

Phenothiazinophanes: Synthesis, Structure, and Intramolecular Electronic Communication

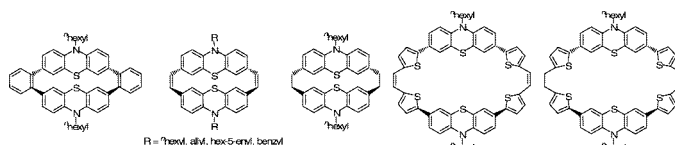
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ABSTRACT



Ortho-phenylene, ethenylene, and ethylene-bridged phenothiazinophanes are synthesized by Suzuki coupling or McMurry dimerization and catalytic hydrogenation at ambient pressure. Intensive intramolecular electronic communication of the phenothiazinyl subunits is found according to cyclic voltammetry. In addition, the macrocycles display blue to green fluorescence with large Stokes shifts. In the solid state, the cyclophanes are arranged in unidimensional stacks. This orientation appears to be favorable for anisotropic charge transport in hole-transport materials for organic field effect transistors (OFET) applications.

In cyclophanes,¹ the π -electron subsystems are placed in close proximity and in a parallel arrangement. Therefore, an intense intramolecular electronic communication established by through-bond and through-space interactions is found.² This overall theme has been exemplified for many arenes, heteroarenes, nonbenzoid π -systems, and even organometallic subunits. The incorporation of cyclophanes in polymers causes a change of the optical and electronical properties of the polymers.³ However, if the π -system itself is bent and unsymmetrical, stereochemical and stereoelectronic implications may arise that manifest in the electronic properties of these cyclophanes. Hence, phenothiazines as a structural motif in cyclophanes should enhance bending as

a consequence of the butterfly conformation of the benzo rings. Phenothiazines belong to an important class of tricyclic nitrogen–sulfur heterocycles.⁴ They display low oxidation potentials and radical cations with distinct, deep colored absorptions⁵ and have become important spectroscopic probes in molecular and supramolecular arrangements for photoinduced electron transfer (PET) studies⁶ and as motifs in organic materials.⁷ The prospect of integrating strongly coupled redox fragments like phenothiazines into conjugated

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(1) For an excellent recent monography, see, e.g.: *Modern Cyclophane Chemistry*; Gleiter, R., Hopf, H., Eds.; Wiley-VCH: Weinheim, 2004.

(2) For a recent review, see, e.g.: Tsuji, T. In *Modern Cyclophane Chemistry*; Gleiter, R., Hopf, H., Eds.; Wiley-VCH: Weinheim, 2004; pp 81–104.

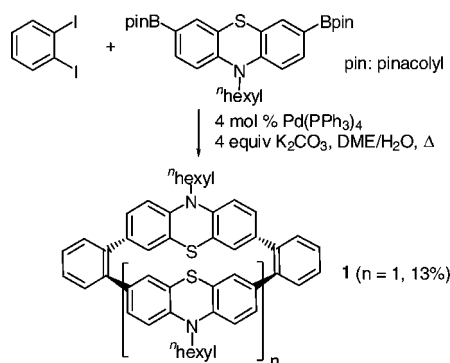
(3) (a) Morisaki, Y.; Chujo, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 6430–6437. (b) Morisaki, Y.; Ishida, T.; Chujo, Y. *Macromolecules* **2002**, *35*, 7872–7877.

(4) Sainsbury, M. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon: Oxford, 1984; Vol. 3, p 995.

(5) For cyclovoltammetric and spectroscopic data of phenothiazine, see, e.g.: (a) Tinker, L. A.; Bard, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 2316–2319. (b) Padusek, B.; Kalinowski, M. K. *Electrochim. Acta* **1983**, *28*, 639. (c) McIntyre, R.; Gerischer, H. *Ber. Bunsen Ges. Phys. Chem.* **1984**, *88*, 963–969.

