Dyes and Pigments 143 (2017) 308–316

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

3-Phenothiazinyl propiolates – Fluorescent electrophores by Sonogashira coupling of ethyl propiolate

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ARTICLE INFO

Article history:
Received 17 March 2017
Received in revised form
22 April 2017
Accepted 23 April 2017
Available online 27 April 2017

Keywords:
Alkynoates
Cross-coupling
Cyclic voltammetry
DFT calculations
Fluorescence
Phenothiazines
Redox systems
Solvatochromism

ABSTRACT

Fluorescent ethyl 3-phenothiazinyl propiolates with reversible Nernstian oxidation potentials were efficiently synthesized by an improved Sonogashira coupling of aryl iodides and ethyl propiolate. The versatility of this modified alkynylation was illustrated by 13 ethyl 3-arylpropiolates in mostly excellent yields with a broad substrate scope. In addition to reversible one-electron oxidations, the title compounds reveal large Stokes shifts, high fluorescence quantum yields, and solvatochromic emission. The photophysical characteristics were corroborated and rationalized by DFT and TD-DFT calculations.

1. Introduction

Phenothiazines bearing conjugated π-substituents in 3- and/or 7-position present interesting classes of functional chromophores [1] that are both luminescent and redox active [2]. In particular, alkynylated phenothiazines [3] have been employed to decorate gold [4] or zinc and iron surfaces [5] with functional reversible redox systems. These systems were readily accessible by Pd-catalyzed alkynylation reactions. However, for synthetic transformations and extended functionalizations, electrophilic three-carbon building blocks such as 3-aryl propiolates, which contain an ester moiety and a conjugated triple bond, are particularly desirable. In heterocycle syntheses, aryl propiolates are for instance particularly valuable as Michael systems [6] or as dienophiles. Most commonly, 3-aryl propiolates are synthesized by the reaction of alkynyl metal species with chloroformates [7]. This methodology, however, only has a limited substrate scope as many functional groups are incompatible with the strongly basic reaction conditions required for the metalation of terminal alkynes. Further limitations arise from the limited availability of the alkyne starting materials. In principle, Sonogashira coupling of aryl halides with alkyl propiolates as alkynyl partner circumvents these problems, thus considerably broadening functional group tolerance and substrate scope. However, electron-poor alkynes such as alkyl propiolates are often less reactive and tend to decompose or undergo self-condensation [8]. In the past years, several approaches have been published that address these issues e. g. by *in situ* generation of alkynylzinc [9] or lithium-indium [10] reagents or by replacement of the aryl halide component by diaryliodonium salts [11] or arylboronic esters [12] To the best of our knowledge, and to our surprise, no direct and general approach to aryl propiolates from aryl halides and alkyl propiolates has been reported to date [13]. We therefore set out to develop a straightforward Sonogashira coupling with ethyl propiolate, compensating its reduced reactivity and diminished stability by carefully adjusting the reaction conditions. In addition, we report the application of this improved methodology to the synthesis of 3-phenothiazinyl ethyl propiolates, interesting novel functional chromophores.

2. Results and discussion

2.1. Synthesis of ethyl aryl propiolates by Sonogashira coupling

For the coupling of aryl iodides **1** a quick screening of the

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http://dx.doi.org/10.1016/j.dyepig.2017.04.049
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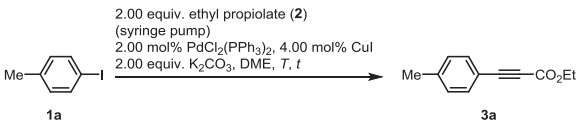
Table 1
Selected optimization reactions for the synthesis of ethyl *p*-tolylpropiolate **3a**.



entry	*T* [°C]	*t* [h]	remark	yield of **3a** (%)[a]
1	90	1		traces
2	40	16		88
3	40	20		96
4	40	20	10 mmol scale	94
5	40	20	without syringe pump	3

[a] Isolated yields after chromatography on silica gel.

stoichiometry, catalyst system, base, and solvent gave the use of 2 equivs of ethyl propiolate (**2**), catalytic amounts of $PdCl_2(PPh_3)_2$ and copper(I) iodide as well as 2 equivs of potassium carbonate in DME as most promising for further optimization studies. As we observed a rapid consumption of ethyl propiolate (**2**) during the course of the reaction, we reasoned that a low stationary concentration by a slow addition of **2** *via* a syringe pump should be beneficial for the coupling product formation. We chose the Sonogashira coupling of 4-iodotoluene (**1a**) with ethyl propiolate (**2**) to give ethyl *p*-tolyl propiolate (**3a**) as a model reaction (Table 1).

While an addition over the course of 1 h at 90 °C gave only traces of the desired product **3a** (Table 1, entry 1), we were delighted to find that decreasing the temperature to 40 °C with a prolonged addition over 16 h already resulted in a yield of 88% of **3a** (Table 1, entry 2). Extending the ethyl propiolate addition to 20 h finally resulted in complete conversion and nearly quantitative isolation of compound **3a** (Table 1, entry 3). The optimized reaction conditions could also be employed on a 10 mmol scale without any significant loss in isolated yield of compound **3a** (Table 1, entry 4). For comparison, the reaction was repeated under the optimized condition without the use of a syringe pump and upon adding the entire amount of ethyl propiolate (**2**) at the beginning of the reaction. This resulted in almost no conversion of **1a** with a drastically reduced yield of **3a** of only 3% (Table 1, entry 5).

With these optimized conditions in hand, we examined the scope of the reaction (Table 2).

To our delight, the functional group tolerance of the reaction proved to be excellent, giving high to nearly quantitative isolated yields for electron-rich (Table 2, entries 1, 4, and 6), electron-poor (Table 2, entries 3, 5, and 10) and sterically hindered substrates (Table 2, entries 6 and 8). The use of 4-iodopyridine (**1g**) resulted in full conversion of the substrate but the desired product **3g** was only isolated in moderate yield, presumably due to the propensity of **3g** for polymerization.

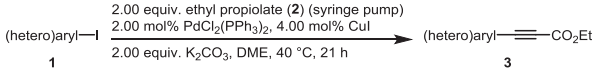
The reaction was additionally employed for the synthesis of phenothiazinyl propiolates, furnishing the desired products **3k** and **3l** in moderate to high yields. In the case of **3l**, the carbon-iodine bond of the bromo-iodo substrate (**1l**) could be selectively addressed, leaving the bromo functionality intact for possible further transformations. Using 3,7-diiodophenothiazine **1m**, phenothiazinyl bis(ethyl propiolate) **3m** was also accessible by double Sonogashira coupling (Scheme 1).

2.2. Photophysical properties of ethyl 3-phenothiazinyl propiolates

The synthesized ethyl phenothiazinyl propiolates **3k**–**m** are yellow in solution and show pronounced fluorescence upon irradiation with UV light (Fig. 1).

