First synthesis and electronic properties of diphenothiazine dumbbells bridged by heterocycles†‡

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According to cyclic voltammetry, symmetrical dumbbell-shaped phenothiazine dyads bridged by heterocycles show intense electronic coupling between the redox-active phenothiazine moieties. Furthermore, the fluorescence of the pyridyl-bridged derivatives can be controlled by p*H* change giving reversibly switchable redox-active biselectrophore dyads.

Introduction

Many reversible redox systems display electronic bi- or multistability (e.g. neutral-radical ion, or even several stable oxidation states) and, therefore, they are highly intriguing as switching functional units (native-doped; ON-OFF) and building blocks in future single-molecule-based molecular electronics.[1] Coupled reversible redox systems can be considered as excellent models for electronically multistable entities, and if integrated in conjugated chains they could constitute a so far unknown class of redox addressable molecular wires. Among many redox active heterocycles, particularly, phenothiazines meet the demanded criteria. They are tricyclic nitrogen-sulfur heterocycles[2] and have become important in medicinal chemistry due to a broad spectrum of pharmacological activity.[3] Most interestingly, phenothiazines are also able to cleave DNA upon photochemical induction.[4] As a consequence of a low oxidation potential, they readily form stable radical cations and some of their physiological activity can be attributed to this circumstance.[5] Furthermore, the radical cations give rise to a fingerprint of characteristic, deep-colored absorptions.[6] Thus, phenothiazine derivatives have become important spectroscopic probes in molecular and supramolecular arrangements for photoinduced electron transfer (PET) studies[7] and as motifs in organic materials.[8]

As part of our program to synthesize and investigate phenothiazinyl based molecular wires,[9–11] we have communicated syntheses, structures, and cyclic voltammetry measurements of directly linked phenothiazinyl dyads, triads and up to heptads[10] that can be regarded as models for polymer-based coupled electrophores. Recently, we reported studies on the correlation of the folding angle of phenothiazines and the electronic properties by introducing sterically demanding aromatic substituents in the 10-position.[11] Here, we present the first synthesis and studies on the electronic properties of dumbbell-shaped diphenothiazines with heterocyclic bridges, displaying tunable redox and, in some cases, fluorescence properties.

Results and discussion

Synthesis

The central ring of phenothiazine contains a nitrogen and a sulfur atom and, therefore, ligation of the nitrogen atoms *via* bridges appears to be a logical connection. Furthermore, increased steric strain and enhanced electronic communication has been previously demonstrated for *p*-phenylene bridges.[12] Thus, the electronic and geometrical modulation by heterocycles as bridges sets the stage for our approach to diphenothiazine dumbbells bridged by heterocycles. Generally, there are two well-established methods in the literature for the amination of (hetero)arenes: the copper-mediated Ullmann-coupling,[13] or the palladium-catalyzed Buchwald-Hartwig reaction.[14] Just recently, Buchwald also reported a catalytic, palladium-free protocol of the Ullmann-coupling.[15] Applying the Buchwald-Hartwig approach, the coupling of 10*H*-phenothiazine (**1**) with dibromo (hetero)arenes (**2–7**) was successfully accomplished in the presence of 3% of $Pd_2(dba)_3 \cdot dba$ as a palladium source, 5% of $HP^tBu_3BF_4$ as a ligand, NaO^tBu as a base, and 1,4-dioxane as a solvent.[16] After refluxing the reaction mixture overnight, the desired coupling products **8–13** were isolated in good yields (Scheme 1).

The structures of *N,N′*-bridged phenothiazine dyads **8–13** were unambiguously assigned by ^1H and ^{13}C NMR, UV/vis, and IR spectroscopy, by mass spectrometry, by correct combustion

