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Synthesis of electroactive hydrazones derived from 3-(10-alkyl-10*H*-phenothiazin-3-yl)-2-propenals and their corresponding 3,3′-bispropenals

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ABSTRACT

3-(10-Alkyl-10*H*-phenothiazin-3-yl)-2-propenals and their corresponding 3,3′-bispropenals that represent a previously unexplored class of functionalised phenothiazine derivatives were prepared upon reacting *N*-alkylated 3-bromo- and 3,7-dibromo-10*H*-phenothiazines with acrolein diethyl acetal under Pd catalysis. The obtained heterocyclic 2,3-unsaturated aldehydes were condensed with *N*-methyl-*N*-phenylhydrazine and *N*,*N*-diphenylhydrazine resulting in mono- and dihydrazones that act as effective hole transporting materials. Thermal, optical, electrochemical and photophysical properties of the synthesised new organic electroactive derivatives have been investigated.

1. Introduction

2,3-Unsaturated aromatic aldehydes are very important precursors in synthetic organic chemistry. For example, cinnamaldehyde and substituted derivatives were used as starting materials for the synthesis of various carbocyclic[1] and heterocyclic[2] compounds, including synthetic analogues of biomolecules.[3] The reaction of cinnamaldehydes with heterocycles bearing the CH-acidic methyl group, afforded butadienyl dyes,[4] while their condensation with aromatic and heteroaromatic hydrazines gave the corresponding hydrazones that were used as charge transporting materials for photoreceptors.[5]

In recent years, efficient protocols have been developed for the preparation of 2,3-unsaturated aromatic aldehydes using the Heck reaction[6] of arylhalides with propenal[7] or its derivatives; the corresponding diethyl acetal,[8] or 3,3-diacetoxypropene.[9] These Pd-catalysed coupling reactions were also applied to the synthesis of several heterocyclic analogues of cinnamaldehyde.[7f,8a,b,9,10,12b] Djakovitch and co-workers[7f] carried out the Heck arylation of acrolein diethyl acetal with 3-bromoquinoline using conditions based on Jeffery's[11] phase-transfer reaction conditions [$Pd(OAc)_2$, *n*-Bu_4NOAc, K_2CO_3, KCl, DMF] and obtained (2*E*)-3-(quinolin-3-yl)-2-propenal with a yield of 79%. However, when 4-bromoisoquinoline and 3-bromobenzothiophene were used in similar coupling reactions, the yields of the target aldehydes were significantly reduced because of substantial dehalogenation of the starting substrates. The reaction of heteroaryl bromides with acrolein acetals in the presence of catalyst systems, such as $[PdCl(C_3H_5)]_2$/*cis*,*cis*,*cis*-1,2,3,4-tetrakis(diphenylphosphinomethyl) cyclopentane or $[Pd(NH_3)_4]$/NaY zeolite afforded the corresponding 2,3-unsaturated heteroaryl aldehydes as the minor product in a mixture with 3-(heteroaryl)propionic esters.[12]

In the present work, we report on the synthesis of 2,3-unsaturated phenothiazinyl aldehydes by the Heck coupling methodology and their further application for the preparation of organic electronic materials. The phenothiazine ring system is present in numerous examples of electroactive organic compounds.[13] However, few studies were devoted solely to the synthesis and characterisation of phenothiazine-based, electroactive hydrazones until now.[14] Heteroaromatic hydrazones are effective functional materials for the preparation of organic photoreceptors, which are widely used on copying machine and laser printer drums.[15] The advantages of hydrazones against other classes of charge transporting materials include efficient charge transporting

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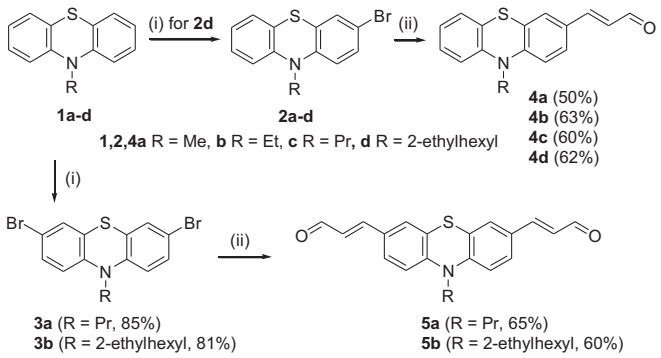
properties, a simple synthesis and a low cost of starting materials.[15b] Therefore, the condensation of 3-(phenothiazin-3-yl)-2-propenals with *N*,*N*-disubstituted arylhydrazines could provide easy access to new heterocyclic hydrazones bearing an extended and fully conjugated π-electron system for use as an efficient charge transporting material for organic photoreceptors.

2. Results and discussion

2.1. Synthesis

It is known that *N*-alkylated 3-bromo- and 3,7-dibromophenothiazines and their corresponding iodo derivatives represent excellent substrates in various Pd-catalysed coupling reactions.[13c,d,16a,b] The most common methods used for the preparation of monobrominated scaffolds involved the direct bromination of *N*-alkylphenothiazines.[13d,17] The alternative approach was based on the bromination of *N*-unsubstituted phenothiazine followed by N-alkylation of the obtained brominated derivatives.[13c,16b] Treatment of *N*-alkylphenothiazines with two equimolar amounts of bromine in acetic acid,[13c,16c,18] or dichloromethane[19] resulted in the corresponding 3,7-dibromo compounds.

In this work, the required 10-alkyl-3-bromophenothiazines **2a**–**c** were synthesised from 10-alkylphenothiazines **1a**–**c** according to literature procedures.[17b,c] 10-(2-Ethylhexyl)-3-bromophenothiazine, **2d**, was obtained by bromination of **1d** with NBS. This reaction was carried out in the presence of a catalytic amount of benzoyl peroxide in CCl_4, which allowed the target product to be obtained with a yield of 60%. In contrast, the yield provided by the previously known synthesis protocol,[13e] based on bromination of **1d** with bromine in pyridine, did not exceed 40%. The heating of **1a** and **1b** in CCl_4 with two equimolar amounts of NBS gave 10-alkyl-3,7-dibromophenothiazines **3a**[17b] and 3**b**[19] with good yields of 85% and 81%, respectively (Scheme 1).



Scheme 1. Reagents and conditions: (i) NBS, CCl_4, benzoyl peroxide, reflux, 2 h; (ii) acrolein diethyl acetal, $Pd(OAc)_2$, n-Bu_4NOAc, K_2CO_3, KCl, DMF, 90 °C, 1.5 h.

Having successfully prepared the brominated scaffolds, we examined their ability to participate in Pd-catalysed couplings with acrolein diethyl acetal. Thus, the Heck reaction of 3-bromo-10-alkyl-10*H*-phenothiazines **2a**–**d** with acrolein diethyl acetal, carried out under conditions optimised by Cacchi and co-workers for the synthesis of 2,3-unsaturated aromatic aldehydes[8a] and following work-up of the formed adducts with hydrochloric acid, afforded 3-(10-alkyl)-10*H*-3-phenothiazinyl-2-propenals **4a**–**d**. These derivatives were isolated by column chromatography with yields of 50–63%. The reaction also produced small amounts of by-products including the corresponding ethyl 3-(10-alkylphenothiazin-3-yl)propanoates that were formed due to hydrogen shifts in the carbopalladated intermediate of the catalytic cycle,[8a] and a 10-alkylphenothiazine derivative due to dehalogenation of the starting substrate.[7f] However, their presence in the reaction mixture was only detected by methods, such as HPLC/MS spectrometry and ^{1}H NMR spectroscopy, and they were not isolated in a pure state.