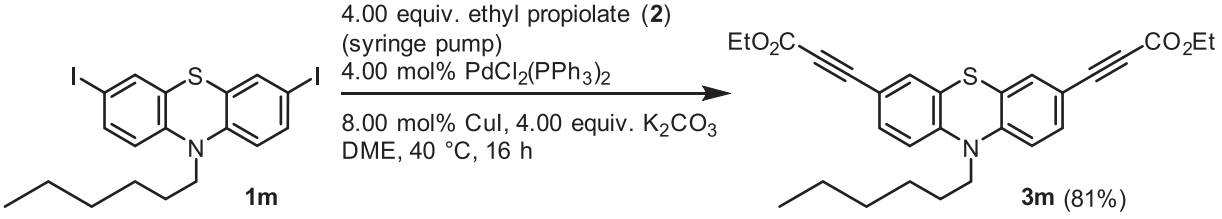
The photophysical properties of all three compounds were studied by absorption and emission spectroscopy in

Table 2
Synthesized ethyl aryl popiolates **3**.



entry	(hetero)aryl iodide 1	yield of propiolate **3** (%)
1	(hetero)aryl = 4-Tol (**1a**)	**3a** (97, 94[a])
2	(hetero)aryl = Ph (**1b**)	**3b** (86)
3	(hetero)aryl = 4-AcC_6H_4 (**1c**)	**3c** (88)
4	(hetero)aryl = 4-$MeOC_6H_4$ (**1d**)	**3d** (97)
5	(hetero)aryl = 4-$F_3CC_6H_4$ (**1e**)	**3e** (83)
6	(hetero)aryl = 2-$MeOC_6H_4$ (**1f**)	**3f** (83)
7	(hetero)aryl = 4-pyridyl (**1g**)	**3g** (50)
8	(hetero)aryl = 9-phenanthryl (**1h**)	**3h** (92)
9	(hetero)aryl = 2-naphthyl (**1i**)	**3i** (96)
10	(hetero)aryl = 3-ClC_6H_4 (**1j**)	**3j** (93)
11	(hetero)aryl = 10-hexyl-10*H*-phenothiazin-3-yl (**1k**)	**3k** (82)
12	(hetero)aryl = 7-brom-10-hexyl-10*H*-phenothiazin-3-yl (**1l**)	**3l** (68)

[a] Prepared on a 10.0 mmol scale.



Scheme 1. Synthesis of diethyl-3,3'-(10-hexyl-10*H*-phenothiazin-3,7-diyl)dipropiolate (**3m**).

Fig. 1. Fluorescence of phenothiazinyl propiolates **3k**–**l** (left to right, λ_{exc} = 365 nm, hand-held UV lamp).

dichloromethane solutions (Table 3).

All compounds show several absorption maxima (Fig. 2), two in the UV at 235–244 and 274–291 nm, respectively. The longest wavelength absorption band can be found between 366 nm (**3l**) and 391 nm (**3m**). For compound **3l**, an additional absorption maximum appears at 337 nm. The highest molar decadic extinction coefficient is found for compound **3m** at 291 nm (48500 $M^{-1}cm^{-1}$).

The emission maxima lie between 514 nm for dipropiolate **3m** and 526 nm for 7-unsubstituted compound **3k** (Fig. 2). This results in remarkably large Stokes shifts of 6100–7900 cm^{-1}, which can be explained to some extent by the push-pull-character of the acceptor-substituted phenothiazine chromophore. The introduction of a weakly electron-withdrawing bromo substituent (compound **3l**) or a second propiolic ester moiety (compound **3m**) in position 7 of the phenothiazine core mitigates this effect, causing a reduction of the Stokes shifts in comparison to compound **3k**. Relative fluorescence quantum yields were determined with coumarin 153 as a standard (Φ_f = 0.53 in ethanol) and show an inverse trend as quantum yields increase from 0.50 for parent compound **3k** over 0.61 for bromo compound **3l** to 0.66 for dipropiolate **3m**.

It is evident upon eyesight that the emission properties of the synthesized phenothiazinyl propiolates **3k**–**m** depend on the solvent system. We therefore performed a solvatochromism study, using ethyl 3-(10-hexyl-10*H*-phenothiazin-3-yl)-propiolate (**3k**) as a model system. With increasing solvent polarity, the emission is shifted bathochromically, ranging from blue fluorescence in cyclohexane to yellow-green fluorescence in *N*,*N*-dimethyl formamide (Fig. 3).

This positive emission solvochromicity was further studied by recording the absorption and emission spectra in the respective solvents (Fig. 4).

As the absorption band remains almost unchanged between 358 and 372 nm, only the absorption in dichloromethane is shown exemplarily. The emission band, however, shows a pronounced dependency on the solvent polarity, spanning a range from 465 nm in cyclohexane to 542 nm in *N*,*N*-dimethyl formamide (Table 4).

A Lippert plot [14] of the respective Stokes shifts $\Delta\tilde{\nu}$ against the orientation polarizabilities Δf of the solvent gives an excellent linear correlation with a fit of $r^2 = 0.95$ (Fig. 5).

Orientation polarizabilities were calculated according to equation (1) from the relative permittivity ε_r and the optical refractive

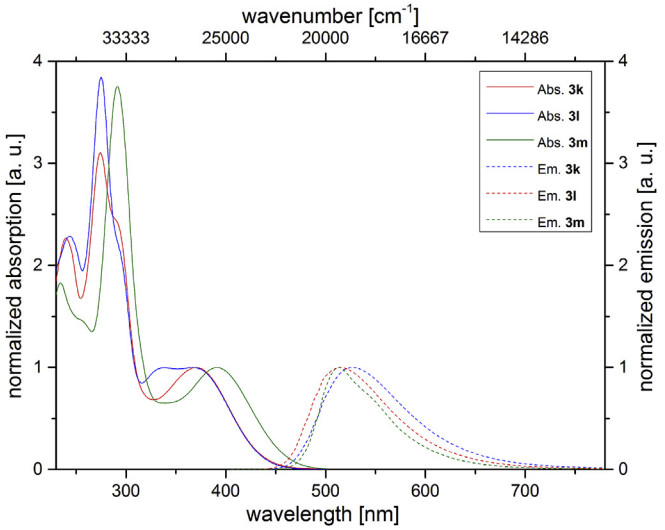


Fig. 2. UV/Vis absorption (solid lines) and emission (dashed lines) spectra of phenothiazinyl propiolates **3k**–**l**. Recorded in dichloromethane, T = 293 K.

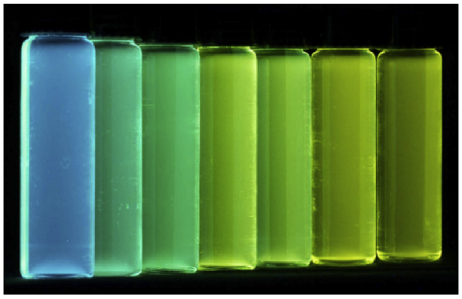
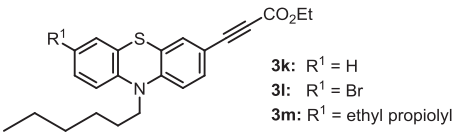


Fig. 3. Fluorescence of **3k** with variable solvent polarity (left to right: cyclohexane, toluene, ethyl acetate, dichloromethane, acetone, *N*,*N*-dimethyl formamide, acetonitrile; λ_{exc} = 365 nm, hand-held UV lamp).

Table 3
Photophysical properties of ethyl phenothiazinyl propiolates **3k**–**m**.



entry	compound	$\lambda_{max,abs}$ [nm] (ε [$M^{-1}cm^{-1}$])[a]	$\lambda_{max,em}$ [nm] (Φ_F)[b,c]	$\Delta\tilde{\nu}$ [cm^{-1}]
1	**3k**	240 (20400), 274 (28100), 371 (9000)	526 (0.50)	7900
2	**3l**	244 (18000), 275 (30300), 337 (7800), 366 (7900)	515 (0.61)	7500
3	**3m**	235 (23500), 291 (48500), 391 (12900)	514 (0.66)	6100

[a] Recorded in dichloromethane, T = 293 K, c(**3**) = 10^{-5} M.
[b] Recorded in dichloromethane, T = 293 K, c(**3**) = 10^{-7} M.
[c] Fluorescence quantum yields were determined relative to coumarin 153 (Φ_F = 0.53) as a standard in ethanol.

