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Synthesis of Functionalized Ethynylphenothiazine Fluorophores

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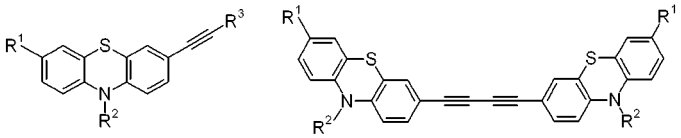
ABSTRACT



R^1 = H, alkynyl(Ar, Het), formyl, Br; R^2 = CH_3, *n*-hexyl; R^3 = (hetero)aryl

Alkynylated and butadiynyl-bridged phenothiazines with variable functionalization can be synthesized in good yields by cross-coupling and condensation approaches. In addition, the structure of the diethynylated phenothiazine (7a) has been corroborated by an X-ray structure analysis. These oligofunctional heterocycles are fluorescent with modest quantum yields (Φ_f = 20–35%) and represent suitable building blocks for novel photoexcitable molecular wires.

Phenothiazines have proven to be a pharmaceutically important class of heterocycles,[1] and due to their pharmacological efficacy they are applied as sedatives, tranquilizers, antiepileptics, antituberculotics, antipyretics, antitumor agents, bactericides, and parasiticides.[2] Interestingly, phenothiazines are able to cleave DNA upon photochemical induction.[3] Fairly early, it was recognized that the low oxidation potentials 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 materials science[7] motifs. Recently, we found a straightforward access to 3-mono- and 3,7-dialkynylated phenothiazines **1** and **2**, interesting building blocks for redox active oligomers.[8] Application of the *Eglinton* coupling to monoalkynylated systems **1** (R^1 = CH_3, *n*-hexyl) gave rise to dumbbell-shaped

† X-ray crystal structure analysis.

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butadiynyl-bridged diphenothiazinyl compounds **3** (Figure 1). Both heterocyclic fragments are electronically coupled

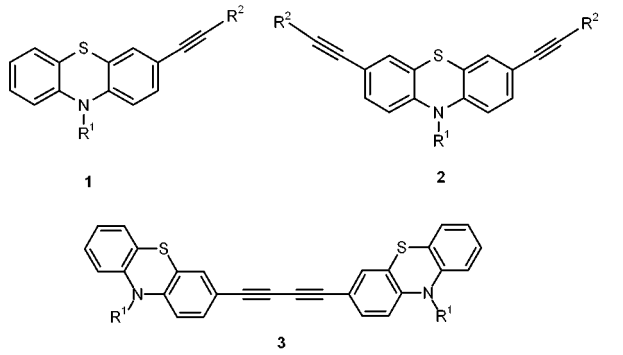


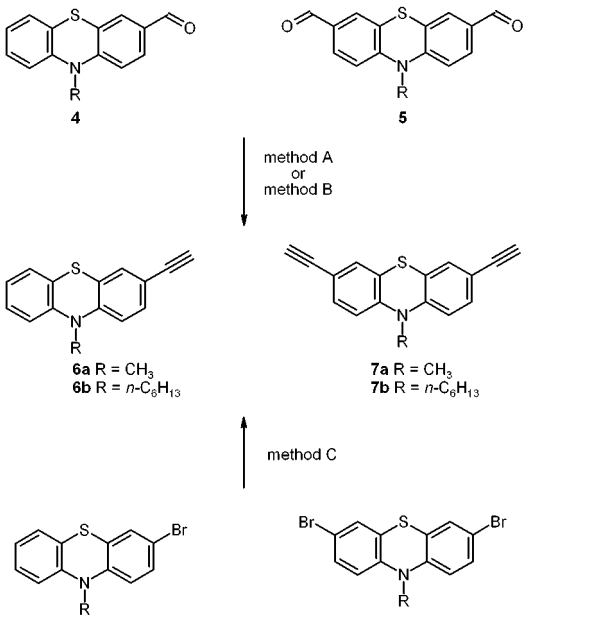
Figure 1.

according to cyclic voltammetry, absorption, and emission spectroscopy.[8] Coupled redox systems integrated in conjugated chains could constitute a so far unknown class of redox addressable molecular wires, in particular, for a redox manipulation of single molecules with nanoscopic scanning techniques.[9,10]

However, the incorporation of redox dumbbells such as **3** into conjugated oligomers, symmetrically or unsymmetrically, demands flexible functionality for cross-coupling and/or condensation approaches. Here, we present the syntheses, structure, and emission properties of alkynylated and butadiynyl-bridged phenothiazines with variable functional groups.

