Synthesis and Electronic Properties of Alkynylated Phenothiazines

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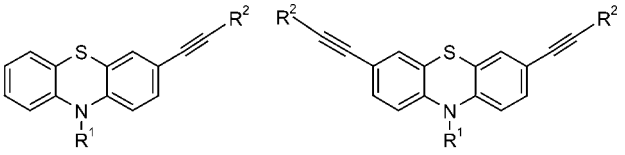
Alkynylated phenothiazines **1**, **2**, **5**, **7**, and **12**–**15** can be synthesized in moderate to excellent yields by sequences of aldehyde–alkyne transformations and/or Sonogashira cross-coupling reactions from suitable phenothiazine aldehydes or bromides. The electronic properties of (hetero)aryl ethynyl-substituted *N*-methyl-phenothiazines (UV/Vis absorption, fluorescence, redox potentials) strongly correlate with Hammett σ_P parameters and indicate that remote substituents transmit their electronic information through π-electron delocalization and the σ-framework. Phenothiazinyl dyads (**7g**, **12**, **13**) and triads (**14**) reveal different degrees of intramolecular electronic coupling as demonstrated by cyclic voltammetry, qualifying them as good model candidates for redox-active molecular wires.

Introduction

Reversible heterocyclic redox systems display electronic bi- or multistability (e.g. neutral-radical ion, or even several stable oxidation states) and so are highly intriguing as switching functional units (native-doped; ON-OFF) and building blocks in future single-molecule-based molecular electronics.[1] Coupled redox systems integrated into conjugated chains could therefore constitute an as yet unknown class of redox-addressable molecular wires, suitable for redox manipulation of single molecules with nanoscopic scanning techniques.[2,3] In particular, phenothiazines,[4] a pharmaceutically important class of heterocycles (known as pharmacophores in sedatives, tranquilizers, anti-epilectic agents, anti-tuberculosis agents, anti-pyretics, anti-tumor agents, bactericides, and parasiticides)[5] possess low and highly reversible first oxidation potentials[4,6] with pronounced propensities to form stable radical cations. Interestingly, this peculiar property is also responsible for their physiological activities[7] and, moreover, phenothiazines have also been found to be able to cleave DNA upon UV irradiation.[8] As a consequence, these favorable electronic properties of phenothiazines have led to their application as electrophore probes in supramolecular assemblies[9] for PET (photo-induced electron transfer) studies and as electron donor components in materials science investigations into such fields as electrically conducting charge-transfer composites.[10] Although alkenylated phenothiazines have been synthesized to address electro-active donor-acceptor systems,[10c,10d,10e] alkynylated phenothiazines such as **1** and **2**, representing interesting building blocks for redox-active oligomers with a rigid-rod arrangement of these electrophores, remained unexplored. We have recently communicated syntheses of the first representatives of 3-mono- and 3,7-dialkynylated phenothiazines **1** and **2**[11] as part of our program to establish a bottom-up approach to redox-active nanometer-sized molecular wires.[12] Here we wish to report synthetic approaches to functionalized alkynylated phenothiazines, their electronic properties and substituent effects according to cyclic voltammetry, absorption and emission spectroscopy, and structure-property relationships by correlation analyses of experimentally obtained and computational data.



1 **2**

Results

Syntheses and Structure of Alkynyl Phenothiazines

The electron-rich natures of phenothiazines necessitate several considerations for selection of suitable synthetic strategies to alkynylated phenothiazines. Synthetically, both aldehyde-alkyne transformations and cross-coupling methodologies allow varied and flexible functionalization. In particular, since phenothiazine carbaldehydes **3** are easily prepared by Vilsmeier[13] or Bergman[14,15] formylations, the alkynylated derivatives **1** and **2** are obtained in good yields according to the two-step Corey–Fuchs procedure[16] (Scheme 1, Method A) or the fairly mild one-step

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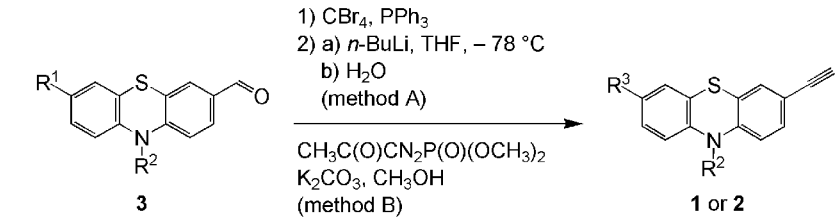
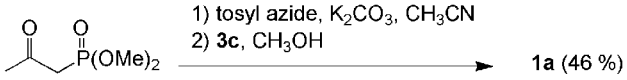


	3a	3b	3c	3d	3e
R^1	H	H	CHO	CHO	Br
R^2	Me	*n*-hexyl	Me	*n*-hexyl	Me

	1a	1b	1c	2a	2b
R^2	Me	*n*-hexyl	Me	Me	*n*-hexyl
R^3	H	H	Br	C≡CH	C≡CH
yields	(76 %,[a] 77 %[b])	(70 %[a])	(60 %[b])	(54 %,[a] 66 %[b])	(78 %[a])

[a] method A
[b] method B



Scheme 1. Ethynylated phenothiazines **1** and **2** by aldehyde transformations

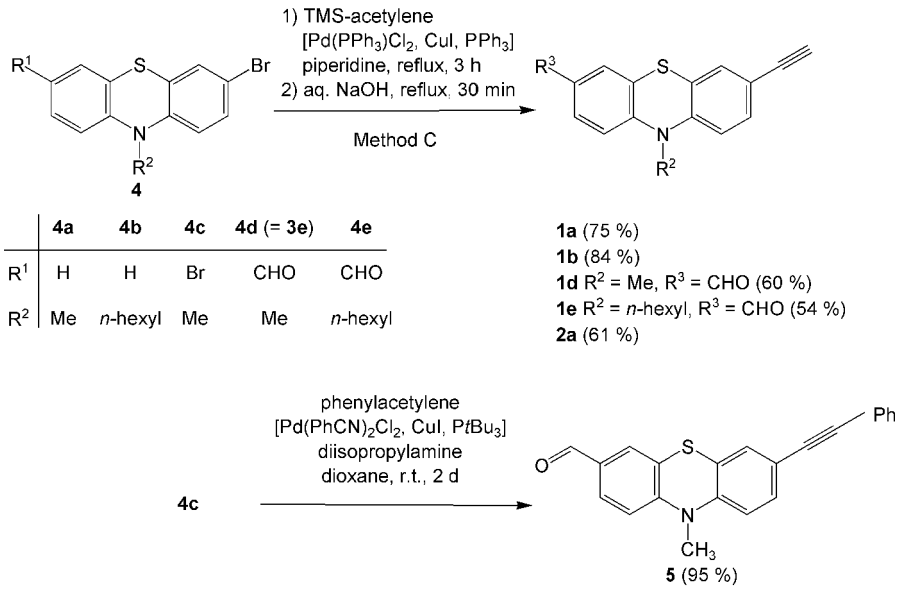
Ohira–Bestmann transformation (Method B).[17] Application of the in situ formation of the diazoketophosphonate by tosyl azide diazo transfer to dimethyl-2-oxo propyl phosphonate in the presence of K_2CO_3 gives the monoethynylated product **1a** in 46% yield (instant Ohira–Bestmann procedure).

Alternatively, we have also applied the Sonogashira ethynylation[18] with piperidine as a base to mono- and dibromo phenothiazines **4**[19,20] to furnish, after subsequent alkaline desilylation, the desired alkynylated derivatives **1** and **2** in one pot and in good yield (Scheme 2, Method C). Furthermore, the application of this cross-coupling reaction is highly compatible with the presence of fragile, base-sensitive functional groups such as aldehydes (compounds **1d** and **1e**). Phenylacetylene was successfully coupled with the bromo aldehyde **4c** under Buchwald–Fu conditions,[21] giving rise to the formation of the aldehyde derivative **5** in excellent yield.

The spectroscopic (^{1}H and ^{13}C NMR, IR, MS) and combustion analytical data unambiguously support the structural assignments of the alkynylated phenothiazines **1**, **2**, and **5**. In particular, the ethynylated phenothiazines **1** and **2** can be clearly identified by the diagnostic appearance of the terminal alkynyl methine proton and carbon resonances between δ = 3.0 and 3.6 (^{1}H NMR) and δ = 74.5 and 82.8 ppm (^{13}C NMR), and also by quaternary carbon nuclei in the ^{13}C NMR spectra between δ = 77.2 and 83.1 ppm. The characteristic CC-triple bond stretching vibrations at 2100 cm^{-1} are generally weak and do not appear clearly in all IR spectra of the compounds **1** and **2**. Another typical characteristic of the alkynylated phenothiazines **1** and **2** is found in the mass spectra. Not only is the molecular peak, representing a radical cation, present for all compounds, but in most cases it is also the basis signal. The fragmentation occurs with the expected loss of the methyl group or direct and α-cleavages of the *n*-hexyl substituent. In addition, an X-ray crystal structure analysis of the diethynylated derivative **2b**[22] (Figure 1) clearly shows the characteristic butterfly conformation[4] of the phenothiazine core unit, with dihedral angles of 152.97 (C2–C1–S1–C12) and 152.73° (C5–C6–N1–C7). The bond lengths of the phenothiazinyl moiety and the triple bonds also lie within the expected margins (C19–C20: 1.169 Å; C21–C22: 1.173 Å). Furthermore, the *N*-hexyl substituent adopts a pseudoequatorial arrangement with only a slight deviation of C13 from coplanarity (dihedral angles: C8–C7–N1–C13: 13.95°; C5–C6–N1–C13: 12.77°).

With ethynylated phenothiazines **1** to hand, the stage was now set for the synthesis of various alkynyl-substituted phenothiazines, as well as bridged dumbbell- or even star-shaped phenothiazine dyads and triads. The terminal alkynes **1** and various (hetero)aryl halides **6** were therefore subjected to Sonogashira coupling conditions to furnish 3-alkynyl-substituted phenothiazines **7** in moderate to good yields as pale yellow to brown solids or as a yellow oil (**7d**) (Scheme 3).

Upon coupling of the ethynyl phenothiazines **1** with diiodo or triiodo (hetero)arenes such as 1,4-diiodobenzene (**8**), 2,5-diiodothiophene (**9**), 3,7-diiodophenothiazine (**10**), or 1,3,5-triiodobenzene (**11**), dumbbell-shaped alkynyl-bridged diphenothiazines **12** and **13** and triphenothiazines with rod-like (**14**) or star-shaped (**15**) alignments of the electrophore units are readily accessible in moderate to excellent yields, as yellow to orange solids (**13**, **15**) or resins (**12**, **14**) with blue to green fluorescence (Scheme 4).



Scheme 2. Ethynylated phenothiazines **1**, **2**, and **5** from bromo phenothiazines by Sonogashira coupling

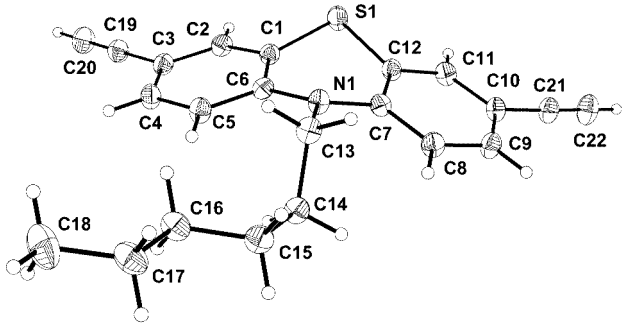


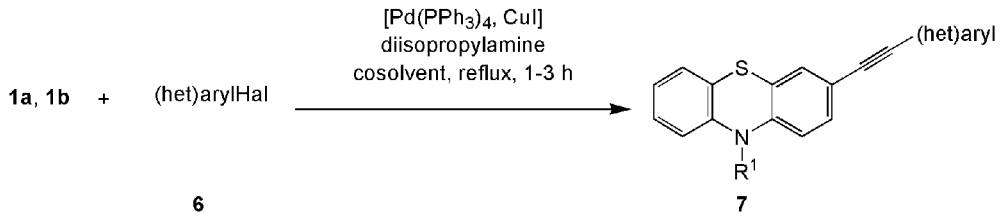
Figure 1. ORTEP plot of the diethynylated *N*-hexylphenothiazine **2b**

The structural assignments of the alkynylated phenothiazines **7** and the oligophenothiazines **12**−**15** are unambiguously supported by spectroscopic (^{1}H and ^{13}C NMR, IR, MS), combustion analytical, and − in the cases of resins and oils − by HRMS data. In the ^{1}H and ^{13}C NMR spectra of the oligophenothiazine derivatives **7g** and **12**−**15**, the appearance of single sets of resonances for the magnetically and chemically equivalent terminal phenothiazinyl ethynyl fragments confirms the highly symmetric solution structures of these dumbbell- or star-shaped entities. The characteristic α- and β-alkyne (with respect to the phenothiazine moiety) carbon resonances in the ^{13}C NMR spectra found between δ = 86.4−94.6 (C_α) and δ = 82.3−89.5 (C_β) can be assigned by increment calculations. The shifts of these signals attest to a significant influence of the electronic nature of the substituent at C_β. Interestingly, in the consanguine series of **7a**, **7b**, **7c**, and **7e** (all representing *p*-phenylene-substituted 3-ethynyl-10-methylphenothiazine derivatives) an excellent correlation of the Δδ [i.e., $\delta(C_\beta) - \delta(C_\alpha)$] and σ_P Hammett substituent parameters can be established (r^2 = 0.9914). In conclusion, this correlation indicates that the electronic substituent effect at the remote *p*-phenyl position is transmitted to the alkynyl bridge by resonance and inductive mechanisms; that is, through delocalization of π-molecular orbitals and the σ-bond framework. In accordance with the mass spectra of the simple alkynylated phenothiazines **1** and **2**, the molecular peak, representing the stable radical cation (vide infra), is also the basis signal and can be found for all compounds **7** and **12**−**15**. Most characteristic for the fragmentation patterns in the EI mass spectra are the expected loss of the methyl group and direct and α-cleavages of the *n*-hexyl substituent.