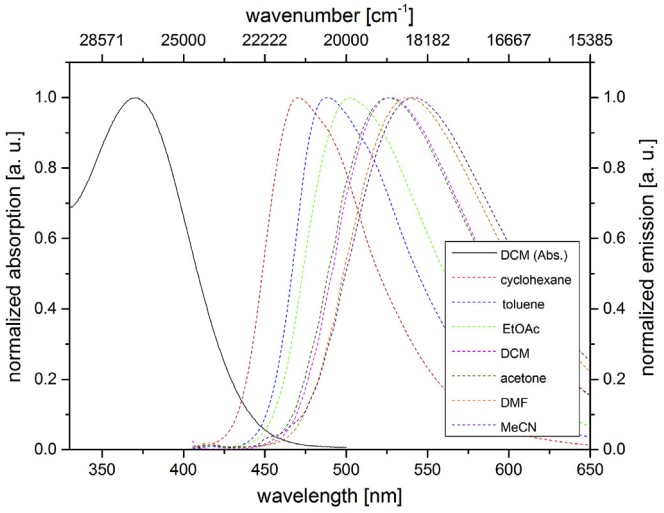


Fig. 4. UV/Vis absorption in dichloromethane (solid line) and emission (dashed lines) spectra in seven solvents of different polarity (recorded at $T = 293$ K).

index n of the respective solvent.

$$\Delta f = \frac{\varepsilon_r - 1}{2\varepsilon r + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (1)$$

The change in dipole moment from the ground to the vibrationally relaxed excited state can be calculated using SI units in the Lippert-Mataga equation (Equation (2))

$$\tilde{\nu}_a - \tilde{\nu}_f = \frac{2\Delta f}{4\pi\varepsilon 0hca^3}(\mu_E - \mu_G)^2 + const \quad (2)$$

where $\tilde{\nu}_a$ and $\tilde{\nu}_f$ represent the absorption and emission maxima (in m^{-1}), μ_E and μ_G are the dipole moments in the excited and ground state (in Cm), ε_0 ($8.8542 \cdot 10^{-12}$ $AsV^{-1}m^{-1}$) is the vacuum permittivity constant, h ($6.6256 \cdot 10^{-34}$ Js) is Planck's constant, c ($2.9979 \cdot 10^8$ ms^{-1}) is the speed of light and a is the radius of the solvent cavity occupied by the molecule (in m).

To estimate the radius of the solvent cavity, the Onsager radius was calculated by a DFT-level optimization of the ground-state structure of **3k** (*vide infra*), followed by a gas phase calculation of the molecular volume. Using a value of 5.6 Å ($5.6 \cdot 10^{-10}$ m), the change in dipole moment was calculated to $\Delta\mu = 11$ D ($3.74 \cdot 10^{-29}$ Cm), clearly indicating a charge transfer character of the involved electronic transition.

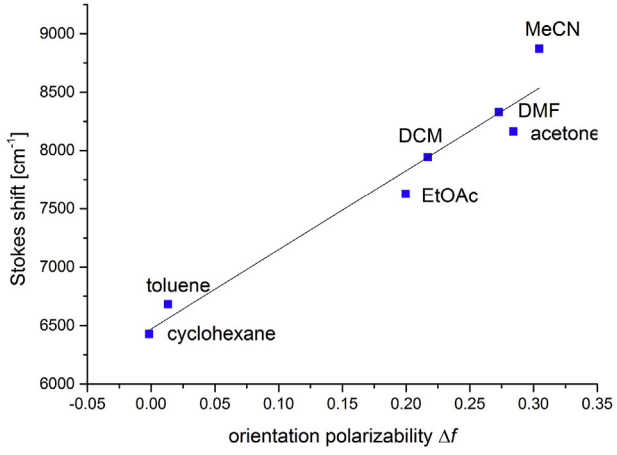


Fig. 5. Lippert plot for compound **3k** ($n = 7$, $r^2 = 0.95$).

Table 4
UV/Vis absorption and emission data for compound **3k** in seven solvents of different polarity.

entry	solvent	$\lambda_{max,abs}$ [nm][a]	$\lambda_{max,em}$ [nm][b]	$\Delta\tilde{\nu}$ [cm^{-1}]
1	cyclohexane	358	465	6400
2	toluene	368	488	6700
3	ethyl acetate	363	502	7600
4	dichloromethane	371	526	7900
5	acetone	369	527	8200
6	*N*,*N*-dimethyl formamide	372	539	8300
7	acetonitrile	366	542	8900

[a] Recorded at $T = 293$ K, c(**3k**) $= 10^{-5}$ M.
[b] Recorded at $T = 293$ K, c(**3k**) $= 10^{-7}$ M.

2.3. Computations of the electronic structure of ethyl 3-phenothiazinyl propiolates

The geometries of the electronic ground-state structures were optimized using Gaussian09 [15] with the hybrid exchange correlation functional CAM-B3LYP [16] and the Pople-311G+(d,p) basis set [17]. As the experimental investigation of the absorption and emission properties was carried out in dichloromethane solutions, we employed the polarizable continuum model (PCM) for dichloromethane as a solvent [18]. All minimum structures were unambiguously confirmed by analytical frequency analysis.

For determining and rationalizing the absorption characteristics, TD-DFT calculations were then performed, again using PCM for dichloromethane as solvent. The results reasonably reproduce the experimentally obtained values. Table 5 summarizes the calculated and measured absorption maxima. In several cases, more than one excited state significantly contributes to the absorption band. For these, all wavelengths are stated.

For all three ethyl 3-phenothiazinyl propiolates **3k**–**m**, the longest wavelength absorption band originates predominatly from the HOMO-LUMO transition. Fig. 6 exemplarily shows the respective Kohn–Sham molecular frontier orbitals for parent compound **3k**.

A shift in coefficient density from the phenothiazine core donor to the ester acceptor is apparent, supporting a pronounced charge-transfer character of the transition. Sufficient overlap is ensured by coefficient density on the ester-substituted phenyl ring of the phenothiazine moiety. This interpretation is in good agreement with the observed large Stokes shift and solvatochromic behavior.

2.4. Electrochemical properties of ethyl 3-phenothiazinyl propiolates

The electrochemical properties of phenothiazinyl propiolates **3k**–**m** were examined using cyclic voltammetry. Fig. 7 exemplarily shows the cyclic voltammogram for parent compound **3k**. All three compounds exhibit Nernstian reversible one-electron oxidations, with no second oxidations appearing in the measuring window. The results are summarized in Table 6. Parent compound **3k** exhibits an oxidation potential at 0.88 V, which is higher than that of literature-known arylethynyl phenothiazines [19]. This is caused by the electron-withdrawing effect of the ester acceptor functionality. The introduction of a second propiolate moiety (compound **3l**) has little effect on the oxidation potential while a bromo substituent in position 7 causes a slight shift to 0.82 V.

3. Conclusions

We have established a straightforward general synthesis of 3-aryl propiolic esters **3** in nearly quantitative yields with excellent

Table 5
TD-DFT calculations (CAM-B3LYP 6-311G+(d,p)) of the absorption maxima for phenothiazinyl propiolates **3k**–**m**.

structure	experimental $\lambda_{max,abs}$ [nm][a]	calculated $\lambda_{max,abs}$ [nm]	most dominant contributions
3k	240	246	HOMO → LUMO + 3 (49%), HOMO − 1 → LUMO (21%)
	274	269	HOMO − 1 → LUMO (43%), HOMO → LUMO + 3 (20%)
		275	HOMO → LUMO + 2 (71%)
	371	353	HOMO → LUMO (82%)
3l	244	247	HOMO → LUMO + 3 (56%), HOMO − 1 → LUMO (19%)
	275	270	HOMO − 1 → LUMO (40%), HOMO → LUMO + 3 (20%)
		284	HOMO → LUMO + 2 (60%), HOMO → LUMO + 1 (23%)
	337	291	HOMO → LUMO + 1 (59%), HOMO → LUMO + 2 (16%)
	366	353	HOMO → LUMO (80%)
3m	235	242	HOMO − 2 → LUMO (38%), HOMO-1 → LUMO+1 (25%), HOMO → LUMO+2 (11%)
	291	272	HOMO − 1 → LUMO (55%), HOMO → LUMO + 3 (11%)
		276	HOMO → LUMO + 2 (58%), HOMO → LUMO + 1 (17%)
		298	HOMO → LUMO + 1 (70%), HOMO → LUMO + 2 (18%)
	391	370	HOMO → LUMO (88%)

[a] Recorded in dichloromethane, $T = 293$ K, $c(\mathbf{3}) = 10^{-7}$ M.