(6) (a) Duesing, R.; Tapolsky, G.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 5378–5379. (b) Jones, W. E., Jr.; Chen, P.; Meyer, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 387–388. (c) Brun, A. M.; Harriman, A.; Heitz, V.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 8657–8663. (d) Burrows, H. D.; Kemp, T. J.; Welburn, M. J. *J. Chem. Soc., Perkin Trans. 2* **1973**, 969–974. (e) Collin, J.-P.; Guillerez, S.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1989**, 776–778. (f) Daub, J.; Engl, R.; Kurzwaga, J.; Miller, S. E.; Schneider, S.; Stockmann, A.; Wasielewski, M. R. *J. Phys. Chem. A* **2001**, *105*, 5655–5665.

Scheme 1. Suzuki Approach to *ortho*-Phenylene-Bridged Phenothiazinophane **1**

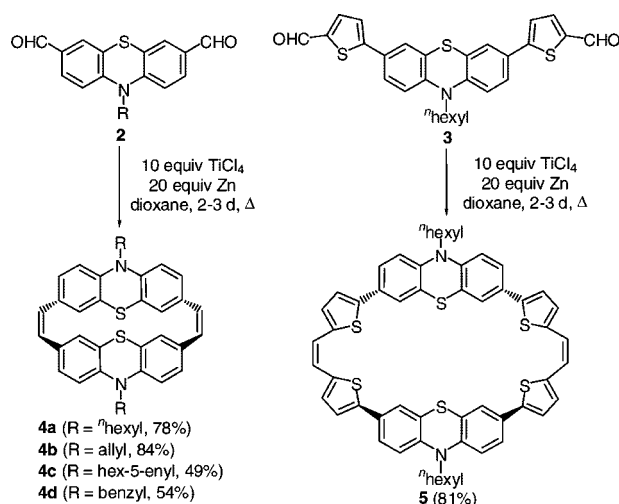


chains could constitute a so far unknown class of redox addressable molecular wires. In this respect, the question arises as to whether communication of two electrophoric subunits in phenothiazinophanes is still operative and to what extent it might occur. As part of our program to synthesize and investigate phenothiazinyl-based molecular wires⁸ and functional molecules,⁹ phenothiazinyl dyads, and triads,¹⁰ we now have focused on the synthesis and studies of phenothiazines embedded in a cyclophane topology. Here, we communicate the synthesis and structures of several phenothiazinophanes as well as the first studies on their electronic properties and their electronic structures.

Upon the basis of our previous experience using borylated phenothiazines in Suzuki couplings, a cross-coupling strategy for the formation of phenothiazinophanes was devised (Scheme 1).

Therefore, upon reacting 1,2-diiodo benzene and 10-*n*-hexyl-3,7-bis-(pinacolyl boryl)-10H-phenothiazine under pseudo high dilution Suzuki conditions,¹¹ the phenothiazinophane **1** was separated and isolated in 13% yield as a colorless crystalline solid. Besides, column chromatography allows the isolation of mixtures of higher macrocycles in minor amounts (identified by mass spectrometry). The molecular structure of **1** was unambiguously supported by

Scheme 2. Synthesis of Ethenylene-Bridged Phenothiazinophanes **4** and **5**



NMR spectroscopy, by MALDI-TOF, and additionally by X-ray structure analysis indicating an *anti* orientation of the phenothiazinyl moieties (see Supporting Information).¹²

Ethenylene-bridged cyclophanes can be readily synthesized by the McMurry coupling¹³ of suitable dialdehydes, and this approach has also been successfully applied to the synthesis of several heterophanes.¹⁴ Therefore, phenothiazinyl dialdehydes **2** are the suitable precursors for the synthesis of ethenylene-bridged phenothiazinophanes.¹⁵ Most conveniently, TiCl₄ and zinc were chosen as reagents as they are inexpensive and easy to handle.¹⁶

Reacting the phenothiazinyl dialdehydes **2** and **3** under McMurry conditions in boiling dioxane¹⁷ under pseudo high dilution for 2–3 days gave rise to the formation of the cyclophanes **4** and **5** in good yields (Scheme 2).