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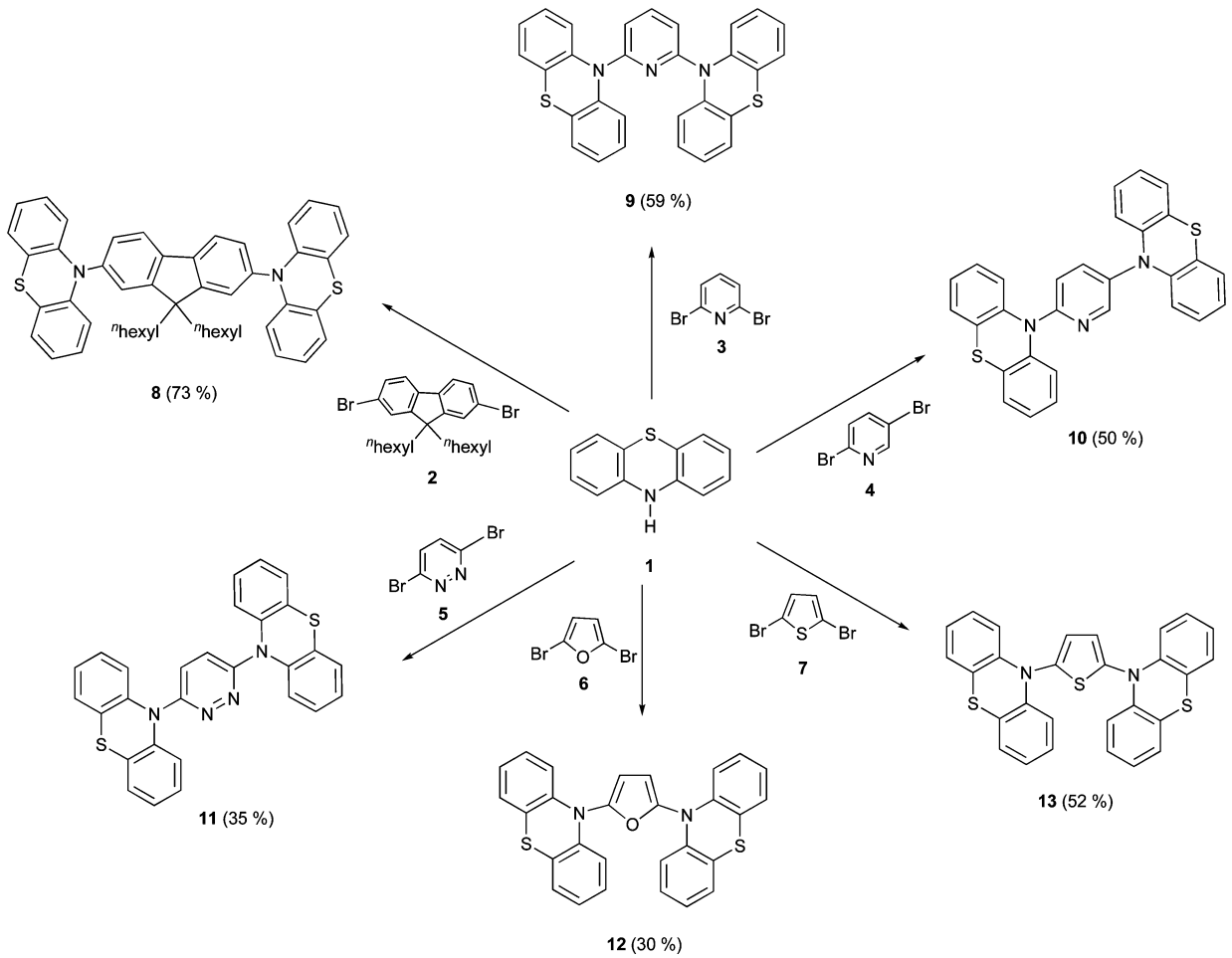
† Dedicated to Prof. Dr Willi Kantlehner on the occasion of his 65th birthday.

‡ Electronic supplementary information (ESI) available: Detailed experimental procedures, and copies of ^1H and ^{13}C NMR spectra of compounds **8–13**; cyclovoltammetric and fluorescence spectra of **8–13**; atomic coordinates of the calculated structures of **11** and **13**. CCDC reference number 689758. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b814850c



Scheme 1 Synthesis of dumbbell-shaped phenothiazine dyads **8–13** (reaction conditions: dibromo arene **2–7** (1 equiv.), 10*H*-phenothiazine (**1**) (2.2 equiv.), $Pd_2(dba)_3$·dba (0.03 equiv.), $PH^tBu_3BF_4$ (0.05 equiv.), NaO^tBu (2.3 equiv.), dry 1,4-dioxane, reflux, 19 h).

analyses, and later by an X-ray structure analysis of the dyad **13** (Fig. 1).‡§¶

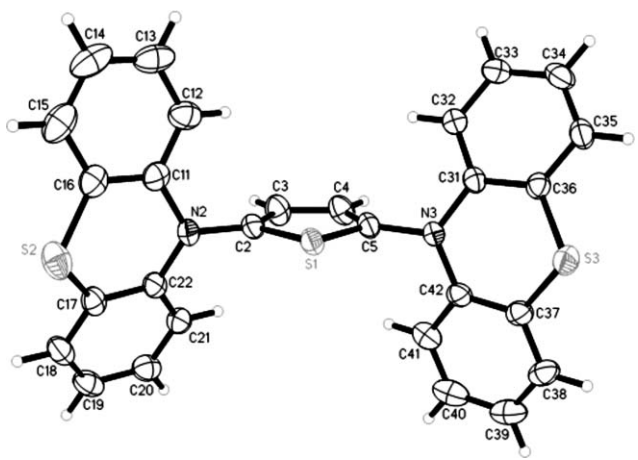


Fig. 1 Molecular structure of 2,5-bis(phenothiazin-10-yl) thiophene (**13**) (ORTEP: 50% probability).

Electronic structure

The electronic structure of the heterocycle-bridged phenothiazine dyads was first considered by computations on the DFT level of theory (B3LYP/6–31+G(d,p)).[17] The structures of 3,6-pyridazine- (**11**) and 2,5-thiophene- (**13**) bridged phenothiazine dyads were

§ X-ray structure analysis. CCDC 689758 (**13**) contains the supplementary crystallographic data for this structure. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). Data were collected on a Bruker APEX diffractometer. Mo K_α radiation ($\lambda = 0.71073$ Å) was used in all cases and the intensities were corrected for absorption effects using SADABS based on the Laue symmetry of the reciprocal space. The structures were solved by direct methods and refined against F^2 with a full matrix least square algorithm by using the SHELXTL software package. Hydrogen atoms were considered at calculated positions and refined using appropriate riding models. Relevant crystal and data collection parameters for the individual structures are given in the following footnote.

