

Butadiynyl-bridged Diphenothiazines – Redox-active Fluorophores and Self-assembly on HOPG

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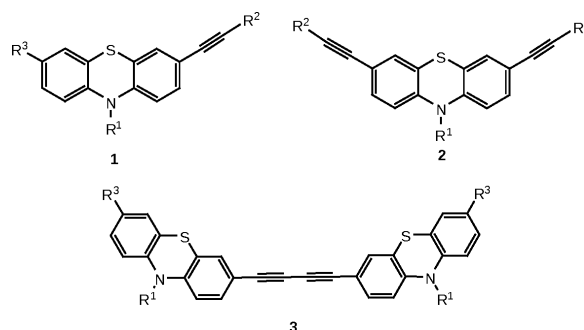
Dedicated to Professor Gerhard Maas on the occasion of his 60th birthday

Ethynyl phenothiazines are oxidatively coupled to symmetrical dumbbell-shaped butadiynyl-bridged diphenothiazines in good yields. These molecules show intense absorption bands, intense blue-green luminescence with large Stokes shifts, and reversible oxidation potentials in the anodic region. Thermally, these butadiynes do not undergo topochemical polymerization, but oligomerizations to oligomeric polycyclic heterocycles with complex structures in the melt. STM images of two representatives on HOPG (highly oriented pyrolytic graphite) show the formation of monolayers adsorbed by attractive π - π interactions.

Key words: Alkynes, Cyclic Voltammetry, Fluorescence, Phenothiazines, STM, Self-assembly

Introduction

Phenothiazines represent a pharmaceutically important class of heterocycles [1] and have found application as sedatives, tranquilizers, anti-epileptics, anti-tuberculous, anti-pyretics, anti-tumor agents, bactericides, and parasitocides [2]. In addition, phenothiazines are able to cleave DNA upon photochemical induction [3]. Fairly early, it became apparent that the low oxidation potential of this class of tricyclic nitrogen-sulfur heterocycles, and their propensity to form stable radical cations play a key role in their physiological activities [4]. More recently, due to their reversible oxidation [1, 5], phenothiazine derivatives have become attractive supramolecular [6] and material scientific [7] motifs. In the past years we have explored syntheses and electronic properties of oligophenothiazines also with respect to their suitability as redox switchable functional π systems. Straightforward syntheses of 3-mono- and 3,7-dialkynylated phenothiazines **1** and **2** have given access to redox active oligomers [8]. By Eglinton coupling of monoethynyl species **1** dumbbell-shaped butadiynyl-bridged diphenothiazines **3** can be obtained in good yields [9]. Here, we report in detail the synthesis and electronic properties of butadiynyl-

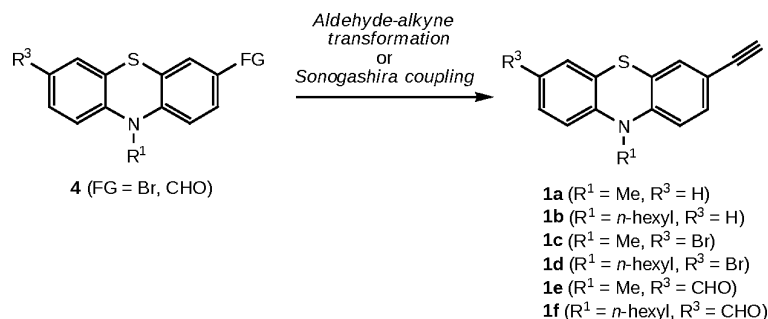


bridged diphenothiazines **3** as well as their thermal behavior and self-assembly on HOPG (highly oriented pyrolytic graphite).

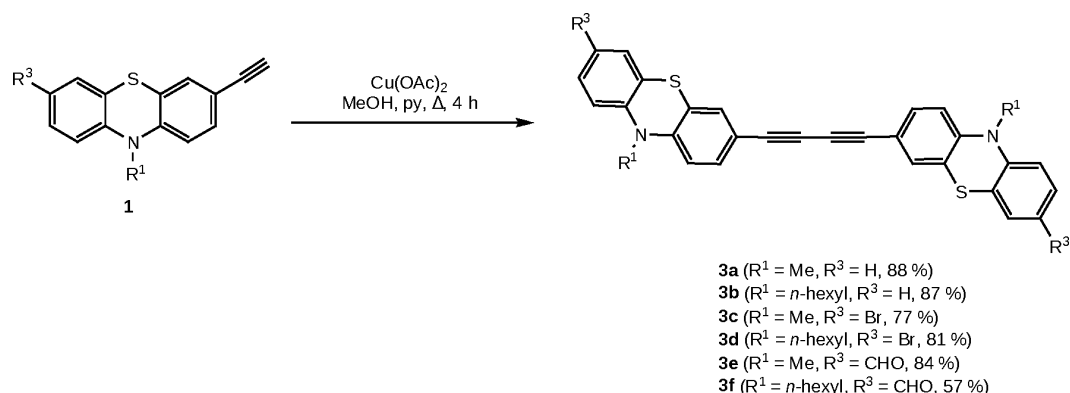
Results and Discussion

Synthesis

Mono- and diethynylated phenothiazines **1** ($R^2 = H$) and **2** ($R^2, R^2 = H, H$) are suitable building blocks for alkynyl-bridged phenothiazine-based redox systems and can be readily prepared by both aldehyde-alkyne transformations and cross-coupling methodologies [8]. In particular, 7-bromo phenothiazine 3-carb-



Scheme 1. General synthesis of 7-functionalized 3-ethynyl *N*-alkyl phenothiazines **1**.



Scheme 2. Synthesis of butadiynyl-bridged diphenothiazines **3** by Eglinton coupling.

aldehydes **4** ($R^3 = \text{Br}$, FG = CHO or $R^3 = \text{CHO}$, FG = Br), obtained by bromination of the phenothiazine 3-carbaldehydes in acetic acid in good yields, can selectively be functionalized to 3-ethynyl *N*-alkyl phenothiazines **1** ($R^2 = \text{H}$) bearing either a 7-bromo ($R^3 = \text{Br}$) or an aldehyde function ($R^3 = \text{CHO}$). Applying this synthetic concept, a series of 7-functionalized and unfunctionalized 3-ethynyl *N*-alkyl phenothiazines **1** are easily synthesized (Scheme 1).

With these 3-ethynyl phenothiazines in hand, oxidative dimerization by the copper-mediated Eglinton coupling [10] in a boiling mixture of methanol and pyridine gives rise to the formation of butadiynyl-bridged diphenothiazines **3** as intensively yellow to yellow-orange solids in good yields (Scheme 2). Most characteristically, upon UV irradiation of solutions of butadiynyl-bridged diphenothiazines **3** intense blue-green emission becomes immediately apparent.

The molecular structures of the dumbbell-shaped diphenothiazines were unambiguously assigned by ^1H and ^{13}C NMR spectra showing due to symmetry only a single set of signals. In the IR spectra the characteristic alkynyl C-H and $\text{C}\equiv\text{C}$ stretching vibrations are found around 3290 cm^{-1} and between 2100 and 2220 cm^{-1} ,

respectively. In the mass spectra the molecular ions are always the base peaks followed by a fragment resulting from α -cleavage of the alkyl side chains. Computations of the truncated model of **3b** on the DFT level show a butterfly angle of the benzo rings of 149.4° (*vide infra*) [11].