The structure of all cyclophanes was unambiguously supported by extensive NMR spectroscopy, mass spectrometry, combustion analyses, and later by an X-ray structure analysis of **4a**, again revealing an *anti* orientation of the phenothiazinyl moieties (Figure 1).¹²

(7) (a) Wheland, R. C.; Gillson, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3916–3925. (b) Berges, P.; Kudnig, J.; Klar, G.; Sanchez-Martinez, E.; Diaz-Calleja, R. *Synth. Met.* **1992**, *46*, 207–219. (c) Knorr, A.; Daub, J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2664–2666. (d) Spreitzer, H.; Scholz, M.; Gescheidt, G.; Daub, J. *Liebigs Ann. Chem.* **1996**, 2069–2077. (e) Spreitzer, H.; Daub, J. *Chem.-Eur. J.* **1996**, *2*, 1150–1158.

(8) (a) Müller, T. J. J. *Tetrahedron Lett.* **1999**, *40*, 6563–6566. (b) Krämer, C. S.; Zeitler, K.; Müller, T. J. J. *Org. Lett.* **2000**, *2*, 3723–3726. (c) Krämer, C. S.; Müller, T. J. J. *Eur. J. Org. Chem.* **2003**, 3534–3548. (d) Sailer, M.; Franz, A. W.; Müller, T. J. J. *Chem.-Eur. J.* **2008**, *14*, 2602–2614.

(9) (a) Sailer, M.; Nonnenmacher, M.; Oeser, T.; Müller, T. J. J. *Eur. J. Org. Chem.* **2006**, 423–435. (b) Sailer, M.; Rominger, F.; Müller, T. J. J. *J. Organomet. Chem.* **2006**, *691*, 299–308. (c) Hauck, M.; Schönhaber, J.; Zuccherro, A. J.; Hardcastle, K. I.; Müller, T. J. J.; Bunz, U. H. F. *J. Org. Chem.* **2007**, *72*, 6714–6725.

(10) (a) Krämer, C. S.; Zeitler, K.; Müller, T. J. J. *Tetrahedron Lett.* **2001**, *42*, 8619–8624. (b) Krämer, C. S.; Zimmermann, T. J.; Sailer, M.; Müller, T. J. J. *Synthesis* **2002**, 1163–1170. (c) Franz, A. W.; Müller, T. J. J. *Synthesis* **2008**, 1121–1125.

(11) Grave, C.; Schlüter, A. D. *Eur. J. Org. Chem.* **2002**, 3075–3098.

(12) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 685260 (**1**), CCDC685261 (**4a**), and CCDC 685262 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44–1223/336–033; E-mail: deposit@ccdc.cam.ac.uk).

(13) For reviews, see, e.g.: (a) McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513–1524. (b) Rieke, R. D.; Kim, S.-H. *J. Org. Chem.* **1998**, *63*, 5235–5239.

(14) (a) Ephritikhine, M.; Villiers, C. *Modern Carbonyl Olefination*; Wiley-VCH Verlag GmbH: Weinheim, New York, Chichester, Brisbane, Singapore, Toronto; 1. Auflage 2004, 223–285. (b) Kawase, T.; Ueda, N.; Tanaka, K.; Seirai, Y.; Oda, M. *Tetrahedron Lett.* **2001**, *42*, 5509–5511. (c) Vogel, E.; Binsack, B.; Hellwig, Y.; Erben, C.; Heger, A.; Lex, J.; Wu, Y. D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2612–2615.

(15) For the first phenothiazinophane, see: (a) Petry, C.; Lang, M.; Staab, H. A.; Bauer, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1711–1714. (b) Independently from our studies, a related phenothiazinophane has just recently been reported. See: Rajakumar, P.; Kanagalatha, R. *Tetrahedron Lett.* **2007**, *48*, 8496–8500.