¶ **Crystal data**: **13**: $C_{28}H_{18}N_2S_3$, $M = 478.62$, triclinic, space group $P\bar{1}$, a = 8.3982(15), b = 8.7381(16), c = 17.245(3) Å, $\alpha = 83.601(5)°$, $\beta = 87.923(4)°$, $\gamma = 62.354(4)°$, V = 1113.9(3) Å^3, T = 200.(2) K, Z = 2, $\rho = 1.427$ g cm^3, crystal dimensions $0.16 \cdots 0.15 \cdots 0.04$ mm^3, $\mu = 0.353$ mm^{-1}, 0.3° omega-scans, 11772 reflections measured, 5501 unique [R(int)= 0.0474], 4126 observed [$I > 2\sigma(I)$], 298 parameters refined, goodness of fit 1.13, wR2 = 0.138, R1 = 0.071 (observed reflections), residual electron density –0.32 to 0.42 eÅ^{-3}, CCDC 689758.

geometry optimized and for further discussion the electron density distribution in the frontier orbitals (HOMO and LUMO) of these lowest energy conformation structures was exclusively taken into account.

In the case of the thiophene bridged phenothiazine dyad **13** an almost C_{2v}-symmetrical structure was obtained by geometry optimization (Fig. 2). Most characteristically, the butterfly structure of the phenothiazinyl moieties is reproduced by the computations. Futhermore, both phenothiazine units adopt the pseudo-equatorial *intra*-configuration, which is typical for *N*-aryl phenothiazines.[18] Due to symmetry, the computed HOMO (Fig. 2, bottom) is predominately localized on both phenothiazine moieties, whereas the LUMO (Fig. 2, top) is localized on the central thiophene. This also represents the intuitive notion, where phenothiazine units can be regarded as strong electron donors whilst the thiophene moiety serves as an acceptor.

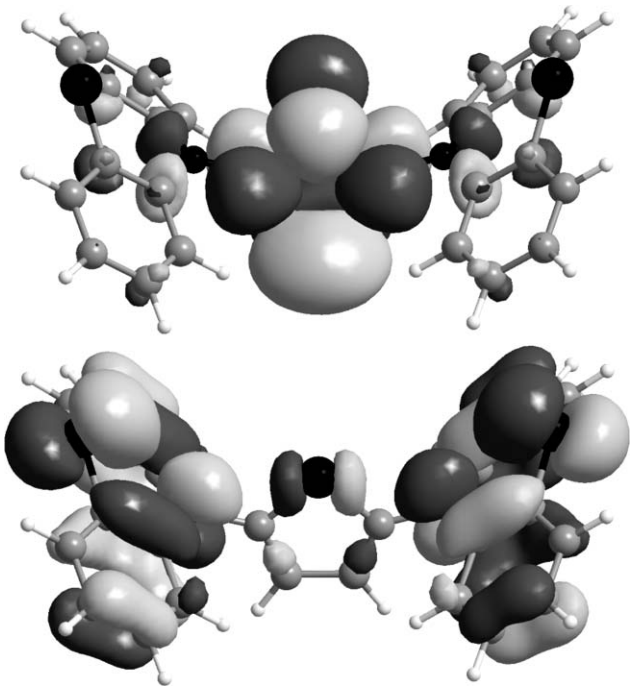


Fig. 2 LUMO (top) and HOMO (bottom) of the *N,N′*-thiophene bridged biphenothiazine **13**.

In addition, calculations were performed for 10,10′-biphenothiazinyl-3,6-pyridazine (**11**), where a C_{2v}-symmetrical structure was also obtained as the energy minimum. Again, the *intra*-configuration of both phenothiazines in the butterfly conformation appears to be the most stable one. However, the electronic structure of **11** with respect to the frontier orbitals reveals a significantly different electron distribution (Fig. 3) in comparison with the thiophene derivative **13**. While the LUMO (Fig. 3, top) of **11** is located mostly in the pyrazidine moiety, the HOMO (Fig. 3, bottom) represents a largely delocalized structure, *i.e.* electron density in all fragments of the molecule.

Electronic spectra, cyclic voltammetry, and fluorescence quenching by protonation of the pyridine bridged dumbbells

The electronic properties of the dumbbell-shaped phenothiazine dyads **8–13** were determined by absorption and emission spectroscopy and by cyclic voltammetry (Table 1). Optical spectroscopy (UV/vis and fluorescence spectra) of systems **8–10** and **12–13** displays weak fluorescence with emission of blue-green light and enormous Stokes shifts (9600–10600 cm^{-1}). Since pyridazine itself is essentially non-fluorescent,[19] expectedly, the pyridazine bridged phenothiazine derivative **11** does not show any detectable emission.

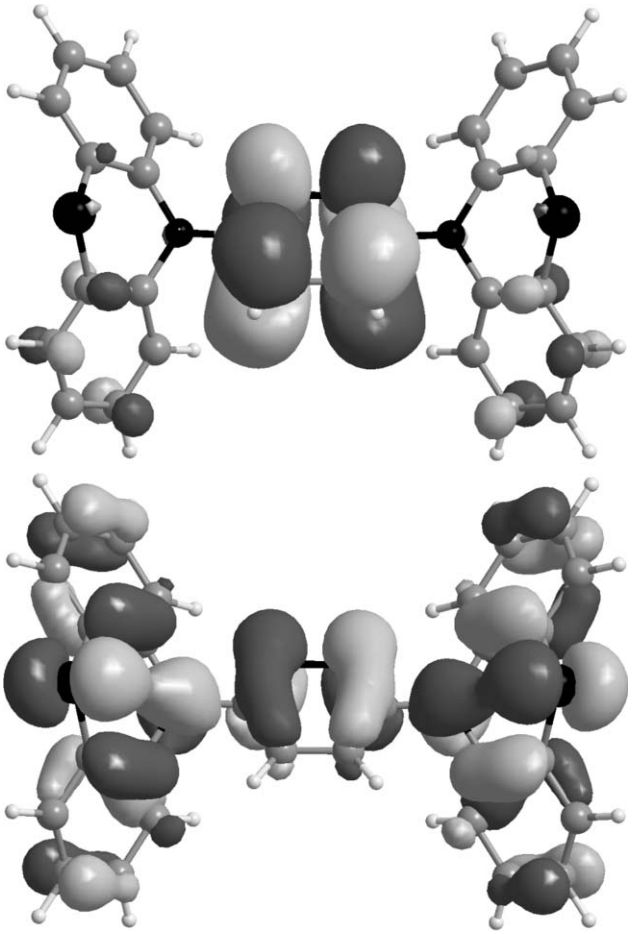


Fig. 3 LUMO (top) and HOMO (bottom) of the *N,N′*-pyridazine bridged biphenothiazine **11**.