Electronic properties (absorption, emission, redox properties)

All butadiynyl-bridged phenothiazines **3** absorb in the UV close to the visible region and display intense blue-green emission (Table 1). Based upon the DFT structure optimization of the truncated butadiyne **3b** (*vide supra*), single point ZINDO-CI computations [12] were performed for assigning the electronic structure of the longest wavelength absorption bands [13]. The three longest wavelength bands of **3b** at 281, 316, and 389 nm are reproduced by the calculations with absorption bands at 285, 306, and 360 nm. The lowest energy band at 360 nm, *i. e.* the S_1 state, displays considerable oscillator strength and consists to 66 % of a HOMO-LUMO transition, where in the sense of a $\pi\text{-}\pi^*$ transition electron density is transferred from the terminal phenothiazine donors

Compound	R ³	R ¹	Absorption λ_{max} (nm)	Emission λ_{max} (nm) (Φ_f)	Stokes shift $\Delta\tilde{\nu}^a$ (cm ⁻¹)
3a	H	Me	281, 315, 388	483 (0.42)	5100
3b	H	<i>n</i> -hexyl	281, 316, 389	485 (0.43)	5100
3c	Br	Me	275, 320sh, 343sh, 388	475 (0.35)	4700
3d	Br	<i>n</i> -hexyl	278, 319sh, 349sh, 389	476 (0.36)	4700
3e	CHO	Me	292, 408	527 (0.31)	5500
3f	CHO	<i>n</i> -hexyl	296, 411	534 (0.32)	5600

Table 1. Selected UV/Vis and emission data recorded in CHCl₃ ($T = 293$ K). The photoluminescence quantum yields Φ_f were determined with perylene as a standard ($\Phi_f = 0.94$). Wavelengths in bold face were used to calculate the Stokes shifts $\Delta\tilde{\nu}$.^a

^a $\Delta\tilde{\nu} = \lambda_{\text{max,abs}} - \lambda_{\text{max,em}}$ (cm⁻¹).

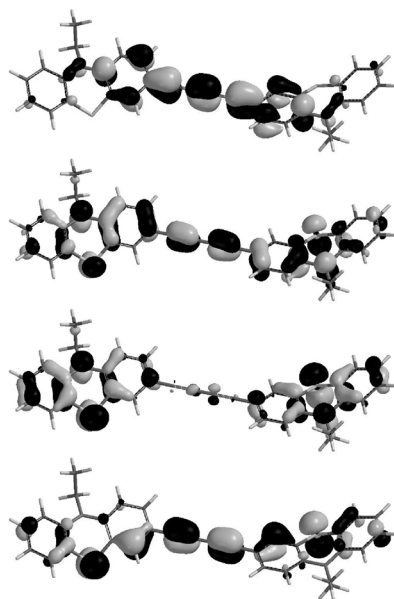


Fig. 1. DFT-computed frontier molecular orbitals (FMOs) of the truncated butadiyne **3b** (from bottom to top): HOMO-2 (−5.77807 eV), HOMO-1 (−5.05490 eV), HOMO (−4.78229 eV), and LUMO (−1.45497 eV).

(HOMO) to the central butadiyne bridge (LUMO) (Fig. 1). The band at 306 nm has a weak oscillator strength based on two higher singlet states, where substantial contributions of HOMO-1-LUMO+2 (14 %), HOMO-LUMO+2 (30 %), and HOMO-1-LUMO+3 (14 %), HOMO-LUMO+3 (31 %), respectively, are found. The higher singlet states arising from the absorption band at 285 nm are again strong with respect to the oscillator strength and consist of HOMO-LUMO (7 %), HOMO-1-LUMO+1 (33 %), and HOMO-2-LUMO (12 %) transitions. The intensity of all three bands can be rationalized qualitatively by consulting the orbital coefficients of the three highest occupied frontier molecular orbitals (FMOs) (Fig. 1). Significant electron density is localized on the phenothiazinyl termini and on the bridge. Therefore, the Franck-Condon factors should be reasonably large duely resulting in substantial transition dipole moments.

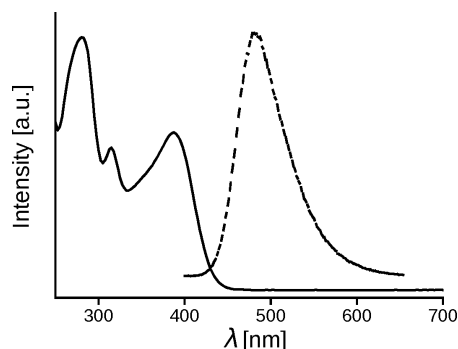


Fig. 2. Normalized absorption and emission spectra of **3a** (recorded in CHCl₃ at 20 °C).

Interestingly, the photoluminescence occurs with substantial quantum yields ($\Phi_f = 0.31$ – 0.43) and remarkable Stokes shifts ($\Delta\tilde{\nu} = 4700$ – 5600 cm⁻¹) (Fig. 2). These substantial Stokes shifts can be attributed to significant geometrical changes upon excitation from a highly non-planar groundstate to a largely planarized excited state [14] and have also been observed for several other classes of phenothiazine derivatives [15]. The *N*-alkyl substituent neither has an influence on the absorption and emission energies nor on the efficiency of the spontaneous emission. Most remarkably, the bromo substituents do not exert their expected heavy atom effect causing a lowering of the fluorescence quantum yields as a consequence of enhanced spin-orbit coupling. As a consequence of a rigid acetylenic framework of the butadiynes, vibrational modes causing relaxation are restricted and, thus, the rod-like butadiynyl-bridged phenothiazines **3** are highly efficient fluorophores both in solution and in the solid state.

According to cyclic voltammetry data, alkynes as conjugating bridges allow intramolecular communication between a remote substituent and a phenothiazine electrophore transmitted through resonance and field effects only to a minor extent [8b]. Therefore, upon considering butadiynes as conjugating bridges this intramolecular electronic communication should be even weaker. Hence, only the diphenothiazinyl buta-

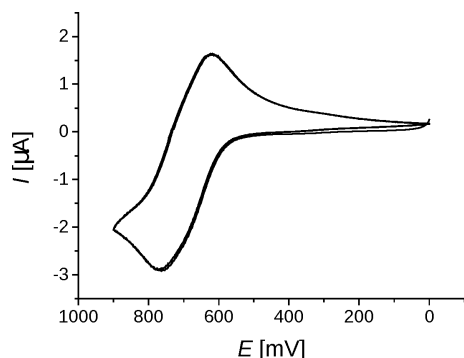


Fig. 3. Cyclic voltammogram of compound **3b** [CH_2Cl_2 ; $T = 293 \text{ K}$; electrolyte: $0.05 \text{ M NBu}_4\text{PF}_6$ (CH_2Cl_2); $\nu = 100 \text{ mV s}^{-1}$; Pt as a working electrode, Ag/AgCl as a reference electrode, and Pt as a counter electrode (determined vs. ferrocene, $E_0^{0/+1} = +450 \text{ mV}$)].

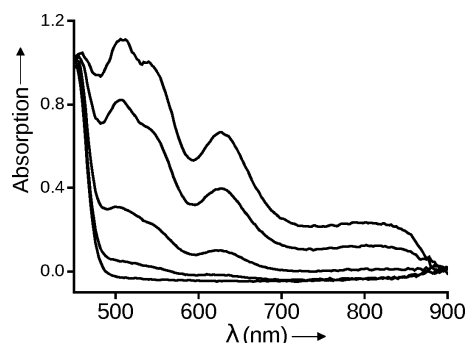


Fig. 4. Absorption difference spectra of compound **3b** in CH_2Cl_2 at $E \text{ (mV)}/I \text{ (mA)} = 433/0, 800/0.05, 900/0.15, 1000/0.24, 1100/0.29$.

diyne dumbbell **3b** was studied by cyclic voltammetry (Fig. 3). A very weak electronic communication can be estimated from the shoulders in the cyclic voltammograms and convolution of the data with a $1/\sqrt{t}$ function. Caused by the strong electron-withdrawing nature of the *sp*-hybridized bridge, the anodically shifted oxidation potentials can be determined at $E_{1/2}^{0/+1} = 804 \text{ mV}$ and $E_{1/2}^{+1/+2} = 845 \text{ mV}$. With a potential separation of $\Delta E = 41 \text{ mV}$ the semiquinone formation constant can be calculated to $K_{\text{SEM}} = 5$. Thus, it can be expected that an oxidation in a spectroelectrochemical experiment should directly furnish the dication.

Gradually increasing the voltage from 433 to 1100 mV leads to a development of long-wavelength bands at 506, 538, 626 and 820 nm (Fig. 4). These bands are in good agreement with a diradical dication resulting from a simultaneous oxidation of both phenothiazine electrophores.

