JOC The Journal of Organic Chemistry

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Phenothiazinyl Rhodanylidene Merocyanines for Dye-Sensitized Solar Cells

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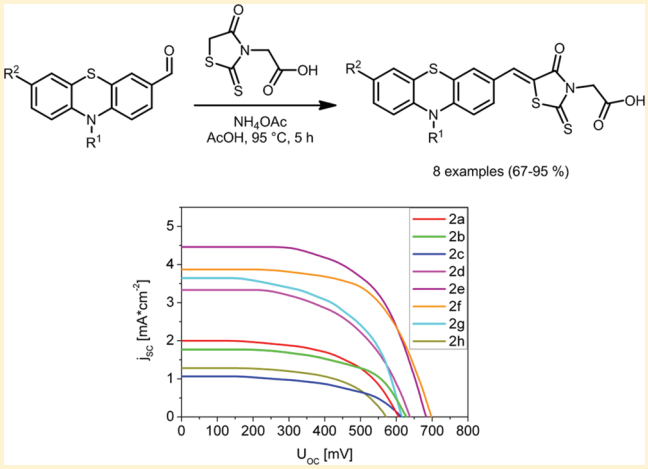
Supporting Information

ABSTRACT: Phenothiazinyl rhodanylidene acetic acid merocyanine dyes with variable substitution pattern on the peripheral benzene ring were synthesized in good to excellent yields by Knoevenagel condensation of the corresponding phenothiazinyl aldehydes and rhodanine-*N*-acetic acid. The electronic properties were investigated by cyclic voltammetry, absorption, and fluorescence spectroscopy. Electron releasing substitution leads to an appreciable lowering of the oxidation potential, bathochromic shift of the absorption band, and minimization of the emission quantum yield. Not least as a consequence of these properties, the compounds are interesting for use as chromophores in dye-sensitized solar cells (DSSC). DSSCs were constructed and successfully tested by determining the characteristic parameters such as incident-photon-to-electron conversion efficiency (IPCE), fill factor (FF), and overall efficiency.



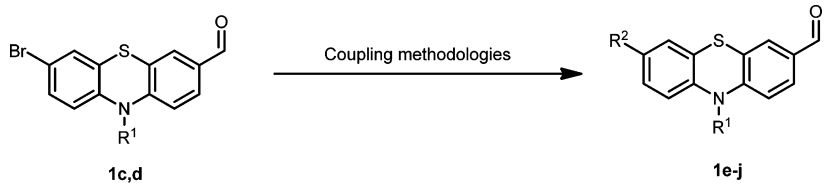
INTRODUCTION

Merocyanines[1] are unsymmetrical and highly dipolar and have adopted a central role among Do−Acc dyes. In particular, merocyanines are well-suited to self-organize in mesoscopic and macroscopic morphologies,[2] and therefore, they have become increasingly important as absorbing chromophores in dye-sensitized solar cells (DSSC)[3] for photovoltaics with a wide range of donor auxochromes. For several reasons, phenothiazines,[4] a class of tricyclic nitrogen−sulfur heterocycles with a broad pharmaceutical profile,[5] are particularly intriguing as redox active donor systems. They possess low and highly reversible first-oxidation potentials[4,6] with a pronounced propensity to form stable radical cations,[7] and their redox and fluorescence properties can be tuned.[8] Furthermore, the inherent folded conformation of phenothiazine[9] with a folding angle of 158.5°, which can be transformed into a stable radical cation with a planar conformation and excellent delocalization,[10] qualifies phenothiazine-based Do−Acc chromophores as excellent models for redox-switchable merocyanines. In addition, phenothiazine derivatives with extended π-conjugated substituents often display intense luminescence upon UV/vis excitation with remarkable Stokes shifts that might be due to solvent relaxation and, in part, to geometry changes in the excited state. As a consequence, the favorable electronic properties of phenothiazines have led to applications as electrophore probes in supramolecular assemblies[11] for photo-induced electron transfer (PET) and sensor studies, and as electron-donor components in material scientific investigations such as electrically conducting charge-transfer composites,[12] polymers,[13] Do−Acc arrangements,[14] and also as chromophores in dye-sensitized photovoltaic cells.[15] As part of our program to synthesize and study oligophenothiazines,[8,16] we have just recently disclosed are general and modular synthetic access to phenothiazinyl merocyanine dyes with variable substitution patterns on the peripheral benzene ring and *N*-methyl rhodanylidene or 2,3-dioxoindanylidene as acceptor units.[17] All these merocyanines revealed a reversible redox behavior that stems from the phenothiazinyl centered oxidation to give stable radical cations. Based upon an excellent correlation of the oxidation potentials with Hammett σ_p parameters, it was not only possible to shift and predictably fine-tune the first oxidation, but also to correlate a remote substituent effect on the luminescence efficiency. Electro-optical absorption, absorption and emission spectroscopy in conjunction with time-dependent DFT computations on selected synthetic model systems rationalize the peculiar highly polar excited state behavior of phenothiazinyl merocyanines. Besides a pronounced emissive solvochromism all merocyanines of the series reveal large Stokes shifts caused by large dipole moment changes upon excitation from the ground to the excited state. Based upon the improved spectral overlap with

Received: December 19, 2011
Published: February 24, 2012

   dx.doi.org/10.1021/jo202608w | *J. Org. Chem.* 2012, 77, 3704−3715

Scheme 1. Synthesis of *N*-Alkyl 7-Substituted 3-Formyl Phenothiazines 1e−1j[a]



1c,d → **1e-j**

1e (R^1 = 2-decyltetradecyl, R^2 = CN, 55%)[a]
1f (R^1 = *n*-hexyl, R^2 = *p*-tolyl, 90%)[b]
1g (R^1 = *n*-hexyl, R^2 = 10-(*n*-hexyl)-10*H*-phenothiazin-3-yl, 89%)[b]
1h (R^1 = 2-decyltetradecyl, R^2 = 10*H*-phenothiazin-10-yl, 22%)[c]
1i (R^1 = 2-decyltetradecyl, R^2 = 9*H*-carbazol-9-yl, 28%)[c]
1j (R^1 = 2-decyltetradecyl, R^2 = pyrrolidin-1-yl, 41%)[d]

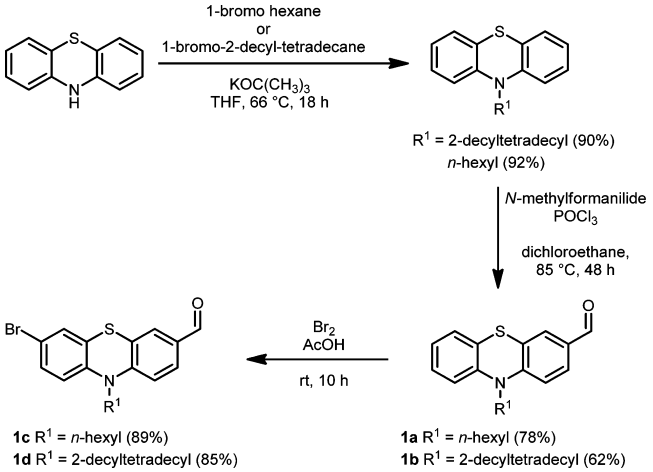
[a]Beller cyanation: $Pd(OAc)_2$, dppf, $K_4[Fe(CN)_6]$, Na_2CO_3, NMP, 120 °C, 18 h. [b]Suzuki coupling: $Pd(PPh_3)_4$, (hetero)aryl boronate, K_2CO_3, DME, H_2O, 95 °C, 10 h. [c]Buchwald-Hartwig coupling: $Pd(dba)_2$, $HP(t\text{-}Bu)_3BF_4$, sec. amine, $NaOC(CH_3)_3$, dry 1,4-dioxane, 110 °C, 26 h. [d]Ullmann coupling: CuI, *L*-proline, sec. amine, K_2CO_3, dry DMSO, 100 °C, 24 h.

the solar spectrum of rhodanylidene moiety,[18] the possibility of its favorable HOMO−LUMO tuning,[19] and the detailed information on the excited state properties of its phenothiazinyl merocyanine derivatives, we set out to synthesize electron-rich phenothiazinyl rhodanylidene acetic acid merocyanines, to study their electronic properties, and to investigate their use and performance in the organic solar cells as sensitizing dyes.

RESULTS AND DISCUSSION

Synthesis. The key reaction for the synthesis of electron-rich phenothiazinyl merocyanines is the Knoevenagel condensation of the corresponding phenothiazinyl carbaldehydes **1** and rhodanine *N*-acetic acid in acetic acid in the presence of ammonium acetate as a catalyst.[17] The 7-substituted phenothiazinyl carbaldehydes **1e−1j** are accessible via cross-coupling methodologies, as previously exemplified with phenothiazines for Suzuki-Miyaura coupling,[16c] Beller cyanation,[8b] or Buchwald-Hartwig- and Ullmann-*N*-arylations,[8c,d] from the *N*-alkyl 7-bromo-3-formyl phenothiazines **1c** and **1d** as key intermediates (Scheme 1). The latter are synthesized in three steps starting from phenothiazine by alkylation, Vilsmeier−Haack formylation and bromination (Scheme 2). For increasing the solubility a 2-decyltetradecyl substituent, the so-called "dovetail" was chosen as side chain. The "dovetail bromide" required for the alkylation can be obtained by bromination of the corresponding alcohol with *N*-bromo succinimide in the presence of triphenylphosphane.

Scheme 2. Synthesis of *N*-Alkyl 7-Bromo-3-formyl Phenothiazines 1c and 1d



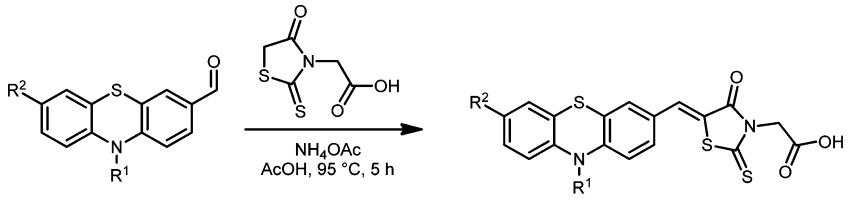
With various *N*-alkyl 3-formyl phenothiazines **1** in hand, Knoevenagel condensation with rhodanine acetic acid as the methylene active condensation partner gave rise to the formation of various electron-rich phenothiazinyl rhodanylidene acetic acid merocyanines **2** in good to excellent yields as red to violet solids (Scheme 3).

The structures of all merocyanines **2** were unambiguously assigned by ^1H and ^{13}C NMR, UV/vis and IR spectroscopy, mass spectrometry, and combustion analysis. Interestingly, although two geometrical isomers for the newly formed double bonds can be expected, the appearance of single sets of the signals in the NMR spectra indicates the stereoselective formation of the Z-isomers in all cases. Previously, the stereoselectivity was additionally corroborated by X-ray structure analysis of two phenothiazinyl merocyanine derivatives.[17]

Photophysical Properties. The phenothiazinyl rhodanylidene acetic acid merocyanine dyes **2a−2f** display four distinct broad, unstructured absorption bands in the UV/vis region at 252−269, 294−307, 358−366, and 462−503 nm (Table 1, Figure 1). In case of dye **2g** an additional band appears at 343 nm instead of the first band, while dye **2h** displays only three absorption bands at 271, 374, and 536 nm. As shown before by comparison of phenothiazinyl rhodanylidene merocyanines, and *N*,*N*-diethyl- and *N*,*N*-diphenylaniline model systems, the longest wavelength absorption arises from the aniline-rhodanylidene merocyanine substructure, whereas the phenothiazinyl specific bands are found at higher energies.[17] A closer look at the spectroscopic data shows a strong dependence of the location of the low-energy absorption bands and their corresponding molar extinction coefficients on the electronic nature of the substituents at the peripheral benzene ring of the phenothiazine. While derivatives with electron-withdrawing groups absorb at higher energies and show their largest molar extinction coefficients at the longest wavelength maxima, electron-donating groups exhibit a deviant behavior. The unsubstituted dye **2a** reveals its longest wavelength absorption at 478 nm, which shifts in the presence of a nitrile acceptor to 462 nm, and bathochromically in case of donor substituted dyes. By choosing *C*-bonded phenothiazine or *N*-bonded pyrrolidine as donor-fragments (**2e**, **2h**), even a shift of 30 or almost 60 to 536 nm is possible. At the same time the molar extinction coefficients of the short wavelength maxima increase strongly, while those of the longest wavelength band drop only

dx.doi.org/10.1021/jo202608w | J. Org. Chem. 2012, 77, 3704−3715

Scheme 3. Synthesis of Electron-rich Phenothiazinyl Rhodanylidene Acetic Acid Merocyanines 2



