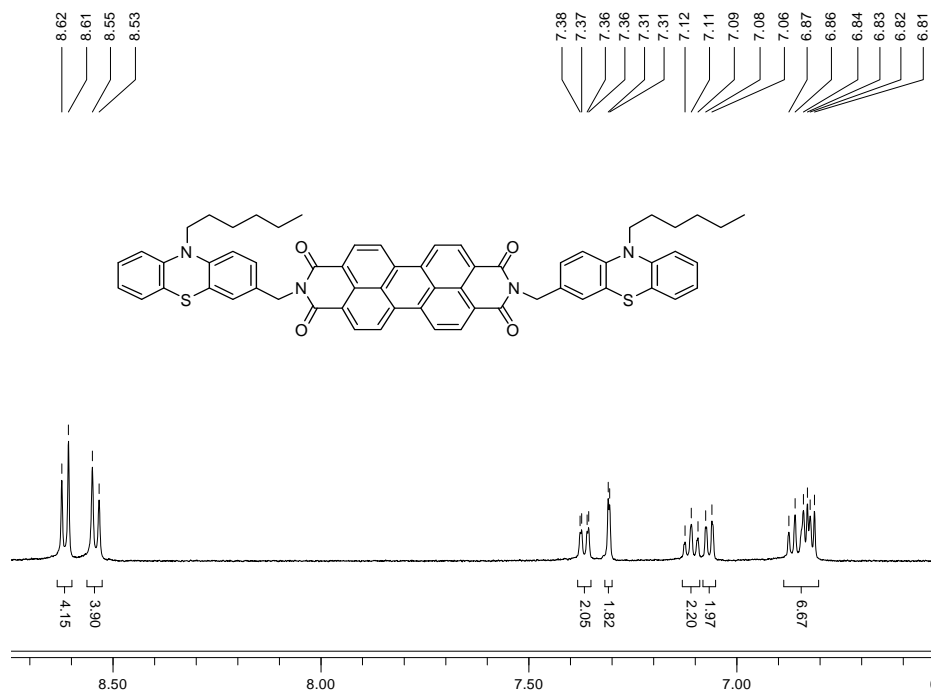
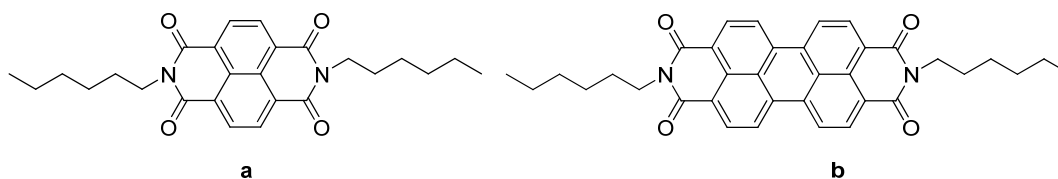


Figure 3 ^1H -NMR spectrum of **11** in CD_2Cl_2 at room temperature.

The structure of the perylene diimides **11** and **12** is confirmed by ^1H si ^{13}C NMR spectra (^{13}C NMR spectra just for derivative **12**, due to the poor solubility of derivative **11**), mass, IR, UV-Vis spectra and correct elemental analysis.

5.2.2. Electronic properties of the naphthalene and perylene diimides with (oligo)phenothiazine units

The electronic properties were investigated using absorption and emission spectroscopy and cyclic voltammetry and were compared to those of the hexyl diimides **a** and **b** showed in scheme 9.



Scheme 9

The absorption spectra of naphthalene diimides **8-10** show characteristic bands for the phenothiazine units in the range of 260-323 nm and characteristic broad bands for the naphthalene imidic core in the range of 342 and 382 nm (Figure 4).