Electronic Structures and Properties of Alkynyl Phenothiazines

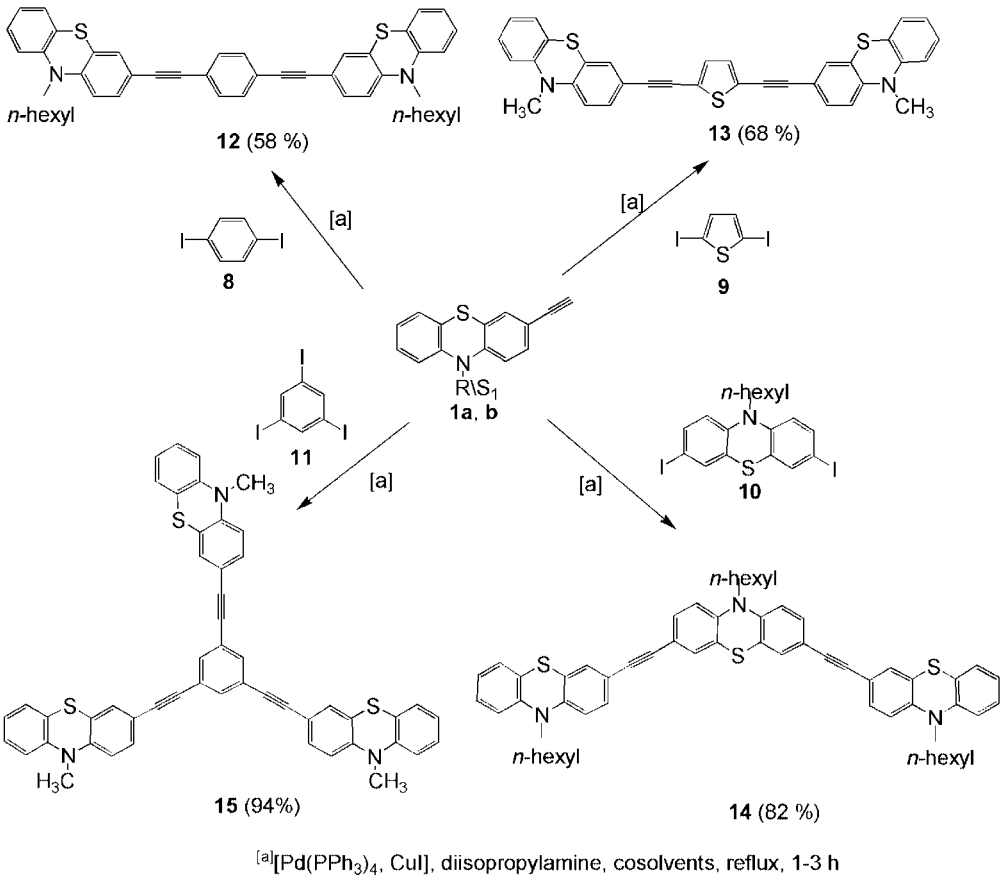
The electronic structures and properties of alkynyl phenothiazines were investigated by experimental (absorption and emission spectra, cyclic voltammetry) and computational methods (DFT calculations)[23] (Table 1).

As a consequence of the weakly electron-withdrawing nature of the ethynyl group (electronegativity χ_P = 3.03;[24] σ_P Hammett substituent parameter: 0.23[25]), resulting in a small inherent push-pull chromophore of alkynylated phenothiazines, the longest-wavelength absorption maxima in the UV/Vis spectra of the ethynylated phenothiazines (**1a**: 319 nm; **1b**: 321 nm) are shifted bathochromically in comparison with methyl- (310 nm) and hexylphenothiazine (311 nm). According to ZINDO/CI calculations[26] on a DFT-optimized structure[23] of **1a**, this absorption band arises from equal contributions from the HOMO−LUMO transition (representing considerable orbital coefficients in the ethynyl side-chain, Figure 2) and transitions within the phenothiazine core (from HOMO and HOMO-1 to LUMO+1 and LUMO+2). Upon UV excitation of the longest-wavelength absorption band, these parent alkynyl phenothiazines exhibit considerable Stokes shifts and spon-



	R^1	(het)aryl	yields
7a	Me	*p*-$C_6H_4NO_2$	(89 %)
7b	Me	*p*-C_6H_4CHO	(60 %)
7c	Me	C_6H_5	(54 %)
7d	*n*-hexyl	C_6H_5	(62 %)
7e	Me	2-thienyl	(72 %)
7f	Me	*p*-C_6H_4OMe	(61 %)
7g	*n*-hexyl	10-*n*-hexylphenothiazin-3-yl	(35 %)

Scheme 3. Alkynylated phenothiazines **7** by Sonogashira coupling



Scheme 4. Dumbbell- and star-shaped alkynyl bridged di- and triphenothiazines **12**−**15**

Table 1. Selected experimentally determined (UV/Vis, fluorescence, half wave redox potentials) and calculated[23] (HOMO, LUMO) electronic properties of alkynylated phenothiazines

	Absorption[a] $\lambda_{max,abs}$ [nm] (ε)	Emission[b] $\lambda_{max,em}$ [nm] (Φ_f)	Stokes shift $\Delta\tilde{\nu}$ [cm^{-1}]	$E_{1/2}$ [mV]	HOMO [eV]	LUMO [eV]
1a	267 (36700), **319** (7200)	**475** (14%)	10300	825	−4.905	−2.161
1b	268 (36400), **321** (6700)	**452** (14%)	9000	800	−4.839	−2.198
1d	255 (20300), 283 (40300), **389** (7800)	**528** (29%)	6800	−	−	−
2a	250 (16200, sh), 274 (55800), **334** (7800)	450	7700	889	−	−
5	295 (49400), **395** (11100)	**533** (29%)	6600	963	−	−
7a	263 (26800), 307 (23600), 408 (15000)	−	−	846, −1048	−5.196	−3.755
7b	248 (23400)[c], 274 (32300, sh), 294 (37700), 320 (24800, sh), 386 (22500)	−	−	828, −1675[d]	−5.095	−3.347
7c	274 (38500)[c], 294 (34400), **344** (12200)	**462** (39%)	7400	798	−4.854	−2.500
7d	276 (31400), 290 (26300, sh), **342** (11100)	**463** (39%)	7600	759	−4.755[e]	−2.509[e]
7e	306 (24300), **354** (14000)	**463** (23%)	6700	806	−4.824	−2.533
7f	274 (31600, sh), 288 (35100), 297 (36100, sh), 338 (14900)	−	−	778	−4.711	−2.301
7g	273 (40900), 293 (34000), **370** (19600)	**462** (26%)	5400	731, 843	−4.547[e]	−2.449[e]
12	272 (34000), 286 (31900), 304 (32600), 318 (34900), **384** (32800)	499	6000	754	−	−
13	270 (51500), 333 (33200), **394** (43700)	**496** (20%)	5200	773	−	−
14	238 (48400)[c], 276 (67500), 296 (79200), **388** (41900)	**481**[f] (43%)	5000	739, 886	−	−
15	278 (96200), 295 (76100, sh), **356** (46600)	**470** (45%)	6800	−	−	−
10-methylphenothiazine	254 (35800), 310 (6100)	−	−	767	−4.807	−1.717
10-hexylphenothiazine	256 (33000), 311 (5100)	−	−	728	−4.702[e]	−1.723[e]
nitrobenzene	258 (qual.)[36]	−	−	−1147	−7.102	−3.822

[a] Recorded in $CHCl_3$. [b] Recorded in $CHCl_3$ (perylene as standard). [c] Recorded in CH_2Cl_2. [d] Irreversible reduction wave. [e] Calculated for the ethyl-substituted derivative. [f] Recorded in $CHCl_3$ [tetrakismethyl 3,4,9,10-perylenetetrakis(carboxylate) as standard]

taneously fluoresce with emission of blue light (**1a**: $\lambda_{max,em}$ = 475 nm; **1b**: $\lambda_{max,em}$ = 452 nm) and modest quantum yields (Φ_f = 14%). Attachment of additional more strongly electron-withdrawing substituents such as formyl groups to the phenothiazine core (**1d**, **5**) produces a tremendous bathochromic and hyperchromic shift of the absorption (**1d**: $\lambda_{max,abs}$ = 389 nm; **5**: $\lambda_{max,abs}$ = 395 nm) and the emission maxima (**1d**: $\lambda_{max,em}$ = 528 nm; **5**: $\lambda_{max,em}$ = 533 nm) as an effect of an additional enhanced push-pull chromophore/fluorophore. Although the Stokes shifts in these rigidified and polarized push-pull chromophores decrease to $\Delta\tilde{\nu}$ = 6700 cm^{-1}, the fluorescence quantum yield is doubled in relation to the parent alkynyl phenothiazines (**1a**, **1b**). Extension of the conjugated system by a phenyl substituent at C_β of the alkynyl side chain (**7c**, **7d**), however, produces not only a bathochromic shift in the absorption but also an increase in the fluorescence quantum yield (Φ_f = 39%). Interestingly, the fluorescence quantum yield does not necessarily depend on the number of phenothiazinyl units, since the star-shaped tris(phenothiazinyl) fluorophore **15**, in which the phenothiazine ethynyl moieties are not in conjugation, emits blue light with the highest quantum yield (Φ_f = 45%) in the investigated series of alkynyl phenothiazines. Apparently, the conjugation of sulfur-containing heterocycles such as phenothiazine (**7g**: Φ_f = 26%; **14**: Φ_f = 43%) and/or thiophene (**7e**: Φ_f = 23%; **13**: Φ_f = 20%) favors and enhances the heavy element-mediated spin-orbit coupling and results in an increased rate of intersystem crossing, and thus in a depopulation of the S_1 state. However, an increased rate of singlet to triplet transfer could prove to be beneficial for the envisioned charge separations of suitably substituted phenothiazines initiated by photoinduced electron transfer.

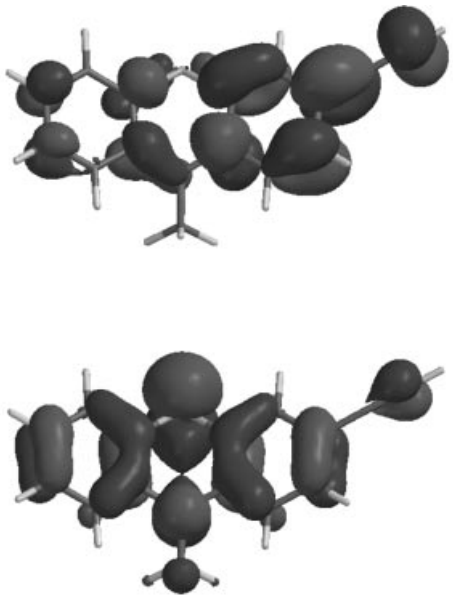


Figure 2. LUMO (top) and HOMO (bottom) of **1a**

In the series of alkynylated *N*-methyl phenothiazines **7a**, **7b**, **7c**, **7e**, and **7f**, a good correlation of the longest-wave-

length absorption band λ_{max} and the σ_P Hammett substituent parameters can be established ($r^2 = 0.9715$, Figure 3), indicating that the transmittance of the electronic substituent nature through resonance and field effects has a considerable influence even on the electronic transitions arising from transitions between the π-type frontier orbitals. Surprisingly, the correlations with σ_R or σ_I Hammett substituent parameters (describing only the resonance or the field influence, respectively) give fairly poor correlations with the electronic spectroscopic data.

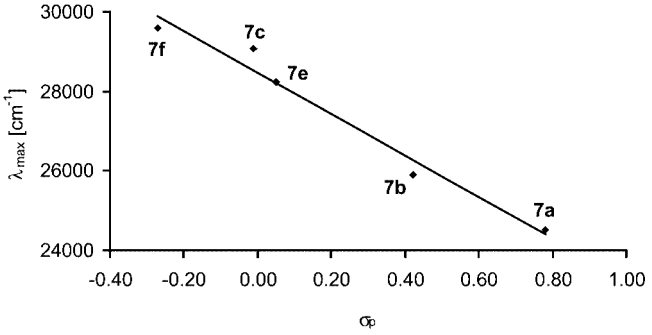


Figure 3. Correlation of the long-wavelength absorption λ_{max} [cm^{-1}] and the Hammett σ_P of (hetero)aryl ethynyl *N*-methyl phenothiazines **7** ($r^2 = 0.9715$)

Examination of the modest solvochromicity ($\Delta\tilde{\nu}_{THF-DMSO} = 540$ cm^{-1}) of the nitrophenyl-substituted alkynyl phenothiazine **7a** (i.e., the most pronounced push-pull system in the series of the alkynyl phenothiazines **7**) reveals a linear correlation ($r^2 = 0.9846$) between Reichardt's solvent polarity $E_T(30)$ values[27] and the longest-wavelength absorption maxima in THF ($\lambda_{max,abs}$ = 404 nm), chloroform ($\lambda_{max,abs}$ = 405 nm), dichloromethane ($\lambda_{max,abs}$ = 407 nm), and DMSO ($\lambda_{max,abs}$ = 413 nm). According to the observed positive solvochromicity (i.e., a bathochromic shift of the charge-transfer band with increasing solvent polarity), a considerable charge-transfer character of the first excited state can be deduced. This charge-transfer band can be interpreted as a highly polarized HOMO-1−LUMO transition (according to ZINDO/CI calculations[26]) in which the HOMO-1 and the LUMO both display significant orbital coefficients in the phenothiazine core and the *p*-nitrophenyl substituent (Figure 4).