Thermal behavior

Since diacetylenes are known to be polymerizable in solid, liquid crystalline, and molten state, as well as in thin films or as monolayers [16], thermal polymerizations in the solid state or in the melt can be envisioned. However, ideal distances ($d = 5 \text{ Å}$, $s = 3.4\text{--}4.0 \text{ Å}$) and angles ($\gamma \sim 45^\circ$) [17] are required for a topochemical polymerization to poly(diacetylenes) [18]. Therefore, DSC (differential scanning calorimetry) was performed for the *N*-methyl and *N*-hexyl butadiynes **3a** and **3b** under nitrogen from 20 to 300°C (Fig. 5). During the complete heating process no weight changes (neither losses nor gains) could be recorded.

The first endothermic phase transition around 50°C can be assigned to the glass temperature T_g . The next sharp endothermic phase transitions at 245°C (**3a**) or 157°C (**3b**) correspond to the melting points. Interestingly, only in the melt exothermic reactions can be observed. The temperature maxima at 269°C (**3a**) and 283°C (**3b**) are associated with reaction enthalpies ΔH_R of -213 (**3a**) and -177 kJ mol^{-1} (**3b**),

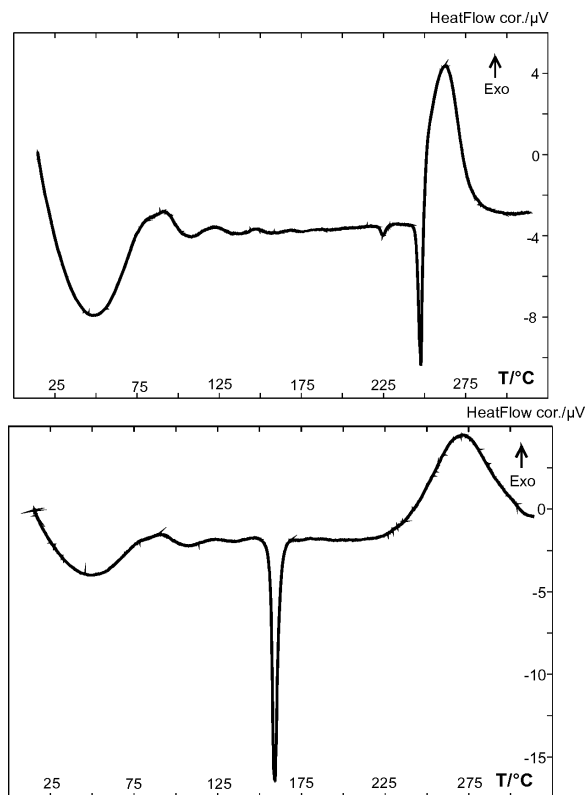


Fig. 5. DSC curves of compounds **3a** (top) and **3b** (bottom) (heating rate 10 K min^{-1}).

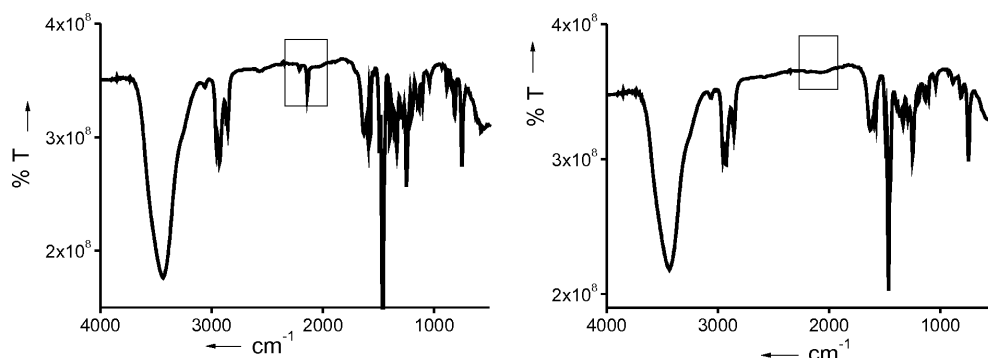


Fig. 6. IR spectra of compound **3a** before (left) and after DSC analysis (right) (recorded in KBr).

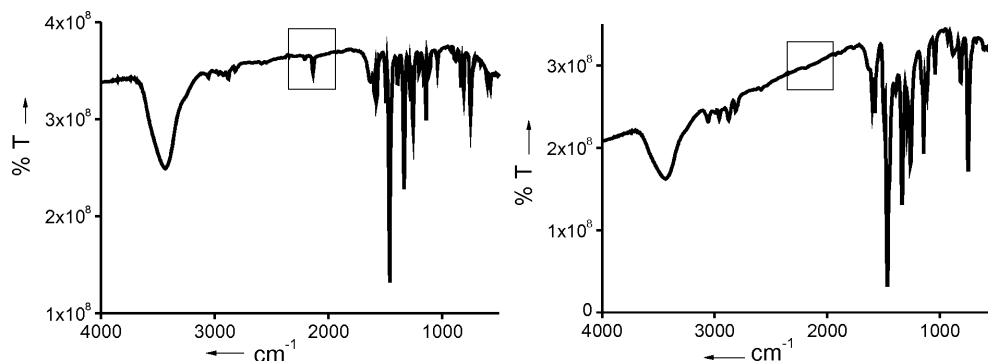


Fig. 7. IR spectra of compound **3b** before (left) and after DSC analysis (right) (recorded in KBr).

respectively. This energy releases are significantly higher than those estimated for the conversion of triple bonds into double and single bonds in polymerizations.

The black-brown residues from the DSC experiments were partially (**3a**) or completely (**3b**) soluble in THF. The residues were investigated by IR spectroscopy, and the supernatants or solutions by SEC (size exclusion chromatography) and MALDI/TOF. In the IR spectra of the DSC samples of **3a** and **3b** (Figs. 6 and 7) the characteristic stretching vibrations of butadiyne carbon-carbon triple bonds at about 2100 cm^{-1} have completely disappeared.

SEC of the soluble residue of the DSC experiment with compound **3b** shows a Gaussian distribution with a broad peak maximum for a molecular weight $M_w = 2734\text{ g mol}^{-1}$ corresponding to an average oligomerization degree of 4.5 monomer units of **3b** ($M_w = 612.91\text{ g mol}^{-1}$) (Fig. 8). This finding is also supported by the mass spectrum of the solution determined by MALDI/TOF. Unambiguously, the mass peaks of the dimer ($M = 1225\text{ u}$), the trimer ($M = 1838\text{ u}$), the

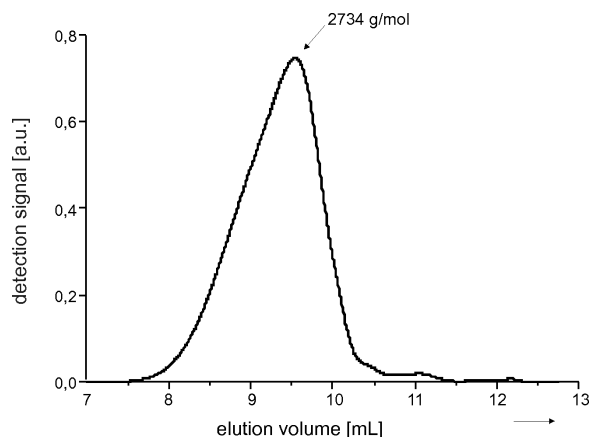


Fig. 8. Size exclusion chromatography (SEC) of compound **3b** after DSC analysis (recorded in THF with polystyrene as a standard).

tetramer ($M = 2450\text{ u}$), and the pentamer ($M = 3062\text{ u}$) can be detected.