The structures of the synthesised propenals, **4a**–**d**, were confirmed by analysis of their spectroscopic data (^{1}H NMR, ^{13}C NMR, ^{15}N NMR, IR, MS). For example, the IR spectrum of **4b** showed a strong band at 1674 cm^{-1} that was attributable to its aldehydic C=O group. The ^{1}H NMR spectrum contained a set of signals that was characteristic of the propenal moiety: a doublet of the aldehyde proton at 9.63 ($^3J_{(CHO,H2)}$=7.8 Hz), a doublet of doublets of H-2 at 6.57 ($^3J_{(CHO,H2)}$=7.8 Hz, $^3J_{(H2,H3)}$=15.8 Hz), and a doublet of H-3 at 7.31 ppm ($^3J_{(H2,H3)}$=15.8 Hz). *E*-Configuration at the C=C double bond unequivocally follows from the magnitude of the vicinal coupling between the alkene protons H-2 and H-3. NOE experiments (NOESY and NOE-difference) of compound **4b** revealed a strong through-space interaction between the aldehyde proton and proton H-3, but no interaction between the aldehyde proton and H-2. This corresponds to the s-trans conformation of the α,β-unsaturated aldehyde moiety. The detailed assignments presented in Fig. 1 were based on the combined application of standard NMR techniques including COSY, TOCSY, HSQC, HMBC, NOE-difference and long-range INEPT spectra with selective excitation.[20]

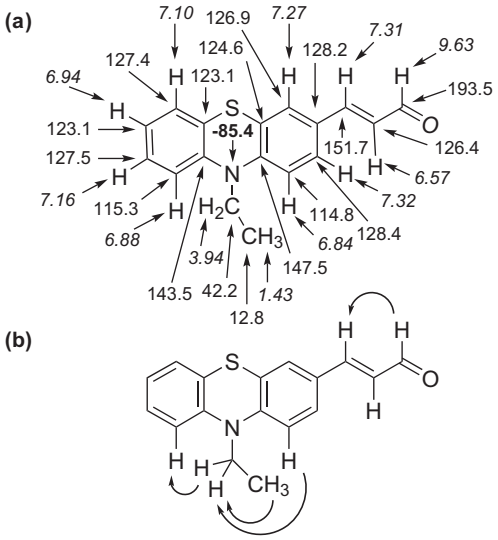
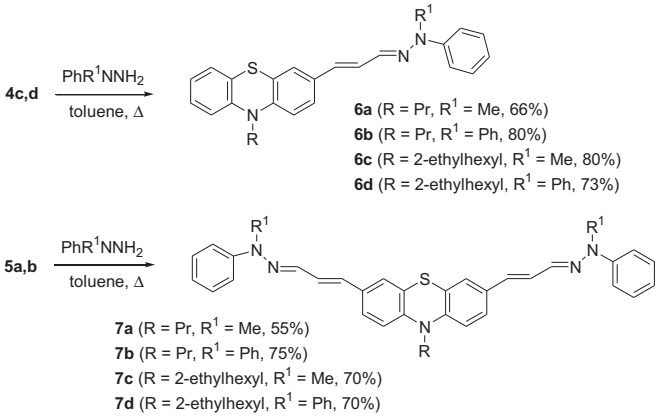


Fig. 1. (a) ^{1}H NMR (italics), ^{13}C NMR (plain) and ^{15}N NMR (bold) chemical shifts [ppm; ref. TMS (^{1}H and ^{13}C) and CH_3NO_2 (^{15}N)] for **4b** in $CDCl_3$. (b) Relevant NOE correlations.

The coupling reactions of 3,7-dibrominated phenothiazines **3a** and **3b** with acrolein diethyl acetal, followed by hydrolysis, afforded bispropenals **5a** and **5b** in satisfactory yields of 65% and 60%, respectively. The ^{1}H and ^{13}C NMR spectra of bispropenal **5a** displayed only nine proton signals and twelve carbon signals, indicating that the compound was a highly symmetrical molecule. The NOE experiments of **5a** revealed an s-trans conformation for the both α,β-unsaturated aldehyde moieties.

Condensation of propenals **4c**, **d** with 1-methyl-1-phenylhydrazine and 1,1-diphenylhydrazine in toluene yielded hydrazones **6a**–**d**, while a similar reaction of bispropenals **5a**, **b** afforded dihydrazones **7a**–**d** (Scheme 2). The ^{1}H NMR spectra of compounds **6a**–**d** and **7a**–**d** contained a characteristic doublet of one of the ethene protons in the region of 6.36–6.64 ppm with vicinal ^3J=15.3–15.9 Hz. This unique signal pattern verified the trans configuration of the ethene moiety.



Scheme 2. Synthesis of hydrazones **6a**–**d** and **7a**–**d**.

2.2. Thermal analysis

The favourable state for hydrazones that are used as charge transporters is a glassy state. The formation of the glassy state of synthesised monohydrazones **6a**–**d** and dihydrazones **7a**–**d** was confirmed by differential scanning calorimetry (DSC) analysis. The melting points (T_m) and glass transition temperatures (T_g) of investigated compounds are presented in Table 1.

Table 1
Data of thermal analysis and ionisation potentials (I_p) of hydrazones **6a**–**d** and **7a**–**d**

Compound	T_m, °C	T_g, °C	I_p, eV
6a	173	41	5.25
6b	no	55	5.28
6c	no	46	5.35
6d	no	no	5.30
7a	226	no	5.15
7b	no	106	5.12
7c	154	72	5.18
7d	no	56	5.22

no – not observed.

These investigations revealed that some of the hydrazones can exist both in crystalline and amorphous states, while others were found only in an amorphous phase in our experiments. Thus, during the first heating of dihydrazone **7c**, the melting point was observed at 154 °C (Fig. 2a). No crystallisation was observed during the second heating, and the only detected glass transition occurred at 72 °C. Glass transition occurs at 56 °C for **7d**, but no melting was observed (Fig. 2b). This indicates that the original state of sample **7d** was amorphous.

Comparison of the DSC analysis results for **6a**–**d** and **7a**–**d** revealed a significant influence of the molecular mass (weight) on the thermal transition data. In general, glass transition temperatures were higher for the dihydrazones, compared with the monohydrazone analogues. These data suggest that introduction of branched aliphatic chains potentially leads to a decreased in T_g in dihydrazone case.

2.3. Optical, electrochemical and photophysical properties

The UV–vis absorption spectra of hydrazones **6a**–**d** and **7a**–**d** were recorded at room temperature in THF (Fig. 3a). The lowest energy absorption bands of monohydrazones **6a**–**d** give maxima in the region of 380–450 nm and a shoulder around 350 nm. The lowest energy absorption band of dihydrazones **7a**–**d** is shifted bathochromically for approximately 20 nm, and the maxima are in the region of 400–420 nm. The shoulders in the absorption spectra of dihydrazones are transformed into the absorption bands with maxima at 350 nm and 400–420 nm of equal intensity.

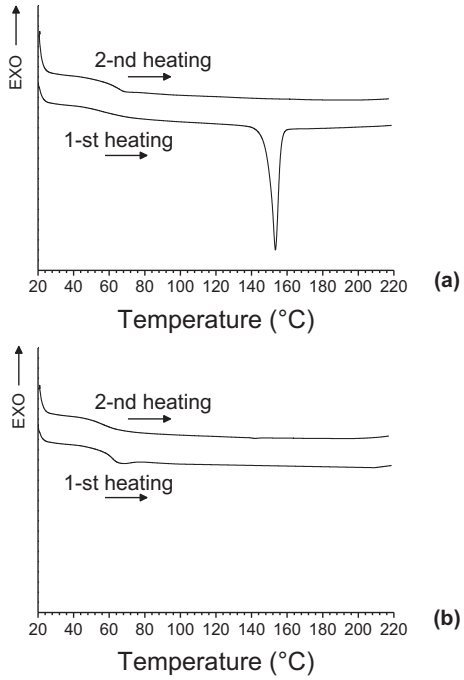


Fig. 2. (a) DSC curves for **7c**, (b) DSC curves for **7d** (heating rate 10 °C/min).