1

2a (R^1 = 2-decyltetradecyl, R^2 = H, 95 %)
2b (R^1 = 2-decyltetradecyl, R^2 = Br, 94 %)
2c (R^1 = 2-decyltetradecyl, R^2 = CN, 92 %)
2d (R^1 = *n*-hexyl, R^2 = *p*-tolyl, 67 %)
2e (R^1 = *n*-hexyl, R^2 = 10-(*n*-hexyl)-10*H*-phenothiazin-3-yl, 68 %)
2f (R^1 = 2-decyltetradecyl, R^2 = 10*H*-phenothiazin-10-yl, 94 %)
2g (R^1 = 2-decyltetradecyl, R^2 = 9*H*-carbazol-9-yl, 91 %)
2h (R^1 = 2-decyltetradecyl, R^2 = pyrrolidin-1-yl, 82 %)

Table 1. Absorption and Emission Properties[a] of the Dyes 2

dye	absorption[b] $\lambda_{max,abs}$ [nm] (ε 10^3[$M^{-1}cm^{-1}$])	emission[c] $\lambda_{max,em}$ [nm] (Φ_f)[d]	Stokes shift $\Delta\tilde{\nu}$ [cm^{-1}][e]
2a	252 (18), 305 (14), 366 (14), 478 (20)	651 (0.01)	5600
2b	256 (28), 297 (20), 361 (21), 473 (29)	643 (0.05)	5600
2c	265 (18), 297 (21), 363 (16), 462 (22)	630 (0.21)	5800
2d	269 (29), 303 (25), 358 (19), 471 (23)	655 (<0.01)	6000
2e	265 (36), 307 (16), 359 (24), 503 (18)	688 (<0.01)	5300
2f	258 (62), 300 (22), 359 (19), 472 (24)	636 (<0.01)	5500
2g	294 (33), 343 (17), 363 (17), 478 (22)	657 (<0.01)	5700
2h	271 (31), 374 (22), 536 (18)	659 (<0.01)	3500

[a]Absorption and emission spectra were measured in CH_2Cl_2, T = 293 K. [b]Recorded in CH_2Cl_2 at c(**2**) = 10^{-3} M. [c]Recorded in CH_2Cl_2 at c(**2**) = 10^{-6} M. [d]Determined with 4-dicyanomethylene-2-methyl-6-[*p*-(dimethylamino)styryl]-4*H*-pyran (DCM) as a standard in DMSO, Φ_f = 0.78. [e]$\Delta\tilde{\nu} = 1/\lambda_{max,abs} - 1/\lambda_{max,em}$.

slightly in comparison to the unsubstituted derivative. Sterically demanding donor-fragments, such as *N*-bonded phenothiazine or carbazole (**2f**, **2g**), show no effect on the location of the absorption bands, which can be explained by an out-of-plane rotation of these substituents resulting in the generation of two noncommunicable π-systems. The appearance of a new broad absorption band at 343 nm in the spectrum of dye **2g** supports this argumentation, because it is in accord with absorption spectra of *N*-alkylated carbazoles.[20] All dyes **2** reveal more or less intense fluorescence and show large Stokes shifts ($\Delta\tilde{\nu}$) in a range from 5300−6000 cm^{-1}, which represents a peculiar and characteristic behavior of many phenothiazine based chromophores (Figure 2). Noticeably, dye **2f** shows only a small shift of 3500 cm^{-1}, what can be ascribed to its low-energy absorption. The broad, unstructured emission bands display maxima at 630−688 nm, depending on the substitution pattern. However the emission intensity as reflected by the fluorescence quantum yields varies significantly with the peripheral benzo substituent on the phenothiazine. The electron-deficient substituted merocyanines **2b**−**2c** exhibit the highest quantum yields of 5 and 21% in this series. Increasing the electron density significantly quenches the fluorescence. While the derivative with the electronically neutral hydrogen (**2a**) shows a fluorescence quantum yield of 1%, for donor-substituted phenothiazinyl merocyanines, the yield decreases considerably.

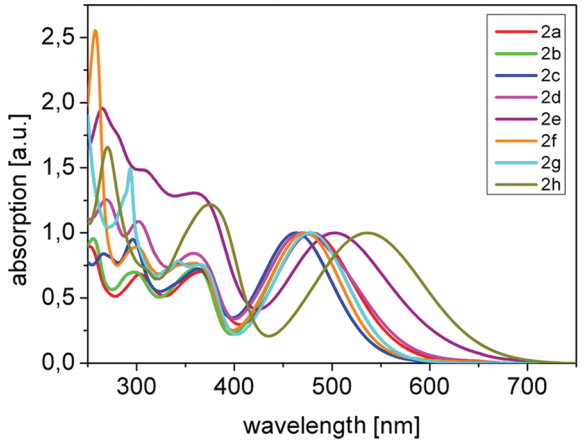


Figure 1. Normalized absorption spectra of **2** (recorded in CH_2Cl_2 at T = 293 K (a.u. = arbitrary units)).

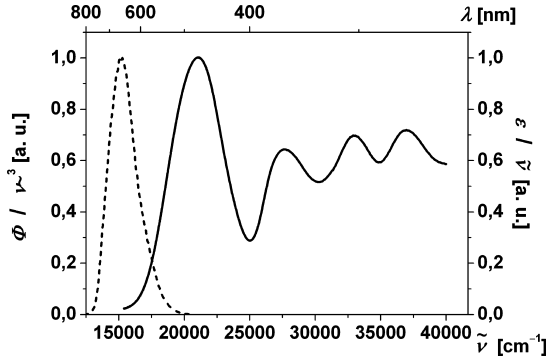


Figure 2. Absorption (solid line) and emission (dashed line) of compound **2d** (recorded in CH_2Cl_2, T = 293 K, excitation wavelength λ_{exc} = 471 nm (a.u. = arbitrary units)).

Electrochemical Properties. The cyclic voltammograms of the dyes **2** exhibit two, in the case of **2e** three, reversible oxidations, typical of phenothiazine derivatives (Table 2). Their potential strongly depends on the electronic nature of the substituent of the peripheral benzene ring. The nitrile substituted derivative as the most electron-deficient dye shows the first oxidation wave at 1116 mV, that is, anodically shifted compared to the unsubstituted dye **2a**. The second oxidation presumably lies outside the measurement range of

dx.doi.org/10.1021/jo202608w | J. Org. Chem. 2012, 77, 3704−3715

Table 2. Cyclovoltammetric Data[a] and Electrochemical Properties of the Dyes 2

dye	$E_0^{0/+1}$[b] [mV]	$E_0^{+1/+2}$[b] [mV]	$E_0^{+2/+3}$[b] [mV]	$E_{1/2}^{0/+1}$ vs NHE[c] [V]	$E_{1/2}^{+1/+2}$ vs NHE[c] [V]	$E_{1/2}^{+2/+3}$ vs NHE[c] [V]	E_{0-0}[d] [eV]	$E(S^+/S^*)$ vs NHE[e] [V]
2a	898	1563		1.10	1.76		2.13	−1.03
2b	970	1614		1.17	1.81		2.16	−0.99
2c	1116			1.31			2.24	−0.93
2d	792	1443		0.99	1.64		2.24	−1.25
2e	686	873	1477	0.88	1.07	1.68	2.03	−1.15
2f	719	1095		0.92	1.29		2.21	−1.29
2g	926	1400		1.12	1.60		2.03	−0.91
2h[f]	423	1044		0.62	1.24		1.99	−1.37

[a]Recorded in CH_2Cl_2, T = 293 K, ν = 100 mV s^{-1}, electrolyte: $[Bu_4N][PF_6]$, Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode. [b]$E_0 = (E_{pa} - E_{pc})/2$ with Fc/Fc^+. [c]$E_{1/2}$: E_0 vs NHE (E_0 (3M KCl/Ag/Ag^+) = 0.198 V vs NHE). [d]E_{0-0} was determined from the cross-section of absorption and emission spectra. [e]Excited state oxidation potential $E(S^+/S^*) = E_{1/2}^{0/+1} - E_{0-0}$. [f]1,1′-Dimethylferrocen was used as an internal standard.

dichloromethane. In contrast, electron-rich substituents reduce the oxidation potentials significantly. In the case of phenothiazine as donor fragment (**2e**) the decrease is 200 mV, or even the double by using pyrrolidine (**2f**). The linear correlation of the oxidation potential of the phenothiazinyl merocyanines with the Hammett substitution parameter σ_p, as previously discussed,[17] seems to proceed at strongly electron pushing substituted dyes. The sterically loaded derivatives **2f** and **2g** are out of ordinary because these compounds are distinguished with comparable high first oxidation potentials of 719 and 926 mV, respectively. A closer look at the absorption behavior and literature measurements gives the evident explanation; the dyes exhibit in a twisted conformation. Both π-systems subsist orthogonally to each other, wherefore there is no communication in the electronic ground state within the bonded fragments. The detected potentials accord with the measurements of the corresponding *N*-alkylated donor fragments ($E_{0,phenothiazine}^{0/+1}$ = 701 mV,[21] $E_{0,carbazole}^{0/+1}$ = 930 mV[22]). With the help of the photophysical and the electrochemical measurement data, we are able to appreciate the HOMO and LUMO energy levels of the synthesized dyes (Table 2). In connection with the fixed energy potentials of a typical DSSC, the standard potential for the conducting band (CB) of TiO_2 to NHE: E_{CB} = −0.5 V, and for the iodide/triiodide (I^-/I_3^-) redox couple to NHE: E = 0.53 V (Figure 3), we can prepare a schematic energy diagram (Figure 4). To ensure a satisfied performance of the solar cell, a high energy HOMO level, below the redox potential, and a low energy LUMO level, above the Fermi energy of the semiconductor, are required to ensure a low energy absorption, uninhibited charge transitions and an easy oxidizability of the dye. These requirements are given for all dyes. While the HOMO energy level, which correlates directly with the measurements of the cyclovoltammetry, shows the prediscussed influence of the electronic nature of the substituents, the LUMO level is less influenced. In general, electron donating groups increase, whereas electron withdrawing groups decrease the accordant value.

Photovoltaic Devices and Solar Cell Performance. To test the dyes **2a**−**2h** as sensitizers in DSSCs, solar cells with nanocrystalline TiO_2 were prepared. The exact preparation is demonstrated in the experimental part and the results, together with the standard **N3** (*cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II)), are summarized in Table 3. The absorption spectra of the adsorbed dyes on the TiO_2 surface are shown in Figure 5. They are similar to the absorption spectra of the dyes in solution. The main difference

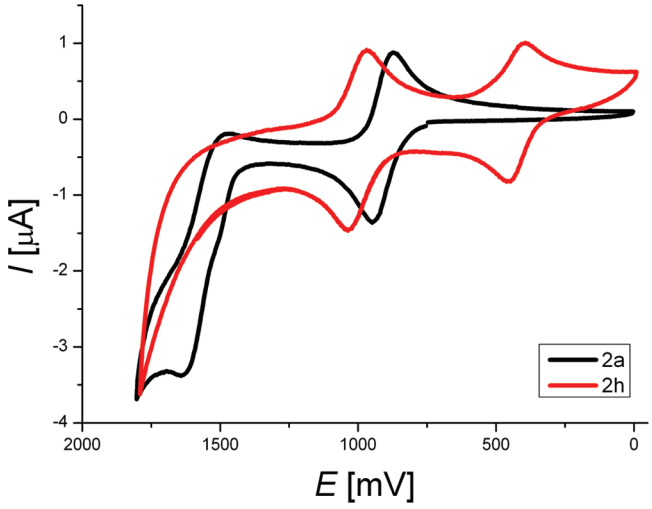


Figure 3. Cyclic voltammogram of dye **2h** (red line) and **2a** (black line) (recorded in CH_2Cl_2, T = 293 K, ν = 100 mVs^{-1}, electrolyte: $[Bu_4N][PF_6]$, Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode).