Comparison with the spectra of 10*H*-phenothiazine (**1**) reveals similar absorption maxima for the phenothiazine dumbbells **8–13**. Therefore, donor (phenothiazine) and acceptor (pyridine, pyridazine, furane, thiophene or fluorene) π-systems are essentially electronically decoupled in the electronic ground state. The absorption spectra of dyads **8–13** are very similar and show a significant longest wavelength band at 303–333 nm, a second intense absorption at 251–259 nm, and in the spectra of **8**, **9**, and **10** a third intense band at 280, 288, and 283 nm, respectively.

The emission spectra of the dyads **8–13** are broad and appear in a range of 443–517 nm. The pyridinyl dyads **9** and **10** show the lowest energy emission maxima at 516 (**9**) and 517 nm (**10**). The dumbbells with electron rich spacers, the furan bridged derivative **12** and the thiophene derivative **13**, present very similar emission maxima at 443 and 444 nm, with a relative increase in emission efficiency compared with the electron deficient spacer pyridine. Concomitantly, the Stokes shift significantly increases from electron rich (**13**, 9600 cm^{-1}) to electron poor dyads

Table 1 Selected (absorption and emission spectra, cyclic voltammetry) electronic properties of dumbbell-shaped phenothiazine dyads **8–13**

Compound	Absorption $\lambda_{max,abs}$ [nm][a]	Emission $\lambda_{max,abs}$ [nm][a]	Stokes shift [cm^{-1}]	$E_0^{0/+1}$ [mV][b]	$E_0^{+1/+2}$ [mV][b]
8	259, 280, **308**	**477**, 506 (sh)	11500	761	–
9	251, 288, **333**	**516**, 552 (sh)	10600	891	1276
10	253, 283, **309**	**517**, 556 (sh)	13000	736	1132
11	253, 303	–	–	851	1155[c]
12	252, **304**	**443**, 503 (sh)	10300	608	954
13	256, **311**	**444**, 512 (sh)	9600	640	1072

[a] Recorded in CH_2Cl_2. [b] Recorded in CH_2Cl_2, $T = 293$ K, $v = 100$ mV/s, electrolyte: $^nBu_4N^+PF_6^-$, Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode. [c] Irreversible oxidation.

(**10**, 13000 cm^{-1}). This finding can be attributed to large geometrical changes upon excitation from a highly nonplanar ground state to an essentially planarized excited state.[20] Hence, electronic communication in the excited state appears to be responsible for the coupling of donor and acceptor.

Cyclic voltammetry clearly shows two reversible single electron anodic oxidations for the dyads **9**, **10**, **12** and **13** (Fig. 4).

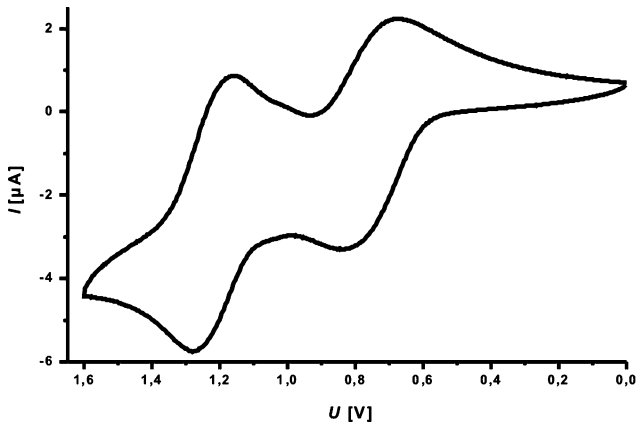


Fig. 4 Cyclic voltammogram of **13** (recorded in CH_2Cl_2, $T = 293$ K, $v = 100$ mV/s, electrolyte: $^nBu_4N^+$ PF_6^-, Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode).

In comparison with 10*H*-phenothiazine ($E_0^{0/+1} = 624$ mV) the first reversible oxidations are shifted anodically, except for the furan bridged derivative **12** which is shifted slightly cathodically ($E_0^{0/+1} = 608$ mV). The anodic shift increases by 270 mV for the 2,6-pyridine bridged **9** ($E_0^{0/+1} = 891$ mV). Interestingly, the second oxidation of **9** appears at 1276 mV. Hence, the strong electronic coupling between both phenothiazinyl units is the consequence of an extended delocalization of the initially formed radical cation. Since the 2,5-pyridine bridged dyad **10** is not symmetrical, two reversible oxidation processes are observed as expected. The first oxidation at 736 mV can be assigned to the more electron-rich phenothiazine moiety located at the 5-position of the central pyridine core. The other phenothiazine, connected to the electron deficient 2-position of pyridine is oxidized at a higher potential of 1132 mV.