Since the strongly exothermic process definitely occurs in the melt, a topochemical polymerization as for perfectly ordered butadiynes can be excluded. How-

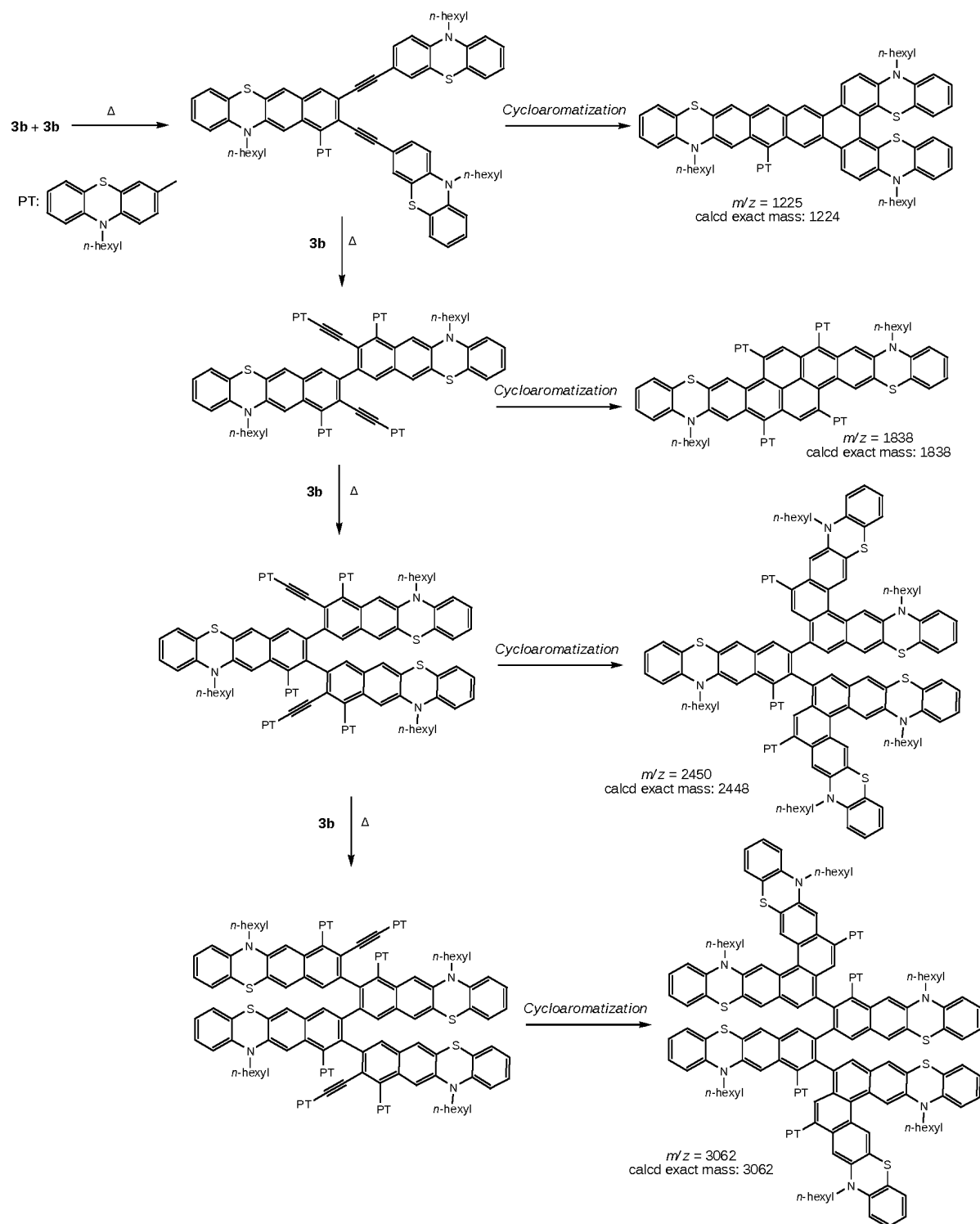


Fig. 9. Tentative mechanism for the formation of polycyclic oligoheterocycles by thermal oligomerization-cyclooligomerization of diphenothiazinyl diyne **3b** based upon MALDI-TOF-determined m/z and calculated exact mass data.

ever, diynes are able to undergo thermally promoted cycloadditions leading to benzoid aromatic units. Furthermore, the initial cycloadducts still contain ethynyl moieties that are able to undergo a thermal cycloisomerization, again under aromatization. Hence, based upon the DSC analysis and the MALDI/TOF data a tentative mechanism for an oligomerization process can be suggested (Fig. 9). In addition, the intense fluorescence of the solution of the thermolysis product of **3b** indicates a rigid structural constitution resulting from multiple benzoid anellations. However, a defined structure of the thermolysate cannot be presented at this time yet. Future studies will focus on the structure elucidation of the thermolysis products of the diynes **3**.

Self-assembly of diynes **3a** and **3b** on HOPG

The regular structure of the diyne **3b** with a rigid and fully delocalized framework (*vide supra*) qualifies this class of compounds for self-assembly on conducting surfaces suitable for STM (scanning tunnel microscopy) investigations. Therefore, the self-assembly of **3b** was studied by STM on highly oriented pyrolytic graphite (HOPG). HOPG has several advantages such as chemical inertness, defect-free planar domains (terraces) and relatively weak dispersive interactions between analyte and substrate, leaving the electronic structure of the analyte unperturbed.

Upon impregnation of HOPG substrates with 10^{-3} M solutions of the diynes **3a** and **3b** in 1-phenyl octane the modified substrates were scanned with a tungsten tip. Bright patterns in the images indicate regions of higher electron density stemming from the extended π electron systems of the individual butadiyne dumbbells. Both molecules share some structural features such as the length of the π -conjugated framework (~ 2.2 nm) and the diameter of the rigid phenothiazine termini defined by the distance from the α -carbon atom of the nitrogen substituent to the hydrogen atom bound to carbon atom 6 (~ 5.5 Å) [19]. Although **3a** and **3b** are electronically essentially identical, two different micrographs were obtained (Figs. 10 and 11).

The *N*-methyl-substituted butadiyne **3a** self-assembles in herring bone lines (Fig. 10), a type of pattern that is often found on pitches and dislocations of HOPG. The lengths of the molecules can be estimated from the computed dimensionality (*vide infra*). From the image, the diameter of the molecules can be calculated to 5.4 Å, indicating that the molecules are

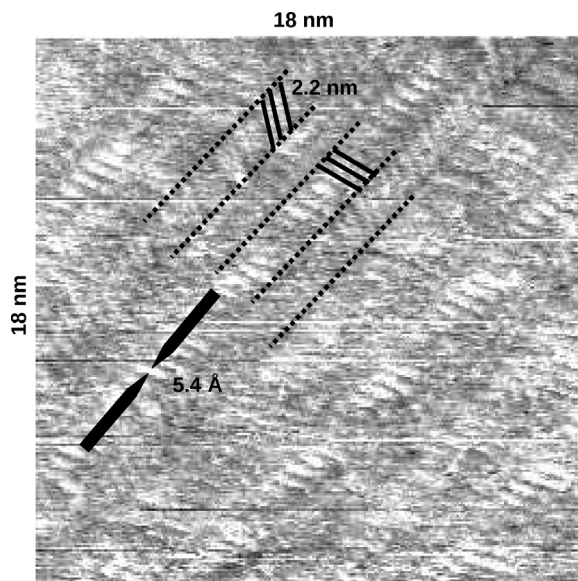


Fig. 10. STM of butadiyne **3a** on HOPG ($I \sim 5$ pA, $U \sim 5$ V, $c(\mathbf{3a}) = 3.4$ mmol L $^{-1}$). (Patterns are indicated by insets of bars with the computed length and diameter of the molecule).