Synthetically, the exploitation of both aldehyde−alkyne transformations and cross-coupling methodologies opens flexible strategies to various functionalizations. Recently, we showed that phenothiazine 3-carbaldehydes **4**[11] and phenothiazine 3,7-biscarbaldehydes **5**,[12] respectively, can be transformed to the alkynylated derivatives **6** and **7** according to the *Corey−Fuchs* protocol[13] in good yields (Scheme 1, method A).[8] Alternatively, the fairly mild conditions of the *Ohira−Bestmann* transformation[14] of **4** and **5** to **6** and **7** opens a new access to alkynylated systems with broad functional group tolerance (method B).[15] Additionally, we have transposed the *Sonogashira* ethynylation[16] to the mono- and dibrominated phenothiazines **8**[17] and **9**[18] to give the

Scheme 1



desired alkynylated derivatives after subsequent alkaline desilylation in one pot (method C).

The X-ray crystal structure analysis of **7a**[19] (Figure 2)

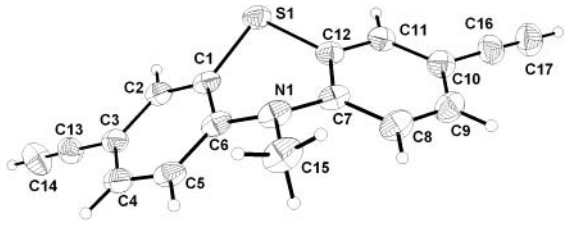


Figure 2.

clearly shows the expected butterfly conformation[1] of the phenothiazine core with dihedral angles of 141.9 (C2−C1−S1−C12) and 140.0° (C5−C6−N1−C7). The bond lengths

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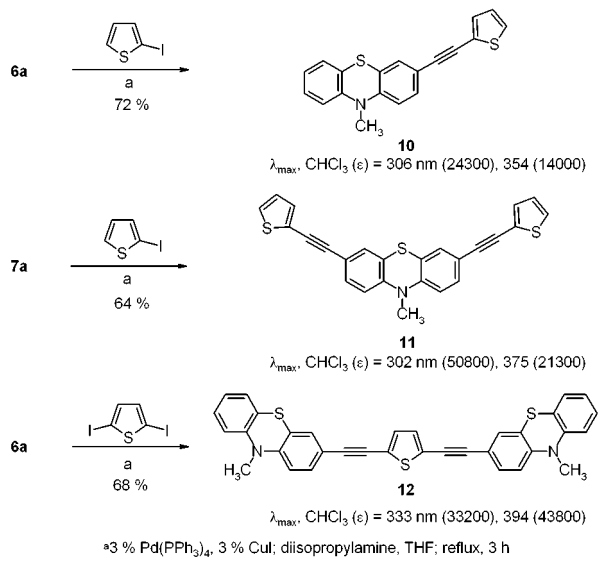
(19) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149969 (**7a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223/336−033. E-mail: deposit@ccdc.cam.ac.uk).

of the phenothiazinyl moiety and the triple bonds lie within the expected margins as well (C16−C17, 1.17 Å; C13−C14, 1.16 Å). Furthermore, the *N*-methyl group adopts a pseudoequatorial arrangement.

The mono- and diethynylated compounds **6** and **7** are suitable building blocks for alkynyl-bridged phenothiazine-based redox systems, and thus, the *Sonogashira* coupling of **6a** and **7a** with 2-iodothiophene and 2,5-diiodothiophene, respectively, give rise to the formation of thienyl-substituted (**10**[20] and **11**) and thienyl-bridged (**12**) ethynyl phenothiazines (Scheme 2).[15]

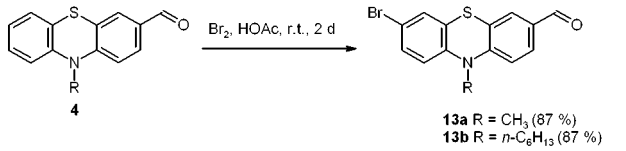
Scheme 2



In the UV/vis spectra of the thienyl ethynylated phenothiazines **10** and **11**, the absorption bands at 306 (**10**) and 302 nm (**11**) arise from transitions of the phenylethynyl thiophene fragments as indicated by the doubling of molar extinction coefficients. However, the longest wavelength bands at 354 (**10**) and 375 nm (**11**) can be attributed to $\pi-\pi^*$ transitions within the extended π-system, i.e., including the conjugation through the nitrogen atom. Interestingly, the thienylethynyl-substituted and thienylethynyl-bridged phenothiazines are fluorescent with modest quantum yields ($\Phi_f = 20\%$) for the spontaneous emission upon irradiation of the longest wavelength absorption band but remarkable Stokes shifts (**10**, λ_{max}(emission) = 463 nm, $\Delta\tilde{\nu} = 5800$ cm^{-1}; **11**: λ_{max}(emission) = 479 nm, $\Delta\tilde{\nu} = 6100$ cm^{-1}; **12**: λ_{max}(emission) = 496 nm, $\Delta\tilde{\nu} = 5500$ cm^{-1}).