Electrochemical data for the alkynyl phenothiazines were obtained by cyclic voltammetry for the compounds **1**, **5**, **7**, and **12**−**14** in the anodic (up to +1.5 V) and the cathodic regions (up to −2.0 V). The first reversible one-electron oxidations $E_0^{0/+1}$ reveal a strong dependence on the electronic nature of close (e.g., the formyl group in **5**) and remote substituents and are found between 700 and 963 mV (Table 1). In comparison with the *N*-methylphenothiazine ($E_0^{0/+1}$ = 767 mV) and *N*-hexylphenothiazine ($E_0^{0/+1}$ = 728 mV) parent systems, this oxidation event can be attributed to the formation of stable *N*-alkyl phenothiazine radical cations. In addition, this assignment is also strongly supported by the electronic structures of the molecules' HOMOs, indicating that the orbital coefficients are largely

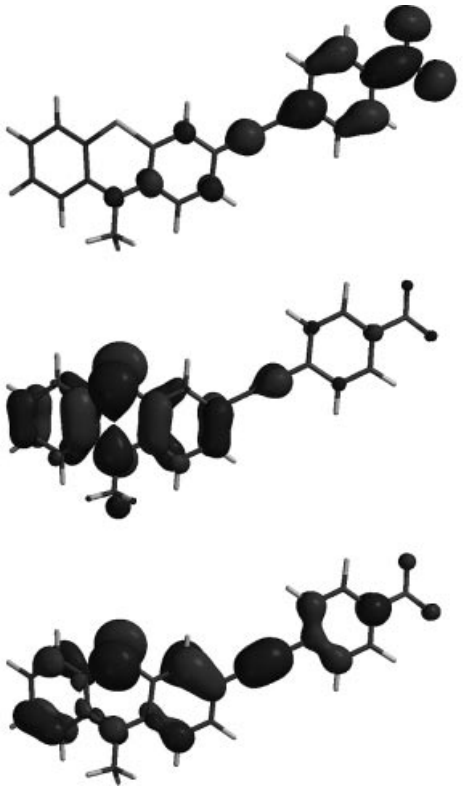


Figure 4. LUMO (top), HOMO (middle), and HOMO-1 (bottom) of **7a**

localized in the phenothiazinyl core (Figures 2 and 4). A closer inspection of the electrochemical behavior of the *p*-nitrophenyl-substituted ethynylphenothiazine **7a** shows, in addition to the reversible one-electron oxidation at $E_0^{0/+1}$ = 864 mV, a reversible reduction wave that can be detected in the cathodic region at $E_0^{0/-1} = -1100$ mV (Figure 5).

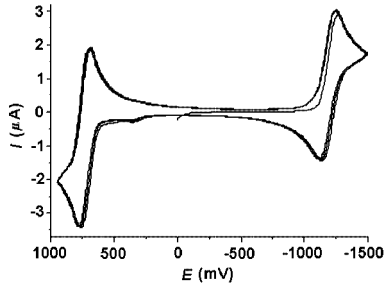


Figure 5. Cyclic voltammogram of **7a** in the anodic and cathodic regions (CH_2Cl_2, 20 °C, Pt disk electrode, reference electrode Ag/AgCl, scan rate = 100 mV/s, supporting electrolyte: $NnBu_4^+PF_6^-$)

In relation to nitrobenzene ($E_0^{0/-1} = -1147$ mV), this radical anion formation is facilitated by the presence of the extended π-electron conjugation and the electron-withdrawing nature of the alkynyl substituent, and so can readily be assigned to a one-electron reduction in the ethynyl *p*-nitrophenyl fragment of compound **7a**. Again, this assignment is supported by the electronic structure of the LUMO (Figure 4), in which the orbital coefficients are to a large extent localized on the ethynyl *p*-nitrophenyl side chain.

Most interestingly, the push-pull chromophore (vide supra) **7a** is an electrochemically amphoteric system that can reversible accept or donate electrons at relatively low voltages, a rather favorable property for hole and electron conductors in OLEDs (organic light-emitting diodes),[28] OFETs (organic field effect transistors),[29] or molecular rectifiers.[1]

For the establishment of structure-electronic property relationships it became apparent that the oxidation potentials $E_0^{0/+1}$ of *N*-methyl- (**1a**, **7c**) and *N*-hexyl alkynylated phenothiazines (**1b**, **7d**), as well as those of the reference compounds 10-methylphenothiazine and 10-hexylphenothiazine, correlate well with the corresponding HOMO energies calculated at the DFT level of theory[23] ($r^2 = 0.956$). Good correlation of the first reversible one-electron oxidation potential $E_0^{0/+1}$ and DFT-calculated HOMO energies in the series of alkynylated *N*-methyl phenothiazines **7a**, **7b**, **7c**, **7f**, and **7g**[23] can therefore be established ($r^2 = 0.9582$) (Figure 6). Rational design of tailor-made alkynyl phenothiazine electrophores with fine-tunable oxidation potentials should now be achievable on the basis of this correlation of experimental and computational electronic properties. As already shown for the electronic spectra (vide supra), the best correlation ($r^2 = 0.9704$) of the electrochemical data and the Hammett substitution parameters can be established between $E_0^{0/+1}$ and σ_P (Figure 7), again indicating that the electronic communication between the remote substituent and the phenothiazine electrophore is transmitted through resonance and field effects.

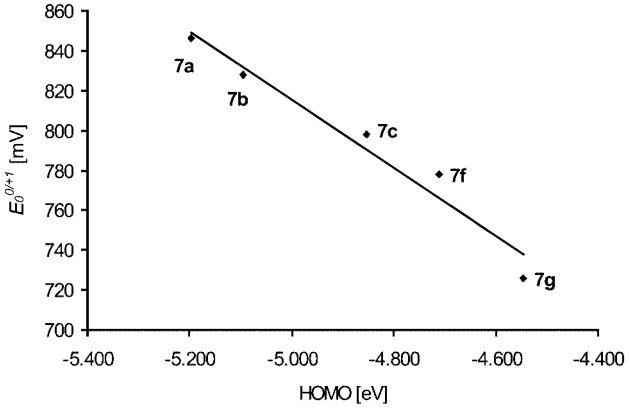


Figure 6. Correlation of the first oxidation potentials $E_0^{0/+1}$ [mV] and the calculated HOMO energies [eV] of (hetero)aryl ethynyl *N*-methyl phenothiazines **7** ($r^2 = 0.9582$).

Finally, our interest focused on the electrochemical behavior of phenothiazinyl dyads (**7g**, **12**, **13**) and triads (**14**) in which the electrophores are linked by alkynyl bridges in a conjugated fashion. Inevitably, the question of intramolecular electronic communication between the phenothiazinyl units arises. The ethynyl-bridged dyad **7g** shows two distinctly separated, fully reversible one-electron oxidation waves ($E_{rev}^{0/+1} = 731$ mV; $E_{rev}^{+1/+2} = 843$ mV) with a potential splitting $\Delta E = 112$ mV (Figure 8).

Thus, for this two-step redox system, the stability of the radical cation is $K_{SEM} = 79$ [i.e., at a potential slightly above $E_{rev}^{0/+1} = 731$ mV, almost 90% of the radical cation

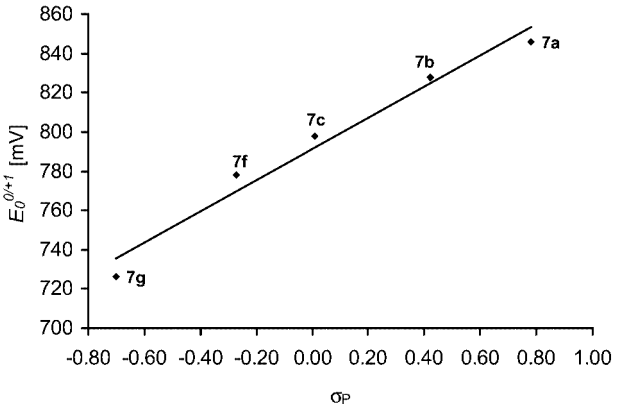


Figure 7. Correlation of the first oxidation potentials $E_0^{0/+1}$ [mV] and the Hammett σ_P coefficients of (hetero)aryl ethynyl *N*-methyl phenothiazines **7** ($r^2 = 0.9704$)

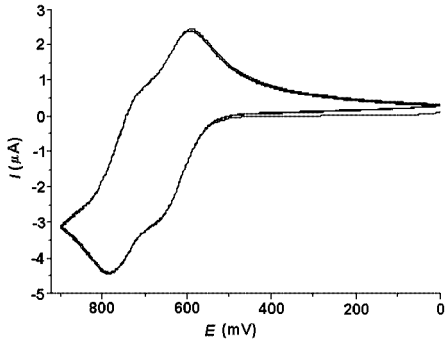


Figure 8. Cyclic voltammogram of **7g** in the anodic region (CH_2Cl_2, 20 °C, Pt disk electrode, reference electrode Ag/AgCl, scan rate = 100 mV/s, supporting electrolyte: $NnBu_4^+PF_6^-$)

$\mathbf{7g^+}$ (vs. the disproportionation in 5% of neutral **7g** and 5% of $\mathbf{7g^{2+}}$) is present in equilibrium]. The potential for the radical cation formation is significantly shifted cathodically with respect to the parent compound **1b** ($E_{rev}^{0/+1} = 800$ mV) as a consequence of the donor effect of the phenothiazinyl substitution. In turn, the second oxidation step from the radical cation to the dication is affected by the presence of a delocalized positive charge and so is shifted anodically with respect to **1b**. Inspection of the calculated electronic structures[23,30] of the frontier molecular orbitals of **7g** (Figure 9) reveals a highly delocalized nature and supports the view that the cathodically shifted first oxidation does not occur from a distinct side of the dyad but rather from the whole entity itself. The two phenothiazinyl subunits therefore clearly display pronounced intramolecular electronic coupling on the timescale of cyclic voltammetry.

A comprehensive interpretation of the electronic structure of the radical cation $\mathbf{7g^+}$ and, in particular, of the dication $\mathbf{7g^{2+}}$, which can adopt either a singlet or a triplet configuration, requires extensive open-shell calculations and spectro-electrochemical studies of this highly symmetrical electrophore dyad.

Interestingly, the oxidation potentials of the dyads **12** ($E_{rev} = 754$ mV) and **13** ($E_{rev} = 773$ mV), in which the phenothiazine electrophores are separated by a 1,4-diethyn-