(16) Lenoir, D. *Synthesis* **1977**, 553–554.

(17) Fürstner, A.; Bogdanović, B. *Angew. Chem., Int. Ed.* **1996**, *35*, 2442–2469.

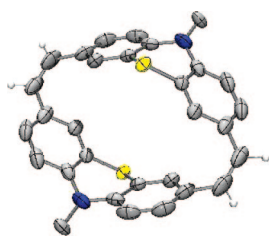
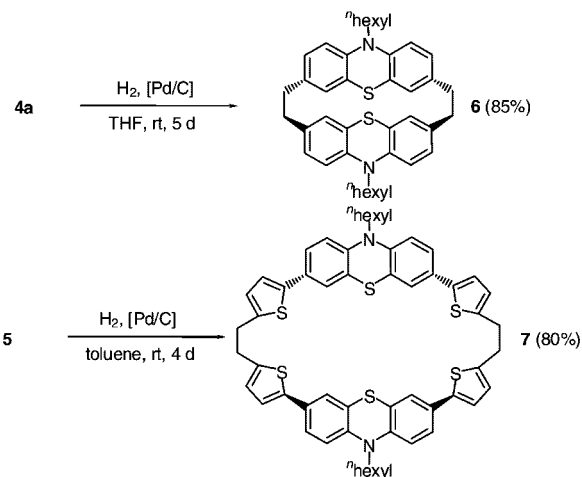


Figure 1. Molecular structure of **4a** (most hydrogen atoms were omitted, and the hexyl substituents were truncated for clarity).

Furthermore, by catalytic hydrogenation of the ethynylene-bridged cyclophanes **4a** and **5**, the ethylene-bridged phenothiazinophanes **6** and **7** were obtained in good yields as crystalline solids (Scheme 3).

Scheme 3. Synthesis of Ethylene-Bridged Phenothiazinophanes **6** and **7** by Hydrogenation



In addition to NMR spectroscopy supporting the C_{2h} symmetry of the cyclophane structure by appearance of a single set of signals for the benzo and ethynylene proton and carbon nuclei, and combustion analytical characterization of **6** and **7**, the structure of cyclophane **6** was corroborated by an X-ray structure analysis that displays an *anti* orientation of the phenothiazinyl moieties (see Supporting Information).¹²

The electronic properties of the phenothiazinophanes **1**, **4**, **5**, **6**, and **7** have been investigated by absorption and emission spectra and cyclic voltammetry (Table 1). Optical spectroscopy (UV/vis and fluorescence spectra) reveals fluorescence with emission of blue to green light and large Stokes shifts ($\Delta\tilde{\nu} = 7900\text{--}9700\text{ cm}^{-1}$), however, with relatively low fluorescence quantum yields Φ_f ¹⁸ ranging

(18) Fluorescence quantum yields were determined with perylene ($\Phi_f = 0.32$) or with coumarine 6 ($\Phi_f = 0.78$) as standards. For a reference, see: Du, H.; Fuh, R. A.; Li, J.; Corkan, A.; Lindsey, J. S. *Photochem. Photobiol.* **1998**, *68*, 141–142.

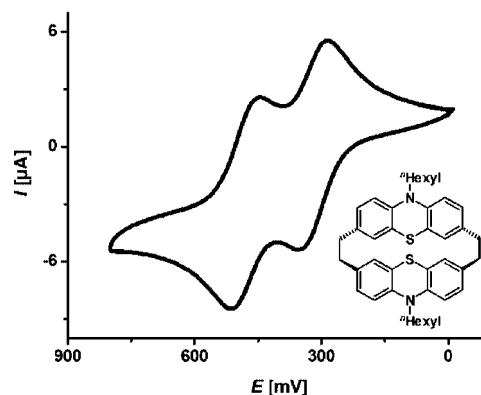


Figure 2. Cyclic voltammogram of **6** in CH_2Cl_2 . $T = 293\text{ K}$; electrolyte, $0.1\text{ M NBu}_4\text{PF}_6$ (CH_2Cl_2); $\nu = 100\text{ mV/s}$; Pt as a working and a counter electrode; Ag/AgCl as a reference electrode (determined vs ferrocene, $E_{0/+1}^{0/+1} = +450\text{ mV}$).

between 2 and 7%. Electrochemical data for **1**, **4**, **5**, **6**, and **7** were obtained by cyclic voltammetry in the anodic region (scan area up to 1.5 V) (Figure 2).