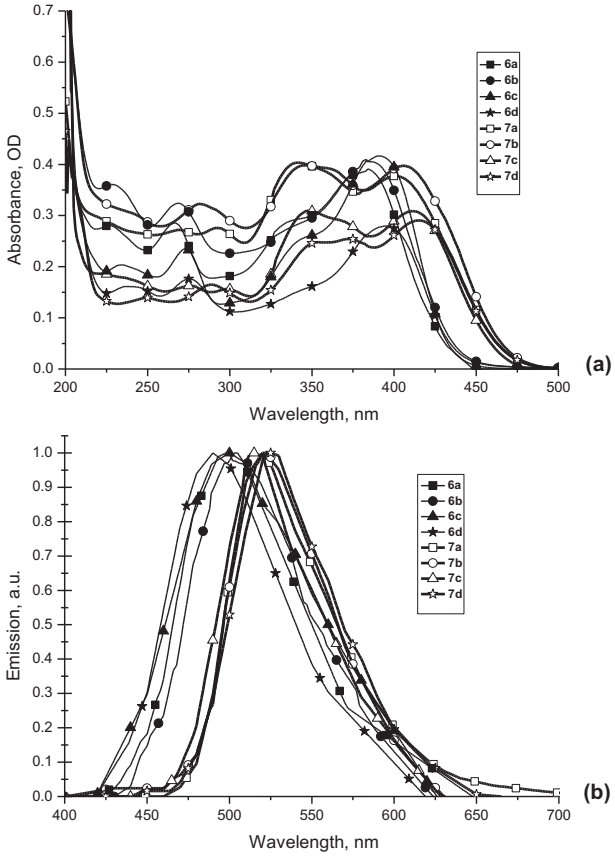


Fig. 3. (a) UV–vis absorption spectra of hydrazones **6a**–**d** and **7a**–**d**, (b) Fluorescence spectra of hydrazones **6a**–**d** and **7a**–**d**.

The fluorescence spectra of hydrazones **6a**–**d** and **7a**–**d** are provided in Fig. 3b. Emission maxima of monohydrazones **6a**–**d** are in the region of 495–500 nm, and dihydrazones **7a**–**d** emit at 520–525 nm. The small differences between the maxima of absorption and fluorescence spectra (~20 nm) of monohydrazones and dihydrazones are attributable to the 'butterfly' shape of the phenothiazine heterocycle[21] and comparing weak conjugation between two branches of hydrazone moieties in these molecules.

The E_{HOMO} and E_{LUMO} energies of the representative hydrazones **6a**, **d**, **7a**, **d** and the reference compound **1c** were measured employing the cyclic voltammetry (CV) technique (Table 2). These values do not represent any absolute solid-state or gas-phase ionization energies, but can be used to compare different compounds relative to one another. The cyclic voltammograms of all synthesized compounds show quasi-reversible oxidation couples. Cyclic voltammograms of investigated compounds are shown in the (Fig. 4). Compared with phenothiazine **1c**, addition of one hydrazone fragment increases E_{HOMO} by 0.1 eV in the case of *N*-methyl-*N*-phenyl hydrazone **6a**, while substitution of the methyl group by a phenyl ring in **6d** diminishes this effect, and E_{HOMO} increases only by 0.04 eV. Addition of a second hydrazone fragment in **7a**, **d** increases E_{HOMO} by another 0.06 eV. Addition of hydrazone fragments also narrows the energy bandgap and reduces E_{LUMO}. Compared with **1c** addition of two hydrazone fragments lowers E_{LUMO} by ~0.8 eV.

The new phenothiazine-based hydrazones were used for charge carrier mobility studies. The xerographic time-of-flight (XTOF) technique[22] was used to characterise the magnitude of the hole-drift mobility for the neat materials. In cases when measurements were impossible due to crystallisation or other irregular layer formations (**6a**, **c** and **7a**), these materials were dispersed in bisphenol Z polycarbonate as a polymer host (PC-Z).

In all the cases investigated, the mobility (μ) is approximated by the formula

$$\mu = \mu_0 e^{\alpha\sqrt{E}} \quad (1)$$

where μ_0 is the zero field mobility, α is Pool–Frenkel parameter and E is electric field strength.

The mobility defining parameters μ_0 and α values as well as the mobility values at the 10^6 V/cm field strength are given in Table 3. Room temperature hole-drift mobilities were found to exceed 10^{-4} cm^2/V s in strong electric fields for neat materials, and for compounds with polymeric binder this parameter was found to be two orders of magnitude lower. The examples of the d*U*/d*t* transients for the corresponding PC-Z blends are shown in Fig. 5.

XTOF measurements reveal that small charge transport transients are within a well-defined transit time on linear plots in the case of **7a** composition with PC-Z (Fig. 6a). The XTOF transients for all the other samples were of disperse character, but the transit time was well observed on lg–lg plots (Fig. 6b).

Table 2
Electrochemical properties of **1c**, **6a**, **d** and **7a**, **d**[a]

Compound	E_{HOMO}, eV[b]	E_{LUMO}, eV[c]	E_g^{opt}, eV[d]	E_{pc}^{ox} vs Fc, V[e]	E_{pa}^{ox} vs Fc, V	$E_{1/2}$ vs Fc, V[a]	E_{onset} vs Fc, V
1c	−5.06	−1.52	3.54	0.33	0.18	0.26	0.18
6a	−4.96	−2.09	2.87	0.22	0.09	0.16	0.08
6d	−5.02	−2.20	2.82	0.27	0.16	0.22	0.15
7a	−4.90	−2.26	2.64	0.13	0.05	0.09	0.03
7d	−4.96	−2.31	2.65	0.20	0.12	0.16	0.09

[a] The CV measurements were carried out at a glassy carbon electrode in dichloromethane solutions containing 0.1 M tetrabutylammonium hexafluorophosphate as electrolyte and Ag/$AgNO_3$ as the reference electrode. Each measurement was calibrated with ferrocene (Fc).
[b] $E_{HOMO} = -4.8 + (E_{1/2} - E_{1/2}^{Fc})$.
[c] $E_{LUMO} = E_{HOMO} - E_g^{opt}$.
[d] The optical band gaps E_g^{opt} estimated from the edges of electronic absorption spectra.
[e] $E_{1/2}=(E_{pa}+E_{pc})/2$; E_{pa} and E_{pc} are peak anodic and peak cathodic potentials, respectively.

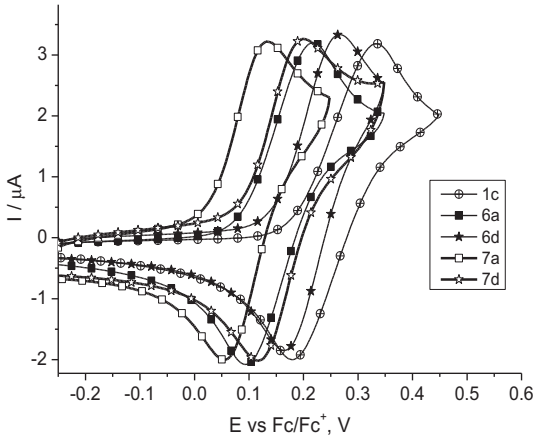


Fig. 4. The cyclic voltammograms of compounds **1c**, **6a**, **d** and **7a**, **d**.

The photoelectron emission in the air spectra were recorded for the investigated hydrazones and I_p values are presented in Table 1. Namely due to the 'butterfly' effect, the ionisation potentials of mono- and dihydrazones are similar and they are slightly lower for dihydrazones **7a**–**d** (5.12–5.22 eV) compared to monohydrazones **6a**–**d** (5.25–5.35 eV).

3. Conclusion

In conclusion, the coupling of 3-bromo- and 3,7-dibromo-10-alkyl-10*H*-phenothiazines with acrolein diethyl acetal under Heck reaction conditions afforded functionalised phenothiazine derivatives possessing 2-propenal moieties as side chains with acceptable yields. Condensation of the latter with *N*,*N*-disubstituted hydrazines gave the corresponding mono- and dihydrazones as new effective organic electroactive materials. Additionally, their ionisation potentials were measured by an electron photoemission technique and were determined to be 5.12–5.35 eV, and their room temperature hole-drift mobilities exceeded 10^{-4} cm^2/V s in strong electric fields for neat materials.