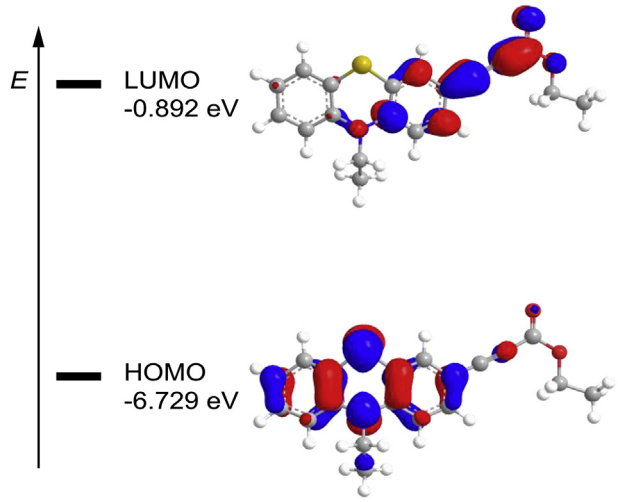


Fig. 6. Selected Kohn-Sham molecular frontier orbitals for **3k**.

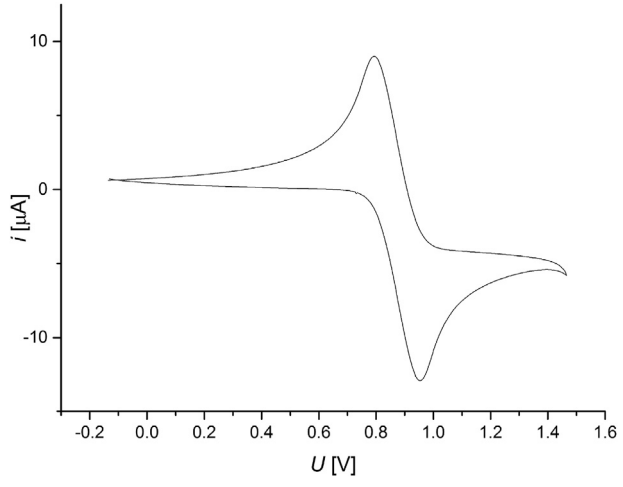
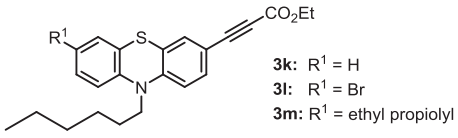


Fig. 7. Cyclic voltammogram of **3k** (recorded in dichloromethane, $T = 293$ K, 0.1 M electrolyte $[Bu_4N][PF_6]$, Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode).

functional group tolerance by a modified Sonogashira coupling of aryl iodides **1** and ethyl propiolate (**2**). The slow addition of propiolate **2** *via* a syringe pump prevents the unproductive

Table 6
Oxidation potentials of ethyl phenothiazinyl propiolates **3k**–**m**.



entry	compound	$E_0^{0/+1}$ [V][a]
1	**3k**	0.88
2	**3l**	0.82
3	**3m**	0.86

[a] Recorded in dichloromethane, $T = 293$ K, 0.1 M electrolyte $[Bu_4N][PF_6]$, Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode (the potentials were corrected to the internal standard of Fc/Fc^+ in CH_2Cl_2 ($E_0^{0/+1} = 450$ mV [20])).

consumption of this substrate. The optimized conditions were then employed for the synthesis of three 3-phenothiazinyl propiolates. Due to conjugation of the ester acceptor substituent to the phenothiazine core *via* the ethynyl bridge, interesting electronic properties such as large Stokes shifts, emission solvatochromy and Nernstian reversible one-electron oxidations are found for these extended π-systems. The experimentally obtained results were corroborated and rationalized by calculations on the DFT and TD-DFT level of theory. Expansion of the synthetic methodology towards novel one-pot syntheses and application of the functionalized phenothiazines for obtaining novel luminescent electrophores are currently underway.

4. Experimental

4.1. General considerations

All reactions were performed in flame-dried Schlenk tubes under a nitrogen atmosphere. Reaction progress was qualitatively monitored by thin layer chromatography using silica gel layered aluminium foil (60 F_{254} Merck, Darmstadt). For detection, UV light of wavelengths 254 and 366 was employed. Column chromatography was performed using silica gel 60 (Macherey Nagel), mesh 230–400. The commercially available chemicals **1a-j** were purchased from Sigma Aldrich, Alfa Aesar, Fluorochem, and ACROS and were used as received without any further purification. The iodo phenothiazines **3k-m** were prepared according to the literature [21]. Ethyl propiolate (**2**) was purchased from Sigma Aldrich. ^1H and ^{13}C NMR spectra were measured on a Bruker Avance III-300 or

Bruker Avance III-600 spectrometer. Chemical shifts are given in ppm (δ) and were referenced to the internal solvent signal: $CDCl_3$ (^1H δ 7.26, ^{13}C δ 77.2) or acetone-d_6 (^1H δ 2.50, ^{13}C δ 39.5). Multiplicities are stated as: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), ddd (doublet of doublet of doublet), m (multiplet). Coupling constants (J) are given in Hz. The assignment of primary (CH_3), secondary (CH_2), tertiary (CH) and quaternary carbon nuclei (C_{quat}) was made using DEPT-135 spectra. Mass-spectrometric investigations were carried out in the Department of Mass Spectrometry of the Institute of Inorganic and Structural Chemistry, Heinrich-Heine-Universität Düsseldorf. IR spectra were recorded using a Shimadzu IRAffinity-1. The intensities of the IR bands are abbreviated as w (weak), m (medium), s (strong). Cyclic voltammetry experiments were performed under argon in dry and degassed CH_2Cl_2 at rt and at scan rates of 100, 250, 500, and 1000 mVs^{-1} using an electrochemical workstation with $[Bu_4N][PF_6]$ (0.1 M) as electrolyte, a 1 mm platinum disk as working electrode, a platinum wire as counter electrode, and a an Ag/AgCl reference electrode. The potentials were corrected to the internal standard of Fc/Fc^+ in CH_2Cl_2 ($E_0^{0/+1} = 450$ mV [20]) Melting points (uncorrected) were measured using a Büchi Melting Point B-540. Combustion analyses were measured on a Perkin Elmer Series II Analyser 2400 in the Institute of Pharmaceutical and Medicinal Chemistry, Heinrich-Heine University, Düsseldorf.

4.2. General procedure for the synthesis of ethyl arylpropiolates 3

Bis(triphenylphosphane)palladium(II)dichloride (14.2 mg, 20.0 μmol, 2.00 mol%) and copper(I) iodide (7.62 mg, 40.0 μmol, 4.00 mol%) were placed in a flame-dried 10 mL Schlenk tube with a magnetic stir bar under a nitrogen atmosphere and the Schlenk tube was evacuated and flushed with nitrogen two more times. DME (3.0 mL) was added and the resulting yellow solution was stirred for several minutes at rt. Aryl iodide **1** (1.00 mmol, 1.00 equiv) and potassium carbonate (276 mg, 2.00 mmol, 2.00 equiv) were added and the vessel was closed and heated to 40 °C. Ethyl propiolate (**2**) (198 mg, 2.00 mmol, 2.00 equiv) was dissolved in DME (0.95 mL) and added slowly over 21 h (1.0 mL syringe, 0.50 mm/min feed rate). After complete addition, the syringe was rinsed in the reaction mixture and stirring was continued for 1 h at 40 °C. Celite® was added to the dark brown mixture and the solvent was removed under reduced pressure. For purification, chromatography on silica gel was performed using manual flash technique or a Biotage *SP4* flash purification system with eluents consisting of *n*-hexane and EtOAc or acetone.