According to spectroscopic and X-ray analyses, phenothiazinophanes are highly symmetric, and their phenothiazinyl moieties are identical due to symmetry. Interestingly, all cyclophanes show cooperative behavior of their first two one-electron oxidations which are fully reversible in most cases in accordance with Nernstian behavior. Upon reduction of the bridging double bonds of **4a** and **5** to give the bisethynylene-bridged cyclophanes **6** and **7**, the first oxidations are expectedly shifted cathodically as a consequence of 3,7-dialkyl substitution. Most remarkably, the cyclophanes display clearly separated first and second one-electron oxidations which can be attributed to an intramolecular electronic communication. The separations of half-wave potentials lie between 113 and 206 mV and reveal a considerable stabilization of the initially formed radical cation by $\sigma\text{--}\pi$ through-bond and through-space interactions. Furthermore, DFT computations¹⁹ reveal that the electron

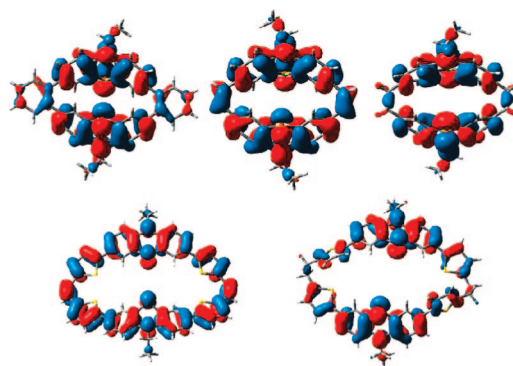


Figure 3. HOMOs of **1** (top left), **4a** (top center), **6** (top right), **5** (bottom left), and **7** (bottom right) as calculated on the level of DFT (B3LYP/6-31+G (d,p)).

Table 1. Selected UV/vis, Fluorescence, and Electrochemical Data of the Cyclophanes **1**, **4**, **5**, **6**, and **7** (Recorded in Dichloromethane at 20 °C, Cyclic Voltammetry in a 0.1 M Solution of NBu₄PF₆ in CH₂Cl₂ as an Electrolyte, Pt as a Working and Counter Electrode, vs Ag/AgCl, at $\nu = 100$ mV)

compd	absorption λ_{max} [nm]	emission λ_{max} [nm]	Stokes shift ^a [cm ⁻¹] (Φ_f)	$E_{1/2}^{0/+1}$ [mV]	$E_{1/2}^{+1/+2}$ [mV]
1	240,268,304, 330	466	8800(7%) ^b	782	913
4a	268,316, 346	522	9700	733	911
4b	266,314, 346	521	9700	767	960
4c	268,316, 346	521	9700	735	912
4d	266,312, 346	519	9600	796	1002
5	248,302,352, 388	572	8300(4%) ^c	445 ^d	680 ^{e,f,g}
6	256, 310	440	9500	611	753
7	242,291, 350	484	7900(3%) ^c	600	713 ^h

^a $\Delta\tilde{\nu} = \lambda_{\text{max,abs}} [\text{cm}^{-1}] - \lambda_{\text{max,em}} [\text{cm}^{-1}]$. ^b Fluorescence quantum yield was determined with perylene as a standard. ^c Fluorescence quantum yield was determined with coumarine 6 as a standard. ^d Quasireversible oxidations. ^e Irreversible oxidation wave. ^f Sharp signal at $E_{1/2}^{+2/+4} = 925$ mV indicating chemically reversible electrode adsorption. ^g Irreversible oxidation wave at 1240 mV and cathodic peak potentials at 1110 and 1050 mV. ^h An additional reversible two electron oxidation is found at $E_{1/2}^{+2/+4} = 1150$ mV.

density is delocalized over the complete molecular framework in the oxidation relevant HOMOs (Figure 3).