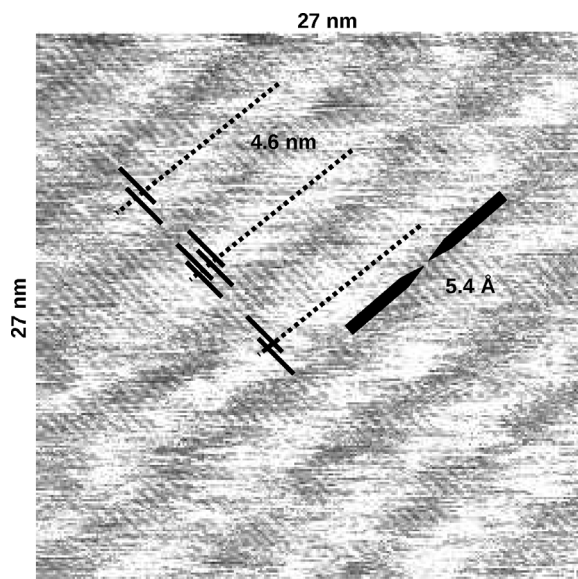
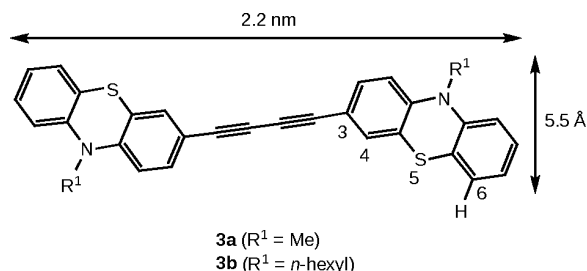


Fig. 11. STM of butadiyne **3b** on HOPG ($I \sim 5$ pA, $U \sim 5$ V, $c(\mathbf{3b}) = 5.4$ mmol L $^{-1}$). (Patterns are indicated by insets of bars with the computed length and diameter of the molecule).

assembled on the graphite surface by attractive π - π interactions in agreement with literature precedence for acetylenic π systems [20]. In contrast, the *N*-hexyl-substituted butadiyne **3b** arranges in a displaced fashion on the graphite surface caused by steric



requirements of the hexyl side chain. Hence, the pitch of the repetitive pattern with 4.6 nm is approximately double the length of the molecule. Again, as for butadiyne **3a**, the diameter of the molecules of **3b** can be directly calculated to 5.4 Å. Therefore, butadiyne **3b** also assembles on the graphite surface by attractive π - π interactions.

Conclusion

Starting from 7-bromo phenothiazine 3-carbaldehydes, functionalized monoethynylated phenothiazines can be readily obtained by alkynylation or aldehyde-alkyne transformation, and these ethynyl phenothiazines can be oxidatively coupled to symmetrical dumbbell-shaped butadiynyl-bridged diphenothiazines in good yields. The electronic properties are in agreement with previous findings for alkynylated phenothiazines and other symmetrical diphenothiazines and manifest in intense absorption bands close to the visible region, intense blue-green luminescence with large Stokes shifts, and reversible oxidation potentials in the anodic region. The nature of the electronic transitions can also be rationalized by DFT and ZINDO-CI computations. Interestingly, the thermal behavior of selected butadiynes do not show topochemical polymerization. However, according to SEC and MALDI-TOF mass spectrometry, oligomerizations to polycyclic heterocycles with complex structures occur. As a consequence of their high π -electron density, butadiynyl-bridged diphenothiazines are well suited for self-assembly on graphite surfaces, as shown by STM images of two representatives. By altering the alkyl substituent on the nitrogen atom from methyl to hexyl without changing the electronic properties, different patterns of the self-assembled layers are obtained. The analysis of the images indicates that the molecules are absorbed in monolayers on HOPG by attractive π - π interactions. Further studies directed towards thermal oligomerizations and nanostructuring of these novel building blocks are currently underway.

Experimental Section

Reagents, catalysts, ligands and solvents were purchased reagent grade and used without further purification. Dichloromethane, methanol, piperidine, THF, pyridine, and triethylamine were dried and distilled according to standard procedures [21]. The phenothiazine alkynes **1a**, **1b** [8b], the diynyl-bridged phenothiazine **3a** [8a], and dimethyl 1-diazo-2-oxopropylphosphonate [22] were prepared according to literature procedures. Column chromatography: silica gel 60 (Merck, Darmstadt), mesh 70–230. TLC: silica gel plates (60 F₂₅₄ Merck, Darmstadt). Melting points (uncorrected values): Büchi Melting Point B-540, Stuart Scientific SMP 3, heating rate 5 K min⁻¹. ¹H and ¹³C NMR spectra: Bruker ARX 300, Varian VXR 400S; CDCl₃ (locked to Me₄Si) [23], [D₆]DMSO (locked to Me₄Si). The assignments of quaternary C, CH, CH₂ and CH₃ has been made by using DEPT spectra. IR: Perkin Elmer FT-IR spectrometer 1000, Bruker Vector 22. UV/Vis: Perkin Elmer UV/Vis Spectrometer Lambda 16, Hewlett Packard 8452 A. Fluorescence spectra: Perkin-Elmer LS 50 B (irradiation at approximately 10 nm less in energy than the longest wavelength absorption maximum). MS: Finnigan MAT 90, Finnigan MAT 95 Q, Finnigan TSQ 700 or JEOL JMS-700. Elemental analyses were carried out in the Microanalytical Laboratories of the Department Chemie, Ludwig-Maximilians-Universität München, and of the Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg.

Electrochemistry: Cyclic voltammetry experiments (EG & G potentiostatic instrumentation) were performed under argon in dry and degassed CH₂Cl₂ at r.t. and at scan rates of 100, 250, and 500 mV s⁻¹. The electrolyte was 0.10 M Bu₄NPF₆. The working electrode was a 1-mm platinum disk, the counter electrode was a platinum wire, and the reference electrode was an Ag/AgCl electrode. The potentials were corrected referring to the internal standard of Fc/Fc⁺ in CH₂Cl₂ ($E_0^{0/+1} = 450$ mV) [24].

Synthesis of 7-bromo-10-*N*-hexyl-10*H*-phenothiazine 3-carbaldehyde

To a solution of 7.94 g (25.5 mmol) of 10-*n*-hexyl-10*H*-phenothiazine 3-carbaldehyde ($R^1 = n\text{-hexyl}$) in 30 mL of glacial acetic acid was added dropwise a solution of 1.30 mL (25.5 mmol) of bromine in 10 mL of glacial acetic acid. The red-brown mixture was stirred at r.t. for 2 d. After addition of 300 mL of water and 600 mL of diethyl ether the organic layer was dried with MgSO₄. The solvents were removed *in vacuo*, and the residue was chromatographed on silica gel (diethyl ether/pentane 1:3) to give 8.66 g (87 %) of 7-bromo 10-*n*-hexyl-10*H*-phenothiazine 3-carbaldehyde as a viscous brown oil. – ¹H NMR (CDCl₃, 300 MHz): δ = 0.87 (t, J = 6.6 Hz, 3 H), 1.28–1.31 (m, 4 H), 1.41 (m_c, 2 H), 1.77 (m_c, 2 H), 3.82 (t, J = 7.2 Hz, 2 H), 6.69 (d, J = 8.6 Hz, 1 H), 6.87 (d, J = 8.4 Hz, 1 H), 7.19 (d, J =

2.2 Hz, 1 H), 7.23 (dd, $J = 8.5$ Hz, $J = 2.2$ Hz, 1 H), 7.54 (d, $J = 1.8$ Hz, 1 H), 7.62 (dd, $J = 8.4$ Hz, $J = 1.8$ Hz, 1 H), 9.78 (s, 1 H). – ^{13}C NMR (CDCl_3 , 75 MHz): $\delta = 13.9$ (CH_3), 22.5 (CH_2), 26.4 (CH_2), 26.5 (CH_2), 31.3 (CH_2), 48.0 (CH_2), 114.9 (CH), 115.7 (C_{quat}), 117.0 (CH), 124.3 (C_{quat}), 126.0 (C_{quat}), 128.3 (CH), 129.7 (CH), 130.2 (CH), 130.2 (CH), 131.2 (C_{quat}), 142.6 (C_{quat}), 150.2 (C_{quat}), 189.8 (CH). – MS (70 eV): m/z (%) = 391 (100) [M , ^{81}Br] $^+$, 389 (96) [M , ^{79}Br] $^+$. – IR (KBr) (cm^{-1}): $\nu = 1688$, 1594, 1462. – UV/Vis (CHCl_3): λ_{max} (nm) (ϵ) = 246 (17200), 277 (20000), 385 (5600). – Anal. for $\text{C}_{19}\text{H}_{20}\text{NSOBr}$ (390.3): calcd. C 58.46, H 5.16, N 3.59, S 8.21, Br 20.47; found C 58.28, H 5.23, N 3.57, S 8.02, Br 20.40.