4.2.1. Ethyl 3-(p-tolyl)propiolate (3a)

According to the GP using 4-iodotoluene (**1a**), 181 mg (0.961 mmol, 96%) of **3a** were obtained as a colorless oil. Purification was performed using manual flash technique (*n*-hexane/EtOAc 30:1). The reaction was repeated on a 10 mmol scale using a 70 mL Schlenk tube and a 10 mL syringe for the addition of ethyl propiolate to give 1.76 g (9.35 mmol, 94%) of **3a**. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.35 (t, 3 H, CH_3, $^3J_H = 7.1$ Hz), 2.37 (s, 3 H, CH_3), 4.29 (t, 2 H, OCH_2, $^3J_H = 7.1$ Hz), 7.15–7.19 (m, 2 H, CH_{Ar}), 7.45–7.49 (m, 2 H, CH_{Ar}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.2 (CH_3), 21.8 (CH_3), 62.1 (OCH_2), 80.5 (C_{quat}), 86.7 (C_{quat}), 116.6 (C_{quat}), 129.5 (CH), 133.1 (CH), 141.4 (C_{quat}), 154.3 (C_{quat}). EI + MS (*m*/*z* (%)): 188 (28) [M^+], 143 (100) [$C_{10}H_7O^{+\cdot}$], 116 (98) [$C_9H_8^{+\cdot}$]. IR: $\tilde{\nu}$[cm^{-1}] = 708 (w), 725 (w), 746 (m), 816 (m), 860 (w), 947 (w), 1018 (w), 1094 (w), 1113 (m), 1165 (s), 1190 (s), 1242 (w), 1287 (s), 1366 (m), 1389 (w), 1447 (w), 1464 (w), 1508 (m), 1607 (w), 1701 (s), 2207 (m), 2236 (w), 2872 (w), 2907 (w), 2926 (w), 2938 (w), 2984 (w), 3032 (w). Anal. calcd. for $C_{12}H_{12}O_2$ (188.2): C 76.57, H 6.43; Found: C 76.65, H 6.73.

4.2.2. Ethyl 3-phenylpropiolate (3b)

According to the GP using iodobenzene (**1b**), 150 mg (0.861 mmol, 86%) of **3b** were obtained as a colorless oil. Purification was performed using manual flash technique (*n*-hexane/EtOAc 50:1). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.36 (t, 3 H, CH_3, $^3J_H = 7.1$ Hz), 4.30 (q, 2 H, OCH_2, $^3J_H = 7.1$ Hz), 7.34–7.40 (m, 2 H, CH_{Ar}), 7.42–7.48 (m, 1 H, CH_{Ar}), 7.57–7.61 (m, 2 H, CH_{Ar}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.2 (CH_3), 62.2 (OCH_2), 80.8 (C_{quat}), 86.2 (C_{quat}), 119.8 (C_{quat}), 128.7 (CH), 130.7 (CH), 133.1 (CH), 154.3 (C_{quat}). EI + MS (*m*/*z* (%)): 174 (12) [M^+], 129 (100) [$C_9H_5O^{+\cdot}$], 102 (66) [$C_8H_6^{+\cdot}$], 75 (14). FT-IR: $\tilde{\nu}$[cm^{-1}] = 606 (w), 756 (w), 860 (w), 922 (w), 947 (w), 1020 (m), 1070 (w), 1096 (w), 1115 (w) 1175 (s), 1188 (s), 1242 (w), 1285 (s), 1368 (w), 1391 (w), 1445 (w), 1491 (w), 1705 (s), 2210 (w), 2236 (w), 2904 (w), 2940 (w), 2984 (w). HRMS (ESI) (*m*/*z*) calcd for $[C_{11}H_{11}O_2]^+$: 175.0754; Found: 175.0753.

4.2.3. Ethyl 3-(4-acetylphenyl)propiolate (3c)

According to the general procedure using 4-iodoacetophenone (**1c**), 191 mg (0.883 mmol, 88%) of **3c** were obtained as a colorless solid. Purification was performed using manual flash technique (*n*-hexane/EtOAc 20:1 → 6:1). Mp 84 °C (lit. 82–83.5 °C [10]). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.36 (t, 3 H, CH_3, $^3J_H = 7.1$ Hz), 2.61 (s, 3 H, CH_3), 4.31 (q, 2 H, OCH_2, $^3J_H = 7.1$ Hz), 7.64–7.68 (m, 2 H, CH_{Ar}), 7.93–7.96 (m, 2 H, CH_{Ar}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.2 (CH_3), 26.8 (CH_3), 62.5 (OCH_2), 83.0 (C_{quat}), 84.6 (C_{quat}), 124.4 (C_{quat}), 128.4 (CH), 133.2 (CH), 138.1 (C_{quat}), 153.8 (C_{quat}), 197.2 (C_{quat}). EI + MS (*m*/*z* (%)): 216 (38) [M^+], 171 (100) [$C_{11}H_7O_2^{+\cdot}$], 144 (73) [$C_{10}H_7O^{+\cdot}$], 129 (74) [$C_9H_5O^{+\cdot}$], 101 (12) [$C_8H_5^{+\cdot}$], 100 (12) [$C_8H_4^{+\cdot}$]. FT-IR: $\tilde{\nu}$[cm^{-1}] = 689 (s), 746 (s), 816 (m), 837 (s), 849 (m), 866 (m), 949 (m), 959 (m), 1009 (m), 1024 (s), 1078 (m), 1173 (s), 1196 (s), 1256 (s), 1259 (s), 1287 (s), 1266 (m), 1400 (m), 1431 (w), 1445 (w), 1458 (m), 1558 (w), 1599 (m), 1682 (s), 1726 (w), 2210 (m), 2247 (w), 2872 (w), 2901 (w), 2926 (w), 2959 (w), 2995 (w). Anal. calcd. for $C_{13}H_{12}O_3$ (216.2): C 72.21, H 5.59; found: C 72.09, H 5.86.

4.2.4. Ethyl 3-(4-methoxyphenyl)propiolate (3d)

According to the general procedure using 4-iodoanisole (**1d**) 198 mg (0.969 mmol, 97%) of **3d** were obtained as a colorless oil. Purification was performed using manual flash technique (*n*-hexane/EtOAc 10:1). ^1H NMR ($CDCl_3$, 600 MHz): δ 1.35 (t, 3 H, CH_3, $^3J_H = 7.1$ Hz), 3.83 (s, 3 H, OCH_3), 4.28 (q, 2 H, OCH_2, $^3J_H = 7.1$ Hz), 6.87–6.89 (m, 2 H, CH_{Ar}), 7.52–7.54 (m, 2 H, CH_{Ar}). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 14.3 (CH_3), 55.5 (OCH_3), 62.1 (OCH_2), 80.3 (C_{quat}), 87.0 (C_{quat}), 111.6 (C_{quat}), 114.4 (CH), 135.1 (CH), 154.5 (C_{quat}), 161.6 (C_{quat}). EI + MS (*m*/*z* (%)): 204 (30) [M^+], 159 (61) [$C_{10}H_7O_2^{+\cdot}$], 142 (100) [$C_9H_8O^{+\cdot}$]. FT-IR: $\tilde{\nu}$[cm^{-1}] = 644 (w), 746 (m), 789 (w), 810 (m), 831 (s), 860 (w), 947 (w), 1022 (s), 1096 (m), 1109 (m), 1159 (s), 1192 (s), 1250 (s), 1285 (s), 1368 (w), 1389 (w), 1443 (w), 1460 (w), 1508 (s), 1603 (m), 1701 (s), 2203 (m), 2236 (w), 2841 (w), 2907 (w), 2938 (w), 2980 (w). HRMS (ESI) (*m*/*z*) calcd. for $[C_{12}H_{13}O_3]^+$: 205.0859; Found: 208.0865.