is the broadening of the longest wavelength band. The absorption extends from 370 to 800 nm compared to 400−700 nm for the dyes in solution. Due to the adsorption on the TiO_2 surface the harvesting of solar light is thus increased. Two reasons could be possible to explain the observed broadening. At first the energy of the π^* level is lowered due to the interaction of the carboxylic acid with the Ti^{4+} ions on the TiO_2 surface. The increased electron delocalization of the π^* level leads to a bathochromic shift of the absorption spectra. Furthermore dye aggregation and excimer formation (J-aggregates) can lead to a broadening of the absorption.[23]

Figure 6 shows the IPCE (incident photo-to-current conversion efficiency) spectra of the DSSCs. Only moderate IPCEs from 8% (**2c**) to 37% (**2f**) were achieved at the absorption maximum of the dyes. One possible reason is a rather low efficiency of electron injection in the conducting band of TiO_2. The photophysical and electrochemical analysis is in line with the measured IPCEs. According to the absorption spectra, the dyes **2e**, **2g** and **2h** should show the best IPCE values at long wavelengths up to 700 nm. In the case of **2e**, we measure efficiencies of 5% at 650 nm. The highest IPCE value (at about 470 nm) shows the dye **2f**. In this spectral range the dye exhibits its absorption maximum with a relative high molar extinction coefficient of 24000 M^{-1} cm^{-1}. At first view the low

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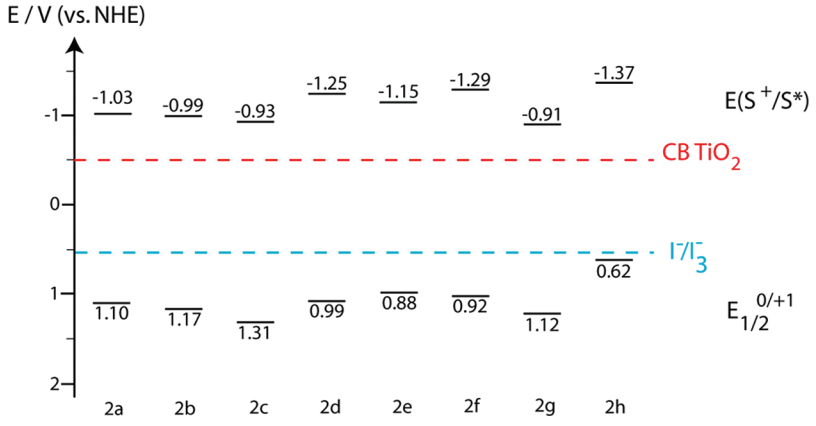

Figure 4. Schematic energy level diagram (HOMO–LUMO) for the dyes **2a–2h**.

Table 3. Photovoltaic Performance DSSCs Based on the Dyes 2[a]

dye	j_{SC} [mA cm^{-2}]	U_{OC} [mV]	FF	η [%]
2a	2.00	607	0.58	0.7
2b	1.77	627	0.59	0.6
2c	1.07	613	0.53	0.4
2d	3.33	638	0.57	1.2
2e	4.46	683	0.60	1.9
2f	3.87	698	0.65	1.8
2g	3.64	615	0.57	1.3
2h	1.28	575	0.58	0.5
N3	11.73	690	0.51	4.1

[a]Measured under irradiation with AM 1.5 G simulated solar light (100 mW cm^{-2}) at room temperature, 13 μm of film thickness, 0.78 cm^2 of working area. The concentrations of the dyes are 0.2 mM in CH_2Cl_2 and of the electrolyte 0.6 M tetrabutylammonium iodide (TBAI), 0.1 M lithium iodide, 0.05 M iodine and 0.5 M 4-*tert*-butylpyridine (TBP) in 5 mL of acetonitrile.

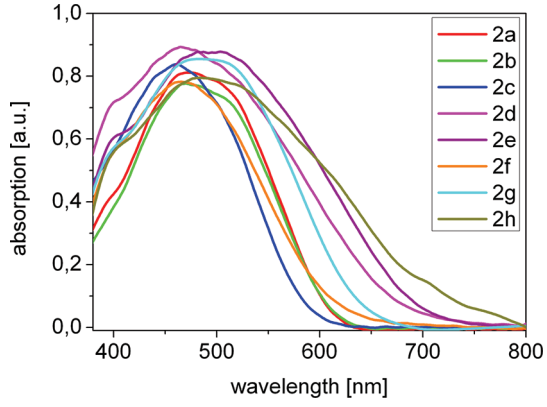

Figure 5. Absorption spectra of the dyes **2** on TiO_2 surface measured in reflection arrangement (the absorption of pure TiO_2 nanoparticles was subtracted).

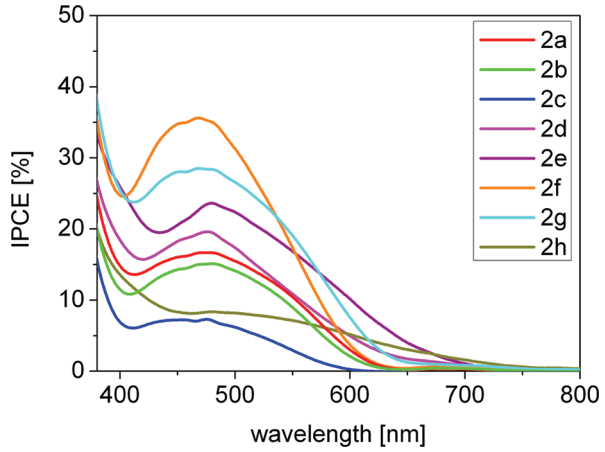

Figure 6. Spectra of the incident photon-to-current conversion efficiencies (IPCE) obtained for nanocrystalline TiO_2 solar cells sensitized by the dyes **2a–2h**.

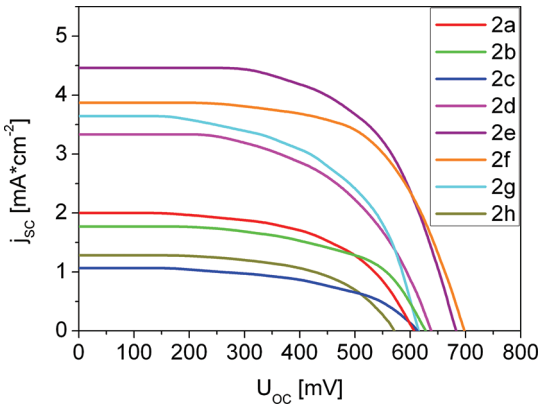

Figure 7. Photocurrent density j_{SC} vs voltage curves of DSSCs based on the dyes **2** with iodine/triiodide electrolyte under irradiation at AM 1.5 simulated solar light (100 mW cm^{-2}).

IPCE value of **2h** surprises as it has the lowest oxidation potential of all dyes and highest absorption in the visible spectral range. Hence, electron detachment should be quite easy and efficient. The explanation is given by the tendency of this dye to form aggregates, resulting in low efficiencies.

The solar cells sensitized with the dyes **2a–2h** show moderate short circuit photocurrent densities j_{sc} from 1.07 (**2c**) to 4.46 (**2e**) mA cm^{-2} and reasonable fill factors in the range 0.51–0.65 (Figure 7). Figure 4 indicates that all energetic positions of the excited state oxidation potential (LUMO) are more negative than the edge of the TiO_2 conduction band (−0.5 V vs NHE[24]). An electron injection from the LUMO of the dyes into the conducting band can take place. The oxidized dyes can be regenerated by accepting electrons from the iodide/triiodide electrolyte, because the ground state (HOMO) of all used dyes are sufficiently more positive than the potential

dx.doi.org/10.1021/jo202608w | J. Org. Chem. 2012, 77, 3704–3715

of the electrolyte (E^0 = 0.53 V[25]). The dye **2e** sensitized SC achieves the best overall conversion efficiency (η) of 1.9%, see Table 3. The energetic positions of HOMO (0.88 V) and LUMO (−1.15 V) and the broad absorption up to 700 nm (extended conjugated π-system) enhance the photovoltaic performance. Keeping in mind that the efficiency of a DSSC prepared from the standard **N3** with the preparation technique described in Section 4 was 4.1%, we achieved reasonable 46% of this value using **2e** as sensitizer. The SC sensitized with dye **2f** shows a similar efficiency (1.8%). In this case, the absorption extents only to 630 nm. However dye **2f** has the highest IPCE-values of all investigated dyes (37% at 470 nm). The dyes **2c** and **2h** represent a group of sensitizers which are not suitable for DSSCs. The overall efficiencies of 0.5% (**2h**) and 0.4% (**2c**) are too low. Dye **2c** features a strong electron withdrawing substituent (cyano group) at the donor part of the molecule. The decreased electron density in the phenothiazine moiety hinders the oxidation of the dye and efficient charge transfer. As stated before, aggregation of dye **2h** is observed during preparation of the DSSC as indicated by the opacity of the solution and precipitation. The precipitated dye in the pores of the TiO_2 film decreases the yield of charge carrier injection so that only low conversion efficiencies are obtained. The neutral substitution (−H) of dye **2a** results in a DSSC overall efficiency of 0.7%. The photocurrent lies in the range between the values of DCCSs based on sensitizers with strong electron push or pull moieties. The bromide substituted dye **2b** achieves similar solar cell efficiencies (η = 0.6%) as dye **2a**. Probably because of the marginally larger bathochromic shift of **2a** (λ_{abs} (max) = 478 nm (**2a**), 473 nm (**2b**)) and its lower fluorescence quantum yield, the efficiencies of dye **2a** sensitized SCs are higher than those of dye **2b** sensitized SCs.

CONCLUSION

A series of new phenothiazinyl rhodanylidene acetic acid merocyanine dyes were successfully synthesized and characterized by photophysical and electrochemical analysis. The dyes exhibit a distinct donor-π-acceptor behavior comprising phenothiazine derivatives as an electron donor and rhodanylidene acetic acid as an electron acceptor. Electron-rich or electron-deficient substituents in the phenothiazine moiety modify the physical and chemical properties of the system. An electron-rich substituent like a second phenothiazinyl group (dye **2e**) decreases the first oxidation potential ($E_0^{0/+1}$ = 686 mV (**2e**)) compared to the unsubstituted phenothiazine and an efficient intramolecular charge transfer can take place. An electron withdrawing group, for example, a cyanide group (dye **2c**), reduces the electron density in the phenothiazine donor, which hinders oxidation of the dye ($E_0^{0/+1}$ = 1116 mV (**2c**)). The substituent also influences the absorption region of the synthesized dyes. A pronounced conjugated π-system shifts the absorption to the red. The electron deficient merocyanines **2b**–**c** exhibit the highest fluorescence quantum yields in this series (5 and 21%). However, a higher electron density in the phenothiazine part quenches the fluorescence significantly. These properties are favorable for a possible application as sensitizer in DSSCs. The obtained efficiencies (IPCE and overall efficiencies) are in good agreement with the photophysical and electrochemical results. The best performance sensitizer dye **2e** (η = 1.9%) corresponds to 46% of the performance of a DSSC prepared with the standard dye **N3** under our experimental conditions. As expected the sensitizer **2c** leads to a low DSSC efficiency (η = 0.5%). Beside the energetic properties the tendency to form aggregates effects the efficiencies of the DSSCs. Dye **2h** has the lowest oxidation potential of all dyes ($E_0^{0/+1}$ = 423 mV). Hence, it should be quite easy to oxidize, but its aggregation results in low efficiencies (η = 0.4%). Furthermore, the steric constitution of the substituent influences the characteristics of the dyes. In the case of the dyes **2f** and **2g** the substituent is rotated out of the plane of the chromophore and conjugation is thus prevented.

The use of phenothiazine based building blocks as sensitizers has several distinct advantages over other sensitizers. At first, the synthesis of phenothiazinyl rhodanylidene acetic acid merocyanine dyes with various substituents is easier, more efficiently compared, and less expensive than the commonly used metal (e.g., ruthenium) complexes. The flexible substitution of the donor or the acceptor moieties, whereby the energetic positions of HOMO and LUMO can be adjusted exactly, is a great advantage of these sensitizers.

Our results show impressively the systematic optical and electrochemical behavior of these compounds. The development of one-pot routes to synthesize other merocyanine dyes with electron-rich substituents in favorable steric constitutions as well as optimal energetic positions of HOMO and LUMO, and their application as sensitizers in DSSCs will be subject of further research.