Finally, an entry to several functionalized alkynylated phenothiazines could be disclosed by bromination of the phenothiazine 3-carbaldehydes **4** in acetic acid to give 7-bromophenothiazine 3-carbaldehydes **13** in good yields (Scheme 3).[21]

Scheme 3



With these unsymmetrically functionalized phenothiazines in hand now a selective functionalization of the bromo or the formyl moiety could be successfully performed. Thus, the Ohira−Bestmann reaction of **13a** furnishes the bromo alkyne **14** (60%) which could be oxidatively dimerized by

(20) **Synthesis of 10**: To a degassed solution of 250 mg (1.05 mmol) of **6a** in 10 mL of dry diisopropylamine and 3 mL of THF were successively added 211 mg (1.03 mmol) of 2-iodo thiophene, 35 mg (0.03 mmol) of $Pd(PPh_3)_4$, and 6 mg (0.03 mmol) of CuI. The reaction mixture was heated to reflux temperature under nitrogen for 3 h. After the solution was cooled to room temperature, the residue was chromatographed on silica gel (diethyl ether/pentane 1:4) to give 239 mg (72%) of **10** as a light yellow solid: mp 141 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.35 (s, 3 H, CH_3), 6.72 (d, J = 8.4 Hz, 1 H), 6.79 (d, J = 8.1 Hz, 1 H), 6.93 (m_c, 1 H), 6.98 (m_c, 1 H), 7.10−7.19 (m, 2 H), 7.22−7.31 (m, 4 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 35.4 (CH_3), 82.5 (C_{quat}), 92.5 (C_{quat}), 113.8 (CH), 114.3 (CH), 116.8 (C_{quat}), 122.8 (C_{quat}), 122.8 (CH), 123.5 (C_{quat}), 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* (%)): 319 (M^+, 100), 304 (74). IR (KBr): $\tilde{\nu}$ 1598 cm^{-1}, 1574, 1519, 1461, 1442, 1328, 1261, 852, 805, 750, 705, 607. UV/vis ($CHCl_3$): λ_{max} (ϵ) 267 nm (26100), 306 (24300), 354 (14000). Anal. Calcd for $C_{19}H_{13}NS_2$ (319.4): 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.

(21) **Synthesis of 13b**: To a solution of 7.94 g (25.5 mmol) of **4** (R = *n*-hexyl) in 30 mL of glacial acetic acid was dropwise added 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 room temperature for 2 d. After addition of 300 mL of water and 600 mL of diethyl ether, the organic layer was dried with $MgSO_4$. 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 **13b** as a vicous brown oil. ^{1}H NMR ($CDCl_3$, 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): δ 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 (M^+, ^{81}Br, 100), 389 (M^+, ^{79}Br, 96). IR (KBr): $\tilde{\nu}$ 1688 cm^{-1}, 1594, 1462. UV/vis ($CHCl_3$): λ_{max} (ϵ) 246 nm (17200), 277 (20000), 385 (5600). Anal. Calcd for $C_{19}H_{20}NSOBr$ (390.3): 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.

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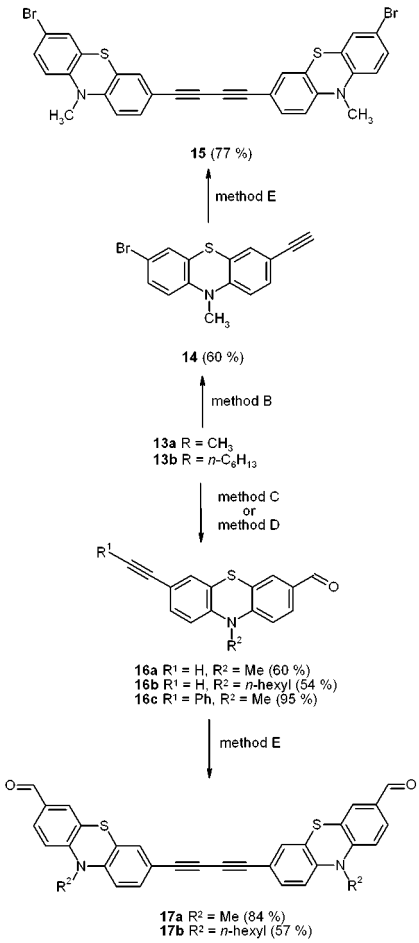
(23) Using the improved variation by Hundertmark, T.; Littke, A. F.; Buchwald, S. L.; Fu, G. C. *Org. Lett.* **2000**, *2*, 1729.