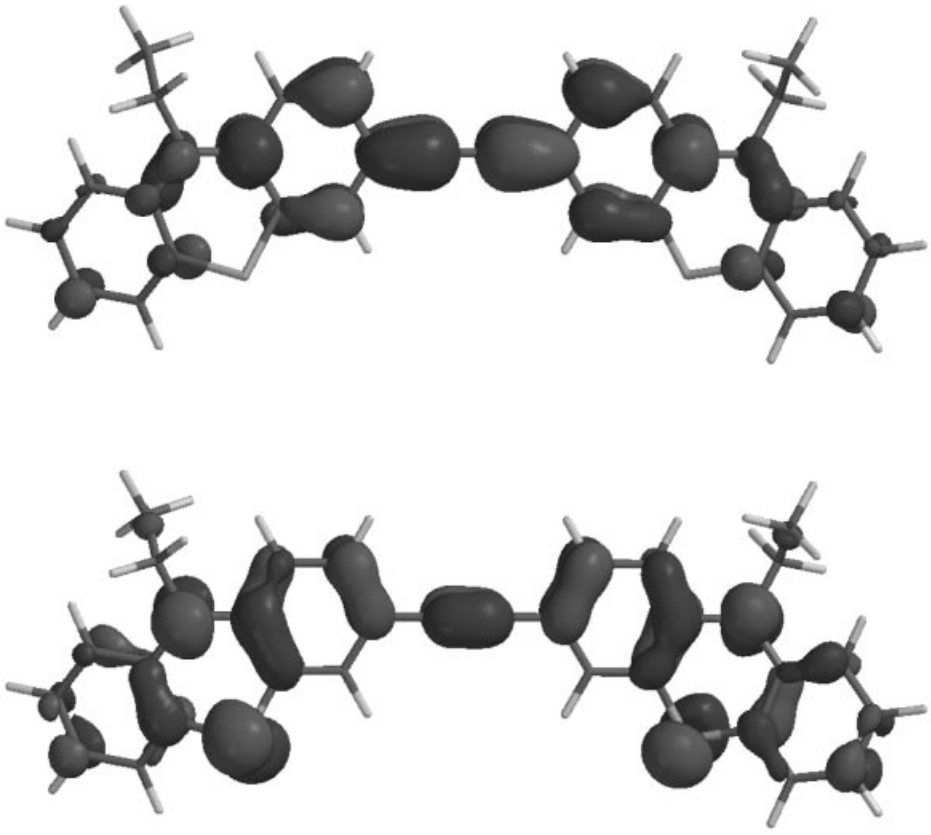


Figure 9. LUMO (top) and HOMO (bottom) of **7g** (calculated for the ethyl-substituted derivative)

ylphenylene (**12**) or a 2,5-diethynylthienylene (**13**) bridge, are not resolved into two stepwise one-electron oxidation waves. In comparison with the *N*-hexylphenothiazine parent system ($E_0^{0/+1}$ = 728 mV), these oxidation events are shifted anodically as a consequence of the electron-withdrawing nature of the diethynyl (hetero)arylene bridge. The anodic peak potential separations $\Delta(E_p^{ox} - E_p^{red})$ are 61 (**12**) and 90 mV (**13**), and the current ratios i_p^c/i_p^a are almost unity, so the oxidation potentials can be assigned to two independent reversible one-electron transfers (i.e., on the timescale of cyclic voltammetry the electrophores in these dyads can be considered to be electronically decoupled). Now, upon extending the oligomeric electrophores from phenothiazinyl dyads to triads a significant difference in the oxidation behavior becomes apparent. In the cyclic voltammogram of the ethynyl-bridged triad **14**, two distinctly separated, fully reversible oxidation waves ($E_{rev}^{0/+2}$ = 739 mV; $E_{rev}^{+2/+3}$ = 886 mV) with a potential splitting ΔE = 147 mV (Figure 10), however, with a relative current ratio of the anodic oxidation wave (or the cathodic reduction wave) of $i_p^{c(0/+2)}/i_p^{c(+2/+3)}$ (or $i_p^{c(+2/0)}/i_p^{c(+3/+2)}$) = 2.

This clearly indicates that the first electron transfer in the anodic region, occurring at a potential comparable to that of the parent *N*-hexylphenothiazine ($E_0^{0/+1}$ = 728 mV), stems from the symmetry equivalent terminal phenothiazine fragments in the sense of two independent one-electron oxidations. The second oxidation represents a one-electron

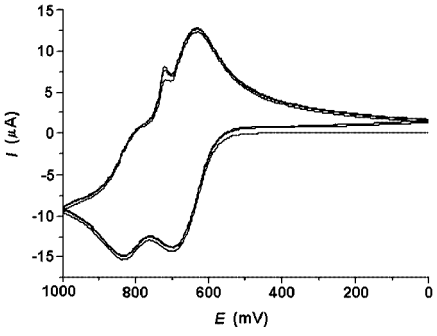


Figure 10. Cyclic voltammogram of **14** in the anodic region (CH_2Cl_2, 20 °C, Pt disk electrode, reference electrode Ag/AgCl, scan rate = 100 mV/s, supporting electrolyte: $NnBu_4^+PF_6^-$)

transfer from the inner phenothiazinyl unit and, as a consequence of the electron-withdrawing nature of the two terminal phenothiazinyl radical cation substituents, appears considerably shifted to higher potential. Thus, from the cyclovoltammetric behavior it can be deduced that the first oxidation event in ethynyl-bridged triads is decoupled, whereas the second oxidation, now occurring at the central phenothiazinyl unit, is subject to the strong electrostatic and resonance influence of the adjacent radical cation moieties. In contrast to triads without ethynyl bridges,[12d] in which three distinct one-electron oxidations can be attributed to intensive intramolecular electronic coupling within

the terphenothiazinyl entity, the ethynyl-bridged triad **14** rather reaches the state of intramolecular electronic coupling after oxidation to a diradical dication species $\mathbf{14}^{2+}$. The elucidation of the electronic structure of the oxidized specimen of **14** and the experimental and computational verification of this hypothesis is in progress and will be reported later.

Conclusion

Standard aldehyde-alkyne and bromide-alkyne transformations can successfully be applied to the corresponding phenothiazine derivatives and provide a straightforward and versatile route to the class of ethynylated *N*-alkyl phenothiazines **1** and **2**, which in turn are valuable building blocks for functionalized, electronically diverse, and extended alkynyl phenothiazines 7 and even oligomeric ethynyl-bridged phenothiazines **12**−**15**. All these new electrophores display interesting electronic properties, such as a modest solvochromicity of push-pull chromophores (**7a**), pronounced blue to green fluorescence upon UV excitation, and a distinct reversible redox behavior for the phenothiazine-phenothiazine$^+$ oxidations. Interestingly, in consanguine series, good correlations between experimentally determined and computed electronic properties and substituent parameters can readily be established. These correlations can now be effectively applied as tools with which to devise, design, and fine-tune tailor-made phenothiazine-based electroactive chromophores and fluorophores that are promising candidates as small-molecule-based molecular wires, molecular rectifiers, and molecular switches in emerging molecular electronics. Syntheses and studies of thiol-functionalized alkynylated phenothiazines for self-assembling monolayers and single-molecule manipulations are currently underway.

Experimental Section

Reagents, catalysts, ligands, and solvents were purchased reagent grade and used without further purification. Dichloromethane, diisopropylamine, dioxane, methanol, piperidine, THF, toluene, and triethylamine were dried and distilled according to standard procedures.[31] The phenothiazine aldehydes **3a**, **3b**,[13] **3e**, and **4e**,[11b] dialdehydes **3c** and **3d**,[14] phenothiazine bromides **4a** and **4b**,[19] and dibromide **4c**,[20] dimethyl 1-diazo-2-oxopropylphosphonate,[17] 3,7-diiodo-*N*-hexylphenothiazine (**10**),[32] and 1,3,5-triiodobenzene (**11**)[33] were prepared according to literature procedures. Column chromatography: silica gel 60 (Merck, Darmstadt), mesh 70−230. TLC: silica gel plates (60 F_{254}, Merck, Darmstadt). Melting points (uncorrected values): Büchi Melting Point B-540, Stuart Scientific SMP 3, heating rate 5 K/min. ^{1}H and ^{13}C NMR spectra: Bruker ARX 300, Varian VXR 400S. $CDCl_3$ (locked to Me_4Si),[34] [D_6]DMSO (locked to Me_4Si). The assignments of quaternary C, CH, CH_2, and CH_3 was carried out by use of 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 below 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 CH_2Cl_2 at room temperature and at scan rates of 100, 250, and 500 mV·s^{-1}. The electrolyte was 0.10 M Bu_4NPF_6. The working electrode was a 1-mm platinum disk, the counter electrode was a platinum wire, and the reference electrode was a Ag/AgCl electrode. The potentials were corrected to the internal standard of Fc/Fc$^+$ in CH_2Cl_2 ($E_0^{0/+1}$ = 450 mV).[35]

Alkynylated Phenothiazines 1 and 2 by the Corey−Fuchs Procedure (Method A, General Procedure 1). a) Synthesis of the Dibromo Olefin: A solution of tetrabromomethane (2 equiv.) in dry dichloromethane (2.8 mmol/mL) was added dropwise under nitrogen to a solution of triphenylphosphane (4 equiv.) in dry dichloromethane (1.9 mmol/mL), cooled to 0 °C by external cooling with ice water. The solution turned orange-yellow, and after the mixture had been stirred for 1 h at room temp., a solution of the corresponding aldehyde **3** (1 equiv., 0.35 mmol/mL) was added dropwise to the reaction mixture. The dark mixture was stirred for 6 days at room temp., after which an equivalent volume of pentane was added under vigorous stirring. The yellow supernatant was decanted from the dark green residue. After the residue had been dissolved in a small amount of dichloromethane, a tenfold volume of pentane was added with vigorous stirring. Again the supernatant was decanted. This procedure was repeated 3−4 times until the decanted supernatant was almost colorless. The solvents of the collected supernatant phases were removed in vacuo to furnish a brown, oily residue. This residue was filtered through a short pad of silica gel with dichloromethane. The volume of the eluate was reduced in vacuo and pentane was carefully added. After the mixture had been allowed to stand in the refrigerator, the crude dibromo olefin had separated and was collected and purified by double crystallization from dichloromethane/pentane.

b) Transformation of the Dibromo Olefin into the Alkyne: A solution of *n*-butyllithium in hexanes (1.6 M, 2.05 equiv.) was added dropwise under nitrogen to a cooled solution (−78 °C) of the dibromo olefin (1 equiv.) in dry THF (0.15 mmol/mL). The brown reaction mixture was then stirred for 2 h at −78 °C, after which the external cooling was removed and a saturated aqueous NH_4Cl solution was added. The organic phase was separated, diluted with diethyl ether, and extracted twice with the same amount of water. After drying with anhydrous magnesium sulfate the solvents were evaporated and the residue was purified by chromatography on silica gel (diethyl ether/pentane) to furnish the alkynylated phenothiazines **1** and **2** as yellow solids, resins, or oils. Further purification could be achieved by recrystallization from a suitable solvent.

Alkynylated Phenothiazines 1 and 2 by the Ohira−Bestmann Procedure (Method B, General Procedure 2): Anhydrous potassium carbonate (2 equiv.) was added under nitrogen to a yellow suspension of the aldehyde **3** (1 equiv.) and dimethyl 1-diazo-2-oxopropylphosphonate (1.5 equiv.) in dry methanol (0.2 mmol/mL). The yellow reaction mixture was stirred at room temp. for 24 h, after which it was diluted with diethyl ether/water and the aqueous phase was extracted with diethyl ether. The combined organic phases were dried with magnesium sulfate and the solvents were evaporated in vacuo. The residue was chromatographed on silica gel (diethyl ether/pentane) to give the alkynylated phenothiazines **1** and **2** as yellow solids, resins, or oils.

Alkynylated Phenothiazines 1 and 2 by Sonogashira Coupling (Method C, General Procedure 3): A suspension of the bromide **4** (1 equiv.), $[Pd(PPh_3)_2Cl_2]$ (0.04 equiv.), CuI (0.04 equiv.), and PPh_3 (0.04 equiv.) in dry piperidine (0.5 mmol/mL) was degassed for 15 min under a constant stream of nitrogen. Trimethylsilylacetylene (1.3 equiv. per bromine) was added to this reaction mixture, which was heated to reflux temp. until complete consumption of the bromide **4** (monitored by TLC). After the mixture had cooled to room temp., NaOH (2 N, 0.5 equiv. per TMS-acetylene) was added to the brown suspension. The mixture was then heated at reflux temp. whilst stirring for 30 min. After the mixture had cooled to room temp., 300 mL of diethyl ether and 500 mL of water were added and the aqueous phase was extracted four times with diethyl ether. The combined organic phases were dried with magnesium sulfate and the solvents were evaporated in vacuo. The residue was chromatographed on silica gel (diethyl ether/pentane) to give the alkynylated phenothiazines **1** and **2** as yellow solids, resins, or oils.

3-Ethynyl-10-methyl-10*H*-phenothiazine (1a). Method A: As described in GP 1, triphenylphosphane (73.6 g, 281 mmol) in dichloromethane (150 mL), tetrabromomethane (46.6 g, 140 mmol) in dichloromethane (50 mL), and the aldehyde **3a** (16.9 g, 70.2 mmol) in dichloromethane (200 mL) furnished the pure dibromo olefin (22.8 g, 82%) as a green/yellow solid after double crystallization from dichloromethane/pentane. Mp. 111−112 °C (methanol). ^{1}H NMR ($CDCl_3$, 300 MHz), δ = 3.37 ppm (s, 3 H), 6.77 (d, *J* = 9.1 Hz, 1 H), 6.81 (d, *J* = 8.3 Hz, 1 H), 6.95 (m, 1 H), 7.12−7.21 (m, 2 H), 7.33−7.37 (m, 3 H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ = 35.3 ppm (CH_3), 87.9 ($C_{quat.}$), 113.6 (CH), 114.2 (CH), 122.8 (CH), 123.3 ($C_{quat.}$), 126.7 (CH), 127.2 (CH), 127.6 (CH), 127.9 (CH), 129.5 ($C_{quat.}$, br), 135.6 (CH), 145.1 ($C_{quat.}$), 145.8 ($C_{quat.}$). MS (70 eV): *m*/*z* (%) = 399 [$^{81}Br_2$ M^+] (54), 397 [$^{81}Br^{79}Br$ M^+] (100), 395 [$^{79}Br_2$ M^+] (51), 384 [$^{81}Br_2$ $M^+ - CH_3$] (27), 382 [$^{81}Br^{79}Br$ $M^+ - CH_3$] (52), 380 [$^{79}Br_2$ $M^+ - CH_3$] (25), 237 [$M^+ - 2$ Br] (42), 237 [$M^+ - CH_3 - 2$ Br] (67), 119 (34), 118 (34). IR (KBr), $\tilde{\nu}$ = 2957 cm^{-1}, 2890, 1597, 1572, 1499, 1461, 1399, 1338, 1257, 1202, 1142, 895, 859, 821, 753, 741. UV/Vis (CH_2Cl_2), λ_{max} (ε): 272 nm (29900), 320 (7600), 342 (7500). $C_{15}H_{11}Br_2NS$ (397.1): calcd. C 45.37, H 2.79, N 3.53; found C 45.65, H 2.69, N 3.63.