EXPERIMENTAL SECTION

General Considerations. Reagents, catalysts, ligands, and solvents were purchased reagent grade and used without further purification. DMSO was dried and distilled from CaH_2 under argon atmosphere. 1-Bromo-2-decyl-tetradecane,[26] 10-hexyl-10*H*-phenothiazine,[8a] 10-hexyl-10*H*-phenothiazine-3-carbaldehyde (**1a**),[27] and 7-bromo-10-hexyl-10*H*-phenothiazine-3-carbaldehyde (**1c**)[28] were prepared according to literature procedures. Column chromatography: silica gel 60, mesh 70–230. TLC: silica gel plates 60 F_{254}.

Instrumentation. Chemical shifts δ in the ^{1}H NMR and ^{13}C NMR spectra are reported in ppm relative to deuterated solvents (CD_2Cl_2, THF-d_8, acetone-d_6, or DMSO-d_6). The assignments of quaternary C, CH, CH_2, and CH_3 signals were made by using DEPT spectra. The absorption spectra of the dyes **2** in solution were recorded on a diode array UV–vis spectrometer. Cyclic voltammetry experiments were performed under argon in dry and degassed CH_2Cl_2 at room temperature and at scan rates of 100, 250, 500, and 1000 mV s^{-1} using an electrochemical workstation. 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 an Ag/AgCl electrode. The potentials were corrected to the internal standard of Fc/Fc$^+$ in CH_2Cl_2 ($E_0^{0/+1}$ = 450 mV).

Preparation of the DSSCs. TiO_2 nanopowder (5 g Aerosil TiO_2 P25) was suspended in nitric acid (1 N) to prepare a suitable TiO_2 paste. This suspension was heated at 80 °C for 24 h.[29] Then, the nitric acid was evaporated and the TiO_2 solid was dried for 3 days at 100 °C. Finally the TiO_2 solid was treated with 25 mL of water, acetylacetone (2.5 g, 24.97 mmol), Triton-X-100 (1.25 g, 1.92 mmol) and polyethylene oxide (M.W. 100000).[30]

We used aluminoborosilicate glass coated with fluorine doped tin oxide (SnO_2:F) as conducting transparent substrate (resistivity ≈ 10 Ω cm^{-2}). The active area was masked with scotch tape and was coated with TiO_2 suspension by use of a glass scraper and dried at 80 °C for 10 min. After removal of the scotch tape, we measured ∼13 μm deposit thickness. This primed photo electrode was sintered in a muffle furnace for ∼45 min at 450 °C. The cooled TiO_2 electrode was immersed in dye solution (0.2 mM in CH_2Cl_2) for 24 h at room temperature. A thin platinum layer was spread on the FTO coating of the counter electrode. Few drops of the active redox couple iodine/iodide (0.1 M lithium iodide, 0.05 M iodine, 0.6 M tetrabutylammonium iodide, and 0.5 M 4-tert-butylpyridine in acetonitrile) were added to the photoelectrode for reduction of the oxidized dyes.

dx.doi.org/10.1021/jo202608w | J. Org. Chem. 2012, 77, 3704–3715

Finally, the counter electrode was clamped to the photoelectrode/electrolyte system.[15]

Measurements of the DSSCs. Measurements of the wavelength dependence of the short circuit current (j_{SC}) were carried out in a light-proof box with a 70 W xenon lamp and a grating monochromator in the spectral range of 300−800 at 1 nm resolution. Data were transmitted to a computer and processed there. The light intensity incident on the electrode (I_{inc}) was measured with a power meter. The IPCE is defined by the following expression:[31]

$$\mathrm{IPCE}(\%) = \frac{j_{sc}(\mathrm{A/cm^2}) \times 1240}{\lambda(\mathrm{nm}) \times I_{inc}(\mathrm{W/cm^2})} \times 100 \quad (1)$$

The photocurrent−voltage (I−V) curves were measured using a 120 W xenon lamp and a special filter, which was focused to give 100 mW cm^{-2} (1 sun) at Air Mass (AM) 1.5 at the surface of the solar cell. The fill factors ff and overall efficiencies η were calculated according to eqs 2 and 3. Here MPP is the "maximum power point" and U_{oc} the open-circuit voltage.[3b]

$$ff = \frac{\mathrm{MPP(W/cm^2)}}{j_{sc}(\mathrm{A/cm^2}) \times U_{oc}(\mathrm{V})} \quad (2)$$

$$\eta(\%) = \frac{j_{sc}(\mathrm{A/cm^2}) \times U_{oc}(\mathrm{V}) \times ff}{I_{inc}(\mathrm{W/cm^2})} \times 100 \quad (3)$$

Optical absorption spectra of the synthesis products were recorded by using a UV−vis spectrophotometer operated at a resolution of 1 nm. The absorption spectra of the electrodes were measured in a reflection arrangement.

10-(2-Decyl-tetradecyl)-10*H*-phenothiazine. 10*H*-Phenothiazine (9.00 g, 45.2 mmol) and potassium *tert*-butoxide (5.73 g, 51.1 mmol) were dissolved in 100 mL of dry THF and stirred for 70 min at room temperature. Then, 1-bromo-2-decyl-tetradecane (31.9 g, 76.4 mmol) was added to the resulting, dark brown solution and the mixture was heated to reflux for 18 h. After cooling to room temperature, the reaction mixture was filtered through a short pad of silica gel, which was washed several times with THF. The solvents were removed *in vacuo* and the crude product was chromatographed on silica gel (*n*-hexane) to give 21.81 g (90%) of 10-(2-decyl-tetradecyl)-10*H*-phenothiazine as a colorless oil. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 0.89 (t, J = 6.9 Hz, 6 H), 1.17−1.43 (m, 40 H), 1.91−2.00 (m, 1 H), 3.73 (d, J = 6.8 Hz, 2 H), 6.88−6.94 (m, 4 H), 7.11−7.18 (m, 4 H). ^{13}C NMR (125.5 MHz, CD_2Cl_2): δ 14.5 (two CH_3), 23.3 (two CH_2), 26.8 (two CH_2), 29.93 (CH_2), 29.95 (CH_2), 30.0 (two CH_2), 30.18 (two CH_2), 30.20 (CH_2), 30.24 (two CH_2), 30.27 (CH_2), 30.5 (two CH_2), 32.1 (two CH_2), 32.5 (two CH_2), 35.0 (CH), 52.0 (CH_2), 116.5 (two CH), 122.8 (two CH), 126.3 (two C_{quat}), 127.7 (two CH), 127.9 (two CH), 146.4 (two C_{quat}). MALDI-TOF MS m/z = 535.3. UV/vis λ_{max} (ε) [nm] = 258 (3400), 311 (6000). IR (film): $\tilde{\nu}$ [cm^{-1}] = 2925 (m), 2852 (m), 2345 (w), 1923 (w), 1594 (m), 1572 (m), 1485 (m), 1459 (s), 1339 (m), 1285 (m), 1250 (s), 1128 (w), 1106 (w), 1039 (m), 926 (w), 848 (w), 748 (s), 726 (m), 625 (w). Anal. Calcd for $C_{36}H_{57}NS$ (535.9): C 80.68, H 10.72, N 2.61. Found: C 81.02, H 11.02, N 2.67.

10-(2-Decyltetradecyl)-10*H*-phenothiazine-3-carbaldehyde (1b). 10-(2-Decyl-tetradecyl)-10*H*-phenothiazine (7.63 g, 14.3 mmol), and *N*-methylformanilide (1.9 mL, 15.6 mmol) were dissolved in 14 mL of dry 1,2-dichloroethane and the reaction mixture was cooled to 0 °C. Phosphorus oxychloride (1.6 mL, 17.7 mmol) dissolved in 3 mL of 1,2-dichloroethane was added dropwise within 4 h to the reaction mixture. The reaction was heated to reflux temperature for 48 h. Then, after cooling to room temperature, 90 mL of an aqueous solution of sodium acetate (40 wt %) was added and the resulting biphasic reaction mixture was stirred for 3 h. The aqueous layer was extracted several times with small amounts of diethyl ether. The combined organic fractions were dried with anhydrous sodium sulfate and the solvents were removed *in vacuo*. The residue was chromatographed on silica gel (*n*-hexane/diethyl ether 25:1) to give 4.67 g (58%) of compound **1b** as a yellow oil. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 0.89 (t, J = 7.0 Hz, 6 H), 1.16−1.44 (m, 40 H), 1.93−2.01 (m, 1 H), 3.80 (d, J = 7.1 Hz, 2 H), 6.93 (dd, J = 0.7, 8.2 Hz, 1 H), 6.96 (d, J = 8.4 Hz, 1 H), 6.98 (dt, J = 1.1, 7.5 Hz, 1 H), 7.15 (dd, J = 1.5, 7.7 Hz, 1 H), 7.19 (dt, J = 1.5, 7.5 Hz, 1 H), 7.59 (d, J = 1.9 Hz, 1 H), 7.65 (dd, J = 1.9, 8.4 Hz, 1 H), 9.79 (s, 1 H). ^{13}C NMR (125.5 MHz, CD_2Cl_2): δ 14.5 (two CH_3), 23.3 (two CH_2), 26.7 (two CH_2), 29.93 (CH_2), 29.95 (CH_2), 30.0 (two CH_2), 30.16 (two CH_2), 30.19 (CH_2), 30.23 (two CH_2), 30.27 (CH_2), 30.5 (two CH_2), 32.0 (two CH_2), 32.50 (CH_2), 32.51 (CH_2), 35.2 (CH), 52.4 (CH_2), 116.2 (CH), 117.3 (CH), 124.1 (CH), 125.5 (C_{quat}), 126.7 (C_{quat}), 128.0 (CH), 128.1 (CH), 128.8 (CH), 130.4 (CH), 131.8 (C_{quat}), 144.7 (C_{quat}), 152.0 (C_{quat}), 190.4 (CH). MALDI-TOF MS m/z = 563.31. UV/vis λ_{max} (ε) [nm] = 276 (19000), 289 (20000), 383 (8000). IR (film): $\tilde{\nu}$ [cm^{-1}] = 2924 (s), 2854 (s), 2721 (w), 2170 (w), 1695 (s), 1587 (m), 1574 (m), 1557 (m), 1494 (m), 1463 (s), 1416 (m), 1376 (m), 1344 (m), 1309 (w), 1288 (w), 1198 (m), 1149 (w), 1102 (m), 898 (w), 816 (w), 747 (m), 690 (w). Anal. Calcd for $C_{37}H_{57}NOS$ (563.9): C 78.80, H 10.19, N 2.48. Found: C 78.60, H 10.37, N 2.49.

7-Bromo-10-(2-decyltetradecyl)-10*H*-phenothiazine-3-carbaldehyde (1d). Bromine (0.8 mL, 15.4 mmol) dissolved in 2 mL of acetic acid was added quickly to a solution of 10-(2-decyltetradecyl)-10*H*-phenothiazine-3-carbaldehyde (**1b**) (8.70 g, 15.4 mmol) in 30 mL of glacial acetic acid. The reaction mixture was stirred at room temperature for 10 h. Then, an oversaturated aqueous solution of Na_2CO_3 was added, and the mixture was stirred for another 2 h. The resulting green reaction mixture was extracted several times with diethylether. The combined organic layers were dried with anhydrous sodium sulfate, and the solvents were removed *in vacuo*. The residue was chromatographed on silica gel (*n*-hexane/diethylether 30:1) to give 8.69 g (88%) of compound **1d** as a yellow viscous oil. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 0.88 (t, J = 7.0 Hz, 6 H), 1.20−1.44 (m, 40 H), 1.89−1.98 (m, 1 H), 3.75 (d, J = 7.2 Hz, 2 H), 6.78 (d, J = 8.6 Hz, 1 H), 6.96 (d, J = 8.4 Hz, 1 H), 7.26 (d, J = 2.2 Hz, 1 H), 7.28 (dd, J = 2.3, 8.6 Hz, 1 H), 7.59 (d, J = 1.9 Hz, 1 H), 7.66 (dd, J = 1.9, 8.4 Hz, 1 H), 9.79 (s, 1 H). ^{13}C NMR (125.5 MHz, CD_2Cl_2): δ 14.5 (two CH_3), 23.3 (two CH_2), 26.7 (two CH_2), 29.93 (CH_2), 29.95 (CH_2), 30.0 (two CH_2), 30.15 (two CH_2), 30.19 (CH_2), 30.23 (two CH_2), 30.27 (CH_2), 30.4 (two CH_2), 31.9 (two CH_2), 32.5 (two CH_2), 35.1 (CH), 52.6 (CH_2), 116.1 (C_{quat}), 116.4 (CH), 118.5 (CH), 126.0 (C_{quat}), 127.8 (C_{quat}), 128.9 (CH), 130.3 (CH), 130.6 (CH), 130.8 (CH), 132.1 (C_{quat}), 144.0 (C_{quat}), 151.6 (C_{quat}), 190.3 (CH). MALDI-TOF MS m/z = 641.30. UV/vis λ_{max} (ε) [nm] = 247 (19000), 276 (24000), 292 (16000), 329 (5000), 383 (7000). IR (film): $\tilde{\nu}$ [cm^{-1}] = 3368 (w), 2925 (s), 2853 (s), 2725 (m), 1695 (s), 1595 (s), 1557 (m), 1456 (s), 1416 (m), 1393 (m), 1337 (m), 1306 (m), 1271 (m), 1198 (s), 1156 (m), 1104 (m), 868 (w), 814 (m), 741 (m), 656 (w), 636 (w), 554 (w). Anal. Calcd for $C_{37}H_{56}BrNOS$ (642.8): C 69.13, H 8.78, N 2.18. Found: C 69.52, H 9.08, N 2.06.