(24) **Synthesis of 16c**: To a solution of 11 mg (0.03 mmol) of $Pd(PhCN)_2Cl_2$, 4 mg (0.02 mmol) of CuI, and 0.24 mL (0.06 mmol) of a 0.25 M solution of P^tBu_3 in dioxane under nitrogen was added 1 mL of dry dioxane to form a brown suspension. To this suspension were added 320 mg (1.00 mmol) of **13a**, 122 mg (1.20 mmol) of phenylacetylene, and a solution of 1.70 mL (1.20 mmol) of dry diisopropylamine in 8 mL of dioxane. The reaction mixture was stirred for 2 d at room temperature. After addition of 10 mL of ethyl acetate, the mixture was filtered through a short plug of silica gel. The solvents were removed from the yellow filtrate in vacuo, and the residue was chromatographed on silica gel (diethyl ether/pentane 1:1) to give 324 mg (95%) of **16c** as a voluminous bright yellow solid: mp 135 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.40 (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 = 8.4 Hz, J = 1.8 Hz, 1 H), 9.79 (s, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 35.9 (CH_3), 88.3 (C_{quat}), 89.9 (C_{quat}), 113.9 (CH), 114.5 (CH),

the copper-mediated Eglinton coupling[22] to give the dibromo diyne **15** in good yields (Scheme 4).[15] Likewise, the

Scheme 4



Sonogashira coupling of **13** with TMSacetylene or phenylacetylene[23] gives rise to the alkynylated aldehydes **16** in decent to excellent yields.[24]

Finally, the Eglinton coupling of **16a** and **16b** leads to the formation of the diformyl diynes **17**[25] in good yields.[15] Interestingly, the butadiynyl-bridged phenothiazines fluoresce with higher quantum yields ($\Phi_f = 32\%$) for the spontaneous emission upon irradiation of the longest wavelength absorption band than the ethynylated compounds **10**, **11**, and **12** but exhibit considerably bathochromically shifted emission maxima and remarkable Stokes shifts (**15**: λ_{max}(emission) = 475 nm, $\Delta\tilde{\nu} = 4700$ cm^{-1}. **17a**: λ_{max}(emission) = 527 nm, $\Delta\tilde{\nu} = 6000$ cm^{-1}. **17b**: λ_{max}(emission) = 534 nm, $\Delta\tilde{\nu} = 6000$ cm^{-1}).

In conclusion, we have shown that alkynylated bromo and alkynylated formyl phenothiazines are easily accessible upon applying the mild conditions of the Ohira−Bestmann formyl−alkyne transformation or the Sonogashira coupling to the novel bromo formyl phenothiazine building block **13**. Thus, the novel functionalized fluorescent dumbbells **15** and **17** can be used as suitable starting materials for further synthetic elaboration toward molecular wires via cross-coupling and/or condensation strategies. Further studies directed toward polymer and oligomer syntheses with these novel ethynylated phenothiazines and their nanostructuration as well as the investigation of the electrochemical and photophysical behaviors are currently underway.

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Supporting Information Available: Tables of data collection parameters, bond lengths and angles, positional and thermal parameter, and least-squares planes for **7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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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), 131.4 (C_{quat}), 131.4 (CH), 143.9 (C_{quat}), 150.3 (C_{quat}), 189.9 (CH). MS (70 eV, *m*/*z* (%)): 341 (M^+, 100). IR (KBr): $\tilde{\nu}$ 1687 cm^{-1}, 1602, 1578, 1468. UV/vis ($CHCl_3$): λ_{max} (ϵ) 295 nm (49000), 395 (11000). Anal. Calcd for $C_{22}H_{15}NSO$ (341.4): 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.

(25) **Synthesis of 17a**: To a solution of 369 mg (1.39 mmol) of **16a** in 6 mL of methanol was added a solution of 379 mg (1.90 mmol) of copper(II) acetate monohydrate in a mixture of 2 mL of methanol and 6 mL of pyridine. This reaction mixture was heated to reflux temperature for 4 h. After the solution was cooled to room temperature, the precipitated solid was collected by suction and washed with methanol to give 308 mg (84%) of a bright yellow powder: mp >250 °C (dec). ^{1}H NMR ($CDCl_3$, 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 (70 eV, *m*/*z* (%)): 528 (M^+, 100), 513 ($M^+ - CH_3$, 22), 498 ($M^+ - 2\ CH_3$, 21). IR (KBr): $\tilde{\nu}$ 2136 cm^{-1}, 1685, 1600, 1576, 1467. UV/vis ($CHCl_3$): λ_{max} (ϵ) 292 nm (74500), 408 (33000). Anal. Calcd for $C_{32}H_{20}N_2S_2O_2$ (528.6): C, 72.70; H, 3.81; N, 5.30; S, 12.13. Found: C, 72.66; H, 3.91; N, 5.42; S, 11.82.