In the second step, this dibromo olefin (7.13 g, 17.9 mmol) in THF (120 mL) was treated with *n*-butyllithium in hexanes (23.0 mL, 36.8 mmol) to give **1a** (3.93 g, 92%) as light yellow crystals after chromatography on silica gel (diethyl ether/pentane, 1:2) and crystallization from diethyl ether/pentane.

Method B: As described in GP 2, the aldehyde **3a** (241 mg, 1.00 mmol), dimethyl 1-diazo-2-oxopropylphosphonate (288 mg, 1.50 mmol), and K_2CO_3 (276 mg, 2.00 mmol) in methanol (5 mL) furnished **1a** (184 mg, 77%) as a light yellow solid after chromatography on silica gel (diethyl ether/pentane, 1:4).

Instant Ohira−Bestmann Procedure: A solution of dimethyl 2-oxopropylphosphonate (660 mg, 3.98 mmol) in dry acetonitrile (15 mL) was added dropwise under nitrogen to a suspension of K_2CO_3 (1.37 g, 9.94 mmol) and tosyl azide (784 mg, 3.98 mmol) in dry acetonitrile (15 mL) and the reaction mixture was stirred for 3 h at room temp., after which a solution of the aldehyde **3a** (800 mg, 3.31 mmol) in dry methanol (60 mL) was added. The yellow suspension was stirred for 16 h at room temp. The solvents were then removed in vacuo and the residue was chromatographed on silica gel (diethyl ether/pentane, 1:4) to give **1a** (364 mg, 46%) as a yellow solid.

Method C: As described in GP 3, the bromide **4a** (1.00 g, 3.42 mmol), $[Pd(PPh_3)_2Cl_2]$ (96 mg, 0.14 mmol), CuI (26 mg, 0.14 mmol), PPh_3 (36 mg, 0.14 mmol) in piperidine (17 mL), and trimethylsilylacetylene (470 mg, 4.79 mmol) in piperidine (3 mL) were allowed to react for 3 h and were then treated with NaOH (2 N, 4 mL) to furnish **1a** (609 mg, 75%) as a light yellow solid after chromatography on silica gel (diethyl ether/pentane, 1:4). R_f (pentane) = 0.30. Mp. 99−102 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ = 3.03 ppm (s, 1 H), 3.35 (s, 3 H), 6.70 (d, *J* = 8.4 Hz, 1 H), 6.80 (dd, *J* = 0.7, 8.1 Hz, 1 H), 6.94 (m, 1 H), 7.10−7.30 (m, 4 H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ = 35.3 ppm (CH_3), 76.8 (CH), 83.2 ($C_{quat.}$), 113.6 (CH), 114.2 (CH), 115.9 ($C_{quat.}$), 122.8 ($C_{quat.}$), 122.85 (CH), 123.5 ($C_{quat.}$), 127.2 (CH), 127.5 (CH), 130.4 (CH), 131.5 (CH), 145.1 ($C_{quat.}$), 146.3 ($C_{quat.}$). MS (EI, 70 eV): *m*/*z* (%) = 237 [M^+] (100), 222 [$M^+ - CH_3$] (85), 118 [M^{2+}] (10). IR (KBr), $\tilde{\nu}$ = 3290 cm^{-1}, 2954, 2927, 2855, 2199, 2106, 1624, 1604, 1579, 1501, 1465, 1398, 1356, 1336, 1297, 1247, 1195, 1153, 883, 814, 758. UV/Vis ($CHCl_3$), λ_{max} (ε): 267 nm (36700), 319 (7200). $C_{15}H_{11}NS$ (237.3): calcd. C 75.92, H 4.67, N 5.90, S 13.51; found C 75.94, H 4.85, N 5.91, S 13.53.

3-Ethynyl-10-*n*-hexyl-10*H*-phenothiazine (1b). Method A: As described in GP 1, triphenylphosphane (31.4 g, 120 mmol) in dichloromethane (130 mL), tetrabromomethane (19.9 g, 60.0 mmol) in dichloromethane (20 mL), and the aldehyde **3b** (8.86 g, 30.0 mmol) in dichloromethane (20 mL) furnished the pure dibromo olefin (11.07 g 79%) as a yellow oil after filtration through silica gel with pentane as eluent, and this was used without further purification.

In the second step, this dibromo olefin (7.01 g, 15.0 mmol) in THF (50 mL) was treated with *n*-butyllithium in hexanes (20 mL, 32 mmol) to give **1b** (4.08 g 89%) as a yellow oil after chromatography on silica gel (pentane).

Method C: As described in GP 3, the bromide **4b** (362 mg, 1.00 mmol), $[Pd(PPh_3)_2Cl_2]$ (28 mg, 0.04 mmol), CuI (8 mg, 0.04 mmol), PPh_3 (10 mg, 0.04 mmol) in piperidine (3 mL) and THF (3 mL), and trimethylsilylacetylene (137 mg, 1.40 mmol) were allowed to react for 2 h at reflux temperature and for 12 h at room temp. and were then treated with NaOH (2 N, 3 mL) to furnish **1a** (259 mg, 84%) as a dark yellow oil after chromatography on silica gel (diethyl ether/pentane, 1:1). R_f (pentane) = 0.16. ^{1}H NMR ($CDCl_3$, 300 MHz), δ = 0.87 ppm (t, *J* = 6.7 Hz, 3 H), 1.28−1.31 (m, 4 H), 1.41 (m, 2 H), 1.77 (m, 2 H), 3.02 (s, 1 H), 3.81 (t, *J* = 7.1 Hz, 2 H), 6.75 (d, *J* = 8.3 Hz, 1 H), 6.83 (d, *J* = 7.9 Hz, 1 H), 6.91 (dt, *J* = 1.1, 7.6 Hz, 1 H), 7.08−7.16 (m, 2 H), 7.22−7.27 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ = 13.9 ppm (CH_3), 22.5 (CH_2), 26.5 (CH_2), 26.7 (CH_2), 31.4 (CH_2), 47.5 (CH_2), 76.8 (CH), 83.1 ($C_{quat.}$), 114.9 (CH), 115.5 (CH), 115.7 ($C_{quat.}$), 122.7 (CH), 124.1 ($C_{quat.}$), 124.8 ($C_{quat.}$), 127.3 (CH), 127.4 (CH), 130.7 (CH), 131.3 (CH), 144.6 ($C_{quat.}$), 145.8 ($C_{quat.}$).

3-Bromo-7-ethynyl-10-methyl-10*H*-phenothiazine (1c). Method B: As described in GP 2, the bromo aldehyde **3e** (585 mg, 1.83 mmol), dimethyl 1-diazo-2-oxopropylphosphonate (432 mg, 2.25 mmol), and K_2CO_3 (415 mg, 3.00 mmol) in methanol (6 mL), after a reaction time of 2 days, furnished **1c** (348 mg, 60%) as a light yellow powder after chromatography on silica gel (diethyl ether/pentane, 1:4). R_f (diethyl ether/pentane, 1:4) = 0.37. Mp. 144−145 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ = 3.04 ppm (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 (s, 2 H), 7.23 (dd, *J* = 1.8, 8.3 Hz, 1 H), 7.28 (dd, *J* = 1.8, 8.4 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ = 35.4 ppm (CH_3), 77.2 ($C_{quat.}$), 82.8 (CH), 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 (70 eV): *m*/*z* (%) = 318 (15) [M^+], 317 [$^{81}Br\ M^+$] (100), 316 (17), 315 [$^{79}Br\ M^+$] (97), 303 (11), 302 [$^{81}Br\ M^+ - CH_3$] (73), 301 (11), 300 [$^{79}Br\ M^+ - CH_3$] (72), 236 [$M^+ - Br$] (26), 221 [$M^+ - CH_3 - Br$] (17), 220 (18), 177 (12). IR (KBr), $\tilde{\nu}$ = 3288 cm^{-1}, 2107, 1597, 1493, 1460, 1384, 1329, 1271, 1250, 1128, 886, 814, 764, 659. UV/Vis ($CHCl_3$), λ_{max} (ε): 268 nm (43900), 325 (8300). HRMS calcd. for $C_{15}H_{10}{}^{79}BrNS$: 314.9717; found 314.9729.

7-Ethynyl-10-methyl-10*H*-phenothiazine-3-carbaldehyde (1d). Method C: As described in GP 3, the bromide **4d** (1.00 g, 3.12 mmol), [$Pd(PPh_3)_2Cl_2$] (22 mg, 0.03 mmol), CuI (12 mg, 0.06 mmol), PPh_3 (24 mg, 0.09 mmol) in piperidine (15 mL), and trimethylsilylacetylene (429 mg, 4.37 mmol) in piperidine (3 mL) were allowed to react for 12 h and were then treated with NaOH (2 N, 2 mL) to furnish **1d** (500 mg, 60%) as a shiny yellow orange powder after chromatography on silica gel (diethyl ether/pentane, 1:1). R_f (diethyl ether/pentane, 1:1) = 0.30. Mp. 181−182 °C. ^1H NMR ($CDCl_3$, 300 MHz), δ = 3.48 ppm (s, 3 H), 3.62 (s, 1 H), 6.94 (d, *J* = 8.5 Hz, 1 H, H_{ar}), 7.11 (d, *J* = 8.4 Hz, 1 H), 7.23 (d, *J* = 1.7 Hz, 1 H), 7.33 (dd, *J* = 1.8, 8.4 Hz, 1 H), 7.59 (d, *J* = 1.8 Hz, 1 H), 7.74 (dd, *J* = 1.8, 8.4 Hz, 1 H), 9.84 (s, 1 H). MS (70 eV): *m*/*z* (%) = 266 (18), 265 [M^+] (100), 251 (12), 250 [$M^+ - CH_3$] (57), 236 [$M^+ - CHO$] (12), 222 [$M^+ - CH_3 - CO$] (26). IR (KBr), $\tilde{\nu}$ = 3235 cm^{-1}, 2107, 1683, 1602, 1578, 1564, 1547, 1470, 1393, 1338, 1315, 1259, 1203, 1154, 1131, 816, 742, 585. UV/Vis ($CHCl_3$), λ_{max} (ε): 255 nm (20400), 283 (40300), 389 (7800). $C_{16}H_{11}NOS$ (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*-phenothiazine-3-carbaldehyde (1e). Method C: As described in GP 3, the bromide **4e** (1.00 g, 2.56 mmol), [$Pd(PPh_3)_2Cl_2$] (54 mg, 0.08 mmol), CuI (15 mg, 0.08 mmol), PPh_3 (20 mg, 0.08 mmol) in piperidine (15 mL) and THF (20 mL), and trimethylsilylacetylene (352 mg, 3.59 mmol) in piperidine (3 mL) were allowed to react for 2 h and were then treated with NaOH (2 N, 4 mL) to furnish **1e** (466 mg, 54%) as a brown yellow oil after chromatography on silica gel (diethyl ether/pentane, 1:3). R_f (diethyl ether/pentane, 1:4) = 0.22. ^1H NMR ($CDCl_3$, 300 MHz), δ = 0.87 ppm (m, 3 H), 1.26−1.32 (m, 4 H), 1.42 (m, 2 H), 1.78 (m, 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* = 1.8, 7.9 Hz, 1 H), 7.54 (d, *J* = 1.8 Hz, 1 H), 7.62 (dd, *J* = 1.9, 8.4 Hz, 1 H), 9.79 (s, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ = 13.9 ppm (CH_3), 22.5 (CH_2), 26.4 (CH_2), 26.6 (CH_2), 31.3 (CH_2), 48.1 (CH_2), 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), 131.4 ($C_{quat.}$), 143.9 ($C_{quat.}$), 149.9 ($C_{quat.}$), 189.8 (CH). MS (70 eV): *m*/*z* (%) = 335 [M^+] (100), 264 [$M^+ - C_5H_{11}$] (45), 250 [$M^+ - C_6H_{13}$] (69), 232 (15), 222 [$M^+ - C_6H_{13} - CO$] (14). IR (KBr), $\tilde{\nu}$ = 3290 cm^{-1}, 3056, 2955, 2927, 2855, 2729, 2108, 1694, 1682, 1601, 1580, 1564, 1496, 1470, 1416, 1398, 1378, 1357, 1336, 1308, 1276, 1246, 1197, 1156, 1102, 1055, 924, 885, 815, 741, 721, 653, 586. UV/Vis ($CHCl_3$), λ_{max} (ε): 256 nm (19000), 284 (32900), 389 (7300). HRMS calcd. for $C_{21}H_{21}NOS$: 335.1344; found 335.1349.