10-(2-Decyltetradecyl)-7-formyl-10*H*-phenothiazine-3-carbonitrile (1e). Anhydrous Na_2CO_3 (0.33 g, 3.11 mmol), $K_4[Fe(CN)_6]$ (0.29 g, 0.79 mmol) (ground to a fine powder and dried under vacuum), $Pd(OAc)_2$ (7.00 mg, 0.03 mmol), 1,1′-bis-(diphenylphosphanyl)ferrocene (35.0 mg, 0.06 mmol) and 7-bromo-10-(2-decyltetradecyl)-10*H*-phenothiazine-3-carbaldehyde (**1d**) (2.00 g, 3.11 mmol) were dissolved in 3 mL of *N*-methylpyrrolidinone under an argon atmosphere and the reaction mixture was stirred at 125 °C for 14 h. After cooling to room temperature, the solution was diluted with deionized water, a saturated aqueous solution of Na_2SO_3, and dichloromethane. The aqueous phase was extracted several times with small portions of dichloromethane, and the combined organic phases were washed with brine and dried with anhydrous sodium sulfate, and the solvents were removed *in vacuo*. The residue was chromatographed on silica gel (*n*-hexane/ethyl acetate 30:1 to 10:1) to give 1.04 g (55%) of compound **1e** as a yellow viscous oil. ^{1}H NMR (500 MHz, acetone-d_6): δ 0.88 (t, J = 6.9 Hz, 6 H), 1.16−1.49 (m, 40 H), 1.96−2.03 (m, 1 H), 4.02 (d, J = 7.3 Hz, 2 H), 7.26 (d, J = 8.6 Hz, 1 H), 7.28 (d, J = 8.5 Hz, 1 H), 7.54 (d, J = 1.9 Hz, 1 H), 7.62 (dd, J = 1.9, 8.5 Hz, 1 H), 7.67 (d, J = 1.9 Hz, 1 H), 7.79 (dd, J = 1.9, 8.4 Hz, 1 H), 9.88 (s, 1 H).^{13}C NMR (125.5 MHz, acetone-d_6): δ 14.5 (two CH_3), 23.4 (two

dx.doi.org/10.1021/jo202608w | J. Org. Chem. 2012, 77, 3704−3715

Table 4. Experimental Details of the Suzuki Cross-Coupling Reaction (GP1)

pinacolylboronate [g] (mmol)	**1c** [g] (mmol)	K_2CO_3 [g] (mmol)	$Pd(PPh_3)_4$ [mg] (μmol)	product [g] (%)
p-tolyl-pinacolyl boronate 0.31 (1.40)	0.60 (1.54)	1.39 (10.1)	49 (42)	0.51 (90) of **1f**
10-hexyl-phenothiazine-3-pinacolyl boronate 0.51 (1.25)	0.54 (1.38)	1.24 (9.00)	43 (38)	0.66 (89) of **1g**

Table 5. Experimental Details of the Buchwald-Hartwig Cross-Coupling Reaction (GP2)

1d [g] (mmol)	amine [g] (mmol)	$NaOC(CH_3)_3$ [g] (mmol)	$[(t\text{-}Bu)_3PH]BF_4$ [mg] (mmol)	$Pd(dba)_2$ [mg] (mmol)	product [g] (%)
2.00 (3.11)	phenothiazine 0.71 (3.60)	0.42 (4.35)	90 (0.31)	90 (0.15)	0.52 (22) of **1h**
1.72 (2.68)	carbazole 0.52 (3.08)	0.36 (3.75)	80 (0.27)	80 (0.14)	0.55 (28) of **1i**

CH_2), 26.7 (two CH_2), 30.2 (three CH_2), 30.35 (CH_2), 30.36 (CH_2), 30.39 (CH_2), 30.41 (CH_2), 30.45 (CH_2), 30.46 (CH_2), 30.49 (CH_2), 30.6 (two CH_2), 31.9 (two CH_2), 32.7 (two CH_2), 35.5 (CH), 52.7 (CH_2), 107.5 (C_{quat}), 118.1 (CH), 118.4 (CH), 118.9 (C_{quat}), 125.8 (C_{quat}), 126.8 (C_{quat}), 129.2 (CH), 131.0 (CH), 131.5 (CH), 133.1 (CH), 133.6 (C_{quat}), 149.5 (C_{quat}), 150.6 (C_{quat}), 190.6 (CH). MALDI-TOF MS m/z = 588.36. UV/vis λ_{max} (ε) [nm] = 248 (11000), 258 (11000), 283 (37000), 384 (7000), 299 (14000). IR (film): $\tilde{\nu}$ [cm^{-1}] = 2926 (m), 2854 (m), 2723 (w), 2226 (m), 1896 (w), 1694 (m), 1602 (m), 1578 (m), 1464 (s), 1375 (w), 1341 (w), 1283 (w), 1197 (s), 1100 (m), 884 (w), 820 (m), 723 (m), 592 (w), 526 (w). Anal. Calcd. for $C_{38}H_{56}N_2OS$ (588.9): C 77.50, H 9.58, N 4.76. Found: C 77.21, H 9.64, N 4.72.

General Procedure for the Suzuki Cross-Coupling Reaction (GP1). Under a nitrogen atmosphere, 1.0 equiv of the pinacolylboronic ester and 7.2 equiv of K_2CO_3 were dissolved in 9 mL of a mixture (2:1) of dimethoxyethane and distilled water (for experimental details, see Table 4). The solution was degassed with nitrogen for 20 min. Then, 1.1 equiv of 7-bromo-10-hexyl-10*H*-phenothiazine-3-carbaldehyde (**1c**) and 3 mol % of $Pd(PPh_3)_4$ were added and the reaction mixture was stirred at 95 °C for 10 h. After cooling to room temperature, the solution was diluted with deionized water, a saturated aqueous solution of Na_2SO_3, and dichloromethane. The aqueous phase was extracted several times with small portions of dichloromethane, the combined organic phases were washed with brine and dried with anhydrous sodium sulfate, and the solvents were removed *in vacuo*. The residue was chromatographed on silica gel to give the aldehydes **1f** and **1g** as yellow resins.

*10-Hexyl-7-p-tolyl-10H-phenothiazine-3-carbaldehyde (**1f**).* According to GP1 and flash chromatography on silica gel (*n*-hexane/acetone 50:1), 0.51 g (90%) of compound **1f** were obtained as a yellow highly viscous resin. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 0.88−0.94 (m, 3 H), 1.30−1.36 (m, 4 H), 1.41−1.48 (m, 2 H), 1.76−1.83 (m, 2 H), 2.38 (s, 3 H), 3.85 (t, J = 7.3 Hz, 2 H), 6.88 (d, J = 8.5 Hz, 1 H), 6.90 (d, J = 8.5 Hz, 1 H), 7.23 (d, J = 8.1 Hz, 2 H), 7.32 (d, J = 2.0 Hz, 1 H), 7.38 (dd, J = 2.0, 8.4 Hz, 1 H), 7.42 (d, J = 8.0 Hz, 2 H), 7.54 (d, J = 1.6 Hz, 1 H), 7.60 (dd, J = 1.6, 8.4 Hz, 1 H), 9.76 (s, 1 H). ^{13}C NMR (125.5 MHz, CD_2Cl_2): δ 14.4 (CH_3), 21.4 (CH_3), 23.2 (CH_2), 27.0 (CH_2), 27.1 (CH_2), 31.9 (CH_2), 48.5 (CH_2), 115.2 (CH), 116.4 (CH), 124.4 (C_{quat}), 124.8 (C_{quat}), 125.8 (CH), 126.3 (CH), 126.7 (two CH), 128.4 (CH), 130.1 (two CH), 130.7 (CH), 131.6 (C_{quat}), 136.8 (C_{quat}), 137.0 (C_{quat}), 137.6 (C_{quat}), 142.8 (C_{quat}), 150.8 (C_{quat}), 190.2 (CH). UV/vis λ_{max} (ε) [nm] = 260 (24000), 289 (41000), 395 (9000). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2925 (m), 2854 (m), 2346 (w), 1686 (s), 1579 (s), 1467 (s), 1244 (m), 1197 (m), 883 (w), 804 (m), 737 (w). ESI HR MS calcd. for ($C_{26}H_{27}NOSNa$) m/z = 424.1706. Found: 424.1703.

*10,10′-Dihexyl-10H,10H′-3,3′-bisphenothiazine-7-carbaldehyde (**1g**).* According to the GP1 and flash chromatography on silica gel (*n*-hexane/acetone 50:1) 0.66 g (89%) of compound **1g** were obtained as a yellow highly viscous resin. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 0.88 (t, J = 6.9 Hz, 3 H), 0.89 (t, J = 7.0 Hz, 3 H), 1.28−1.38 (m, 8 H), 1.39−1.50 (m, 4 H), 1.74−1.86 (m, 4 H), 3.85 (t, J = 7.2 Hz, 2 H), 3.90 (t, J = 7.3 Hz, 2 H), 6.87−6.95 (m, 5 H), 7.12 (dd, J = 1.4, 7.6 Hz, 1 H), 7.14 - 7.19 (m, 1 H), 7.29 (dd, J = 2.1, 8.1 Hz, 2 H), 7.33 (dd, J = 2.4, 5.7 Hz, 1 H), 7.34 (dd, J = 2.3, 5.6 Hz, 1 H), 7.56 (d, J = 1.9 Hz, 1 H), 7.63 (dd, J = 1.9, 8.4 Hz, 1 H), 9.77 (s, 1 H). ^{13}C NMR (125.5 MHz, CD_2Cl_2): δ 14.30 (CH_3), 14.32 (CH_3), 23.15 (CH_2), 23.17 (CH_2), 27.0 (CH_2), 27.1 (CH_2), 27.2 (CH_2), 27.3 (CH_2), 31.9 (CH_2), 32.0 (CH_2), 48.0 (CH_2), 48.6 (CH_2), 115.3 (CH), 116.0 (CH), 116.1 (CH), 116.7 (CH), 122.9 (CH), 124.5 (C_{quat}), 124.7 (C_{quat}), 124.9 (C_{quat}), 125.4 (CH), 125.5 (CH), 125.7 (CH), 125.9 (CH), 127.8 (CH), 127.9 (CH), 128.5 (CH), 130.7 (CH), 131.7 (C_{quat}), 134.1 (C_{quat}), 135.8 (C_{quat}), 142.8 (C_{quat}), 142.9 (C_{quat}), 145.1 (C_{quat}), 145.6 (C_{quat}), 150.9 (C_{quat}), 190.3 (CH). MALDI-TOF MS m/z = 592.2. UV/vis λ_{max} (ε) [nm] = 289 (48000), 399 (12000). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2924 (m), 2825 (m), 1686 (s), 1602 (m), 1578 (m), 1459 (s), 1414 (m), 1376 (m), 1333 (m), 1242 (s), 1196 (s), 873 (w), 806 (m), 745 (m). Anal. Calcd. for $C_{37}H_{40}N_2OS_2$ (592.9): C 74.96, H 6.80, N 4.73. Found: C 74.94, H 7.08, N 4.65.