4.2.5. Ethyl 3-(4-(trifluoromethyl)phenyl)propiolate (3e)

According to the general procedure using 4-iodobenzotrifluoride (**1e**), 202 mg (0.834 mmol, 83%) of **3e** were obtained as a colorless oil. Purification was performed using manual flash technique (*n*-hexane/EtOAc 50:1). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.36 (t, 3 H, CH_3, $^3J_H = 7.1$ Hz), 4.29 (q, 2 H, OCH_2, $^3J_H = 7.1$ Hz), 7.62–7.65 (m, 2 H, CH_{Ar}), 7.67–7.71 (m, 2 H, CH_{Ar}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.2 (CH_3), 62.1 (OCH_2), 82.4 (C_{quat}), 83.9 (C_{quat}), 123.6 (q, C_{quat}, $^5J_F = 1$ Hz), 123.7 (q, C_{quat}, $^1J_F = 273$ Hz), 125.7 (q, CH, $^3J_F = 4$ Hz), 132.3 (q, C_{quat}, $^2J_F = 33$ Hz), 133.3 (CH), 153.7 (C_{quat}). EI + MS (*m*/*z* (%)): 242 (4) [M^+], 197 (100) [$C_{10}H_4F_3O^{+\cdot}$], 170 (69) [$C_9H_5F_3^{+\cdot}$]. FT-IR: $\tilde{\nu}$[cm^{-1}] = 741 (m), 749 (m), 843 (s), 947 (w), 1016 (s), 1065 (s), 1107 (s), 1126 (s), 1167 (s), 1198 (s), 1283 (s), 1321

(s), 1368 (m), 1406 (m), 1449 (w), 1516 (w), 1616 (w), 1709 (s), 2214 (w), 2239 (m), 2878 (w), 2909 (w), 2941 (w), 2988 (w). Anal. calcd. for $C_{12}H_9F_3O_2$ (242.2): C 59.51, H 3.75; found: C 59.46, H 3.97.

4.2.6. Ethyl 3-(2-methoxyphenyl)propiolate (3f)

According to the general procedure using 2-iodoanisole (**1f**), 170 mg (0.832 mmol, 83%) of **3f** were obtained as a colorless oil. Purification was performed using manual flash technique (*n*-hexane/EtOAc 30:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.35 (t, 3 H, CH_3, ^3J_H = 7.1 Hz), 3.90 (s, 3 H, OCH_3) 4.30 (q, 2 H, OCH_2, ^3J_H = 7.1 Hz), 6.88–6.96 (m, 2 H, CH_{Ar}), 7.40 (ddd, 1 H, CH_{Ar}, ^3J_H = 8.4 Hz, 7.5 Hz, ^4J_H = 1.8 Hz), 7.51–7.54 (m, 1 H, CH_{Ar}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.2 (CH_3), 55.9 (OCH_3), 62.1 (OCH_2), 83.2 (C_{quat}), 84.7 (C_{quat}), 108.9 (C_{quat}), 110.9 (CH), 120.6 (CH), 132.4 (CH), 135.0 (CH), 154.3 (C_{quat}), 161.6 (C_{quat}). EI + MS (*m*/*z* (%)): 204 (42) [M^+], 159 (31) [$C_{10}H_7O_2^{+\cdot}$], 132 (100) [$C_9H_8O^{+\cdot}$], 115 (21) [$C_8H_3O^{+\cdot}$], 103 (11), 77 (16) [$C_6H_5^{+\cdot}$]. FT-IR: $\tilde{\nu}$[cm^{-1}] = 608 (m), 746 (s), 789 (w), 810 (w), 858 (w), 945 (w), 1018 (s), 1045 (m), 1074 (w), 1094 (w), 1113 (m), 1161 (s), 1184 (s), 1223 (m), 1244 (s), 1277 (s), 1298 (s), 1366 (w), 1466 (w), 1435 (m), 1464 (m), 1491 (m), 1576 (w), 1597 (m), 1701 (s), 2210 (m), 2839 (w), 2872 (w), 2938 (w), 2861 (w), 2980 (w), 3076 (w). Anal. calcd. for $C_{12}H_{12}O_3$ (204.2): C 70.58, H 5.92; Found: C 70.31, H 6.19.

4.2.7. Ethyl 3-(pyridin-4-yl)propiolate (3g)

According to the general procedure using 4-iodopyridine (**1g**), 88.0 mg (0.502 mmol, 50%) of **3g** were obtained as a light brown oil which turned black within a few hours upon exposure to laboratory atmosphere. Purification was performed using manual flash technique (*n*-hexane/EtOAc 9:1 → 4:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.34 (t, 3 H, CH_3, ^3J_H = 7.1 Hz), 4.30 (q, 2 H, OCH_2, ^3J_H = 7.1 Hz), 7.39–7.41 (m, 2 H, CH_{Ar}), 8.64–8.66 (m, 2 H, CH_{Ar}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1 (CH_3), 62.7 (OCH_2), 82.2 (C_{quat}), 83.9 (C_{quat}), 126.2 (CH), 128.0 (C_{quat}), 150.2 (CH), 153.3 (C_{quat}). EI + MS (*m*/*z* (%)): 175 (16) [M^+], 130 (100) [$C_8H_4NO^{+\cdot}$], 103 (29) [$C_7H_5N^{+\cdot}$], 75 (11). FT-IR: $\tilde{\nu}$[cm^{-1}] = 669 (w), 748 (m), 818 (m), 858 (w), 953 (w), 989 (w), 1020 (m), 1065 (w), 1096 (w), 1113 (w), 1190 (s), 1217 (m), 1285 (s), 1368 (m), 1406 (m), 1447 (w), 1466 (w), 1474 (w), 1489 (w), 1537 (w), 1589 (m), 1709 (s), 2218 (w), 2245 (w), 2940 (w), 2984 (w), 3042 (w). HRMS (ESI) (*m*/*z*) calcd. for $[C_{10}H_{10}NO_2]^+$: 176.0708; Found: 176. 0706.

4.2.8. Ethyl 3-(phenanthren-9-yl)propiolate (3h)

According to the general procedure using 9-iodophenanthrene (**1h**), 252 mg (0.919 mmol, 92%) of **3h** were obtained as a light yellow solid. Purification was performed using manual flash technique (*n*-hexane/EtOAc 30:1). Mp 85 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.42 (t, 3 H, CH_3, ^3J_H = 7.2 Hz), 4.38 (q, 2 H, OCH_2, ^3J_H = 7.1 Hz), 7.62 (ddd, 1 H, CH_{Ar}, ^3J_H = 8.0 Hz, 7.1 Hz, ^4J_H = 1.2 Hz), 7.68–7.75 (m, 3 H, CH_{Ar}), 7.86–7.89 (m, 1 H, CH_{Ar}), 8.19 (s, 1 H, CH_{Ar}), 8.39–8.45 (m, 1 H, CH_{Ar}), 8.64–8.71 (m, 2 H, CH_{Ar}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.3 (CH_3), 62.3 (OCH_2), 84.7 (C_{quat}), 85.0 (C_{quat}), 116.3 (C_{quat}), 122.8 (CH), 126.7 (CH), 127.3 (CH), 127.6 (CH), 127.7 (CH), 128.9 (CH), 129.2 (CH), 130.1 (C_{quat}), 130.7 (C_{quat}), 130.8 (C_{quat}), 131.3 (C_{quat}), 135.6 (CH), 154.3 (C_{quat}). EI + MS (*m*/*z* (%)): 274 (38) [M^+], 229 (21) [$C_{17}H_{19}O^{+\cdot}$], 202 (100) [$C_{16}H_{10}^{+\cdot}$]. FT-IR: $\tilde{\nu}$[cm^{-1}] = 667 (w), 723 (s), 746 (s), 766 (s), 804 (w), 854 (m), 889 (m), 920 (w), 1016 (m), 1074 (m), 1109 (m), 1148 (w), 1192 (s), 1211 (s), 1233 (m), 1260 (s), 1319 (m), 1368 (w), 1379 (w), 1452 (w), 1474 (w), 1692 (s), 2210 (m), 2857 (w), 2905 (w), 2863 (w), 2978 (w), 3366 (w). HRMS (ESI) (*m*/*z*) calcd. for $[C_{19}H_{15}O_2]^+$: 275.1067; Found: 275.1067.