As a consequence of an average intramolecular distance of the central thiazinyl cores of 6.0 Å (as extracted from X-ray structure analyses) and the mutual orthogonalization of the bridges and the phenothiazinyl moieties, π – π through-bond interactions are very unlikely for **1**, **4**, **6**, and **7**; however, cyclophane **5** opens this pathway by efficient π -conjugation. With this respect, these phenothiazinophanes can be classified a Robin–Day class II electron transfer system.²⁰

Finally, as a consequence of high molecular symmetry, of ellipsoidal shape, and *anti*-orientation of the phenothiazinyl cores, intermolecular stacking and its influence on crystal packing can be expected. Indeed, the molecules are organizing along the crystallographic *z*-axis with intermolecular benzo ring distances of 8.0–11.8 Å (Figure 4).¹² Hence,

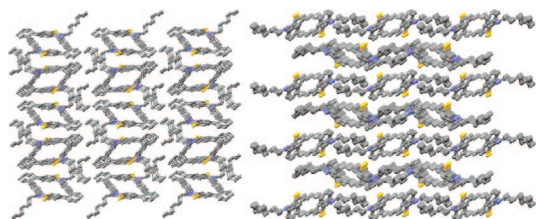


Figure 4. Crystal packing of phenothiazinophanes **1** (left) and **4a** (right) (views along the crystallographic *z*-axes, hydrogen atoms were omitted for clarity).

structural anisotropy, a prerequisite for solid state phenomena such as electrical charge transport in semiconductors in the direction of the intermolecular stacks,²¹ can be expected. In particular, phenothiazines are able to form π -mers upon interaction of radical cation and neutral species.²² As recently

demonstrated for triphenylamine-based cyclophanes,²³ phenothiazinophanes should be good candidates as novel organic field effect transistors (OFET).

In conclusion, we have developed a general synthesis to ethynylene and ethylene-bridged phenothiazinophanes applying McMurry dimerization to phenothiazinyl aldehydes. All representatives reveal intensive intramolecular electronic communication of the phenothiazinyl subunits according to cyclic voltammetry. DFT calculations show that the HOMOs of the cyclophanes possess a fully delocalized structure, and communication over the bridges rather likely occurs by σ – π interaction. In the solid state, the cyclophanes are arranged in unidimensional stacks, a favorable orientation for anisotropic hole-transport in OFET applications.

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Supporting Information Available: Experimental procedures, spectroscopic and analytical data of compounds **1**, **4**, **5**, **6**, and **7**, ¹H and ¹³C NMR spectra, crystallographic data of compounds **1**, **4a**, and **6**, and molecular modeling coordinates of structures **1**, **4a**, **6**, **5**, and **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(20) (a) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, 247–422. (b) Bott, A. W. *Curr. Sep.* **1997**, 61–66. (c) Stoll, M. E.; Lovelace, S. R.; Geiger, W. E.; Schimanke, H.; Hyla-Kryspin, I.; Gleiter, R. *J. Am. Chem. Soc.* **1999**, 121, 9343–9351.

(21) Facchetti, A.; Mushrush, M.; Yoon, M.-H.; Hutchison, G. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, 126, 13859–13874.

(22) Sun, D.; Rosokha, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **2004**, 126, 1388–1401.

(23) Song, Y.; Di, C.; Yang, X.; Li, S.; Xu, W.; Liu, Y.; Yang, L.; Shuai, Z.; Zhang, D.; Zhu, D. *J. Am. Chem. Soc.* **2006**, 128, 15940–15941.

(19) As implemented in: *PC Spartan 02*; Wavefunction Inc.: Irvine, CA, 2002.