3,7-Diethynyl-10-methyl-10*H*-phenothiazine (2a). Method A: As described in GP 1, triphenylphosphane (78.0 g, 297 mmol) in dichloromethane (200 mL), tetrabromomethane (49.2 g, 148 mmol) in dichloromethane (25 mL), and dialdehyde **3c** (10.0 g, 37.1 mmol) in dichloromethane (500 mL) furnished the pure bis(dibromo olefin) (14.4 g, 67%) as light yellow crystals after recrystallization from acetone. R_f (diethyl ether/pentane, 1:2) = 0.54. Mp. 108 °C ($CHCl_3$/hexane). ^1H NMR ($CDCl_3$, 300 MHz), δ = 3.37 ppm (s, 3 H), 6.76 (d, *J* = 9.1 Hz, 2 H), 7.32−7.37 (m, 6 H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ = 35.3 ppm (CH_3), 88.3 ($C_{quat.}$), 113.8 (CH), 122.8 ($C_{quat.}$), 126.8 (CH), 128.1 (CH), 129.9 ($C_{quat.}$), 135.4 (CH), 145.1 ($C_{quat.}$). MS (70 eV): *m*/*z* (%) = 585 [$^{81}Br_4\ M^+$] (17), 583 [$^{81}Br_3{}^{79}Br\ M^+$] (68), 581 [$^{81}Br_2{}^{79}Br_2\ M^+$] (100), 579 [$^{81}Br^{79}Br_3\ M^+$] (68), 577 [$^{79}Br_4\ M^+$] (17), 568 [$^{81}Br_3{}^{79}Br\ M^+ - CH_3$] (21), 566 [$^{81}Br_2{}^{79}Br_2\ M^+ - CH_3$] (28), 564 [$^{81}Br^{79}Br_3\ M^+ - CH_3$] (19), 246 [$M^+ - 4$ Br] (33). IR (KBr), $\tilde{\nu}$ = 1603 cm^{-1}, 1580, 1549, 1507, 1474, 1463, 1422, 1339, 1272, 1257, 1203, 1172, 1163, 1134, 1117, 913, 891, 884, 847, 826, 807, 732, 716, 698, 684. UV/Vis (CH_2Cl_2), λ_{max} (ε): 286 nm (52400), 371 (11200). $C_{17}H_{11}Br_4NS$ (581.0): calcd. C 35.15, H 1.91, N 2.41; found C 35.41, H 1.92, N 2.40.

In the second step, this bis(dibromo olefin) (6.45 g, 11.1 mmol) in THF (250 mL) was treated with *n*-butyllithium in cyclohexane (2 M, 22.0 mL, 44.0 mmol) to give **2a** (2.33 g, 80%) as light yellow crystals after chromatography on silica gel (diethyl ether/isohexane, 1:4) and crystallization from diethyl ether/pentane.

Method B: As described in GP 2, the dialdehyde **3c** (269 mg, 1.00 mmol), dimethyl 1-diazo-2-oxopropylphosphonate (576 mg, 3.00 mmol), and K_2CO_3 (276 mg, 2.00 mmol) in a mixture of methanol (10 mL) and dichloromethane (5 mL) furnished **2a** (172 mg, 66%) as a light yellow powder after chromatography on silica gel (diethyl ether/pentane, 1:2).

Method C: As described in GP 3, the dibromide **4c** (10.0 g, 26.9 mmol), [$Pd(PPh_3)_2Cl_2$] (760 mg, 1.08 mmol), CuI (210 mg, 1.08 mmol), PPh_3 (280 mg, 1.08 mmol) in piperidine (17 mL), and trimethylsilylacetylene (9.90 mL, 70.0 mmol) in piperidine (50 mL) were allowed to react for 3 h and were then treated with NaOH (2 N, 25 mL) to furnish **2a** (4.28 g, 61%) as a light yellow solid after chromatography on silica gel (diethyl ether/pentane, 1:4). **2a**: Mp. 141 °C (ethanol). ^1H NMR ($CDCl_3$, 200 MHz), δ = 3.05 ppm (s, 2 H), 3.38 (s, 3 H), 6.69 (d, *J* = 8.4 Hz, 2 H), 7.22 (m_c, 2 H), 7.27 (dd, *J* = 2.0, 8.4 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ = 35.5 ppm (CH_3), 77.2 (CH), 82.8 ($C_{quat.}$), 113.9 (CH), 116.4 ($C_{quat.}$), 122.9 ($C_{quat.}$), 130.5 (CH), 131.7 (CH), 145.5 ($C_{quat.}$). MS (70 eV): *m*/*z* (%) = 261 [M^+] (100), 246 [$M^+ - CH_3$] (40), 131 [M^{2+}] (8). IR (KBr), $\tilde{\nu}$ = 2093 cm^{-1}, 1612, 1576, 1460, 1389, 1333, 1257, 1200, 1157, 1135, 888, 817. UV/Vis (CH_2Cl_2), λ_{max} (ε): 250 nm (16200, sh), 274 (55800), 334 (7800). $C_{17}H_{11}NS$ (261.4): calcd. C 78.13, H 4.24, N 5.36; found C 77.94, H 4.13, N 5.10.

3,7-Diethynyl-10-*n*-hexyl-10*H*-phenothiazine (2b). Method A: As described in GP 1, triphenylphosphane (16.75 g, 64.00 mmol) in dichloromethane (30 mL), tetrabromomethane (10.6 g, 32.0 mmol) in dichloromethane (10 mL), and dialdehyde **3d** (2.53 g, 7.45 mmol) in dichloromethane (20 mL) furnished the pure bis(dibromo olefin) (4.21 g, 87%) as a pale yellow, crystalline solid after absorptive filtration through silica gel (diethyl ether/pentane, 1:1). R_f (diethyl ether/pentane, 1:2) = 0.54. Mp. 108 °C ($CHCl_3$/hexane). ^1H NMR ($CDCl_3$, 300 MHz), δ = 3.37 ppm (s, 3 H), 6.76 (d, *J* = 9.1 Hz, 2 H), 7.32−7.37 (m, 6 H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ = 35.3 ppm (CH_3), 88.3 ($C_{quat.}$), 113.8 (CH), 122.8 ($C_{quat.}$), 126.8 (CH), 128.1 (CH), 129.9 ($C_{quat.}$), 135.4 (CH), 145.1 ($C_{quat.}$). MS (70 eV): *m*/*z* (%) = 585 [$^{81}Br_4\ M^+$] (17), 583 [$^{81}Br_3{}^{79}Br\ M^+$] (68), 581 [$^{81}Br_2{}^{79}Br_2\ M^+$] (100), 579 [$^{81}Br^{79}Br_3\ M^+$] (68), 577 [$^{79}Br_4\ M^+$] (17), 568 [$^{81}Br_3{}^{79}Br\ M^+ - CH_3$] (21), 566 [$^{81}Br_2{}^{79}Br_2\ M^+ - CH_3$] (28), 564 [$^{81}Br^{79}Br_3\ M^+ - CH_3$] (19), 246 [$M^+ - 4$ Br] (33). IR (KBr), $\tilde{\nu}$ = 1603 cm^{-1}, 1580, 1549, 1507, 1474, 1463, 1422, 1339, 1272, 1257, 1203, 1172, 1163, 1134, 1117, 913, 891, 884, 847, 826, 807, 732, 716, 698, 684. UV/Vis (CH_2Cl_2), λ_{max} (ε): 286 nm (52400), 371 (11200). $C_{17}H_{11}Br_4NS$ (581.0): calcd. C 35.15, H 1.91, N 2.41; found C 35.41, H 1.92, N 2.40.

In the second step, this bis(dibromo olefin) (2.30 g, 3.53 mmol) in THF (20 mL) was treated with *n*-butyllithium in hexanes (1.6 M, 10 mL, 16 mmol) to give **2b** (1.05 g, 90%) as a yellow solid after chromatography on silica gel (diethyl ether/isohexane, 1:4). ^{1}H NMR ($CDCl_3$, 300 MHz), δ = 0.87 ppm (t, *J* = 6.9 Hz, 3 H), 1.26−1.31 (m, 6 H), 1.76 (m, 2 H), 3.05 (s, 2 H), 3.80 (t, *J* = 7.1 Hz, 2 H), 6.74 (d, *J* = 8.5 Hz, 2 H), 7.20 (d, *J* = 1.9 Hz, 2 H), 7.26 (dd, *J* = 1.9, 8.4 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ = 13.9 ppm (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 ($C_{quat.}$), 115.1 (CH), 116.2 ($C_{quat.}$), 124.0 ($C_{quat.}$), 130.7 (CH), 131.4 (CH), 145.0 ($C_{quat.}$).

10-Methyl-7-phenylethynyl-10*H*-phenothiazine-3-carbaldehyde (5): According to a modified Buchwald−Fu procedure, [$Pd(PhCN)_2Cl_2$] (11 mg, 0.03 mmol), CuI (4 mg, 0.02 mmol), and a 0.25 M solution of P*t*Bu_3 in dioxane (0.24 mL, 0.06 mmol) under nitrogen were successively added in 1 mL of dry dioxane to form a brown suspension. Bromide **4d** (320 mg, 1.00 mmol), phenylacetylene (122 mg, 1.20 mmol), and dry diisopropylamine (1.70 mL, 1.20 mmol) in dioxane (8 mL) were then added successively. The dark brown solution was stirred at room temp. for 2 days, after which it was diluted with ethyl acetate (10 mL). The reaction mixture was filtered through a short plug of silica gel to remove a colorless precipitate. The solvents were evaporated from this yellow orange solution in vacuo and the residue was chromatographed on silica gel (diethyl ether/pentane, 1:1) to furnish pure **5** (324 mg, 95%) as a voluminous, shiny, yellow solid. R_f (diethyl ether/pentane, 1:1) = 0.46. Mp. 135 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ = 3.40 ppm (s, 3 H), 6.75 (d, *J* = 8.4 Hz, 1 H), 6.83 (d, *J* = 8.2 Hz, 1 H), 7.26 (d, *J* = 1.6 Hz, 1 H), 7.31−7.35 (m, 4 H), 7.48−7.51 (m, 2 H), 7.57 (d, *J* = 1.8 Hz, 1 H), 7.64 (dd, *J* = 1.8, 8.4 Hz, 1 H), 9.79 (s, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ = 35.9 ppm (CH_3), 88.3 ($C_{quat.}$), 89.9 ($C_{quat.}$), 113.9 (CH), 114.5 (CH), 118.5 ($C_{quat.}$), 122.6 ($C_{quat.}$), 123.1 ($C_{quat.}$), 123.5 ($C_{quat.}$), 127.9 (CH), 128.2 (CH), 128.3 (CH), 129.9 (CH), 130.4 (CH), 131.2 (CH), 128.3 (CH), 131.4 ($C_{quat.}$), 131.4 (CH), 143.9 ($C_{quat.}$), 150.3 ($C_{quat.}$), 189.9 (CH). MS (70 eV): *m*/*z* (%) = 342 (25), 341 [M^+] (100), 327 (12), 326 [$M^+ - CH_3$] (52), 170 [M^{2+}] (9). IR (KBr), $\tilde{\nu}$ = 1687 cm^{-1}, 1602, 1578, 1564, 1505, 1488, 1468, 1395, 1373, 1338, 1313, 1270, 1252, 1201, 1154, 1129, 895, 814, 756, 690. UV/Vis ($CHCl_3$), λ_{max} (ε): 295 nm (49000), 395 (11000). $C_{22}H_{15}NSO$ (341.4): calcd. C 77.39, H 4.43, N 4.10, S 9.39; found C 77.06, H 4.43, N 4.03, S 9.37.

Sonogashira Coupling of Ethynylated Phenothiazines with (Hetero)aryl Halides (General Procedure): A mixture of **1** or **2** (1.05 equiv.), a monohalide (1.0 equiv.; 0.5 equiv. of a dihalide or 0.33 equiv. of a trihalide), a palladium catalyst (0.03 equiv. per halogen atom), and CuI (0.03 equiv.) in toluene (5 mL) and diisopropylamine (5 mL) was degassed with nitrogen for 5 min and then stirred at room temp., after which it was heated at reflux temperature for the indicated times until all alkyne had been consumed. After cooling to room temp. the reaction mixture was diluted with diethyl ether, THF, or dichloromethane (dependent on the solubility) and filtered through Celite 454 to give a clear, orange/red solution. The solvents were evaporated in vacuo and the residue was chromatographed on silica gel with diethyl ether/pentane to furnish the alkynylated phenothiazines as yellow, orange, or red solids or resins. Further purification could be achieved in many cases by recrystallization.