3-Bromo-7-ethynyl-10-methyl-10H-phenothiazine (**1c**)

In a 25 mL two-neck flask were placed 585 mg (1.83 mmol) of 7-bromo-10-methyl-10H-phenothiazine 3-carbaldehyde, 432 mg (2.25 mmol) of dimethyl-1-diazo-2-oxopropyl phosphonate, and 6 mL of dry methanol. To this yellow suspension was added 415 mg (3.00 mmol) of K_2CO_3 . The mixture was stirred 2 d at r. t. Then, 50 mL of dichloromethane and 50 mL of water were added. The aqueous phase was extracted three times 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 (diethyl ether/pentane 1 : 4) to give 348 mg (60 %) of **1c** as a voluminous colorless solid. M. p. 144–145 °C. – ^1H NMR (CDCl_3 , 300 MHz): $\delta = 3.04$ (s, 1 H), 3.31 (s, 3 H), 6.62 (d, $J = 8.5$ Hz, 1 H), 6.68 (d, $J = 8.4$ Hz, 1 H), 7.22–7.25 (m, 3 H), 7.28 (dd, $J = 8.4$ Hz, $J = 1.8$ Hz, 1 H). – ^{13}C NMR (CDCl_3 , 75 MHz): $\delta = 35.4$ (CH_3), 77.2 (CH), 82.8 (C_{quat}), 113.8 (CH), 115.1 (C_{quat}), 115.3 (CH), 116.3 (C_{quat}), 122.7 (C_{quat}), 125.0 (C_{quat}), 129.4 (CH), 130.2 (CH), 130.4 (CH), 131.7 (CH), 144.3 (C_{quat}), 145.8 (C_{quat}). – MS (EI+, 70 eV): m/z (%) = 318 (15), 317 (100) [M] $^+$, 316 (17), 315 (97), 303 (11), 302 (73), 301 (12), 300 (72), 236 (26), 221 (17), 220 (18), 177 (12). – IR (KBr): ν (cm^{-1}) = 3288 (m), 2107 (w), 1597 (w), 1493 (w), 1460 (ss), 1384 (w), 1329 (s), 1271 (w), 1250 (m), 1128 (m), 886 (w), 814 (s), 764 (w), 659 (w). – UV/Vis (CHCl_3): λ_{max} (nm) (ϵ) = 268 (43900), 325 (8300). – R_f (diethyl ether/pentane 1 : 4) = 0.37. – HRMS: $m/z = 314.9729$ (calcd. 314.9717 for $\text{C}_{15}\text{H}_{10}^{79}\text{BrNS}$, [M] $^+$).

3-Bromo-7-ethynyl-10-hexyl-10H-phenothiazine (**1d**)

In a 25 mL two-neck flask were placed 390 mg (1.00 mmol) of 7-bromo 10-*n*-hexyl-10H-phenothiazine 3-carbaldehyde, 288 mg (1.50 mmol) of dimethyl-1-diazo-2-oxopropyl phosphonate, 5 mL of dry methanol and 3 mL of dry dichloromethane. To this brown solution was added 415 mg (3.00 mmol) of K_2CO_3 . The yellow-orange suspen-

sion was stirred 2 d at r. t. Then, 50 mL of dichloromethane and 50 mL of water were added. The aqueous phase was extracted three times 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 (diethyl ether/pentane 1 : 4) to give 287 mg (74 %) of **1d** as a light-brown oil. – ^1H NMR (CDCl_3 , 300 MHz): $\delta = 0.86$ (t, $J = 6.7$ Hz, 3 H), 1.25–1.30 (m, 4 H), 1.40 (mc, 2 H), 1.74 (mc, 2 H), 3.03 (s, 1 H), 3.77 (t, $J = 7.2$ Hz, 2 H), 6.67 (d, $J = 8.7$ Hz, 1 H), 6.73 (d, $J = 8.4$ Hz, 1 H), 7.20 (s, 2 H), 7.23–7.28 (m, 2 H). – ^{13}C NMR (CDCl_3 , 75 MHz): $\delta = 13.9$ (CH_3), 22.5 (CH_2), 26.5 (CH_2), 26.6 (CH_2), 31.3 (CH_2), 47.6 (CH_2), 77.1 (CH), 82.8 (C_{quat}), 114.8 (C_{quat}), 115.0 (CH), 116.1 (C_{quat}), 116.6 (CH), 124.1 (C_{quat}), 126.4 (C_{quat}), 129.6 (CH), 130.0 (CH), 130.7 (CH), 131.5 (CH), 143.7 (C_{quat}), 145.4 (C_{quat}). – MS (EI+, 70 eV): m/z (%) = 388 (21), 387 (100) [M] $^+$, 386 (21), 385 (94), 316 (35), 314 (32), 303 (19), 302 (97), 301 (19), 300 (91), 284 (11), 282 (11), 235 (12), 222 (12), 221 (19), 220 (20), 177 (13). – IR (Film, KBr): ν (cm^{-1}) = 3293 (m), 2955 (s), 2927 (s), 2855 (s), 2107 (w), 1597 (m), 1491 (s), 1461 (ss), 1398 (m), 1332 (m), 1268 (s), 1250 (s), 1196 (m), 1105 (w), 883 (w), 808 (s). – UV/Vis (CHCl_3): λ_{max} (nm) (ϵ) = 269 (37900), 324 (7000). – R_f (diethyl ether/pentane 1 : 4) = 0.79. – Anal. for $\text{C}_{20}\text{H}_{20}\text{BrNS}$ (386.3): calcd. C 62.18, H 5.22, N 3.62, S 8.30, Br 20.68; found C 62.55, H 5.30, N 3.61, S 8.28, Br 19.97.

7-Ethynyl-10-methyl-10H-phenothiazinyl-3-carbaldehyde (**1e**)

In a 25 mL two-neck flask 1.00 g (3.12 mmol) of 7-bromo 10-methyl-10H-phenothiazine 3-carbaldehyde, 22 mg (0.03 mmol) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, 12 mg (0.06 mmol) of CuI , 24 mg (0.09 mmol) of triphenylphosphane, and 15 mL of distilled piperidine were degassed with nitrogen for 10 min. Then, 429 mg (4.37 mmol) of (trimethylsilyl)acetylene was added, and the reaction mixture was heated to reflux temperature 12 h. After cooling to r. t. the brown suspension was diluted with diethyl ether and filtered over celite. The solvents were concentrated *in vacuo* to a few milliliters. After addition of 88 mg (1.56 mmol) of KOH in 5 mL methanol the mixture was heated to reflux temperature for 30 min. After extraction and removal of the solvents *in vacuo* the residue was chromatographed on silica gel (diethyl ether/pentane 1 : 1) to give 500 mg (60 %) of **1e** as a bright-orange solid. M. p. 181–182 °C. – ^1H NMR (CDCl_3 , 300 MHz): $\delta = 3.48$ (s, 3 H), 3.62 (s, 1 H), 6.98 (d, $J = 8.4$ Hz, 1 H), 7.11 (d, $J = 8.4$ Hz, 1 H), 7.23 (d, $J = 1.7$ Hz, 1 H), 7.33 (dd, $J = 8.4$ Hz, $J = 1.8$ Hz, 1 H), 7.59 (d, $J = 1.8$ Hz, 1 H), 7.74 (dd, $J = 8.4$ Hz, $J = 1.8$ Hz, 1 H), 9.84 (s, 1 H). – MS (EI+, 70 eV): m/z (%) = 266 (19), 265 (100) [M] $^+$, 251 (12), 250 (57), 236 (12), 222 (26). – IR (KBr): ν (cm^{-1}) = 3235 (w), 1683 (s), 1602 (m), 1578 (s), 1564 (w),

1547 (w), 1471 (ss), 1394 (w), 1338 (s), 1315 (w), 1259 (m), 1203 (s), 1154 (w), 1131 (w), 816 (m). – UV/Vis (CHCl₃): $\lambda_{\max}$ (nm) (ϵ) = 255 (20300), 283 (40300), 389 (7800). – R_f (diethyl ether/pentane 1 : 1) = 0.30. – Anal. for C₁₆H₁₁NOS (265.3): calcd. C 72.43, H 4.18, N 5.28, S 12.08; found C 72.16, H 4.18, N 5.17, S 11.91.