Most remarkably, the cyclic voltammogram of **11** (Fig. 5) shows a separation of both anodic oxidations by more than 300 mV. Based upon the large potential separation a pronounced stability of the radical cation $\mathbf{11}^+$ by extended delocalization is deduced. Therefore, dumbbell **11** can be assigned as a Robin-Day class III system.[21] On the other hand the voltammogram of **8** containing a

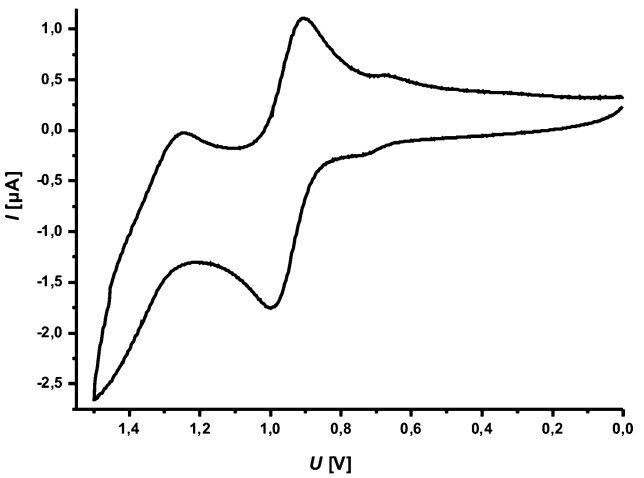


Fig. 5 Cyclic voltammogram of **11** (recorded in CH_2Cl_2, $T = 293$ K, $v = 100$ mV/s, electrolyte: $^nBu_4N^+$ PF_6^-, Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode).

2,7-fluorenylene spacer reveals only one single reversible oxidation with perfect Nernstian behavior. Hence, in comparison to the symmetrical phenothiazine dyads **9**, **11**, **12**, and **13**, the phenothiazine units in the symmetrical 2,7-fluorene bridged (**8**) derivative seem to be electronically decoupled according to cyclic voltammetry.

The pyridyl bridged phenothazine dyads **9** and **10** contain a basic moiety. Although protonation of many phenothiazine derivatives with mineral acids has been reported to lead to the formation of radical cations,[2,22] we recently reported that titration of phenothiazine derivatives containing other basic nitrogen atoms with TFA in methylene chloride reproducibly gives acid-base reactions and no radical cation formation.[9d] Here, we even have measured the absorption spectra to the NIR (see ESI‡) and could not detect any radical cation specific bands. Hence, protonation of the pyridyl nitrogen atom can be plausibly assumed to cause a redshift (**9**: 334 nm; $\mathbf{9\text{-}H^+}$: 371 nm) of the absorption (Fig. 6) by lowering the HOMO-LUMO gap.

Therefore, the ground state pK_a of the conjugate pyridinium salt of **9** was determined to be 4.34 assuming a quantitative protonation of the basic nitrogen atom, hence, setting $c(H^+) = c_0(TFA)$ as a good approximation for TFA as a strong acid. In comparison with pyridine ($pK_a = 5.23$)[23] the pyridyl bridged dyad **9** is less basic by one order of magnitude. A plausible explanation is the –I effect of the phenothiazinyl nitrogen atoms that is exerted by an almost orthogonal arrangement of the bridge and the phenothiazine. Therefore, an interesting effect on the emission properties upon protonation can be anticipated. Hence,

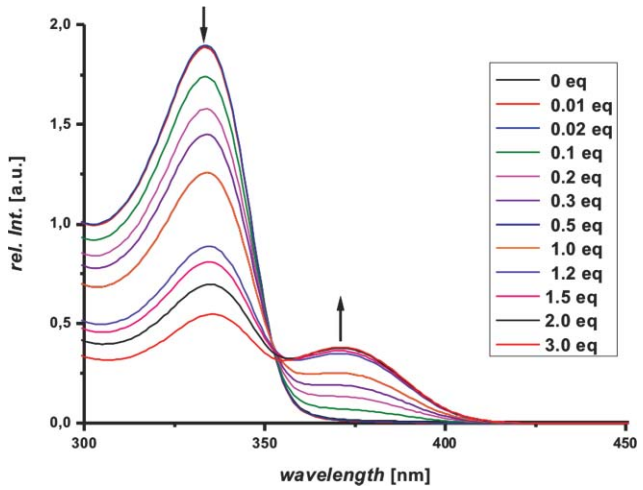


Fig. 6 Absorption spectra of **9** in the presence of increasing amounts of TFA (recorded in CH_2Cl_2, $c_0(\mathbf{9}) = 10^{-4}$ *M*, $T = 293$ K).

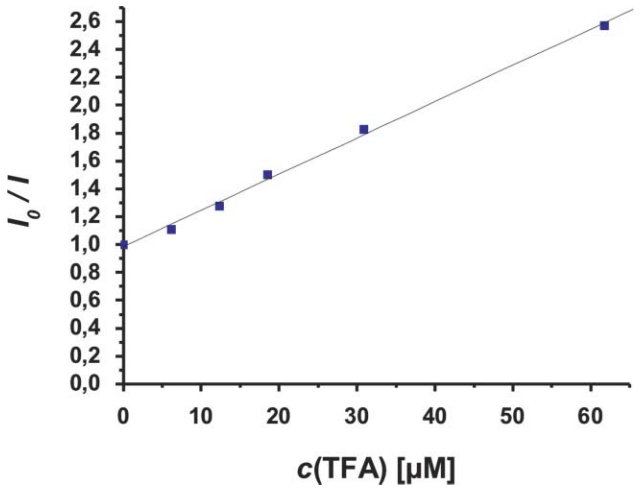


Fig. 8 Stern-Volmer plot of **9** ($c_0(\mathbf{9}) = 10^{-6}$ *M* in dichloromethane, $T = 293$ K, $\lambda_{max,em}$ at 517 nm; $\Phi_0/\Phi = 0.986 + 26015\ \mathrm{Lmol^{-1}}\ [H^+]$; $r^2 = 0.98211$).