10-Methyl-3-(4-nitrophenylethynyl)-10*H*-phenothiazine (7a): As described in the GP, **1a** (250 mg, 1.05 mmol), 4-iodo(nitro)benzene (**6a**, 250 mg, 1.00 mmol), [$(Ph_3P)_4Pd$] (35 mg, 0.03 mmol), and CuI (6 mg, 0.03 mmol), after stirring at room temp. for 2.5 h and being heated at reflux temp. for 15 min, furnished **7a** (321 mg, 89%) as a dark brown solid after recrystallization from dichloromethane. R_f (diethyl ether/pentane, 1:4) = 0.36. Mp. 188−190 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ = 3.39 ppm (s, 3 H), 6.76 (d, *J* = 8.3 Hz, 1 H), 6.82 (d, *J* = 7.9 Hz, 1 H), 6.95 (m, 1 H), 7.12−7.18 (m, 2 H), 7.30−7.36 (m, 2 H), 7.60 (d, *J* = 8.8 Hz, 2 H), 8.19 (d, *J* = 8.8 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ = 35.5 ppm (CH_3), 87.8, ($C_{quat.}$), 94.6 ($C_{quat.}$), 113.9 (CH), 114.4 (CH), 115.8 ($C_{quat.}$), 122.6 ($C_{quat.}$), 123.7 (br., $C_{quat.}$), 123.1 (CH), 123.6 (CH), 123.7 ($C_{quat.}$), 127.2 (CH), 127.7 (CH), 130.1 (CH), 130.1 (CH), 130.5 ($C_{quat.}$), 132.0 (CH), 144.9 ($C_{quat.}$), 146.7 ($C_{quat.}$). MS (70 eV): *m*/*z* (%) = 359 (23), 358 [M^+] (100), 343 [$M^+ - CH_3$] (27), 328 [$M^+ - NO$] (24), 313 [$M^+ - HNO_2$] (15), 297 [$M^+ - NO_2 - CH_3$] (23), 296 [$M^+ - HNO_2 - CH_3$] (13). IR (KBr), $\tilde{\nu}$ = 2902 cm^{-1}, 1629, 1591, 1573, 1512, 1464, 1339, 1260, 1141, 1106, 860, 815, 748, 688. UV/Vis ($CHCl_3$), λ_{max} (ε): 264 nm (23600), 306 (19800), 405 (12200); (CH_2Cl_2): 263 (26000), 306 (24000), 407 (15000); (DMSO): 265 (27000), 306 (22600), 413 (13000); (THF): 262 (26700), 304 (24700), 404 (15800); (pentane): 261 (qual.), 389 (qual.); (MeOH): 261 (qual.), 299 (qual.), 397 (qual.). $C_{22}H_{14}N_2O_2S$ (358.4): calcd. C 70.37, H 3.94, N 7.81, S 8.94; found C 70.07, H 4.12, N 7.52, S 8.75.

3-(4-Formylphenylethynyl)-10-methyl-10*H*-phenothiazine (7b): As described in the GP, **1a** (237 mg, 1.00 mmol), 4-bromobenzaldehyde (**6b**, 185 mg, 1.00 mmol), [$(Ph_3P)_4Pd$] (35 mg, 0.03 mmol), and CuI (6 mg, 0.03 mmol), after being heated at reflux temp. for 3 days, furnished **7b** (224 mg, 66%) as a yellow, voluminous solid after chromatography on silica gel (CH_2Cl_2/hexane, 1:4). R_f (CH_2Cl_2/hexane, 1:3) = 0.53. Mp. 174−175 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ = 3.36 ppm (s, 3 H), 6.75 (d, *J* = 8.4 Hz, 1 H), 6.80 (d, *J* = 8.1 Hz, 1 H), 6.94 (m, 2 H), 7.14−7.19 (m, 2 H), 7.29 (d, *J* = 1.6 Hz, 1 H), 7.33 (dd, *J* = 1.9, 8.4 Hz, 1 H), 7.60 (d, *J* = 8.2 Hz, 2 H), 7.82 (d, *J* = 8.2 Hz, 2 H), 9.99 (s, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ = 35.4 ppm (CH_3), 88.6 ($C_{quat.}$), 93.2 ($C_{quat.}$), 113.8 (CH), 114.3 (CH), 116.2 ($C_{quat.}$), 122.7 ($C_{quat.}$), 123.6 ($C_{quat.}$), 123.0 (CH), 127.2 (CH), 127.6 (CH), 129.6 (CH), 129.8 ($C_{quat.}$), 130.0 (CH), 131.3 (CH), 131.9 (CH), 135.2 ($C_{quat.}$), 145.0 ($C_{quat.}$), 146.4 ($C_{quat.}$), 191.4 (CH). MS (EI+, 70 eV): *m*/*z* (%) = 342 (26), 341 [M^+] (100), 327 (14), 326 [$M^+ - CH_3$] (58). IR (KBr), $\tilde{\nu}$ = 2201 cm^{-1}, 1688, 1633, 1598, 1575, 1512, 1465, 1396, 1338, 1262, 1210, 1141, 857, 830, 751. UV/Vis (CH_2Cl_2), λ_{max} (ε): 248 nm (23400), 274 (32300, sh), 294 (37700), 320 (24800, sh), 386 (22500). $C_{22}H_{15}NOS$ (341.4): calcd. C 77.39, H 4.43, N 4.10, S 9.39; found C 76.89, H 4.40, N 4.01, S 9.42.

10-Methyl-3-phenylethynyl-10*H*-phenothiazine (7c): As described in the GP, **1a** (238 mg, 1.00 mmol), iodobenzene (**6c**, 204 mg, 1.00 mmol), [$Pd(PPh_3)_2Cl_2$] (21 mg, 0.03 mmol), and CuI (6 mg, 0.03 mmol) in triethylamine (15 mL) and THF (7 mL), after being heated at reflux temp. for 24 h, furnished **7c** (250 mg, 80%) as a light yellow powder after chromatography on silica gel (diethyl ether/pentane, 1:25). R_f (diethyl ether/pentane, 1:25) = 0.58. Mp. 135−137 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ = 3.38 ppm (s, 3 H), 6.75 (d, *J* = 8.5 Hz, 1 H), 6.82 (d, *J* = 8.1 Hz, 1 H), 6.95 (t, *J* = 7.3 Hz, 4 H), 7.16 (m, 2 H), 7.32 (m, 5 H), 7.49−7.52 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ = 35.4 ppm (CH_3), 88.8 ($C_{quat.}$), 89.2 ($C_{quat.}$), 113.8 (CH), 114.2 (CH), 117.2 ($C_{quat.}$), 122.8 (CH), 122.9 ($C_{quat.}$), 123.4 ($C_{quat.}$), 123.5 ($C_{quat.}$), 127.2 (CH), 127.5 (CH), 128.0 (CH), 128.3 (CH), 129.9 (CH), 130.9 (CH), 131.4 (CH), 145.2 ($C_{quat.}$), 145.8 ($C_{quat.}$). MS (70 eV): *m*/*z* (%) = 314 (24), 313 [M^+] (100), 299 (15), 298 [$M^+ - CH_3$] (64), 149 (10). IR (KBr), $\tilde{\nu}$ = 3056 cm^{-1}, 2977, 2924, 2226, 1627, 1594, 1574, 1500, 1464, 1442, 1396, 1334, 1259, 1156, 1038, 853, 816, 754, 691. UV/Vis (CH_2Cl_2),

λ_{max} (ε): 240 nm (22500), 274 (38500), 294 (34400), 344 (12200). HRMS calcd. for $C_{21}H_{15}NS$: 313.0925; found 313.0959.

10-*n*-Hexyl-3-phenylethynyl-10*H*-phenothiazine (7d): As described in the GP, **1b** (75 mg, 0.24 mmol), iodobenzene (**6c**, 47 mg, 0.23 mmol), $[Pd(PPh_3)_4]$ (8 mg, 0.01 mmol), and CuI (3 mg, 0.01 mmol) in diisopropylamine (2 mL) and THF (4 mL), after being heated at reflux temp. for 12 h, furnished **7d** (55 mg, 62%) as a green yellow oil after chromatography on silica gel (diethyl ether/pentane, 1:25). R_f (diethyl ether/pentane, 1:25) = 0.51. ^{1}H NMR ([D$_6$]acetone, 300 MHz), δ = 0.84 ppm (m, 3 H), 1.28 (m, 4 H), 1.45 (m, 2 H), 1.78 (m, 2 H), 3.95 (t, *J* = 7.0 Hz, 2 H), 6.95 (m, 1 H), 7.00−7.04 (m, 2 H), 7.13 (dd, *J* = 1.3, 7.6 Hz, 1 H), 7.20 (m, 1 H), 7.26 (d, *J* = 1.9 Hz, 1 H), 7.33−7.40 (m, 4 H), 7.49−7.52 (m, 2 H). ^{13}C NMR ([D$_6$]acetone, 75 MHz), δ = 14.2 ppm (CH_3), 23.2 (CH_2), 27.0 (CH_2), 27.4 (CH_2), 32.1 (CH_2), 47.9 (CH_2), 89.5 ($C_{quat.}$), 89.9 ($C_{quat.}$), 116.5 (CH), 116.9 (CH), 117.7 ($C_{quat.}$), 123.7 (CH), 124.2 ($C_{quat.}$), 124.7 ($C_{quat.}$), 125.7 ($C_{quat.}$), 128.0 (CH), 128.5 (CH), 129.1 (CH), 129.4 (CH), 130.4 (CH), 131.7 (CH), 132.1 (CH), 145.5 ($C_{quat.}$), 146. 5 ($C_{quat.}$). MS (70 eV): *m*/*z* (%) = 384 (25), 383 [M$^+$] (95), 312 [M$^+$ − C_5H_{11}] (31), 299 (31), 298 [M$^+$ − C_6H_{13}] (100), 280 (12). IR (KBr), $\tilde{\nu}$ = 3060 cm^{-1}, 2954, 2926, 2855, 2203, 1595, 1498, 1463, 1444, 1399, 1364, 1334, 1266, 1250, 1195, 1156, 1142, 1104, 1040, 912, 881, 815, 752, 690. UV/Vis ($CHCl_3$), λ_{max} (ε) 276 nm (31400), 290 (26300), 342 (11100). HRMS calcd. for $C_{26}H_{25}NS$: 383.1708; found 383.1707.

10-Methyl-3-thien-2-ylethynyl-10*H*-phenothiazine (7e): As described in the GP, **1a** (250 mg, 1.05 mmol), 2-iodothiophene (**6d**, 211 mg, 1.03 mmol), $[(Ph_3P)_4Pd]$ (35 mg, 0.03 mmol), and CuI (6 mg, 0.03 mmol), after being heated at reflux temp. for 3 h, furnished **7d** (239 mg, 72%) as a pale yellow solid after chromatography on silica gel with diethyl ether/pentane (1:4) and diethyl ether. R_f (diethyl ether/pentane, 1:4) = 0.50. Mp. 141 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ = 3.35 ppm (s, 3 H), 6.72 (d, *J* = 8.4 Hz, 1 H), 6.79 (d, *J* = 8.1 Hz, 1 H), 6.93 (m, 1 H), 6.98 (m, 1 H), 7.10−7.19 (m, 2 H), 7.22−7.31 (m, 4 H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ = 35.8 ppm (CH_3), 82.5 ($C_{quat.}$), 92.5 ($C_{quat.}$), 113.8 (CH), 114.3 (CH), 116.8 ($C_{quat.}$), 122.8 ($C_{quat.}$), 122.9 (CH), 123.5 ($C_{quat.}$), 122.8 (CH), 126.9 (CH), 127.0 (CH), 127.2 (CH), 127.5 (CH), 129.7 (CH), 130.8 (CH), 131.5 (CH), 145.1 ($C_{quat.}$), 145.9 ($C_{quat.}$). MS (70 eV): *m*/*z* (%) = 321 (11), 320 (22), 319 [M$^+$] (100), 305 (18), 304 [M$^+$ − CH_3] (74), 159 (11), 152 (11). IR (KBr), $\tilde{\nu}$ = 3097 cm^{-1}, 3055, 2883, 2819, 1598, 1574, 1519, 1493, 1461, 1442, 1426, 1394, 1358, 1328, 1261, 1242, 1215, 1141, 1117, 1105, 1037, 873, 852, 805, 750, 705, 607. UV/Vis ($CHCl_3$), λ_{max} (ε): 267 nm (26100), 306 (24300), 354 (14000). $C_{19}H_{13}NS_2$ (319.4): calcd. C 71.44, H 4.10, N 4.38, S 20.07; found C 71.20, H 4.22, N 4.26, S 19.87.

3-(4-Methoxyphenylethynyl)-10-methyl-10*H*-phenothiazine (7f): As described in the GP, **1a** (250 mg, 1.05 mmol), 4-iodoanisole (**6e**, 235 mg, 1.00 mmol), $[(Ph_3P)_4Pd]$ (35 mg, 0.03 mmol), and CuI (6 mg, 0.03 mmol), after being heated at reflux temp. for 1.5 h, furnished **7e** (250 mg, 70%) as a pale yellow solid after chromatography on silica gel with diethyl ether/pentane (1:4) and diethyl ether. R_f (diethyl ether/pentane, 1:4) = 0.31. Mp. 160−161 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ = 3.37 ppm (s, 3 H), 3.82 (s, 3 H), 6.73 (m, 1 H), 6.80 (d, *J* = 8.2 Hz, 1 H), 6.83 (d, *J* = 8.7 Hz, 2 H), 6.93 (t, *J* = 6.6 Hz, 1 H), 7.12−7.19 (m, 2 H), 7.25−7.34 (m, 2 H), 7.43 (d, *J* = 8.8 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ = 35.3 ppm (CH_3), 55.2 (CH_3), 87.4 ($C_{quat.}$), 89.2 ($C_{quat.}$), 113.7 (CH), 113.9 (CH), 114.2 (CH), 115.5 ($C_{quat.}$), 117.5 ($C_{quat.}$), 122.7 (CH), 122.8 ($C_{quat.}$), 123.3 ($C_{quat.}$), 127.1 (CH), 127.5 (CH), 129.7 (CH), 130.7 (CH), 132.8 (CH), 145.2 ($C_{quat.}$), 145.5 ($C_{quat.}$), 159.4 ($C_{quat.}$). MS (70 eV): *m*/*z* (%) = 344 (23), 343 [M$^+$] (100), 329 (15), 328 [M$^+$ − CH_3] (60), 313 [M$^+$ − CH_2O] (10), 285 (17), 171 [M^{2+}] (9), 164 (6). IR (KBr), $\tilde{\nu}$ = 2929 cm^{-1}, 1605, 1572, 1515, 1464, 1393, 1334, 1286, 1246, 1179, 1143, 1106, 1027, 853, 834, 801, 752, 607, 537. UV/Vis ($CHCl_3$), λ_{max} (ε): 297 nm (36100), 338 (14900). $C_{22}H_{17}NOS$ (343.4): calcd. C 76.94, H 4.99, N 4.08, S 9.33; found C 76.70, H 5.00, N 4.06, S 9.63.