4. Experimental

4.1. General

The melting points were determined in open capillary tubes with a Melt-Temp (Electrothermal) melting point apparatus and are uncorrected. The DSC measurements were carried out on a Mettler DSC 30 calorimeter at a scan rate of 10 °C/min. Infrared spectra were recorded on a Perkin Elmer Spectrum One spectrometer using potassium bromide pellets. ^{1}H NMR spectra were recorded at

Table 3
Hole-drift mobility data for pure compounds and mixtures with PC-Z

Transport material, host polymer	d (μm)	μ_0 ($cm^2\ V^{-1}\ s^{-1}$)[a]	μ ($cm^2\ V^{-1}\ s^{-1}$)[b]	α ($cm^{1/2}\ V^{-1/2}$)
6a[c]	7	$\sim 2.0\times10^{-6}$	5.5×10^{-4}	~0.0056
6a+PC-Z, 1:1	10	9.5×10^{-8}	1.6×10^{-5}	0.0051
6b	3.6	0.6×10^{-6}	5.4×10^{-4}	0.0068
6c+PC-Z, 1:1	5.5	5.0×10^{-8}	1.3×10^{-5}	0.0056
6d	3.2	1.7×10^{-6}	4.6×10^{-4}	0.0056
7a+PC-Z, 1:3	6	2.7×10^{-8}	2.4×10^{-6}	0.0045
7b	3.8	0.8×10^{-6}	1.3×10^{-3}	0.0073
7c	3.7	4.4×10^{-6}	9×10^{-4}	0.0053
7d	5.1	1.9×10^{-6}	8×10^{-4}	0.0061

[a] Mobility value at zero field strength.
[b] Mobility value at 10^6 V cm^{-1} field strength.
[c] Crystallisation at the perimeter of film started.

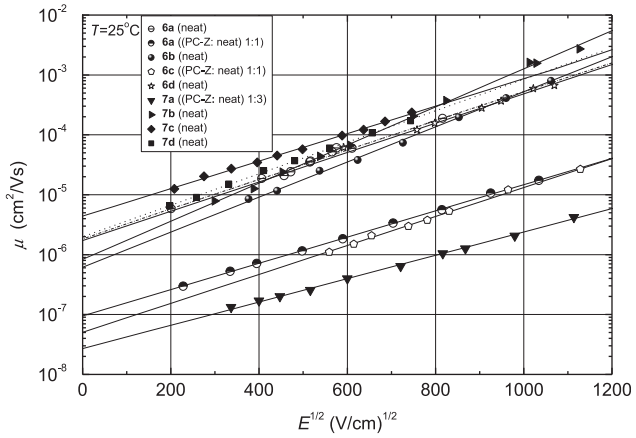


Fig. 5. Electric field dependencies of the hole-drift mobilities of hydrazones **6** and **7**.

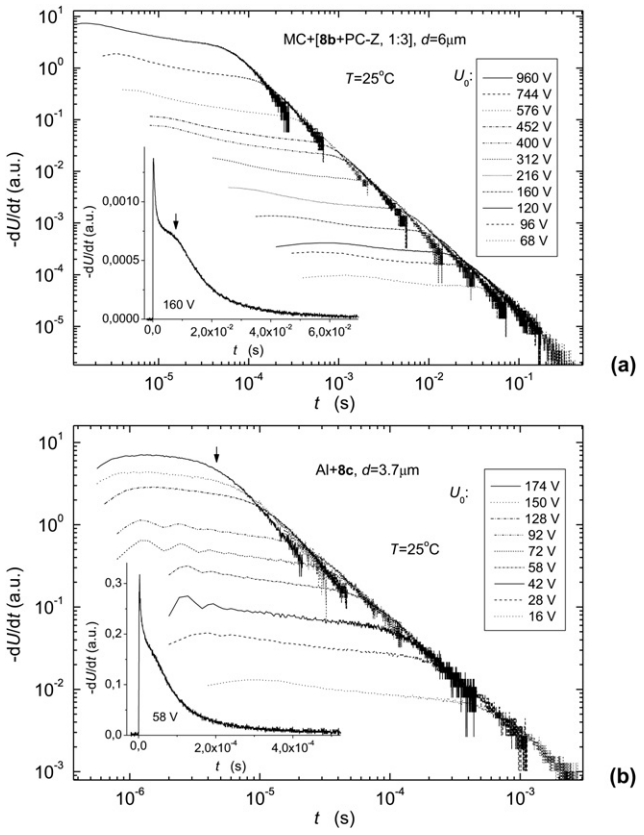


Fig. 6. (a) XTOF transients for **7a** dispersed in PC-Z with a mass ratio of 1:3. The insert shows one transient curve in a linear scale, where the transit time is marked by an arrow. (b) XTOF transients in a double logarithmic scale for **7c**. The arrow indicates the hole transient time at the highest potential and the insert shows a typical transient curve in a linear scale.

300 MHz on a Varian Unity Inova and at 500 MHz on a Bruker Avance 500 spectrometers; ^{13}C NMR spectra were registered at 75 and 125 MHz, respectively. Chemical shifts, expressed in parts per million, were relative to tetramethylsilane (TMS). ^{15}N NMR spectra (50.69 MHz) were obtained on a Bruker Avance 500 spectrometer using a 'directly' detecting broadband observe probe and were referenced against neat, external nitromethane (coaxial capillary). UV–vis spectra were recorded on Perkin Elmer Lambda 35 UV/vis spectrometer. Fluorescence spectra were recorded on Hitachi MPF-4 spectrometer. Mass spectra were recorded on a Waters Micromass ZQ instrument. Elemental analyses were measured with a CE-440 elemental analyzer, Model 440 CHN/O/S. For thin layer chromatographic (TLC) analyses, Merck precoated TLC plates (silica gel 60 F_{254}) were used. Starting 10-alkyl-10*H*-phenothiazines were synthesized by alkylation of 10*H*-phenothiazine with corresponding alkylhalides in DMF applying sodium hydroxide as a base according to a procedure outlined in the literature.[13d]

4.1.1. Cyclic-voltammetry measurements. The electrochemical studies were carried out by a three-electrode assembly cell from Bio-Logic SAS and a micro-AUTOLAB Type III potentiostat–galvanostat. The measurements were carried out with a glassy carbon electrode in dichloromethane solutions containing 0.1 M tetrabutylammonium hexafluorophosphate as electrolyte, Ag/$AgNO_3$ as the reference electrode and a Pt wire counter electrode.

4.1.2. Ionization energy measurements. The ionization potentials (I_p) of the sample films were estimated by performing electron photoemission spectroscopy in air, as described in Ref. 18.

4.1.3. Hole mobility measurements. The sample films for mobility measurements were prepared by dissolving the compounds and polycarbonate PC-Z (Iupilon Z-200 from Mitsubishi Gas Chemical Co.) using mass ratio of 1:1 or 1:3 or neat in tetrahydrofuran and thoroughly stirring the solution before casting the films. The compounds dispersed in PC-Z were casted on polyester film with conductive Al layer serving as the sample substrate. Smooth, transparent and highly uniform films obtained indicated homogeneous dispersion of hydrazone molecules in the polymer host.

The hole-drift mobility was measured by XTOF technique.[20] Electric field was created by positive corona charging. The charge carriers were generated at the layer surface by illumination with pulses of nitrogen laser (pulse duration was 1 ns, wavelength 337 nm). The layer surface potential decrease as a result of pulse illumination was up to 1–5% of initial potential before illumination. The capacitance probe that was connected to the wide frequency band electrometer measured the speed of the surface potential decrease dU/dt. The transit time t_t was determined by the kink on the curve of the dU/dt transient in linear or double logarithmic scale. The drift mobility was calculated by the formula $\mu=d^2/U_0t_t$, where d is the layer thickness, U_0 – the surface potential at the moment of illumination.