the fluorescence was monitored upon titration with trifluoroacetic acid (TFA) in methylene chloride (Fig. 7). The fluorescence of both compounds **9** and **10** develops in a similar fashion upon continuous addition of aliquots of TFA. Whereas the free bases **9** and **10** display emission at 517 nm and 516 nm, respectively, after addition of 0.1–5 equivalents of TFA the emission is noticeably quenched. The Stern-Volmer constant K_{SV} of **9** was determined to 26015 $\mathrm{Lmol^{-1}}$ (Fig. 8).

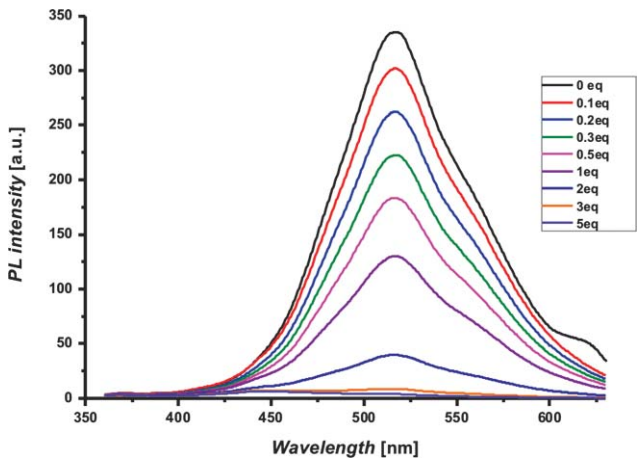


Fig. 7 Emission spectra of **9** in the presence of increasing amounts of TFA (recorded in CH_2Cl_2, $c(\mathbf{9}) = 10^{-6}$ *M*, $T = 293$ K).

By definition of steady-state quenching[24] the Stern-Volmer constant K_{SV} can be regarded as $k_q\tau$ of the fluorophore **9** where k_q is the rate constant for quenching and τ is the life time of the excited state. On the other hand the Stern-Volmer constant K_{SV} also represents the pK_a (4.42) of the fluorophore **9** in the electronic ground state and matches with the pK_a obtained from absorption spectroscopy (4.34). The linear behavior accounts for quenching by protonation at a single site, *i.e.* the pyridyl nitrogen atom. Static fluorescence quenching has been reported for several azine derivatives.[24,25] Interestingly, protonated pyridines substituted with strongly electron donating aryl or disubstituted amino groups[26,27] are known to undergo intramolecular deactivation of the S_1 state by charge transfer from the amino donor to the electron deficient pyridinium moiety. This pathway is also favored by the strong electron donor capacity of phenothiazines as supported by cyclovoltammetric data. Hence, photo induced charge transfer is the mechanistic origin for the non-radiative deactivation of the excited-state which is additionally favored by the reduced HOMO-LUMO gap in agreement with energy gap law.[28] However, this process is reversible, since the protonated species can be neutralized with a base leading to a recovery of the original fluorescence signal. Therefore, pyridyl bridged diphenothiazine dumbbells are p*H*-sensitive fluorescent sensors.

Conclusions

In conclusion, we have presented the synthesis and electronic properties of dumbbell-shaped phenothiazine dyads. The introduction of the heterocyclic bridge can be easily accomplished by the Buchwald-Hartwig aryl amination. The symmetrical systems **9**, **12** and **13** show intense electronic coupling between the redox-active phenothiazinyl units as shown by cyclovoltammetry. Futhermore, we could demonstrate that the emission of derivatives **9** and **10** in CH_2Cl_2 can be switched off by the addition of TFA and switched on by neutralizing the sample solution as a consequence of the enhanced basicity of the pyridines by the electron rich phenothiazine moieties. Therefore, these phenothiazine derivatives represent a new class of tunable molecules, reversibly switchable by redox processes and by p*H* changes. Further studies towards emission switching in phenothiazine derivatives and intramolecular electronic communication in symmetrical dumbbell-shaped diphenothiazines are currently underway.

Experimental

Reagents, catalysts and ligands were purchased reagent grade and used without further purification. The solvents used were dried and distilled according to standard procedures.[29] 2,5-Dibromofuran[30] (**6**) and 9,9′-dihexyl-2,7-dibromofluorene[31] (**2**) were prepared according to the literature. Column chromatography: silica gel 60, mesh 70–230. TLC: silica gel plates. ^{1}H and ^{13}C NMR spectra: CD_2Cl_2, (locked to Me_4Si). The assignments of quaternary C, CH, CH_2 and CH_3 have been made by using

DEPT spectra. Elemental analyses were carried out in the Microanalytical Laboratories, Institut für Pharmazeutische Chemie, Heinrich-Heine University, Düsseldorf, Germany.

Fluorescence measurements (Perkin-Elmer LS-55) were performed in dry and degassed CH_2Cl_2 at room temperature. To avoid re-absorption and re-emission effects the concentrations were strictly kept below 1 μM. The solutions were irradiated at approximately 10 nm less in energy than the longest wavelength absorption maximum.