1,2-Bis(10-hexyl-10*H*-phenothiazin-3-yl)ethyne (7g): As described in the GP, **1b** (338 mg, 1.10 mmol), 3-bromo-10-hexyl-10*H*-phenothiazine (**6f** = **4b**, 362 mg, 1.00 mmol), $[(Ph_3P)_4Pd]$ (35 mg, 0.03 mmol), CuI (100 mg, 0.53 mmol), and triphenylphosphane (262 mg, 1.00 mmol), after being heated at reflux temp. for 36 h, furnished **7g** (206 mg, 35%) as a pale yellow solid after chromatography on silica gel with diethyl ether/pentane (1:4) and diethyl ether. R_f (diethyl ether/pentane, 1:10) = 0.36. Mp. 127−129 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ = 0.86 ppm (m, 6 H), 1.29 (m, 8 H, CH_2), 1.40 (m, 4 H), 1.77 (m, 4 H), 3.79 (t, *J* = 7.0 Hz, 4 H), 6.74 (d, *J* = 8.2 Hz, 2 H), 6.82 (d, *J* = 8.1 Hz, 2 H), 6.89 (m, 2 H), 7.08−7.14 (m, 4 H), 7.22−7.26 (m, 4 H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ = 14.0 ppm (CH_3), 22.6 (CH_2), 26.6 (CH_2), 26.8 (CH_2), 31.4 (CH_2), 47.5 (CH_2), 88.6 ($C_{quat.}$), 115.0 (CH), 115.4 (CH), 117.1 ($C_{quat.}$), 122.6 (CH), 124.2 ($C_{quat.}$), 124.7 ($C_{quat.}$), 127.3 (CH), 127.4 (CH), 130.0 (CH), 130.5 (CH), 144.7 ($C_{quat.}$), 145.1 ($C_{quat.}$). MS (70 eV): *m*/*z* (%) = 590 (14), 589 (33), 588 [M$^+$] (100), 503 [M$^+$ − C_6H_{13}] (18), 418 [M$^+$ − 2 C_6H_{13}] (18). IR (KBr), $\tilde{\nu}$ = 2954 cm^{-1}, 2926, 2854, 1632, 1599, 1576, 1499, 1465, 1398, 1363, 1336, 1293, 1252, 1193, 1138, 1105, 815 (m), 748 (s). UV/Vis ($CHCl_3$), λ_{max} (ε): 273 nm (40900), 293 (34000), 370 (19600). HRMS calcd. for $C_{38}H_{40}N_2S_2$: 588.2633; found 588.2607.

1,4-Bis[2-(10-*n*-hexyl-10*H*-phenothiazin-3-yl)ethynyl)-benzene (12): As described in the GP, **1b** (307 mg, 1.00 mmol), 1,4-diiodobenzene (**8**, 164 mg, 0.50 mmol), $[(Ph_3P)_2PdCl_2]$ (10 mg, 0.01 mmol), and CuI (3 mg, 0.02 mmol), after stirring at room temp. for 3 days, furnished **12** (200 mg, 58%) as a dark yellow resin after chromatography on silica gel with diethyl ether/pentane (1:8). R_f (diethyl ether/pentane, 1:8) = 0.22. ^{1}H NMR ($CDCl_3$, 300 MHz), δ = 0.80 ppm (t, *J* = 6.9 Hz, 6 H), 1.22−1.35 (m, 12 H), 1.72 (m, 4 H), 3.76 (t, *J* = 7.2 Hz, 4 H) 6.71 (d, *J* = 8.4 Hz, 2 H), 6.77 (d, *J* = 8.1 Hz, 2 H), 6.83 (t, *J* = 7.2 Hz, 2 H), 6.87−7.07 (m, 4 H), 7.18−7.24 (m, 4 H), 7.37 (s, 4 H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ = 14.0 ppm (CH_3), 22.6 (CH_2), 26.6 (CH_2), 26.8 (CH_2), 31.4 (CH_2), 47.6 (CH_2), 89.0 ($C_{quat.}$), 90.8 ($C_{quat.}$), 115.0 (CH), 115.5 (CH), 116.7 ($C_{quat.}$), 122.7 (CH), 123.0 ($C_{quat.}$), 124.1 ($C_{quat.}$), 124.8 ($C_{quat.}$), 127.3 (CH), 127.5 (CH), 130.1 (CH), 130.8 (CH), 131.3 (CH), 144.5 ($C_{quat.}$), 145.5 ($C_{quat.}$). MS (FAB+): *m*/*z* (%) = 690 (45), 689 (92), 688 [M$^+$] (100), 603 [M$^+$ − C_6H_{13}] (24), 518 [M$^+$ − 2 C_6H_{13}] (29). IR (KBr), $\tilde{\nu}$ = 2953 cm^{-1}, 2926, 2854, 1596, 1574, 1511, 1462, 1398, 1363, 1334, 1294, 1250, 1193, 1159, 1102, 1040, 835, 814, 746. UV/Vis ($CHCl_3$), λ_{max} (ε): 272 nm (34000), 286 (31900), 304 (32600), 318 (34900), 384 (32800). HRMS calcd. for $C_{46}H_{44}N_2S_2$: 688.2943; found 688.2952.

2,5-Bis[2-(10-methyl-10*H*-phenothiazin-3-yl)ethynyl)thiophene (13): As described in the GP, **1a** (250 mg, 1.05 mmol), 2,5-diiodo thiophene (**9**, 173 mg, 0.51 mmol), $[(Ph_3P)_4Pd]$ (20 mg, 0.02 mmol), and CuI (3 mg, 0.02 mmol), after being heated at reflux temp. for 3 h, furnished **13** (194 mg, 68%) as a dark yellow, microcrystalline solid after chromatography on silica gel with THF/hexane (1:2) and recrystallization from THF/methanol. R_f (THF/hexane, 1:2) = 0.24. Mp. 191−192 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ = 3.36 ppm (s, 6 H), 6.71 (d, *J* = 8.4 Hz, 2 H), 6.79 (d, *J* = 8.0 Hz, 2 H), 6.94 (m, 2 H), 7.09−7.19 (m, 6 H), 7.25 (d, *J* = 1.8 Hz, 2 H), 7.29 (dd, *J* = 1.8, 8.4 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ = 35.4 ppm (CH_3), 82.3 ($C_{quat.}$), 93.6 ($C_{quat.}$), 113.8 (CH), 114.3 (CH),

116.4 ($C_{quat.}$), 122.7 ($C_{quat.}$), 123.5 ($C_{quat.}$), 124.6 ($C_{quat.}$), 122.9 (CH), 127.2 (CH), 127.6 (CH), 129.7 (CH), 130.9 (CH), 131.4 (CH), 145.0 ($C_{quat.}$), 146.1 ($C_{quat.}$). MS (70 eV): *m*/*z* (%) = 556 (23), 555 (40), 554 [M^+] (100), 539 [$M^+ - CH_3$] (21), 524 [$M^+ - 2\ CH_3$] (24), 262 [$M - 2\ CH_3)^{2+}$] (19). IR (KBr), $\tilde{\nu}$ = 3055 cm^{-1}, 2883, 2819, 2202, 1597, 1574, 1521, 1462, 1393, 1334, 1260, 1156, 1140, 1121, 842, 812, 750. UV/Vis ($CHCl_3$), λ_{max} (ε): 270 nm (51500), 333 (33200), 394 (43700). $C_{34}H_{22}N_2S_3$ (554.7) calcd.: calcd. C 73.61, H 4.00, N 5.05, S 17.34; found C 73.45, H 4.03, N 4.89, S 17.59.

10-*n*-Hexyl-3,7-bis(10-*n*-hexyl-10*H*-phenothiazin-3-ylethinyl)-10*H*-phenothiazine (14): As described in the GP, **1b** (145 mg, 0.47 mmol), 10-hexyl-3,7-diiodo-10*H*-phenothiazine, (**10**, 120 mg, 0.22 mmol), [$PdCl_2(PPh_3)_2$] (10 mg, 0.01 mmol), and CuI (4 mg, 0.01 mmol), after being heated at 70 °C (oil bath temp.) for 2 days, furnished **14** (165 mg, 82%) as a shiny, orange resin after chromatography on silica gel with diethyl ether/pentane (1:50) and diethyl ether (collection of an orange band with a green fluorescence upon UV excitation). R_f (diethyl ether/pentane 1:50) = 0.17. ^1H NMR ($CDCl_3$, 300 MHz), δ = 0.87 ppm (m, 9 H), 1.30 (m, 12 H), 1.42 (m, 6 H), 1.78 (m, 6 H), 3.82 (br. s, 6 H), 6.76 (dd, *J* = 2.6, 8.3 Hz, 4 H), 6.84 (d, *J* = 8.1 Hz, 2 H), 6.90 (m, 2 H), 7.09−7.16 (m, 4 H), 7.22−7.26 (m, 8 H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ = 13.9 ppm (CH_3), 22.5 (CH_2), 26.5 (CH_2), 26.6 (CH_2), 26.7 (CH_2), 26.8 (CH_2), 31.3 (CH_2), 31.4 (CH_2), 47.5 (CH_2), 47.55 (CH_2), 88.4 ($C_{quat.}$), 88.8 ($C_{quat.}$), 114.9 (CH), 115.1 (CH), 115.4 (CH), 117.1 ($C_{quat.}$), 117.5 ($C_{quat.}$), 122.6 (CH), 124.1 ($C_{quat.}$), 124.2 ($C_{quat.}$), 124.7 ($C_{quat.}$), 127.3 (CH), 127.4 (CH), 130.0 (CH), 130.5 (CH), 130.6 (CH), 144.4 ($C_{quat.}$), 144.7 ($C_{quat.}$), 145.1 ($C_{quat.}$). MS (FAB+): *m*/*z* (%) = 896 (25), 895 (55), 894 (96), 893 [M^+] (100), 892 (31), 823 (10), 822 [$M^+ - C_5H_{11}$] (15), 811 (10), 810 (20), 809 (30), 808 [$M^+ - C_6H_{13}$] (27), 725 (10), 724 (16), 723 [$M^+ - 2\ C_6H_{13}$] (15), 666 [$M^+ - 2\ C_6H_{13} - C_4H_9$] (12), 665 (16), 654 [$M^+ - 2\ C_6H_{13} - C_5H_{11}$] (14), 653 (19), 641 (13), 640 (23), 639 (35), 638 [$M^+ - 3\ C_6H_{13}$] (34), 621 (10), 620 (14). IR (KBr), $\tilde{\nu}$ = 2953 cm^{-1}, 2927, 2854, 1628, 1580, 1496, 1468, 1398, 1361, 1334, 1295, 1264, 1251, 1193, 1142, 1104, 881, 814, 748. UV/Vis (CH_2Cl_2), λ_{max} (ε): 238 nm (48400), 276 (67500), 296 (79200), 388 (41900). $C_{58}H_{59}N_3S_3$ (894.3) calcd.: calcd. C 77.89, H 6.65, N 4.69, S 10.75; found C 78.13, H 6.62, N 4.81, S 10.65.

1,3,5-Tris(10-methyl-10*H*-phenothiazin-3-ylethinyl)benzene (15): As described in the GP, **1a** (250 mg, 1.05 mmol), 1,3,5-triiodobenzene (**11**, 150 mg, 0.33 mmol), [$(Ph_3P)_4Pd$] (35 mg, 0.03 mmol), and CuI (4 mg, 0.03 mmol), after being heated at reflux temp. for 5 h, furnished **15** (244 mg, 94%) as a yellow solid after chromatography on silica gel with THF/hexane (1:1). R_f (THF/hexane, 1:1) = 0.36. Mp. 247−248 °C. ^1H NMR ($CDCl_3$, 200 MHz), δ = 3.36 ppm (s, 9 H), 6.74 (d, *J* = 8.4 Hz, 6 H), 6.80 (d, *J* = 8.2 Hz, 6 H), 6.95 (t, *J* = 7.4 Hz, 3 H), 7.12−7.22 (m, 6 H), 7.26−7.35 (m, 9 H), 7.54 (s, 3 H). MS (70 eV): *m*/*z* (%) = 784 (53), 783 [M^+] (100), 738 [$M^+ - 3\ CH_3$] (12), 391 [M^{2+}] (10). IR (KBr), $\tilde{\nu}$ = 2208 cm^{-1}, 1598, 1570, 1497, 1464, 1443, 1393, 1335, 1286, 1259, 1155, 1141, 1039, 982, 874, 813, 749. UV/Vis ($CHCl_3$), λ_{max} (ε): 278 nm (96200), 295 (76100, sh), 356 (46600). HRMS calcd. for $C_{51}H_{33}N_3S_3$: 783.1837; found 783.1844.

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