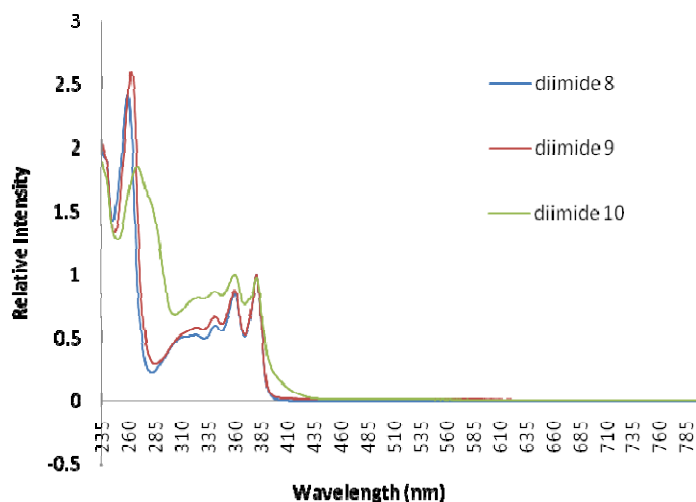


Figure 4 UV-Vis spectra of compounds **8-10** in CH_2Cl_2 at room temperature.

The perylene derivatives **11** and **12** exhibit the characteristic absorption bands for the perylene imidic unit in the range of 460 and 528 nm, next to those expected for the phenothiazine component (Figure 5).

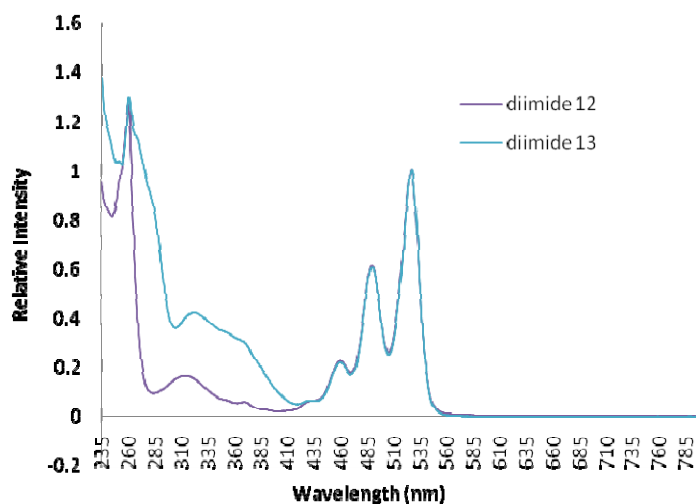


Figure 5 UV-Vis spectra of compounds **11** and **12** in CH_2Cl_2 at room temperature.

Table 1 summarizes the UV-Vis data of the diimidic derivatives **8-12**.

	λ_{\max} (ϵ) (nm)				
8	260 (70600)	323 (15200)	343 (17500)	361 (24800)	382 (29300)
9	263 (80100)	325 (17800)	342 (20400)	361 (26800)	382 (30700)
10	269 (97100)	343 (45400)	361 (52300)	382 (51000)	-
11	260 (122200)	313 (15700)	460 (21300)	491 (58700)	527 (96300)
12	261 (113500)	323 (36900)	460 (19100)	491 (53100)	528 (87900)

Table 1 UV-vis data of phenothiazine diimides **8-12**.

The synthesized diimides are decoupled in the ground state as shown by cyclic voltammetry. The cyclic voltammograms appear as superpositions of the oxidation waves corresponding to the electron donor component (phenothiazine) and of the reduction waves corresponding to the electron acceptor unit (arylene diimidic core).

Table 2 summarizes the redox potentials of the compounds **8-12** and of the reference diimides **a** and **b**.

	$E_0^{0/+1}$ mV	$E_0^{+1/+2}$ mV	$E_0^{0/+2}$ mV	$E_0^{0/-1}$ mV	$E_0^{-1/-2}$ mV
8	730	-	-	-612	-1073
9	809			-580	-1015
10	659	804	1481	-595	-1014
11	721	-	-	-566	-751
12	568	794	-	-592	-810
a	-	-	-	-657	-1084
b	-	-	-	-584	-780

Table 2 Redox potentials of phenothiazine diimides **8-12** and model compounds **a** and **b**.