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, 500, and 1000 mVs^{-1}. The electrolyte was Bu_4NPF_6 (0.025 M). 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).[32]

General procedure (GP)

Under inert conditions 10*H*-phenothiazine **1** (2.2 eq), bromo derivatives **2–7** (1 eq.), $Pd_2(dba)_3$·dba (0.03eq.), PH^tBuF_4 (0.05 eq.), NaO^tBu (2.3 eq.) and anhydrous 1,4-dioxane were placed in a pressure tube. The reaction mixture was stirred at 101 °C for 19 h. After cooling to r.t., the solution was diluted with deionized water, saturated Na_2SO_3 solution and methylene chloride. The aqueous phase was extracted with small portions of methylene chloride, the combined organic phases were dried with anhydrous $MgSO_4$ and the solvents were removed in vacuo. The residue was chromatographed on silica gel (hexane) to furnish the products **8–13** as solids or resins.

3,6-[10,10′]Biphenothiazinyl-9,9-dihexyl-9*H*-fluorene (8). This compound was synthesized according to the **GP** and after purification by flash chromatography on silica gel (hexane) **8** (800 mg, 73%) was obtained as a colourless resin. Mp. 227 °C. R_f (hexane/acetone 10:1): 0.51 ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 0.76 (t, $J = 7.0$ Hz, 6H), 1.07 (m, 16H), 2.04 (t, $J = 8.3$ Hz, 4H), 6.27 (dd, $J = 1.5$ Hz, $J = 8.0$ Hz, 4H), 6.84 (m, 8H), 7.03 (dd, $J = 2.0$ Hz, $J = 7.3$ Hz, 4H), 7.39 (dd, $J = 1.5$ Hz, $J = 8.0$ Hz, 2H), 7.44 (d, $J = 1.5$ Hz, 2H), 8.02 (d, $J = 8$ Hz, 2H). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 13.4 (CH_3), 22.0 (CH_2), 23.6 (CH_2), 29.1 (CH_2), 31.2 (CH_2), 39.8 (CH_2), 55.5 ($C_{quat.}$), 115.4 (CH), 119.3 ($C_{quat.}$), 121.8 (CH), 122.1 ($CH_{.}$), 125.6 (CH), 126.2 (CH), 126.5 (CH), 129.4 (CH), 139.7 ($C_{quat.}$), 140.0 ($C_{quat.}$), 144.1 ($C_{quat.}$), 153.7 ($C_{quat.}$). IR (KBr) ν = 2953, 2925, 2853, 1592, 1483, 1461, 1442, 1305, 1259, 1237, 1121, 1043, 924, 825, 744, 673, 613, 546 cm^{-1}. UV/Vis: λ_{max} (ε) = 259 (164700), 280 (49600), 308 (35200). MS (MALDI) *m/z*: 728.234 (M^+). Anal. calcd. for $C_{49}H_{48}N_2S_2$: C 80.72, H 6.64, N 3.84, found: C 80.72, H 6.79, N 3.82.

10,10′-Biphenothiazinyl-2,6-pyridine (9). This compound was synthesized according to the **GP** and after purification by flash chromatography on silica gel (hexane) **9** (1.72 g, 59%) was obtained as a colorless solid. Mp.138 °C. R_f (hexane/acetone 5:1): 0.45. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 6.33 (d, $J = 8.0$ Hz, 2H), 7.21 (m, 9H), 7.39 (dd, $J = 1.5$ Hz, $J = 7.5$ Hz, 4H), 7.46 (dd, $J = 2.0$ Hz, $J = 8.0$ Hz, 4H). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 100.9 (CH), 125.2 (CH), 126.7 (CH), 127.6 (CH), 127.7 (CH), 133.1 ($C_{quat.}$), 138.5 (CH), 141.0 ($C_{quat.}$), 155.2 ($C_{quat.}$). IR (KBr) ν = 1594, 1575, 1476, 1429, 1345, 1301, 1254, 1194, 1169,1124, 1087, 1033, 940, 861, 778, 752, 731, 695, 659, 635, 612, 546, 523 cm^{-1}. UV/Vis: λ_{max} (ε) = 251 (39000),288 (10900), 333 (17600). MS (EI^+) *m/z* (%): 475 (5, M^{n+2}), 474 (15, M^{n+1}), 473.0 (30, M^+), 274 (20), 242 (35), 198 (100), 154 (23), 127 (8). Anal. calcd. for $C_{29}H_{19}N_3S_2$: C 73.54, H 4.04, N 8.87, found: C 73.31, H 3.86, N 8.82.

10,10′-Biphenothiazinyl-2,5-pyridine (10). This compound was synthesized according to the **GP** and after purification by flash chromatography on silica gel (hexane) **10** (1.07 g, 50%) was obtained as a colourless solid. Mp. 220 °C. R_f (hexane/acetone 5:1): 0.50. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 6.29 (dd, $J = 1.5$ Hz, $J = 8.0$ Hz, 2H), 6.82 (dt, $^dJ = 1.5$ Hz, $^tJ = 7.5$ Hz, 2H), 6.88 (dt, $^dJ = 1.5$ Hz, $^tJ = 7.5$ Hz, 2H), 7.01 (dd, $J = 1.5$ Hz, $J = 7.5$ Hz, 2H), 7.09 (m, 1H), 7.23 (dt, $^dJ = 1.0$ Hz, $J = 7.5$ Hz, 2H), 7.37 (dt, $^dJ = 1.5$ Hz, $^tJ = 7.5$ Hz, 2H), 7.48 (m, 3H), 7.75 (dd, $J = 1.0$ Hz, $J = 8.0$ Hz 2H), 8.18 (m, 1H). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 109.8 (CH), 115.7 (CH), 120.1 ($C_{quat.}$), 122.3 ($CH_{.}$), 125.8 (CH), 126.4 (CH), 126.6 (CH), 126.7 (CH), 127.4 (CH), 127.9 (CH), 130.0 (C_{quat}), 133.3 (C_{quat}), 140.0 (CH), 140.4 (C_{quat}), 144.0 (C_{quat}), 149.5 (CH), 155.1 (C_{quat}). IR (KBr) ν = 1602, 1584, 1551,1475, 1460, 1440, 1385, 1307, 1259, 1233, 1127, 1082, 1044, 824, 746, 621, 540 cm^{-1}. UV/Vis: λ_{max} (ε) = 253 (107800), 283 (26400), 309 (26900). MS (MALDI) *m/z*: 472.941 (M^+). Anal. calcd. for $C_{29}H_{19}N_3S_2$: C 73.54, H 4.04, N 8.87, found: C 73.65, H 4.13, N 8.64.