General Procedure for the Buchwald-Hartwig Cross-Coupling Reaction (GP2). Under a nitrogen atmosphere, 1.0 equiv of 7-bromo-10-(2-decyltetradecyl)-10*H*-phenothiazine-3-carbaldehyde (**1d**), 1.15 equiv of the amine, 1.4 equiv of sodium *tert*-butoxide, 0.10 equiv of tris-*tert*-butylphosphonium tetrafluoroborate and 0.05 equiv of bis(dibenzylidene acetone)palladium(0) were dissolved in 4 mL of dry 1,4-dioxane (for experimental details, see Table 5). Then, the reaction mixture was stirred at 110 °C for 26 h. After cooling to room temperature, the solution was diluted with deionized water, a saturated aqueous solution of Na_2SO_3, and dichloromethane. The aqueous phase was extracted several times with small portions of dichloromethane, the combined organic phases were washed with brine, dried with anhydrous sodium sulfate, and the solvents were removed *in vacuo*. The residue was chromatographed on silica gel to give the products **1h** and **1i** as resins.

*10-(2-Decyltetradecyl)-10H-[3,10′-biphenothiazine]-7-carbaldehyde (**1h**).* According to the GP2 and flash chromatography on silica gel (*n*-hexane/diethylether 20:1), 0.52 g (22%) of compound **1h** were obtained as a yellow highly viscous resin. ^{1}H NMR (300 MHz, acetone-d_6): δ 0.86 (t, J = 7.0 Hz, 3 H), 0.87 (t, J = 7.0 Hz, 3 H), 1.15−1.53 (m, 40 H), 2.07−2.15 (m, 1 H), 4.04 (d, J = 7.2 Hz, 2 H), 6.25−6.30 (m, 2 H), 6.72−6.92 (m, 4 H), 6.99−7.04 (m, 2 H), 7.23−7.30 (m, 3 H), 7.38 (d, J = 8.5 Hz, 1 H), 7.67 (d, J = 1.9 Hz, 1 H), 7.79 (dd, J = 1.9, 8.4 Hz, 1 H), 9.84 (s, 1 H). ^{13}C NMR (75 MHz, acetone-d_6): δ 14.4 (two CH_3), 23.4 (two CH_2), 26.78 (CH_2), 26.81 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 29.6 (CH_2), 29.8 (CH_2), 30.1 (CH_2), 30.16 (CH_2), 30.18 (CH_2), 30.35 (two CH_2), 30.41 (CH_2), 30.6 (CH_2), 32.02 (CH_2), 32.04 (two CH_2), 32.7 (two CH_2), 35.4 (CH), 52.6 (CH_2), 117.0 (two CH), 117.4 (CH), 119.7 (CH), 121.0 (two C_{quat}), 123.5 (two CH), 126.2 (C_{quat}), 127.5 (CH), 127.95 (two CH), 128.0 (C_{quat}), 129.1 (CH), 130.3 (CH), 130.8 (CH), 131.0 (CH), 132.9 (C_{quat}), 137.2 (C_{quat}), 145.0 (two C_{quat}), 145.2 (C_{quat}), 151.7 (C_{quat}), 190.5 (CH). MALDI-TOF MS m/z = 760.4. UV/vis λ_{max} (ε) [nm] = 258 (48000), 277 (44000), 382 (12000). IR (film): $\tilde{\nu}$ [cm^{-1}] = 2920 (s), 2851 (m), 2722 (w), 1690 (s), 1591 (m), 1574 (w), 1497 (w), 1460 (s), 1443 (s), 1402 (w), 1373 (w), 1337 (w), 1306 (m), 1267 (m), 1236 (m), 1198 (m), 1153 (w), 1128 (w), 1098 (w), 1082 (w), 1043 (w), 995 (w), 957 (w), 922 (w), 897 (w), 881 (w), 820 (m), 741 (s), 717 (m), 703 (w), 687 (w), 635 (m), 617 (w). Anal. Calcd. for $C_{49}H_{64}N_2OS_2$ (760.5): C 77.32, H 8.47, N 3.68. Found: C 77.01, H 8.56, N 3.51.

*7-(9H-Carbazol-9-yl)-10-(2-decyltetradecyl)-10H-phenothiazine-carbaldehyde (**1i**).* According to the GP2 and flash chromatography on silica gel (*n*-hexane/diethylether 20:1), 0.55 g (28%) of compound

dx.doi.org/10.1021/jo202608w | J. Org. Chem. 2012, 77, 3704−3715

1i were obtained as a yellow highly viscous resin. ^{1}H NMR (300 MHz, acetone-d_6): δ 0.79−0.90 (m, 6 H), 1.15−1.50 (m, 40 H), 2.07−2.13 (m, 1 H), 3.98 (d, J = 7.1 Hz, 2 H), 7.18 (d, J = 8.4 Hz, 1 H), 7.23−7.45 (m, 9 H), 7.66 (d, J = 1.8 Hz, 1 H), 7.72 (dd, J = 1.8, 8.4 Hz, 1 H), 8.19 (d, J = 7.7 Hz, 2 H), 9.83 (s, 1 H). ^{13}C NMR (75 MHz, acetone-d_6): δ 14.4 (two CH_3), 23.3 (two CH_2), 26.75 (CH_2), 26.78 (CH_2), 30.1 (CH_2), 30.16 (CH_2), 30.18 (CH_2), 30.3 (CH_2), 30.36 (two CH_2), 30.38 (two CH_2), 30.42 (two CH_2), 30.60 (CH_2), 30.62 (CH_2), 31.98 (CH_2), 32.00 (CH_2), 32.62 (CH_2), 32.64 (CH_2), 35.3 (CH), 52.5 (CH_2), 110.5 (two CH), 117.2 (CH), 118.9 (CH), 120.7 (two CH), 121.1 (two CH), 124.1 (two C_{quat}), 126.1 (C_{quat}), 126.6 (CH), 126.9 (two CH), 127.2 (CH), 127.3 (C_{quat}), 129.0 (CH), 130.8 (CH), 132.8 (C_{quat}), 133.8 (C_{quat}), 141.7 (two C_{quat}), 144.4 (C_{quat}), 151.7 (C_{quat}), 190.4 (CH). MALDI-TOF MS m/z = 728.4. UV/vis λ_{max} (ε) [nm] = 282 (46000), 293 (44000), 328 (13000), 341 (13000), 386 (12000). IR (film): $\tilde{\nu}$ [cm^{-1}] = 3055 (w), 2922 (s), 2851 (m), 2722 (w), 1690 (s), 1599 (m), 1580 (m), 1557 (w), 1503 (m), 1464 (s), 1452 (s), 1412 (m), 1373 (m), 1333 (m), 1312 (m), 1273 (m), 1228 (s), 1198 (s), 1148 (m), 1119 (w), 1098 (w), 1026 (w), 1016 (w), 1003 (w), 970 (w), 918 (m), 897 (m), 881 (m), 818 (m), 748 (s), 723 (s), 685 (m), 642 (m), 615 (m). Anal. Calcd. for $C_{49}H_{64}N_2OS$ (729.1): C 80.72, H 8.85, N 3.84. Found: C 80.49, H 8.94, N 3.83.

*10-(2-Decyltetradecyl)-7-(pyrrolidin-1-yl)-10H-phenothiazine-3-carbaldehyde (**1j**).* Under a nitrogen atmosphere 7-bromo-10-(2-decyltetradecyl)-10*H*-phenothiazine-3-carbaldehyde (**1d**) (1.53 g, 2.38 mmol) pyrrolidine (0.60 mL, 7.14 mmol), potassium carbonate (0.66 g, 4.76 mmol), copper(I)iodide (0.03 g, 0.24 mmol), and *L*-proline (0.09 g, 0.48 mmol) were dissolved in 3 mL of dry DMSO. After 20 h at 100 °C, pyrrolidine (0.30 mL, 3.57 mmol), potassium carbonate (0.33 g, 2.38 mmol), copper(I)iodide (0.02 g, 0.16 mmol), and L-proline (0.03 g, 0.16 mmol) were added, and the brown reaction mixture was stirred for 24 h at 100 °C. After cooling to room temperature, the solution was diluted with deionized water, a saturated aqueous solution of Na_2SO_3, and dichloromethane. The aqueous phase was extracted several times with small portions of dichloromethane, the combined organic phases were washed with brine and dried with anhydrous sodium sulfate, and the solvents were removed *in vacuo*. The residue was chromatographed on silica gel (*n*-hexane/diethylether 20:1 to *n*-hexane/diethylether 10:1) to give 0.61 g (41%) of compound **1j** as an orange highly viscous resin. ^{1}H NMR (300 MHz, acetone-d_6): δ 0.85−0.91 (m, 6 H), 1.19−1.46 (m, 40 H), 1.93−2.02 (m, 5 H), 3.21 (t, J = 6.5 Hz, 4 H), 3.85 (d, J = 7.2 Hz, 2 H), 6.36 (d, J = 2.7 Hz, 1 H), 6.41 (dd, J = 2.7, 8.8 Hz, 1 H), 6.92 (d, J = 8.8 Hz, 1 H), 7.06 (d, J = 8.5 Hz, 1 H), 7.57 (d, J = 1.9 Hz, 1 H), 7.66 (dd, J = 1.9, 8.4 Hz, 1 H), 9.76 (s, 1 H). ^{13}C NMR (75 MHz, acetone-d_6): δ 14.4 (two CH_3), 23.4 (two CH_2), 26.0 (two CH_2), 26.8 (two CH_2), 30.12 (two CH_2), 30.14 (two CH_2), 30.35 (two CH_2), 30.37 (CH_2), 30.41 (two CH_2), 30.5 (CH_2), 30.6 (two CH_2), 32.0 (two CH_2), 32.7 (two CH_2), 35.5 (CH), 48.4 (two CH_2), 52.3 (CH_2), 110.9 (CH), 111.5 (CH), 115.9 (CH), 118.7 (CH), 126.0 (C_{quat}), 126.5 (C_{quat}), 128.6 (CH), 130.7 (CH), 131.4 (C_{quat}), 133.2 (C_{quat}), 146.1 (C_{quat}), 153.2 (C_{quat}), 190.1 (CH). MALDI-TOF MS m/z = 632.3. UV/vis λ_{max} (ε) [nm] = 268 (12000), 352 (5000), 422 (5000). IR (film): $\tilde{\nu}$ [cm^{-1}] = 2920 (s), 2851 (s), 2718 (w), 1686 (s), 1607 (m), 1584 (m), 1551 (w), 1508 (s), 1474 (s), 1460 (s), 1422 (m), 1368 (m), 1342 (m), 1309 (m), 1298 (m), 1275 (m), 1244 (s), 1196 (s), 1167 (m), 1146 (m), 1103 (m), 1055 (w), 987 (m), 918 (w), 897 (w), 880 (w), 812 (m), 793 (m), 745 (m), 721 (m), 709 (m), 685 (w), 648 (w), 625 (w). Anal. Calcd. for $C_{41}H_{64}N_2OS$ (633.0): C 77.79, H 10.19, N 4.43. Found: C 77.96, H 10.44, N 4.21.

General Procedure for the Knoevenagel-Condensation Reaction (GP3). A mixture of 1.0 equiv of the phenothiazinyl carbaldehydes **1**, 1.0 equiv of ammonium acetate, and 1.1 equiv of rhodanine-*N*-acetic acid at a 0.5 m concentration of glacial acetic acid was stirred at 95 °C for 5 h (for experimental details, see Table 6). After cooling to room temperature, the solution was diluted with deionized water, a saturated aqueous solution of Na_2SO_3, and dichloromethane. The aqueous phase was extracted several times with small portions of dichloromethane, the combined organic phases were washed with brine, dried with sodium sulfate, and the solvents were removed *in vacuo*. The residue was chromatographed on silica gel to give the products **2** as red to violet solids.