4.2.9. Ethyl 3-(naphthalen-2-yl)propiolate (3i)

According to the general procedure using 2-iodonaphthalene (**1i**), 215 mg (0.959 mmol, 96%) of **3i** were obtained as a colorless solid. Purification was performed using manual flash technique (*n*-hexane/EtOAc 30:1). Mp 56 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.38 (t, 3 H, CH_3, ^3J_H = 7.1 Hz), 4.33 (q, 2 H, OCH_2, ^3J_H = 7.1 Hz), 7.50–7.59 (m, 3 H, CH_{Ar}), 7.81–7.85 (m, 3 H, CH_{Ar}), 8.15–8.16 (m, 1 H, CH_{Ar}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.3 (CH_3), 62.3 (OCH_2), 81.0 (C_{quat}), 86.7 (C_{quat}), 116.9 (C_{quat}), 127.1 (CH), 128.00 (CH), 128.04 (CH), 128.3 (CH), 128.4 (CH), 128.5 (CH), 132.7 (C_{quat}), 134.0 (C_{quat}), 134.4 (CH), 154.2 (C_{quat}). EI + MS (*m*/*z* (%)): 224 (33) [M^+], 179 (47) [$C_{13}H_7O^{+\cdot}$], 152 (100) [$C_{12}H_8^{+\cdot}$]. FT-IR: $\tilde{\nu}$[cm^{-1}] = 644 (m), 711 (m), 745 (s), 824 (s), 862 (m), 905 (m), 955 (w), 970 (m), 1028 (s), 1115 (m), 1126 (m), 1167 (s), 1200 (s), 1234 (s), 1252 (m), 1269 (s), 1285 (s), 1346 (w), 1366 (m), 1393 (w), 1497 (w), 1593 (w), 1624 (w), 1692 (s), 1701 (s), 2212 (m), 2266 (w), 2907 (w), 2986 (w), 3059 (w), 3372 (w). HRMS (ESI) (*m*/*z*) calcd. for $[C_{15}H_{13}O_2]^+$: 225.0910; Found: 225.0912.

4.2.10. Ethyl 3-(3-chlorophenyl)propiolate (3j)

According to the general procedure using 1-chloro-4-iodobenzene (**1j**), 194 mg (0.930 mmol, 93%) of **3j** were obtained as a light yellow oil. Purification was performed using manual flash technique (*n*-hexane/EtOAc 49:1). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.36 (t, 3 H, CH_3, ^3J_H = 7.1 Hz), 4.30 (q, 2 H, OCH_2, ^3J_H = 7.1 Hz), 7.29–7.34 (m, 1 H, CH_{Ar}), 7.41–7.48 (m, 2 H, CH_{Ar}), 7.56–7.58 (m, 1 H, CH_{Ar}). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 14.1 (CH_3), 62.3 (OCH_2), 81.5 (C_{quat}), 84.1 (C_{quat}), 121.4 (C_{quat}), 129.9 (CH), 130.9 (CH), 131.0 (CH), 132.6 (CH), 134.5 (C_{quat}), 153.7 (C_{quat}). EI + MS (*m*/*z* (%)): 210 (6) [M^+, ^{37}Cl], 208 (17) [M^+, ^{35}Cl], 165 (33) [$C_9H_4O^{37}ClO^{+\cdot}$], 163 (100) [$C_9H_4O^{35}ClO^{+\cdot}$], 138 (22) [$C_8H_5^{37}Cl^{+\cdot}$], 136 (67) [$C_8H_5^{35}Cl^{+\cdot}$], 99 (15) [$C_8H_3^{+\cdot}$]. FT-IR: $\tilde{\nu}$[cm^{-1}] = 608 (w), 679 (s), 746 (m), 785 (m), 833 (w), 860 (w), 881 (w), 943 (w), 961 (w), 1022 (m), 1080 (m), 1094 (m), 1113 (w), 1184 (s), 1258 (m), 1368 (m), 1558 (m), 1589 (w), 1705 (s), 2214 (w), 2239 (w), 2907 (w), 2983 (2), 2984 (w), 3069 (w). HRMS (ESI) (*m*/*z*) calcd. for $[C_{11}H_{10}^{35}ClO_2]^+$: 209.0364; Found: 209.0363.

4.2.11. Ethyl 3-(10-hexyl-10H-phenothiazin-3-yl)propiolate (3k)

According to the general procedure using 10-hexyl-3-iodo-10*H*-phenothiazine (**1k**) [19], 313 mg (0.825 mmol, 82%) of **3k** were obtained as an orange resin. Purification was performed using manual flash technique (*n*-hexane/acetone 10:1), followed by a second purification step using the flash purification system (*n*-hexane). ^{1}H NMR (acetone-d_6, 300 MHz): δ 0.82–0.87 (m, 3 H; CH_3), 1.25–1.34 (m, 7 H; CH_2, CH_3), 1.41–1.51 (m, 2 H; CH_2), 1.74–1.84 (m, 2 H; CH_2), 3.96–4.00 (m, 2 H, NCH_2), 4.25 (q, 2 H, OCH_2, ^3J_H = 7.1 Hz), 6.96–7.01 (m, 1 H, CH_{Ar}), 7.04–7.08 (m, 2 H, CH_{Ar}), 7.12–7.16 (m, 1 H, CH_{Ar}), 7.22 (ddd, 1 H, CH_{Ar}, ^3J_H = 8.2 Hz, 7.2 Hz, ^4J_H = 1.6 Hz), 7.34 (d, 1 H, CH_{Ar}, ^4J_H = 1.9 Hz, 7.45 (dd, 1 H, CH_{Ar}, ^3J_H = 8.5 Hz, ^4J_H = 2.0 Hz). ^{13}C NMR (acetone-d_6, 75 MHz): δ 14.2 (CH_3), 14.4 (CH_3), 23.3 (CH_2), 27.0 (CH_2), 27.4 (CH_2), 32.1 (CH_2), 48.1 (NCH_2), 62.4 (OCH_2), 81.8 (C_{quat}), 86.2 (C_{quat}), 113.4 (C_{quat}), 116.6 (CH), 117.2 (CH), 124.2 (CH), 124.3 (C_{quat}), 125.8 (C_{quat}), 128.1 (CH), 128.7 (CH), 131.8 (CH), 133.6 (CH), 144.9 (C_{quat}), 148.7 (C_{quat}), 154.3 (C_{quat}). EI + MS (*m*/*z* (%)): 379 (100) [M^+], 334 (8) [$C_{18}H_{14}NOS^{+\cdot}$], 308 (60) [$C_{18}H_{14}NO_2S^{+\cdot}$], 294 (57) [$C_{17}H_{12}NO_2S^{+\cdot}$], 266 (11), 222 (35) [$C_{14}H_8NS^{+\cdot}$]. FT-IR: $\tilde{\nu}$[cm^{-1}] = 629 (w), 669 (w), 694 (w), 745 (s), 814 (m), 858 (m), 883 (m), 964 (w), 1026 (m), 1103 (m), 1165 (s), 1238 (s), 1250 (m), 1271 (m). Anal. calcd. for $C_{23}H_{25}NO_2S$ (379.5): C 72.79, H 6.64, N 3.69, S 8.45; Found: C 72.58, H 6.51, N 3.47, S 8.48.