7-Ethynyl-10-*n*-hexyl-10*H*-phenothiazinyl-3-carbaldehyde (1f)

In a screw cap vessel 377 mg (0.96 mmol) of 7-bromo 10-*n*-hexyl-10*H*-phenothiazine 3-carbaldehyde, 27 mg (0.04 mmol) of Pd(PPh₃)₂Cl₂, 7 mg (0.04 mmol) of CuI, 20 mg (0.08 mmol) of triphenylphosphane, 20 mL of distilled piperidine, and 10 mL of THF were degassed with nitrogen for 30 min. Then, 190 mg (1.93 mmol) of (trimethylsilyl)acetylene was added, and the reaction mixture was heated to 100 °C 24 h. After cooling to r.t. the brown suspension was diluted with diethyl ether and filtered over celite. The solvents were concentrated *in vacuo* to a few milliliters. After addition of 39 mg (0.7 mmol) of KOH in 5 mL of methanol the mixture was heated to reflux temperature for 30 min. After extraction and removal of the solvents *in vacuo* the residue was chromatographed on silica gel (diethyl ether/pentane 1 : 4) to give 240 mg (74 %) of **1f** as a yellow-brown oil. – ¹H NMR (CDCl₃, 300 MHz): δ = 0.87 (m_c, 3 H), 1.26–1.32 (m, 4 H), 1.42 (m_c, 2 H), 1.78 (m_c, 2 H), 3.06 (s, 1 H), 3.85 (t, J = 7.1 Hz, 2 H), 6.77 (d, J = 8.4 Hz, 1 H), 6.88 (d, J = 8.5 Hz, 1 H), 7.20 (d, J = 1.8 Hz, 1 H), 7.26 (dd, J = 7.9 Hz, J = 1.8 Hz, 1 H), 7.54 (d, J = 1.8 Hz, 1 H), 7.62 (dd, J = 8.4 Hz, J = 1.9 Hz, 1 H), 9.79 (s, 1 H). – ¹³C NMR (CDCl₃, 75 MHz): δ = 13.9 (CH₃), 22.5 (CH₂), 26.4 (CH₂), 26.6 (CH₂), 31.3 (CH₂), 48.1 (CH₂), 74.5 (CH), 82.6 (C_{quat}) 115.0 (CH), 115.5 (CH), 117.2 (C_{quat}), 123.9 (C_{quat}), 124.5 (C_{quat}), 128.4 (CH), 130.1 (CH), 130.8 (CH), 131.4 (C_{quat}), 131.6 (CH), 143.9 (C_{quat}), 149.9 (C_{quat}), 189.8 (CH). – MS (EI+, 70 eV): m/z (%) = 336 (23), 335 (100) [M]⁺, 264 (45), 251 (18), 250 (69), 232 (15), 222 (14). – IR (KBr): ν (cm^{−1}) = 3290 (ss), 3056 (w), 2955 (ss), 2927 (ss), 2855 (ss), 2729 (m), 2108 (m), 1694 (ss), 1682 (ss), 1601 (ss), 1580 (ss), 1564 (ss), 1496 (s), 1470 (s), 1416 (s), 1398 (ss), 1378 (ss), 1357 (ss), 1336 (ss), 1308 (ss), 1276 (ss), 1246 (ss), 1197 (ss), 1156 (s), 1102 (m), 1055 (w), 924 (m), 885 (m), 815 (ss), 741 (m), 721 (m), 653 (m), 586 (m). – UV/Vis (CHCl₃): $\lambda_{\max}$ (nm) (ϵ) = 256 (19000), 284 (32900), 389 (7300). – R_f (diethyl ether/pentane 1 : 4) = 0.22. – HRMS: m/z = 335.1349 (calcd. 335.1344 for C₂₁H₂₁NOS, [M]⁺).

General procedure (GP) for the synthesis of butadiynyl-bridged diphenothiazines 3 by Eglinton coupling

To a 0.1 M solution of 1 equiv. of a 3-ethynyl *N*-alkyl phenothiazine **1** in a mixture of methanol and pyridine (1 : 2)

1 equiv. of copper(II) acetate monohydrate was added, and the light-green suspension was degassed with nitrogen for 10 min. Then, the reaction mixture was heated to reflux temperature for 3–5 h. After cooling to r.t. the precipitate was collected by suction and washed with 100 mL of methanol. For removing last traces of pyridine the residue was purified by absorptive filtration over a short plug of silica gel. The hexyl-substituted compounds were reasonably soluble for purification by flash chromatography. The butadiynyl-bridged diphenothiazines **3** were obtained as crystalline or microcrystalline bright-yellow to orange solids.

1,4-Bis-(10-*n*-hexyl-10*H*-phenothiazin-3-yl)-buta-1,3-diyne (3b)

According to the GP the reaction of 598 mg (1.94 mmol) of **1b** and 353 mg (1.94 mmol) of copper(II) acetate monohydrate furnished 520 mg (87 %) of **3b** as a bright-yellow powder. Crystallization by slow evaporation of a dichloromethane solution gave yellow needles suitable for X-ray structure analysis. M.p. 157–158 °C. – ¹H NMR (CDCl₃, 300 MHz): δ = 0.86 (t, J = 9.0 Hz, 6 H), 1.29 (m_c, 8 H), 1.41 (m_c, 4 H), 1.77 (m_c, 4 H), 3.80 (t, J = 7.2 Hz, 4 H), 6.73 (d, J = 7.2 Hz, 2 H), 6.83 (d, J = 8.4 Hz, 2 H), 6.90 (t, J = 6.3 Hz, 2 H), 7.07–7.13 (m, 4 H), 7.21–7.28 (m, 4 H). – ¹³C NMR (CDCl₃, 75 MHz): δ = 13.9 (CH₃), 22.6 (CH₂), 26.6 (CH₂), 26.8 (CH₂), 31.4 (CH₂), 47.6 (CH₂), 74.1 (C_{quat}), 81.3 (C_{quat}), 114.9 (CH), 115.4 (C_{quat}), 115.6 (CH), 122.9 (CH), 124.0 (C_{quat}), 124.8 (C_{quat}), 127.4 (CH), 127.5 (CH), 130.8 (CH), 131.8 (CH), 144.3 (C_{quat}), 146.1 (C_{quat}). – MS (EI+, 70 eV): m/z (%) = 614 (40), 613 (40), 612 (100) [M]⁺, 528 (10), 527 (25), 443 (10), 442 (28). – IR (KBr): ν (cm^{−1}) = 2954 (m), 2928 (m), 2855 (m), 2139 (w), 1629 (br, w), 1596 (m), 1572 (m), 1491 (w), 1459 (ss), 1397 (w), 1334 (m), 1249 (m), 1203 (w), 1135 (w), 1135 (w), 884 (w), 841 (w), 817 (w), 748 (m). – UV/Vis (CHCl₃): $\lambda_{\max}$ (nm) (ϵ) = 243 (38100), 281 (46100), 316 (24900), 389 (29200). – Anal. for C₄₀H₄₀N₂S₂ (612.9): calcd. C 78.39, H 6.58, N 4.57, S 10.46; found C 78.14, H 6.51, N 4.42, S 10.25.