10,10′-Biphenothiazinyl-3,6-pyridazine (11). This compound was synthesized according to the **GP** and after purification by flash chromatography on silica gel (hexane) **11** (346 mg, 35%) was obtained as a yellow resin. Mp. 231 °C. R_f (hexane/acetone 5:1): 0.32 ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.04 (s, 2H), 7.16 (dt, $^dJ = 1.0$ Hz, $^tJ = 7.5$ Hz, 4H), 7.27 (dt, $^dJ = 1.0$ Hz, $J = 7.5$ Hz, 4H), 7.37 (dd, $J = 1.5$ Hz, $J = 7.5$ Hz, 4H), 7.52 (dd, $J = 1.0$ Hz, $J = 7.5$ Hz, 4H). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 120.1 (CH), 124.8 (CH), 125.3 (CH), 126.8 (CH), 127.5 (CH), 130.8 ($C_{quat.}$), 140.8 ($C_{quat.}$), 154.9 ($C_{quat.}$). IR (KBr) ν = 2967, 2371, 2345, 1774, 1725, 1655, 1627, 1578, 1533, 1509,1478, 1460, 1417, 1364, 1314, 1259, 1233, 1084, 1027, 947, 825, 803, 754, 695, 665, 623, 546 cm^{-1}. UV/Vis: λ_{max} (ε) = 253 (25600), 303 (10400). MS (MALDI) *m/z*: 474.9 (M^+). Anal. calcd. for $C_{28}H_{18}N_4S_2$·0.5 H_2O: C 69.54, H 3.96, N 11.58, found: C 69.31, H 4.16, N 11.13.

10,10′-Biphenothiazinyl-2,5-furan (12). This compound was synthesized according to the **GP** and after purification by flash chromatography on silica gel (hexane) **12** (800 mg, 30%) was obtained as an orange resin. Mp. 200 °C. R_f (hexane/acetone 5:1): 0.48 ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 6.59 (s, 2H), 6.78 (d, J= 8 Hz, 4H), 6.95 (t, $J = 7.5$ Hz, 4H), 7.09 (t, $J = 7.5$ Hz, 4H), 7.13 (d, $J = 8.0$ Hz, 4H). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 108.2 (CH), 116.3 (CH), 122.1 ($C_{quat.}$), 123.4 ($CH_{.}$), 126.5 (CH), 126.8 (CH), 142.7 ($C_{quat.}$), 144.8 ($C_{quat.}$). IR (KBr) ν = 1615, 1589, 1568, 1462, 1443, 1300, 1253, 1234, 1169, 1126, 1085, 1039, 986, 916, 825, 746, 718, 677, 661 cm^{-1}. UV/Vis: λ_{max} (ε) = 252 (80700), 304 (8200). MS (EI^+) *m/z* (%): 464 (10, M^{n+2}), 463 (21, M^{n+1}), 462 (48, M^+), 236 (100), 198 (100), 154 (21). Anal. calcd. for $C_{28}H_{18}N_2OS_2$: C 72.70, H 3.92, N 6.06, found: C 72.13, H 3.72, N 5.84.

10,10′-Biphenothiazinyl-2,5-thiophene (13). This compound was synthesized according to the **GP** and after purification by flash chromatography on silica gel (hexane) **13** (250 mg, 52%) was obtained as a yellow solid. Mp. 215 °C. R_f (hexane/acetone 5:1):

0.45 ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 6.91 (d, $J = 8.5$ Hz, 4H), 6.95 (d, $J = 7.5$ Hz, 4H), 7.06 (m, 2H), 7.10 (m, 8H). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 116.9 (CH), 121.8 ($C_{quat.}$), 123.3 ($CH_{.}$), 126.4 (CH), 126.5 (CH), 126.9 (CH), 141.7 ($C_{quat.}$), 143.3 ($C_{quat.}$). IR (KBr) $\nu =$ 1589, 1556, 1461, 1442, 1302, 1251, 1234, 1198, 1168, 1128, 1042, 915, 814, 750, 712, 659, 631, 562 cm^{-1}. UV/Vis: λ_{max} (ε) = 256 (46300), 311 (5100). MS (EI^{+}) m/z (%): 480 (17, M^{n+2}), 479 (20, M^{n+1}), 478.0 (50, M), 279 (3), 247 (10), 198 (M-278, 100), 154 (3), 127 (4). Anal. calcd. for $C_{28}H_{18}N_2S_3 \cdot 0.25\ CH_2Cl_2$: C 70.26, H 3.79, N 5.85, found: C 70.27, H 3.53, N 5.56.

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