Table 6. Experimental Details of the Knoevenagel-Condensation Reaction (GP3)

aldehyde **1** [g] (mmol)	rhodanine *N*-acetic acid [g] (mmol)	ammonium acetate [mg] (mmol)	acetic acid [mL]	dye **2** [g] (%)
1.130 (2.000) of **1b**	0.420 (2.200)	154 (2.00)	4.0	1.402 (95) of **2a**
1.240 (1.920) of **1d**	0.404 (2.113)	148 (1.92)	4.0	1.473 (94) of **2b**
1.060 (1.800) of **1e**	0.379 (1.980)	139 (1.80)	3.5	1.262 (92) of **2c**
0.246 (0.613) of **1f**	0.128 (0.674)	47 (0.61)	1.2	0.235 (67) of **2d**
0.751 (0.634) of **1g**	0.133 (0.697)	49 (0.63)	1.3	0.330 (68) of **2e**
0.540 (0.710) of **1h**	0.149 (0.781)	55 (0.71)	1.4	0.623 (94) of **2f**
0.511 (0.702) of **1i**	0.147 (0.772)	54 (0.70)	1.4	0.575 (91) of **2g**
0.490 (0.774) of **1j**	0.163 (0.851)	60 (0.77)	1.5	0.512 (82) of **2h**

*(Z)-2-(5-((10-(2-Decyltetradecyl)-10H-phenothiazine-3-yl)-methylene)-4-oxo-2-thioxothiazolidine-3-yl)acetic Acid (**2a**).* According to the GP3 and flash chromatography on silica gel (dichloromethane to dichloromethane/methanol/acetic acid 87:12:1), 1.402 g (95%) of compound **2a** were obtained as a red solid; mp 73−79 °C. ^{1}H NMR (500 MHz, DMSO-d_6/CS_2 1:1): δ 0.89 (m, 6 H), 1.17−1.44 (m, 40 H), 1.86−1.95 (m, 1 H), 3.83 (d, J = 7.1 Hz, 2 H), 4.69 (s, 2 H), 6.98 (dt, J = 0.9, 7.4 Hz, 1 H), 7.02 (d, J = 8.0 Hz, 1 H), 7.10 (d, J = 8.7 Hz, 1 H), 7.13 (dd, J = 1.4, 7.7 Hz, 1 H), 7.19 (dt, J = 1.4, 7.7 Hz, 1 H), 7.37 (d, J = 2.1 Hz, 1 H), 7.46 (dd, J = 2.1, 8.6 Hz, 1 H), 7.74 (s, 1 H). ^{13}C NMR (125.5 MHz, DMSO-d_6/CS_2 1:1): δ 14.0 (two CH_3), 22.4 (two CH_2), 25.7 (two CH_2), 28.99 (CH_2), 29.00 (CH_2), 29.05 (CH_2), 29.06 (CH_2), 29.21 (CH_2), 29.23 (CH_2), 29.26 (CH_2), 29.29 (two CH_2), 29.31 (CH_2), 29.57 (CH_2), 29.58 (CH_2), 30.8 (two CH_2), 31.6 (two CH_2), 34.2 (CH), 44.9 (CH_2), 51.0 (CH_2), 116.4 (CH), 116.7 (CH), 118.8 (C_{quat}), 123.3 (CH), 123.6 (C_{quat}), 125.4 (C_{quat}), 127.1 (C_{quat}), 127.2 (CH), 127.5 (CH), 129.3 (CH), 130.7 (CH), 132.8 (CH), 143.5 (C_{quat}), 147.8 (C_{quat}), 166.1 (C_{quat}), 167.0 (C_{quat}), 192.1 (C_{quat}). MALDI-TOF MS m/z = 736.34. UV/vis λ_{max} (ε) [nm] = 252 (18000), 305 (14000), 366 (14000), 478 (20000). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2923 (s), 2825 (s), 1707 (m), 1585 (s), 1561 (m), 1492 (m), 1459 (s), 1403 (m), 1329 (s), 1270 (m), 1196 (s), 1108 (m), 1056 (m), 806 (w), 752 (w), 581 (w). ESI HRMS calcd. for $C_{42}H_{60}N_2O_3S_3$: 736.37661. Found: 736.37764.

*(Z)-2-(5-((7-Bromo-10-(2-decyltetradecyl)-10H-phenothiazine-3-yl)-methylene)-4-oxo-2-thioxothiazolidine-3-yl)acetic Acid (**2b**).* According to the GP3 and flash chromatography on silica gel (dichloromethane to dichloromethane/methanol/acetic acid 87:12:1), 1.473 g (94%) of compound (**2b**) were obtained as red solid; mp 97−102 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ 0.87 (t, J = 6.9 Hz, 3 H), 0.88 (t, J = 6.9 Hz, 3 H), 1.13−1.48 (m, 40 H), 1.91−2.02 (m, 1 H), 3.89 (d, J = 7.1 Hz, 2 H), 4.87 (s, 2 H), 7.02 (d, J = 8.7 Hz, 1 H), 7.18 (d, J = 8.6 Hz, 1 H), 7.30 (d, J = 2.2 Hz, 1 H), 7.34 (d, J = 2.2 Hz, 1 H), 7.37 (dd, J = 2.1, 8.7 Hz, 1 H), 7.47 (dd, J = 2.2, 8.6 Hz, 1 H), 7.66 (s, 1 H).^{13}C NMR (75 MHz, acetone-d_6): δ 14.4 (two CH_3), 23.4 (two CH_2), 26.7 (two CH_2), 30.1 (four CH_2), 30.32 (CH_2), 30.34 (CH_2), 30.38 (CH_2), 30.42 (two CH_2), 30.45 (CH_2), 30.59 (CH_2), 30.60 (CH_2), 31.93 (two CH_2), 32.68 (two CH_2), 35.4 (CH), 45.4 (CH_2), 52.4 (CH_2), 116.0 (C_{quat}), 117.8 (CH), 119.3 (CH), 120.7 (C_{quat}), 126.3 (C_{quat}), 127.7 (C_{quat}), 128.7 (C_{quat}), 130.4 (CH), 130.5 (CH), 131.3 (CH), 131.8 (CH), 133.4 (CH), 144.5 (C_{quat}), 148.8 (C_{quat}), 167.4 (C_{quat}), 167.4 (C_{quat}), 193.8 (C_{quat}). MALDI-TOF MS m/z = 814.3. UV/vis λ_{max} (ε) [nm] = 256 (28000), 297 (20000), 361 (21000), 473 (29000). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2923 (s), 2852 (s), 1702 (m), 1588 (s), 1589 (s), 1492 (m), 1460 (s), 1403 (m), 1329 (s),

dx.doi.org/10.1021/jo202608w | J. Org. Chem. 2012, 77, 3704−3715

1251 (m), 1196 (s), 1111 (m), 1056 (m), 744 (m), 628 (w), 538 (w). Anal. Calcd. for $C_{42}H_{59}BrN_2O_3S_3$ (816.0): C 61.82, H 7.29, N 3.43. Found: C 61.94, H 7.45, N 3.38.

*(Z)-2-(5-((7-Cyano-10-(2-decyltetradecyl)-10H-phenothiazine-3-yl)-methylene)-4-oxo-2-thioxothiazolidine-3-yl)acetic Acid (**2c**).* According to the GP3 and flash chromatography on silica gel (dichloromethane to dichloromethane/methanol/acetic acid 87:12:1) 1.262 g (92%) of compound (**2c**) was obtained as a red solid; mp 92−97 °C. ^{1}H NMR (500 MHz, acetone-d_6/CS_2 4:1): δ 0.79−0.93 (m, 6 H), 1.12−1.41 (m, 40 H), 1.80−1.88 (m, 1 H), 3.87 (d, J = 6.7 Hz, 2 H), 4.61 (s, 2 H), 7.18 (d, J = 8.4 Hz, 1 H), 7.20 (d, J = 8.4 Hz, 1 H), 7.39 (d, J = 1.7 Hz, 1 H), 7.48 (dd, J = 1.6, 8.6 Hz, 1H), 7.56 (d, J = 1.6 Hz, 1 H), 7.61 (dd, J = 1.6, 8.5 Hz, 1H), 7.72 (s, 1 H).^{13}C NMR (75 MHz, acetone-d_6/CS_2 4:1): δ 15.0 (two CH_3), 23.8 (two CH_2), 27.00 (CH_2), 27.03 (CH_2), 30.39 (CH_2), 30.40 (CH_2), 30.5 (two CH_2), 30.65 (three CH_2), 30.69 (two CH_2), 30.72 (CH_2), 31.0 (two CH_2), 32.1 (two CH_2), 32.9 (two CH_2), 35.6 (CH), 39.9 (CH_2), 52.4 (CH_2), 107.4 ($C_{quat.}$), 117.3 (CH), 117.7 (CH), 118.4 (C_{quat}), 122.1 (C_{quat}), 125.9 (C_{quat}), 126.4 (C_{quat}), 129.3 (CH), 129.7 (C_{quat}), 130.2 (CH), 131.0 (CH), 131.3 (CH), 132.3 (CH), 146.6 (C_{quat}), 148.7 (C_{quat}), 167.0 (C_{quat}), 167.2 (C_{quat}), 192.2 (C_{quat}). MALDI-TOF MS m/z = 761.3. UV/vis λ_{max} (ε) [nm] = 265 (18000), 297 (21000), 363 (16000), 462 (22000). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2924 (s), 2852 (s), 2224 (m), 1707 (m), 1594 (m), 1572 (s), 1499 (w), 1461 (s), 1401 (m), 1329 (m), 1353 (m), 1196 (s), 1112 (m), 1055 (m), 885 (w), 817 (w), 719 (w), 581 (w). ESI HRMS calcd. for $C_{43}H_{59}N_3O_3S_3$: 761.37185. Found: 761.36752.

*(Z)-2-(5-((10-Hexyl-7-p-tolyl-10H-phenothiazine-3-yl)-methylene)-4-oxo-2-thioxothiazolidine-3-yl)acetic Acid (**2d**).* According to the GP3 and flash chromatography on silica gel (dichloromethane to dichloromethane/methanol 22:3) and crystallization (dichloromethane/*n*-hexane), 0.235 g (67%) of compound (**2d**) were obtained as violet crystals; mp 125 °C. ^{1}H NMR (500 MHz, THF-d_8): δ 0.88 (t, J = 6.8 Hz, 3 H), 1.25−1.40 (m, 4 H), 1.43−1.50 (m, 2 H), 1.82 (quint, J = 7.4 Hz, 2 H), 2.34 (s, 3 H), 3.96 (t, J = 7.1 Hz, 2 H), 4.79 (s, 2 H), 7.03 (d, J = 8.5 Hz, 1 H), 7.06 (d, J = 8.6 Hz, 1 H), 7.19 (d, J = 8.0 Hz, 2 H), 7.32 (d, J = 1.8 Hz, 1 H), 7.37 (d, J = 1.5 Hz, 1 H), 7.38−7.44 (m, 2 H), 7.46 (d, J = 8.0 Hz, 2 H), 7.65 (s, 1 H). ^{13}C NMR (125.5 MHz, THF-d_8): δ 14.5 (CH_3), 21.3 (CH_3), 23.7 (CH_2), 27.5 (CH_2), 27.8 (CH_2), 32.6 (CH_2), 45.4 (CH_2), 48.5 (CH_2), 116.6 (CH), 117.2 (CH), 120.8 (C_{quat}), 124.9 (C_{quat}), 126.0 (C_{quat}), 126.3 (CH), 126.7 (CH), 127.1 (two CH), 128.8 (C_{quat}), 130.4 (three CH), 131.5 (CH), 133.1 (CH), 137.4 (C_{quat}), 137.7 (C_{quat}), 137.8 (C_{quat}), 143.6 (C_{quat}), 148.5 (C_{quat}), 167.6 (C_{quat}), 167.7 (C_{quat}), 193.9 (C_{quat}). MALDI-TOF MS m/z = 574.1. UV/vis λ_{max} (ε) [nm] = 269 (29000), 303 (25000), 358 (19000), 471 (23000). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2924 (m), 1707 (m), 1655 (w), 1637 (w), 1572 (s), 1473 (s), 1404 (m), 1364 (m), 1323 (s), 1193 (s), 1107 (m), 1051 (m), 804 (m). ESI HRMS calcd. for $C_{31}H_{30}N_2O_3S_3$: 574.14185. Found: 574.13156.