1,4-Bis[7-bromo-10-methyl-10*H*-phenothiazin-3-yl]-buta-1,3-diyne (3c)

According to the GP the reaction of 292 mg (0.92 mmol) of **1c** and 221 mg (1.11 mmol) of copper(II) acetate monohydrate furnished 223 mg (77 %) of **3c** as a bright-yellow microcrystalline solid. M.p. 242–245 °C. – ¹H NMR (CDCl₃, 300 MHz): δ = 3.34 (s, 6 H), 6.65 (d, J = 8.4 Hz, 2 H), 6.72 (d, J = 8.4 Hz, 2 H), 7.23–7.33 (m, 8 H). – MS (EI+, 70 eV): m/z (%) = 633 (19), 632 (62), 631 (34), 630 (M⁺, 100), 629 (16), 628 (47), 617 (10), 615 (18), 600 (18), 315 (10), 301 (11), 300 (18). – IR (KBr): ν (cm^{−1}) = 2138 (w), 1595 (w), 1492 (w), 1459 (ss), 1384 (w), 1331 (s),

1270 (w), 1259 (w), 1152 (w), 1130 (w), 804 (w). – UV/Vis (CHCl₃): λ_{max} (nm) (ϵ) = 275 (56900), 320 (26600, sh), 343 (25500, sh), 388 (31400). – Anal. for C₃₀H₁₈Br₂N₂S₂ (630.4): calcd. C 57.16, H 2.88, N 4.44, S 10.17, Br 25.35; found C 56.84, H 2.95, N 4.41, S 9.96, Br 24.46.

1,4-Bis[7-bromo-10-hexyl-10H-phenothiazin-3-yl]-buta-1,3-diyne (3d)

According to the GP the reaction of 210 mg (0.54 mmol) of **1d** and 163 mg (0.81 mmol) of copper(II) acetate monohydrate furnished after chromatography on silica gel (diethyl ether/pentane 1 : 10) 169 mg (81 %) of **3d** as a yellow microcrystalline solid. M.p. 150–154 °C. – ¹H NMR (CDCl₃, 300 MHz): δ = 0.87 (t, J = 6.6 Hz, 6 H), 1.28–1.30 (m, 8 H), 1.40 (m_c, 4 H), 1.75 (m_c, 4 H), 3.77 (t, J = 7.1 Hz, 4 H), 6.67 (d, J = 8.4 Hz, 2 H), 6.74 (d, J = 8.6 Hz, 2 H), 7.20 (s, 4 H), 7.23–7.30 (m, 4 H). – ¹³C NMR (CDCl₃, 75 MHz): δ = 13.9 (CH₃), 22.5 (CH₂), 26.5 (CH₂), 26.6 (CH₂), 31.3 (CH₂), 47.7 (CH₂), 74.2 (C_{quat}), 81.2 (C_{quat}), 115.0 (C_{quat}), 115.1 (CH), 115.7 (C_{quat}), 116.7 (CH), 124.1 (C_{quat}), 126.3 (C_{quat}), 129.7 (CH), 130.0 (CH), 130.9 (CH), 132.0 (CH), 143.5 (C_{quat}), 145.7 (C_{quat}). – MS (EI+, 70 eV): m/z (%) = 771 (42), 770 (100) [M]⁺, 769 (14), 768 (34), 687 (11), 685 (13), 602 (10), 600 (17). – IR (KBr): ν (cm^{−1}) = 2952 (m), 2927 (m), 2855 (w), 2138 (w), 1594 (m), 1490 (m), 1458 (ss), 1397 (m), 1331 (w), 1268 (w), 1244 (m), 1147 (w), 809 (m). – UV/Vis (CHCl₃): λ_{max} (nm) (ϵ) = 278 (54300), 319 (24500, sh), 349 (23200, sh), 389 (29000). – R_f (diethyl ether/pentane 1 : 10) = 0.36. – HRMS: m/z = 768.0820 (calcd. 768.0843 for C₄₀H₃₈⁷⁹Br₂N₂S₂, [M]⁺).

1,4-Bis[7-formyl-10-methyl-10H-phenothiazin-3-yl]-buta-1,3-diyne (3e)

According to the GP the reaction of 369 mg (1.39 mmol) of **1e** and 379 mg (1.90 mmol) of copper(II) acetate monohydrate furnished 308 mg (84 %) of **3e** as a bright-yellow solid. M.p. 250 °C (dec.). – ¹H NMR (CDCl₃, 300 MHz): δ = 3.44 (s, 6 H), 6.77 (d, J = 8.4 Hz, 2 H), 6.88 (d, J = 8.3 Hz, 2 H), 7.32 (m_c, 4 H), 7.60 (s, 2 H), 7.67 (d, J = 8.3 Hz, 2 H), 9.82 (s, 2H). – MS (EI+, 70 eV): m/z (%) = 530 (16), 529 (36), 528 (100) [M]⁺, 513 (22), 498 (21). – IR (KBr): ν (cm^{−1}) = 2136 (w), 1686 (s), 1601 (m), 1576 (s), 1468 (ss),

1374 (w), 1336 (s), 1314 (w), 1259 (m), 1200 (s), 1154 (m), 1130 (m), 1107 (w), 814 (m). – UV/Vis (CHCl₃): λ_{max} (nm) (ϵ) = 292 (74400), 408 (33000). – Anal. for C₃₂H₂₀N₂O₂S₂ (528.6): calcd. C 72.70, H 3.81, N 5.30, S 12.13; found C 72.66, H 3.81, N 5.42, S 11.82.

1,4-Bis[7-formyl-10-hexyl-10H-phenothiazin-3-yl]-buta-1,3-diyne (3f)

According to the GP the reaction of 275 mg (0.82 mmol) of **1f** and 223 mg (1.12 mmol) of copper(II) acetate monohydrate furnished after chromatography on silica gel (diethyl ether/pentane 1 : 1) 156 mg (57 %) of **3f** as a bright-orange powder. M.p. 150–153 °C. – ¹H NMR (CDCl₃, 300 MHz): δ = 0.88 (m_c, 6 H), 1.32 (m_c, 8 H), 1.43 (m_c, 4 H), 1.79 (m_c, 4 H), 3.86 (t, J = 7.2 Hz, 4 H), 6.78 (d, J = 8.5 Hz, 2 H), 6.89 (d, J = 8.5 Hz, 2 H), 7.21 (d, J = 1.9 Hz, 2 H), 7.29 (dd, J = 8.4 Hz, J = 1.9 Hz, 2 H), 7.55 (d, J = 1.9 Hz, 2 H), 7.63 (dd, J = 8.4 Hz, J = 1.9 Hz, 2 H), 9.79 (s, 2 H). – ¹³C NMR (CDCl₃, 75 MHz): δ = 13.9 (CH₃), 22.6 (CH₂), 26.4 (CH₂), 26.6 (CH₂), 31.3 (CH₂), 48.2 (CH₂), 74.5 (C_{quat}), 81.1 (C_{quat}), 115.1 (CH), 115.6 (CH), 116.7 (C_{quat}), 124.0 (C_{quat}), 124.3 (C_{quat}), 128.4 (CH), 130.1 (CH), 131.0 (CH), 131.5 (C_{quat}), 132.1 (CH), 144.3 (C_{quat}), 149.7 (C_{quat}), 189.9 (CH). – MS (EI+, 70 eV): m/z (%) = 670 (23), 669 (49), 668 (100) [M]⁺, 583 (20), 499 (12), 498 (32). – IR (KBr): ν (cm^{−1}) = 2960 (m), 2925 (m), 2852 (m), 2139 (w), 1693 (ss), 1560 (m), 1576 (s), 1563 (m), 1471 (ss), 1419 (m), 1396 (s), 1378 (s), 1356 (m), 1261 (ss), 1246 (ss), 1200 (ss), 1148 (s), 1101 (ss, br), 1022 (ss, br), 886 (w), 805 (ss), 741 (w). – UV/Vis (CHCl₃): λ_{max} (nm) (ϵ) = 296 (63200), 411 (27400). – R_f (diethyl ether/pentane 1 : 1) = 0.33. – HRMS: m/z = 668.2501 (calcd. 668.2531 for C₄₂H₄₀N₂O₂S₂, [M]⁺).

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