4.2.12. Ethyl-3-(7-bromo-10-hexyl-10H-phenothiazin-3-yl) propiolate (3l)

Departing from the GP, the reaction was performed on a 4.00 mmol scale. Using 10-hexyl-7-bromo-3-iodo-10*H*-phenothiazine (**1l**) [19], 1.24 g (2.71 mmol, 68%) of **3l** were obtained as an orange resin that crystallized slowly. Purification was performed

using manual flash technique (*n*-hexane → *n*-hexane/acetone 50:1 → 25:1 → 10:1). Mp 60–65 °C. ^{1}H NMR (acetone-d$_6$, 300 MHz): δ 0.81–0.87 (m, 3 H; CH_3), 1.25–1.30 (m, 7 H, CH_2, CH_3), 1.40–1.50 (m, 2 H; CH_2), 1.73–1.83 (m, 2 H; CH_2), 3.95–4.00 (m, 2 H, NCH_2), 4.25 (q, 2 H, OCH_2, ^3J_H = 7.1 Hz), 7.01 (d, 1 H, CH_{Ar}, ^3J_H = 8.7 Hz), 7.09 (d, 1 H, CH_{Ar}, ^3J_H = 8.5 Hz), 7.30 (d, 1 H, CH_{Ar}, ^4J_H = 2.3 Hz), 7.33–7.37 (m, 3 H, CH_{Ar}), 7.47 (dd, 1 H, CH_{Ar}, ^3J_H = 8.5 Hz, ^4J_H = 2.0 Hz). ^{13}C NMR (acetone-d$_6$, 75 MHz): δ 14.2 (CH_3), 14.4 (CH_3), 23.2 (CH_2), 27.0 (CH_2), 27.2 (CH_2), 32.1 (CH_2), 48.1 (NCH_2), 62.5 (OCH_2), 81.9 (C_{quat}), 85.9 (C_{quat}), 113.8 (C_{quat}), 115.7 (C_{quat}), 116.8 (CH), 118.6 (CH), 124.9 (C_{quat}), 126.8 (C_{quat}), 130.1 (CH), 131.2 (CH), 131.9 (CH), 133.8 (CH), 144.3 (C_{quat}), 148.2 (C_{quat}), 154.3 (C_{quat}). EI + MS (*m*/*z* (%)): 459 (100) [M^+ (^{81}Br)], 457 (100) [M^+ (^{79}Br)], 414 (9) [$C_{21}H_{19}^{81}BrNOS^{+\cdot}$], 412 (9) [$C_{21}H_{19}^{79}BrNOS^{+\cdot}$], 388 (59) [$C_{18}H_{13}^{81}BrNO_2S^{+\cdot}$], 386 (62) [$C_{18}H_{13}^{79}BrNO_2S^{+\cdot}$], 374 (80) [$C_{17}H_{11}^{81}BrNO_2S^{+\cdot}$], 372 (71) [$C_{17}H_{11}^{79}BrNO_2S^{+\cdot}$], 356 (10), 354 (10), 346 (17), 344 (15), 328 (10), 302 (52) [$C_{14}H_7^{81}BrNS^{+\cdot}$], 300 (52) [$C_{14}H_7^{79}BrNS^{+\cdot}$], 222 (13), 220 (19), 177 (12), 149 (15), 43 (13) [$C_3H_7^+$]. FT-IR: $\tilde{\nu}$[cm^{-1}] = 652 (w), 689 (w), 719 (w), 743 (m), 766 (m), 793 (s), 829 (m), 862 (m), 968 (w), 995 (w), 1030 (m), 1107 (m), 1159 (m), 1180 (s), 1238 (m), 1271 (m), 1304 (w), 1352 (m), 1368 (w), 1393 (m), 1456 (s), 1595 (m), 1703 (m), 2205 (m), 2270 (w), 2853 (w), 2868 (w), 2926 (w). Anal. calcd. for $C_{23}H_{24}BrNO_2S$ (458.4): C 60.26, H 5.28, N 3.06, S 6.99; Found: C 60.54, H 5.18, N 3.05, S 7.16.

4.2.13. Diethyl-3,3'-(10-hexyl-10H-phenothiazin-3,7-diyl) dipropiolate (**3m**)

Departing from the GP, 1.00 equiv of 10-hexyl-3,7-diiodo-10*H*-phenothiazine (**1m**) [19] were employed and all other reactants were doubled, giving 385 mg (0.810 mmol, 81%) of **3m** as an orange solid. Purification was performed twice using manual flash technique (*n*-hexane/acetone 10:1, then 20:1). An analytic sample for photophysical characterization was recrystallized from *n*-hexane. Mp 93 °C. ^{1}H NMR (acetone-d$_6$, 300 MHz): δ 0.83–0.88 (m, 3 H; CH_3), 1.24–1.36 (m, 10 H, CH_2, CH_3), 1.41–1.53 (m, 2 H; CH_2), 1.76–1.85 (m, 2 H; CH_2), 4.01–4.05 (m, 2 H, NCH_2), 4.25 (q, 4 H, OCH_2, ^3J_H = 7.1 Hz), 7.13 (d, 2 H, CH_{Ar}, ^3J_H = 8.6 Hz), 7.37 (d, 2 H, CH_{Ar}, ^4J_H = 1.9 Hz), 7.48 (d, 2 H, CH_{Ar}, ^3J_H = 8.5 Hz, ^4J_H = 2.0 Hz). ^{13}C NMR (acetone-d$_6$, 75 MHz): δ 14.2 (CH_3), 14.3 (CH_3), 23.2 (CH_2), 26.9 (CH_2), 27.2 (CH_2), 32.1 (CH_2), 48.3 (NCH_2), 62.5 (OCH_2), 82.0 (C_{quat}), 85.7 (C_{quat}), 114.5 (C_{quat}), 117.1 (CH), 124.8 (C_{quat}), 131.9 (CH), 133.8 (CH), 147.3 (C_{quat}), 154.2 (C_{quat}). EI + MS (*m*/*z* (%)): 475 (100) [M^+], 430 (14) [$C_{26}H_{24}NO_3S^{+\cdot}$], 404 (51) [$C_{23}H_{18}NO_4S^{+\cdot}$], 390 (61) [$C_{22}H_{16}NO_4S^{+\cdot}$], 372 (11), 318 (28) [$C_{19}H_{12}NO_2S^{+\cdot}$], 290 (17), 246 (23) [$C_{16}H_{18}NS^{+\cdot}$]. FT-IR: $\tilde{\nu}$[cm^{-1}] = 692 (m), 704 (m), 745 (s), 789 (w), 822 (s), 856 (m), 874 (m), 910 (w), 949 (m), 966 (m), 1028 (m), 1061 (m), 1105 (s), 1148 (s), 1175 (s), 1242 (m), 1269 (s), 1290 (m), 1300 (m), 1360 (m), 1379 (m), 1396 (m), 1460 (m), 1474 (s), 1572 (m), 1697 (s), 2199 (m), 2266 (w), 2567 (w), 2872 (w), 2922 (w), 2938 (w), 2955 (w), 3375 (w). Anal. calcd. for $C_{28}H_{29}NO_4S$ (475.6): C 70.71, H 6.15, N 2.95, S 6.74; Found: C 70.65, H 6.20, N 2.80, S 6.79.

Acknowledgements

The authors cordially thank the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft (Mu 1088/9-1) for financial support.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2017.04.049.

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