The redox potentials are in the known range for the phenothiazine derivatives and naphthalene and perylene diimides (Figure 8).

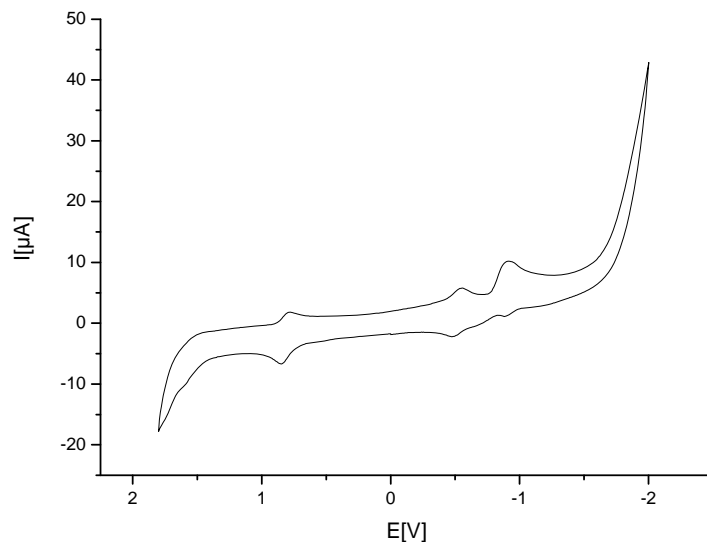


Figure 8 Cyclic voltammogram of **8** (CH_2Cl_2 , 20°C , scan rate=100 mV/s, supporting electrolyte: ${}^n\text{Bu}_4\text{NPF}_6$; Pt working electrode, Pt wire counter electrode, Ag/AgCl reference electrode).

In the case of derivative **8** the reversible oxidation curve corresponding to the phenothiazine component is observed in the anodic region, and the two reversible reduction waves assigned to the diimidic centre are observed in the cathodic region.

5.3. Conclusions

Five new arylene diimides with (oligo)phenothiazine units were synthesized in good yields by condensation of the (oligo)phenothiazine amines with arylene bisanhydrides. UV-Vis spectra and cyclic voltammetry appear as superpositions of the electron donor component and electron acceptor component and confirm their mutual decoupling in the electronic ground state.

General Conclusions

New phenothiazine derivatives with terminal thioacetate and mercapto units were synthesized and used as ligands for experiments of chemisorption on gold surfaces. New (hetero)aryl derivatives were synthesized as useful precursors for more complex structures such as macrocycles.

Suzuki intermolecular macrocyclization afforded new azobenzene cyclic dimers with phenothiazine units. The reaction mixtures were difficult to purify due to the formation in large amounts of oligomers and polymers, undesired but present products in the macrocyclization reactions. These compounds due to the presence of photosensitive azobenzene unit can be used as intermediates in the construction of molecular machines.

Suzuki-Miyaura cross-coupling between phenothiazine and different (hetero)arenes furnished new diphenothiazines bridged by (hetero)aromatics in good yields. Absorption and emission spectroscopy show fluorescence with emission of yellow to orange light, high quantum yields and large Stokes Shifts. Cyclic voltammetry confirms the expected electronic behaviour for the phenothiazine component in the anodic region and the coupling of the phenothiazine units in the electronic ground state.

The condensation of naphthalene and perylene bisanhydrides with (oligo)phenothiazine amines afforded new symmetrical redox active diimides in good yields. The electronic properties of these derivatives were studied by means of UV-Vis spectroscopy and cyclic voltammetry. These diimides are decoupled in the electronic ground state and the fluorescence of both phenothiazine and diimide centre is quenched.

Key words: phenothiazine, thioacetate, azobenzene, macrocycle, redox, diimide, cyclic voltammetry, fluorescence, Suzuki, Stokes shifts.