4.1.4. Reagents. General chemicals were of the best grade available, supplied by Aldrich Chemical Co. and were used without further purification. Starting 10-alkyl-10*H*-phenothiazines were synthesized by alkylation of 10*H*-phenothiazine with corresponding alkylhalides in DMF applying sodium hydroxide as a base according to a procedure outlined in the literature.[13d] 10-Alkyl-3-bromophenothiazines **2a–c**

were prepared from the corresponding 10-alkyl-10*H*-phenothiazines according to the reported procedures.[17b,c]

4.2. Synthetic procedures

*4.2.1. General procedure for the bromination of 10-alkyl-10H-phenothiazines (compounds **2d**, **3a**, **b**).* A double-necked round bottomed flask was charged with the appropriate 10-alkyl-10*H*-phenothiazine (5 mmol) dissolved in boiling CCl_4 (20 mL). Then NBS (0.89 g, 5 mmol, for monobromination or 1.78 g, 10 mmol, for dibromination) and benzoyl peroxide (48 mg, 0.2 mmol, for monobromination or 96 mg, 0.4 mmol, for dibromination) were added to the solution in 10 portions to the refluxing solution during 1 h and the mixture was refluxed additionally for 1 h after the last portion was added. Then the reaction mixture was washed with hot water (3×20 mL, 50 °C), organic layer was dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane as eluent.

*4.2.1.1. 3-Bromo-10-(2-ethylhexyl)-10H-phenothiazine (**2d**).* Yield 1.17 g (60%), resinous substance. The ^{1}H NMR spectrum of **2d** was in good agreement with that described in literature.[13e]

*4.2.1.2. 3,7-Dibromo-10-propyl-10H-phenothiazine (**3a**).* Yield 1.69 g (85%), resinous substance; IR (KBr, cm^{-1}): ν 3060, 2963, 2930, 2872. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.98 (3H, t, J=7.5 Hz), 1.76 (2H, sex, J=7.5 Hz), 3.71 (2H, t, J=7.5 Hz), 6.65 (2H, d, J=8.4 Hz), 7.19–7.23 (4H, m). The ^{13}C NMR spectrum of **3a** was in good agreement with that described in literature.[23]

*4.2.1.3. 3,7-Dibromo-10-(2-ethylhexyl)-10H-phenothiazine (**3b**).* Yield 1.89 g (81%), resinous substance. The ^{1}H and ^{13}C spectrum of **3b** was in good agreement with that described in literature.[19]

4.3. General procedure for the preparation of 3-(10-alkyl-10*H*-phenothiazin-3-yl)-2-propenals 4 and 5

To a stirred solution of 10-alkyl-3-bromo-10*H*-phenothiazine (1.0 mmol) **2** in dry DMF (4 mL) under argon atmosphere acrolein diethyl acetal (0.458 mL, 3.0 mmol), tetrabutylammonium acetate (0.604 g, 2.0 mmol), potassium carbonate (0.208 g, 1.5 mmol), potassium chloride (0.074 g, 1.0 mmol) and palladium (II) acetate (0.006 g, 0.03 mmol) were added and the mixture was stirred for 1.5 h at 90 °C. After cooling, 2 M hydrochloric acid was added slowly (to pH 4–5) and the reaction mixture was stirred at room temperature for 10 min. Then, it was extracted with dichloromethane (3×8 mL), combined dichloromethane solution was washed with water, dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/ethyl acetate (2/1 for **5a** or 4/1 for **4a**–**d**, **5b**).

Similar procedure was used to prepare bispropenals **5a** and **5b** from 10-alkyl-3,7-dibromo-10*H*-phenothiazines **3a** and **3b**. The only difference in the procedure is that the molar ratio of the reagents with **3a** and **3b** was increased twice.

*4.3.1. (E)-3-(10-Methyl-10H-phenothiazin-3-yl)-2-propenal (**4a**).* Yield 50%, orange crystals, mp 129–131 °C (from ethanol); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.40 (3H, s), 6.55 (1H, dd, J=15.9, 7.8 Hz), 6.79 (1H, d, J=8.4 Hz), 6.83 (1H, dd, J=8.4, 1.2 Hz), 6.97 (1H, dt, J=7.5, 1.2 Hz), 7.11–7.22 (2H, m), 7.30–7.36 (3H, m), 9.63 (1H, d, J=7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 35.6, 114.1, 114.5, 122.4, 123.2, 124.1, 126.5, 126.7, 127.2, 127.7, 128.3, 128.6, 144.5, 148.4, 151.7, 193.5; IR (KBr, cm^{-1}): ν 3047, 2965, 2899, 2819, 1667, 1616, 1592, 1570; MS *m*/*z* (%): 268 ($M+H^+$). Anal. Calcd for $C_{16}H_{13}NOS$: C, 71.88; H, 4.90; N, 5.24. Found: C, 71.49; H, 5.00; N, 5.33.

*4.3.2. (E)-3-(10-Ethyl-10H-phenothiazin-3-yl)-2-propenal (**4b**).* Yield 63%, yellow crystals, mp 104–106 °C (from ethanol); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.43 (3H, t, J=7.0 Hz), 3.94 (2H, q, J=7.0 Hz), 6.57 (1H, dd, J=15.8, 7.8 Hz), 6.84 (1H, d, J=8.5 Hz), 6.88 (1H, dd, J=8.2, 1.0 Hz), 6.94 (1H, dt, J=7.5, 1.0 Hz), 7.10 (1H, dd, J=7.5, 1.5 Hz), 7.16 (1H, ddd, J=8.2, 7.5, 1.5 Hz), 7.27 (1H, d, J=2.1 Hz), 7.31 (1H, d, J=15.8 Hz), 7.32 (1H, dt, J=8.5, 2.1 Hz), 9.63 (1H, d, J=7.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 12.8, 42.2, 114.8, 115.3, 123.08, 123.11, 124.6, 126.4, 126.9, 127.4, 127.5, 128.2, 128.4, 143.5, 147.5, 151.7, 193.5; ^{15}N NMR (50 MHz, $CDCl_3$): δ 296.4 (-85.4); IR (KBr, cm^{-1}): ν 3056, 2978, 2936, 2869, 1674; MS *m*/*z* (%): 282 ($M+H^+$, 100). Anal. Calcd for $C_{17}H_{15}NOS$: C, 72.57; H, 5.37; N, 4.98. Found: C, 72.93; H, 5.36; N, 4.90.

*4.3.3. (2E)-3-(10-Propyl-10H-phenothiazin-3-yl)-2-propenal (**4c**).* Yield 60%, yellow resinous substance; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.01 (3H, t, J=7.4 Hz, CH_3), 1.80–1.84 (2H, m), 3.81 (2H, t, J=7.2 Hz), 6.55 (1H, dd, J=15.9, 7.8 Hz), 6.82 (1H, d, J=8.5 Hz), 6.85 (1H, d, J=8.2 Hz), 6.94 (1H, t, J=7.5 Hz), 7.10 (1H, dd, J=7.6, 1.6 Hz), 7.15 (1H, m, J=7.5, 8.2, 1.6 Hz), 7.26 (1H, d, J=2.0 Hz), 7.29 (1H, dd, J=15.9 Hz), 7.31 (1H, dd, J=8.5, 2.0 Hz), 9.62 (1H, d, J=7.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 11.2, 19.9, 49.4, 115.2, 115.6, 123.1, 123.6, 125.1, 126.4, 127.0, 127.40, 127.42, 128.1, 128.3, 143.8, 147.8, 151.7, 193.4; ^{15}N NMR (50 MHz, $CDCl_3$): δ 293.8 (−88.0); IR (KBr, cm^{-1}): ν 3057, 2963, 2931, 2872, 2817, 1673, 1618, 1596, 1573; MS *m*/*z* (%): 296 ($M+H^+$, 100). Anal. Calcd for $C_{18}H_{17}NOS$: C, 73.19; H, 5.80; N, 4.74. Found: C, 73.15; H, 5.80; N, 4.77.