*(Z)-2-(5-((10,10′-Dihexyl-10H,10′H-3,3′-biphenothiazine-7-yl)-methylene)-4-oxo-2-thioxothiazolidine-3yl)acetic Acid (**2e**).* According to the GP3 followed by flash chromatography on silica gel (dichloromethane to dichloromethane/methanol 22:3) and crystallization (dichloromethane/*n*-hexane) 0.330 g (68%) of compound (**2e**) was obtained as violet crystals; mp 198 °C. ^{1}H NMR (500 MHz, DMSO-d_6/CS_2 4:1): δ 0.83−1.00 (m, 6 H), 1.26−1.39 (m, 6 H), 1.39−1.55 (m, 6 H), 1.76 (quint, J = 7.2 Hz, 4 H), 3.88 (t, J = 7.0 Hz, 2 H), 3.91 (t, J = 7.1 Hz, 2 H), 4.55 (s, 2 H), 6.88−6.97 (m, 3 H), 6.99 (d, J = 8.6 Hz, 1 H), 7.05 (d, J = 8.7 Hz, 1 H), 7.08 (dd, J = 1.1, 7.6 Hz, 1 H), 7.13−7.19 (m, 1 H), 7.25−7.31 (m, 3 H), 7.35 (d, J = 1.8 Hz, 1 H), 7.37 (d, J = 1.7 Hz, 1 H), 7.43 (dd, J = 1.8, 8.6 Hz, 1H), 7.65 (s, 1 H). ^{13}C NMR (75 MHz, DMSO-d_6/CS_2 4:1): δ 13.9 (two CH_3), 22.3 (two CH_2), 25.9 (CH_2), 26.0 (CH_2), 26.2 (CH_2), 26.3 (CH_2), 31.0 (CH_2), 31.1 (CH_2), 45.4 (CH_2), 46.6 (CH_2), 47.0 (CH_2), 115.6 (CH), 115.8 (two CH), 116.4 (CH), 118.7 (C_{quat}), 122.4 (CH), 122.8 (C_{quat}), 123.3 (C_{quat}), 123.6 (C_{quat}), 124.2 (C_{quat}), 124.28 (C_{quat}), 124.30 (CH), 124.34 (CH), 125.1 (CH), 125.3 (CH), 126.9 (C_{quat}), 127.0 (CH), 127.5 (CH), 129.2 (CH), 131.0 (CH), 132.8 (CH), 134.2 (C_{quat}), 141.6 (C_{quat}), 143.8 (C_{quat}), 144.4 (C_{quat}), 146.7 (C_{quat}), 166.3 (C_{quat}), 167.3 (C_{quat}), 192.4 (C_{quat}). MALDI-TOF MS m/z = 765.22. UV/vis λ_{max} (ε) [nm] = 265 (36000), 307 (16000), 359 (24000), 503 (18000). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2923 (m), 2852 (m), 2346 (w), 1719 (m), 1561 (s), 1459 (s), 1400 (m), 1328 (m), 1246 (m), 1192 (s), 1105 (m), 802 (m), 745 (m). ESI HRMS calcd. for $C_{42}H_{43}N_3O_3S_4$: 765.21873. Found: 765.21937.

*(Z)-2-(5-((10-(2-Decyltetradecyl)-10H-3,10′biphenothiazine)-7-yl)-methylene)-4-oxo-2-thioxothiazolidine-3-yl)acetic Acid (**2f**).* According to the GP3 and flash chromatography on silica gel (dichloromethane to dichloromethane/methanol/acetic acid 87:12:1) 0.623 g (94%) of (**2f**) was obtained as a red solid; mp 83−88 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 0.83−0.89 (m, 6 H), 1.17−1.43 (m, 40 H), 2.06−2.13 (m, 1 H), 4.01 (d, J = 7.1 Hz, 2 H), 4.85 (s, 2 H), 6.27 (dd, J = 1.2, 8.1 Hz, 2 H), 6.78−6.89 (m, 4 H), 7.00 (dd, J = 1.7, 7.4 Hz, 2 H), 7.22−7.28 (m, 3 H), 7.34−7.39 (m, 2 H), 7.50 (dd, J = 2.1, 8.7 Hz, 1 H), 7.66 (s, 1 H). ^{13}C NMR (125.5 MHz, acetone-d_6): δ 14.4 (two CH_3), 23.4 (two CH_2), 26.78 (CH_2), 26.81 (CH_2), 30.1 (two CH_2), 30.17 (CH_2), 30.2 (CH_2), 30.35 (CH_2), 30.37 (CH_2), 30.40 (CH_2), 30.41 (CH_2), 30.44 (two CH_2), 30.60 (CH_2), 30.63 (CH_2), 32.01 (CH_2), 32.03 (CH_2), 32.66 (CH_2), 32.67 (CH_2), 35.4 (CH), 45.4 (CH_2), 52.5 (CH_2), 117.0 (two CH), 117.9 (CH), 119.6 (CH), 120.6 (C_{quat}), 120.9 (two C_{quat}), 123.5 (two CH), 126.6 (C_{quat}), 127.4 (two CH), 127.7 (C_{quat}), 127.9 (two CH), 128.8 (C_{quat}), 130.4 (CH), 130.5 (CH), 131.0 (CH), 131.8 (CH), 133.4 (CH), 137.1 (C_{quat}), 145.0 (two C_{quat}), 145.2 (C_{quat}), 148.8 (C_{quat}), 167.4 (C_{quat}), 167.5 (C_{quat}), 193.9 (C_{quat}). MALDI-TOF MS m/z = 933.3. UV/vis λ_{max} (ε) [nm] = 258 (62000), 300 (22000), 359 (19000), 472 (24000). IR: $\tilde{\nu}$ [cm^{-1}] = 2920 (s), 2851 (s), 1712 (s), 1587 (m), 1572 (s), 1460 (s), 1442 (s), 1400 (s), 1366 (m), 1323 (s), 1312 (s), 1302 (s), 1267 (s), 1236 (s), 1194 (s), 1111 (s), 1055 (s), 1045 (m), 983 (m), 957 (m), 922 (m), 908 (m), 864 (w), 816 (m), 741 (s), 718 (m), 634 (m). Anal. Calcd. for $C_{54}H_{67}N_3O_3S_4$ (934.4): C 69.41, H 7.23, N 4.50. Found: C 69.39; H 7.27; N 4.47.

*(Z)-2-(5-((7-(9H-Carbazol-9-yl)-10-(2-decyltetradecyl)-10H-phenothiazine-3-yl)-methylene)-4-oxo-2-thioxothiazolidine-3-yl)acetic Acid (**2g**).* According to the GP3 and flash chromatography on silica gel (dichloromethane to dichloromethane/methanol/acetic acid 87:12:1), 0.575 g (91%) of compound (**2g**) were obtained as a red solid; mp 79−85 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ 0.80−0.88 (m, 6 H), 1.14−1.51 (m, 40 H), 2.07−2.09 (m, 1 H), 3.92 (d, J = 7.1 Hz, 2 H), 4.85 (s, 2 H), 7.09 (d, J = 8.6 Hz, 1 H), 7.21−7.42 (m, 11 H), 7.60 (s, 1 H), 8.17 (d, J = 7.7 Hz, 2 H). ^{13}C NMR (75 MHz, acetone-d_6): δ 14.4 (two CH_3), 23.3 (two CH_2), 26.76 (CH_2), 26.80 (CH_2), 30.10 (CH_2), 30.11 (CH_2), 30.17 (CH_2), 30.20 (CH_2), 30.37 (CH_2), 30.39 (CH_2), 30.40 (two CH_2), 30.44 (two CH_2), 30.61 (CH_2), 30.63 (CH_2), 32.01 (CH_2), 32.03 (CH_2), 32.6 (CH_2), 32.7 (CH_2), 35.4 (CH), 45.4 (CH_2), 52.4 (CH_2), 110.5 (two CH), 117.7 (CH), 118.8 (CH), 120.5 (C_{quat}), 120.9 (two CH), 121.1 (two CH), 124.2 (two C_{quat}), 126.5 (C_{quat}), 126.6 (CH), 126.9 (two CH), 127.0 (C_{quat}), 127.1 (CH), 128.7 (C_{quat}), 130.5 (CH), 131.7 (CH), 133.4 (CH), 133.7 (C_{quat}), 141.7 (two C_{quat}), 144.4 (C_{quat}), 148.8 (C_{quat}), 167.4 (two C_{quat}), 193.9 (C_{quat}). MALDI-TOF MS m/z = 901.4. UV/vis λ_{max} (ε) [nm] = 294 (33000), 343 (17000), 363 (17000), 478 (22000). IR: $\tilde{\nu}$ [cm^{-1}] = 2920 (s), 2851 (m), 1711 (m), 1593 (m), 1572 (m), 1461 (s), 1400 (m), 1323 (s) 1323 (m), 1229 (m), 1193 (s), 1111 (m), 1056 (m), 912 (w), 813 (m), 746 (s), 723 (s). Anal. Calcd. for $C_{54}H_{67}N_3O_3S_3$ (902.3): C 71.88, H 7.48, N 4.66. Found: C 71.72, H 7.63, N 4.65.

*(Z)-2-(5-((10-(2-Decyltetradecyl)-7-(pyrrolidine-1-yl)-10H-phenothiazine-3-yl)-methylene)-4-oxo-2-thioxothiazolidine-3-yl)acetic Acid (**2h**).* According to the GP3 and flash chromatography on silica gel (dichloromethane to dichloromethane/methanol/acetic acid 87:12:1), 0.512 g (82%) of compound (**2h**) were obtained as a red solid; mp 78−83 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 0.90 (t, J = 6.9 Hz, 3 H), 0.91 (t, J = 6.9 Hz, 3 H), 1.16−1.43 (m, 40 H), 1.92−1.99 (m, 1 H), 2.02 (t, J = 6.4 Hz, 4 H), 3.26 (s, 4 H), 3.72 (d, J = 5.6 Hz, 2 H), 4.86 (s, 2 H), 6.36−6.44 (m, 2 H), 6.77 (d, J = 8.7 Hz, 1 H), 6.86 (d, J = 8.6 Hz, 1 H), 7.22 (s, 1 H), 7.30 (d, J = 7.6 Hz, 1 H), 7.62 (s, 1 H). ^{13}C NMR (125.5 MHz, CD_2Cl_2): δ 14.7 (two CH_2), 23.5 (two CH_2), 26.1 (two CH_2), 26.99 (CH_2), 27.01 (CH_2), 30.17 (CH_2), 30.18 (CH_2), 30.3 (two CH_2), 30.4 (two CH_2), 30.47 (two CH_2),

dx.doi.org/10.1021/jo202608w | J. Org. Chem. 2012, 77, 3704−3715

30.50 (two CH_2), 30.8 (two CH_2), 32.2 (two CH_2), 32.7 (two CH_2), 35.6 (CH), 45.0 (CH_2), 48.8 (two CH_2), 52.3 (CH_2), 111.4 (CH), 111.5 (CH), 115.9 (CH), 118.0 (CH), 118.8 (C_{quat}), 126.2 (C_{quat}), 126.5 (C_{quat}), 126.8 (C_{quat}), 130.1 (CH), 131.6 (CH), 133.4 (C_{quat}), 134.1 (CH), 145.4 (C_{quat}), 167.3 (C_{quat}), 167.4 (C_{quat}), 171.3 (C_{quat}), 192.9 (C_{quat}). MALDI-TOF MS m/z = 805.3. UV/vis λ_{max} (ε) [nm] = 271 (31000), 374 (22000), 536 (18000). IR: $\tilde{\nu}$ [cm^{-1}] = 2920 (s), 2851 (s), 1708 (m), 1595 (m), 1572 (s), 1508 (m), 1474 (s), 1458 (s), 1402 (m), 1363 (m), 1321 (s), 1298 (m), 1277 (m), 1251 (s), 1225 (s), 1190 (s), 1105 (s), 1053 (s), 986 (m), 957 (m), 903 (m), 874 (m), 795 (m), 743 (m), 722 (m), 690 (m), 661 (m), 619 (m). Anal. Calcd for $C_{46}H_{67}N_3O_3S_3$ (806.2): C 68.53, H 8.38, N 5.21. Found: C 68.35, H 8.30, N 5.12.

■ ASSOCIATED CONTENT

Supporting Information

Selected ^1H and ^{13}C NMR spectra of compounds **1b**, **1d**−**1j**, **2a**−**2h**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from Evonik Stiftung (stipend for T.M.) and the Fonds der Chemischen Industrie is gratefully acknowledged.

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