*4.3.4. (2E)-3-[10-(2-Ethylhexyl)-10H-phenothiazin-3-yl]-2-propenal (**4d**).* Yield 62%, deep orange resinous substance; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.83–0.90 (6H, m), 1.23–1.48 (8H, m), 1.87–1.97 (1H, m), 3.76 (2H, d, J=7.2 Hz), 6.57 (1H, dd, J=15.9, 7.8 Hz), 6.85–6.98 (3H, m), 7.13–7.20 (2H, m), 7.29–7.36 (3H, m), 9.63 (1H, d, J=7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.4, 13.9, 23.0, 23.9, 28.5, 30.5, 35.9, 51.2, 115.8, 116.3, 123.2, 124.7, 126.3, 126.5, 127.3, 127.4, 127.6, 128.18, 128.24, 144.4, 148.5, 151.7, 193.4. IR (KBr, cm^{-1}): ν 3057, 2963, 2931, 2872, 2817, 2733, 1674; MS *m*/*z* (%): 367 ($M+H^+$, 100). Anal. Calcd for $C_{23}H_{27}NOS$: C, 75.57; H, 7.45; N, 3.83. Found: C, 75.73; H, 7.68; N, 4.07.

*4.3.5. (E)-3-{7-[(E)-2-Formyl-1-ethenyl]-10-propyl-10H-phenothiazin-3-yl}-2-propenal (**5a**).* Yield 65%, red crystals, mp 180–182 °C (from ethanol); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.03 (3H, t, J=7.4 Hz), 1.84 (2H, m), 3.85 (2H, t, J=7.2 Hz), 6.57 (2H, dd, J=15.8, 7.7 Hz), 6.85 (2H, d, J=8.4 Hz), 7.34 (2H, dd, J=8.4, 1.0 Hz), 7.27 (2H, d, J=1.0 Hz), 7.31 (2H, d, J=15.8 Hz), 9.64 (2H, d, J=7.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 11.1, 20.0, 49.7, 115.6, 124.3, 127.0, 127.03, 128.4, 129.0, 146.4, 151.0, 193.2; ^{15}N NMR (50 MHz, $CDCl_3$): δ 305.4 (−76.4); IR (KBr, cm^{-1}): ν 3052, 3018, 2971, 2958, 2929, 2813, 2726, 1671; MS *m*/*z* (%): 350 ($M+H^+$, 100). Anal. Calcd for $C_{21}H_{19}NO_2S$: C, 72.18; H, 5.48; N, 4.01. Found: C, 72.38; H, 5.57; N, 4.11.

*4.3.6. (E)-3-{10-(2-Ethylhexyl)-7-[(E)-2-formyl-1-ethenyl]-10H-phenothiazin-3-yl}-2-propenal (**5b**).* Yield 60% as a deep orange resinous substance; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.82–0.91 (3H, m), 0.87 (3H, t, J=7.2 Hz), 1.20–1.45 (8H, m), 1.85–1.95 (1H, m), 3.78 (2H, d, J=7.2 Hz), 6.57 (2H, dd, J=15.9, 7.5 Hz), 6.90 (2H, d, J=8.4 Hz), 7.30–7.38 (6H, m), 9.63 (2H, d, J=7.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.4, 13.9, 22.9, 23.8, 28.4, 30.5, 36.1, 51.4, 116.3, 125.5, 127.0, 127.4, 128.3, 129.1, 147.2, 151.2, 193.3. IR (KBr, cm^{-1}): ν 3051, 2957, 2925, 2856, 2729, 1674. MS *m*/*z* (%): 420 ($M+H^+$, 100). Anal. Calcd for $C_{26}H_{29}NO_2S$: C, 74.43; H, 6.97; N, 3.34. Found: C, 73.95; H, 7.46; N, 3.28.

4.4. General procedure for synthesis of hydrazones 6 and 7

The corresponding aldehyde **4** (or **5**) (2 mmol) was dissolved in toluene (2 mL) and the corresponding phenylhydrazine (3 mmol) was added to the reaction mixture (6 mmol of hydrazine was used with aldehyde **5**). The reaction mixture was refluxed for 0.5–1.0 h for preparing the 1,1-diphenylhydrazones, and it was refluxed for 2–5 h for preparing the 1-phenyl-1-methylhydrazones. All hydrazones were purified by column chromatography on silica gel (eluent for **6a**, **b**, **7a-b**: *n*-hexane/ethyl acetate 4:1 (v/v), eluent for **6c**, **d**: *n*-hexane/ethyl acetate 15:1 (v/v)). Solution was concentrated under reduced pressure and the residue was vacuum dried.

*4.4.1. (E)-3-[10-Propyl-10H-phenothiazin-3-yl]-2-propenal 1-methyl-1-phenylhydrazone (**6a**).* Propenal **4c** (590 mg, 2 mmol) and 1-methyl-1-phenylhydrazine (366 mg, 3 mmol) were used to prepare **6a** according to the general procedure after refluxing for 3 h. Product was crystallized from ethanol. Yield: 528 mg (66%), yellow crystals, mp 171–173 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.01 (3H, t, J=7.5 Hz), 1.83 (2H, m), 3.37 (3H, s), 3.81 (2H, t, J=7.2 Hz), 6.60 (1H, d, J=15.9 Hz), 6.79–7.32 (13H, m), 7.50 (1H, d, J=8.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.3, 20.1, 33.6, 49.2, 115.4 (2× C), 115.5 (2× C), 120.8, 122.4, 124.2, 125.0, 125.1, 125.5, 125.7, 127.2, 127.4, 129.0 (2× C), 131.6, 132.2, 135.6, 144.7, 144.8, 147.5. IR (KBr, cm^{-1}): ν 3026, 2957, 2923, 2869, 1596, 1571, 1500, 1457. MS m/z (%): 400 (M+H$^+$, 100). Anal. Calcd for $C_{25}H_{25}N_3S$: C, 75.15; H, 6.31; N, 10.52. Found: C, 75.24; H, 6.18; N, 10.49.

*4.4.2. (E)-3-[10-Propyl-10H-phenothiazin-3-yl]-2-propenal 1,1-diphenylhydrazone (**6b**).* Propenal **4c** (590 mg, 2 mmol) and 1,1-diphenylhydrazine hydrochloride (662 mg, 3 mmol) were used to prepare **6b** according to the general procedure after refluxing for 0.5 h. Yield 738 mg (80%), yellow resinous substance; T_g 55 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.01 (3H, t, J=7.5 Hz), 1.85 (2H, m), 3.80 (2H, t, J=7.5 Hz), 6.37 (1H, d, J=15.3 Hz), 6.77–7.45 (19H, m). NMR (75 MHz, $CDCl_3$): δ 11.2, 20.1, 49.3, 115.3, 115.4, 122.4 (4× C), 124.2, 124.5 (2× C), 124.9, 125.1, 125.6, 127.2, 127.4, 128.2, 129.0, 129.7 (4× C), 131.5, 133.1, 138.7, 143.5 (2× C), 144.68, 144.72. IR (KBr, cm^{-1}): ν 3035, 2961, 2929, 2869, 1588, 1574, 1494, 1463. MS m/z (%): 462 (M+H$^+$, 100). Anal. Calcd for $C_{30}H_{27}N_3S$: C, 78.06; H, 5.90; N, 9.10. Found: C, 78.25; H, 5.85; N, 8.72.

*4.4.3. (E)-3-[10-(2-Ethylhexyl)-10H-phenothiazin-3-yl]-2-propenal 1-methyl-1-phenylhydrazone (**6c**).* Propenal **4d** (731 mg, 2 mmol) and 1-methyl-1-phenylhydrazine (366 mg, 3 mmol) were used to prepare **6c** according to the general procedure after refluxing for 4 h. Yield 752 mg (80%), yellow resinous substance; T_g 46 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.91 (6H, t, J=7.5 Hz), 1.26–1.55 (8H, m), 1.94–2.02 (1H, m), 3.37 (3H, s), 3.76 (2H, d, J=7.5 Hz), 6.62 (1H, d, J=15.9 Hz), 6.84–7.16 (5H, m), 7.21–7.42 (9H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.4, 14.0, 23.0, 23.9, 28.5, 30.6, 33.1, 35.7, 50.9, 115.2 (2× C), 115.8, 120.5, 122.4, 125.2, 125.3, 125.88, 125.94, 127.1, 127.5, 129.0 (2× C), 131.67, 131.72, 134.8, 145.1, 145.3, 147.5. IR (KBr, cm^{-1}): ν 3058, 3034, 2955, 2923, 2854, 1597. MS m/z (%): 471 (M+H$^+$, 100). Anal. Calcd for $C_{30}H_{35}N_3S$: C, 76.72; H, 7.51; N, 8.95. Found: C, 77.13; H, 7.72; N, 8.76.

*4.4.4. (E)-3-[10-(2-Ethylhexyl)-10H-phenothiazin-3-yl]-2-propenal 1,1-diphenylhydrazone (**6d**).* Propenal **4d** (731 mg, 2 mmol) and 1,1-diphenylhydrazine hydrochloride (662 mg, 3 mmol) were used to prepare **6d** according to the general procedure after refluxing for 1.5 h. Yield 777 mg (73%), yellow resinous substance; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85–0.90 (6H, m), 1.23–1.49 (8H, m), 1.90–1.98 (1H, m), 3.73 (2H, d, J=6.9 Hz), 6.38 (1H, d, J=15.9 Hz), 6.79–7.05 (5H, m), 7.13–7.22 (10H, m), 7.40–7.45 (4H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.4, 14.0, 23.0, 23.9, 28.5, 30.6, 35.8, 51.0, 115.8, 115.9, 122.4 (4× C), 124.4 (2× C), 125.16, 125.22, 125.4, 125.9, 127.1, 127.6, 128.4, 129.4, 129.7 (4× C), 131.5, 133.0, 138.5, 143.5 (2× C), 145.25, 145.32. IR (KBr, cm^{-1}): ν 3059, 3037, 2956, 2924, 2854, 1589. MS m/z (%): 503 (M+H$^+$, 100). Anal. Calcd for $C_{35}H_{37}N_3S$: C, 79.05; H, 7.01; N, 7.90. Found: C, 79.42; H, 6.91; N, 8.33.

*4.4.5. (E)-3-{7-[(E)-2-Formyl-1-ethenyl]-10-propyl-10H-phenothiazin-3-yl}-2-propenal di(1-methyl-1-phenylhydrazone) (**7a**).* Bispropenal **5a** (698 mg, 2 mmol) and 1-methyl-1-phenylhydrazine (733 mg, 6 mmol) were used to prepare **7a** according to the general procedure after refluxing for 5 h. Yield 1.229 g (55%), orange crystals, mp 224–226 °C (from ethanol); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.02 (3H, t, J=7.5 Hz), 1.78–1.90 (2H, m), 3.37 (6H, s), 3.80 (2H, t, J=7.2 Hz), 6.59 (2H, d, J=15.9 Hz), 6.62–7.32 (18H, m), 7.39 (2H, d, J=9.0 Hz). NMR (75 MHz, $CDCl_3$): δ 11.2, 20.1, 33.4, 49.3, 115.3, 115.4 (4× C), 120.7, 124.2, 124.3, 125.0, 125.4, 126.0, 129.0 (4× C), 131.8, 135.1, 144.0, 147.5. IR (KBr, cm^{-1}): ν 3027, 2962, 2925, 2867, 1596, 1547, 1498, 1475. MS m/z (%): 558 (M+H$^+$, 30). Anal. Calcd for $C_{35}H_{35}N_5S$: C, 75.37; H, 6.33; N, 12.56. Found: C, 75.67; H, 6.33; N, 12.39.

*4.4.6. (E)-3-{7-[(E)-2-Formyl-1-ethenyl]-10-propyl-10H-phenothiazin-3-yl}-2-propenal di(1,1-diphenylhydrazone) (**7b**).* Bispropenal **5a** (590 mg, 2 mmol) and 1,1-diphenylhydrazine hydrochloride (1324 mg, 6 mmol) were used to prepare **7b** according to the general procedure after refluxing for 1 h. Yield 738 mg (75%), deep yellow glassy substance; T_g 106 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.01 (3H, t, J=7.5 Hz), 1.81 (2H, sext, J=7.5 Hz), 3.78 (2H, t, J=7.5 Hz), 6.36 (2H, d, J=14.7 Hz), 6.75 (2H, d, J=9.0 Hz), 6.92 (2H, d, J=9.3 Hz), 7.02 (4H, t, J=9.0 Hz), 7.13–7.22 (14H, m), 7.39–7.45 (8H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.2, 20.0, 49.3, 115.2 (2× C), 122.4 (8× C), 124.2 (2× C), 124.4 (4× C), 125.0 (2× C), 125.3 (2× C), 125.6 (2× C), 129.7 (8× C), 131.6 (2× C), 132.8 (2× C), 138.4 (2× C), 143.5 (4× C), 144.1 (2× C). IR (KBr, cm^{-1}): ν 3035, 2960, 2927, 2869, 1587. MS m/z (%): 683 (M+H$^+$, 100). Anal. Calcd for $C_{45}H_{39}N_5S$: C, 79.26; H, 5.76; N, 10.27. Found: C, 79.63; H, 6.02; N, 10.21.

*4.4.7. (E)-3-{10-(2-Ethylhexyl)-7-[(E)-2-formyl-1-ethenyl]-10H-phenothiazin-3-yl}-2-propenal di(1-methyl-1-phenylhydrazone) (**7c**).* Bispropenal **5b** (839 mg, 2 mmol) and 1-methyl-1-phenylhydrazine (733 mg, 6 mmol) were used to prepare **7c** according to the general procedure after refluxing for 4 h. Yield 879 mg (70%), light brown resinous substance; T_g 72 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.9–0.95 (6H, m), 1.29–1.54 (8H, m), 1.95–2.03 (1H, m), 3.40 (6H, s), 3.77 (2H, d, J=7.2 Hz), 6.64 (2H, d, J=16.2 Hz), 6.86 (2H, d, J=9.0 Hz), 6.96–7.06 (4H, m), 7.26–7.44 (14H, m). NMR (75 MHz, $CDCl_3$): δ 10.5, 14.0, 23.0, 23.9, 28.5, 30.6, 33.2 (2× C), 36.0, 51.1, 115.3 (4× C), 115.9 (2× C), 120.6 (2× C), 125.2 (2× C), 125.3 (2× C), 125.5 (2× C), 126.1 (2× C), 129.0 (4× C), 131.7 (2× C), 131.9 (2× C), 134.9 (2× C), 144.7 (2× C), 147.6 (2× C). IR (KBr, cm^{-1}): ν 3026, 2958, 2923, 2857, 1596. MS m/z (%): 629 (M+H$^+$, 100). Anal. Calcd for $C_{40}H_{45}N_5S$: C, 76.52; H, 7.22; N, 11.15. Found: C, 76.35; H, 7.47; N, 11.31.

*4.4.8. (E)-3-{10-(2-Ethylhexyl)-7-[(E)-2-formyl-1-ethenyl]-10H-phenothiazin-3-yl}-2-propenal di(1,1-diphenylhydrazone) (**7d**).* Bispropenal **5b** (839 mg, 2 mmol) and 1,1-diphenylhydrazine hydrochloride (1324 mg, 6 mmol) were used to prepare **7d** according to the general procedure after refluxing for 2 h. Yield 1.052 g (70%), light brown resinous substance; T_g 56 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85–0.90 (6H, m), 1.24–1.48 (8H, m), 1.86–1.99 (1H, m), 3.71 (2H, d, J=7.2 Hz), 6.37 (2H, d, J=15.3 Hz), 6.79 (2H, d, J=9.0 Hz), 6.92–7.05 (4H, m), 7.15–7.22 (16H, m), 7.40–7.45 (8H, m). NMR (75 MHz, $CDCl_3$): δ 10.4, 14.0, 23.0, 23.9, 28.5, 30.6, 35.9, 51.1, 115.8 (2× C), 122.4 (8× C), 124.4 (4× C), 125.26 (2× C), 125.33 (2× C), 125.4 (2× C), 125.5 (2× C), 129.7 (8× C), 131.7 (2× C), 132.8 (2× C), 138.5 (2× C), 143.5 (4× C), 144.8 (2× C). IR (KBr, cm^{-1}): ν 3036, 2956, 2924, 2855, 1588. MS m/z (%): 753

($M+H^+$, 100). Anal. Calcd for $C_{50}H_{49}N_5S$: C, 79.86; H, 6.57; N, 9.31. Found: C, 80.12; H, 6.91; N, 9.03.

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References and notes

1. (a) Kano, T.; Tanaka, Y.; Maruoka, K. *Org. Lett.* **2006**, *8*, 2687; (b) Nagy, I.; Hajós, G.; Riedl, Z.; Egyed, O.; Pápai, I. *Tetrahedron* **2007**, *63*, 4730; (c) Brazier, J. B.; Cavill, J. L.; Elliot, R. L.; Evans, G.; Gibbs, T. J. K.; Jones, I. L.; Platts, J. A.; Tomkinson, N. C. O. *Tetrahedron* **2009**, *65*, 9961; (d) Ma, Y.; Jin, S.; Kan, Y.; Zhang, Y. J.; Zhang, W. *Tetrahedron* **2010**, *66*, 3849.
2. For the recent examples: (a) Sridharan, V.; Perumal, P. T.; Avendaño, C.; Menéndez, C. *Tetrahedron* **2007**, *63*, 4407; (b) Kumar, A.; Maurya, R. A. *Tetrahedron* **2008**, *64*, 3477; (c) Jiang, J.; Yu, J.; Sun, X.-X.; Rao, Q.-Q.; Gong, L.-Z. *Angew. Chem., Int. Ed.* **2008**, *47*, 2458; (d) Cui, P.; Xu, L.; Shi, Z.; Gan, L. *J. Org. Chem.* **2011**, *76*, 4210; (e) Zhou, Y.-Q.; Wang, N.-X.; Zhou, S.-B.; Huang, Z.; Cao, L. *J. Org. Chem.* **2011**, *76*, 669.
3. (a) Huang, C.; Da, S.; Li, Y.; Li, Y. *J. Nat. Prod.* **1997**, *60*, 277; (b) Crimmins, M. T.; Haley, M. W. *Org. Lett.* **2006**, *8*, 4223; (c) Hadden, M.; Nieuwenhuyzen, M.; Osborne, D.; Stevenson, P. J.; Thomson, N.; Walker, A. D. *Tetrahedron* **2006**, *62*, 3977.
4. (a) Šačkus, A.; Amankavičienė, V.; Degutytė, R. *Chemija* **1999**, *10*, 218; (b) Krieg, R.; Eitner, A.; Günther, W.; Schürer, C.; Lindenau, J.; Halbhuber, K.-J. *J. Mol. Histol.* **2008**, *39*, 169; (c) Vedernikov, A. I.; Ushakov, E. N.; Kuz'mina, L. G.; Churakov, A. V.; Strelenko, Y. A.; Wörner, M.; Braun, A. M.; Howard, J. A. K.; Alfimov, M. V.; Gromov, S. P. *J. Phys. Org. Chem.* **2010**, *23*, 195; (d) Sergeeva, T. I.; Gromov, S. P.; Vedernikov, A. I.; Kapichnikova, M. S.; Alfimov, M. V.; Möbius, D.; Zaitsev, S. Y. *Colloids Surf., A* **2005**, *264*, 207.
5. Sakai, K.; Hashimoto, M.; Tsutsui, K. U.S. Patent 4,332,948, 1982; (b) Ando, O.; Murayama, T.; Ono, H.; Suzuki, T. U.S. Patent 4,987,045, 1991; (c) Liu, J.-M.; Shen, S.-Y.; Teng, K.-F. U.S. Patent 5,453,343, 1995.
6. (a) Heck, R. F.; Nolley, J. P. *J. Org. Chem.* **1972**, *37*, 2320; (b) Jeffery, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1287; (c) Heck, R. F. Vinyl Substitution with Organopalladium Intermediates In; Trost, B. M., Fleming, I., Semmelhack, M. F., Eds. . *Comprehensive Organic Synthesis*; Pergamon: Oxford, 1991; Vol. 4, pp 833–863.
7. (a) Unroe, M. R.; Reinhardt, B. A. *Synthesis* **1987**, 981; (b) Kobayashi, S.; Ueda, T.; Fukuyama, T. *Synlett* **2000**, 883; (c) Linkelstein, B. L.; Benner, E. A.; Hendrixson, M. C.; Kranis, K. T.; Rauh, J. J.; Sethuraman, M. R.; McCann, S. F. *Bioorg. Med. Chem.* **2002**, *10*, 599; (d) Gupta, A. K.; Song, C. H.; Oh, C. H. *Tetrahedron Lett.* **2004**, *45*, 4113; (e) Nejjar, A.; Pinel, C.; Djakovitch, L. *Adv. Synth. Catal.* **2003**, *345*, 612; (f) Noël, S.; Djakovitch, L.; Pinel, C. *Tetrahedron Lett.* **2006**, *47*, 3839.
8. (a) Battistuzzi, G.; Cacchi, S.; Fabrizi, G. *Org. Lett.* **2003**, *5*, 777; (b) Najera, C.; Botella, L. *Tetrahedron* **2005**, *61*, 9688; (c) Pan, K.; Noël, S.; Pinel, C.; Djakovitch, L. *J. Organomet. Chem.* **2008**, *693*, 2863; (d) Alacid, E.; Nhjera, C. *Eur. J. Org. Chem.* **2008**, *18*, 3102; (e) Djakovitch, L.; Pinel, C. *Curr. Org. Synth.* **2009**, *6*, 54; (f) Noël, S.; Pinel, C.; Djakovitch, L. *Org. Biomol. Chem.* **2006**, *4*, 3760.
9. Berthiol, F.; Doucet, H.; Santelli, M. *Catal. Lett.* **2005**, *102*, 281.
10. Kleizienė, N.; Arbačiauskienė, E.; Holzer, W.; Šačkus, A. *Molbank* **2009**, M644.
11. Jeffery, T. *Tetrahedron Lett.* **1994**, *35*, 4103.
12. (a) Lemhadri, M.; Doucet, H.; Santelli, M. *Tetrahedron* **2004**, *60*, 11533; (b) Noël, S.; Luo, C.; Pinel, C.; Djakovitch, L. *Adv. Synth. Catal.* **2007**, *349*, 1128.
13. For recent examples: (a) Wu, J. U.S. Patent 7,897,311, 2011; (b) Franz, A. W.; Stoycheva, S.; Himmelhaus, M.; Müller, T. J. J. *Beilstein J. Org. Chem.* **2010**, *6*, doi:10.3762/bjoc.6.72; (c) Sailer, M; Franz, A. W.; Müller, T. J. J. *Chem.—Eur. J.* **2008**, *14*, 2602; (d) Park, M.-J.; Lee, J.; Park, J.-H.; Lee, S. K.; Lee, J.-I.; Chu, H.-Y.; Hwang, D.-H.; Shim, H.-K. *Macromolecules* **2008**, *41*, 3063; (e) Vaitkeviciene, V.; Kruzinauskiene, A.; Grigalevicius, S.; Grazulevicius, J. V.; Rutkaite, R.; Jankauskas, V. *Synth. Met.* **2008**, *158*, 383; (f) Qiu, X.; Lu, R.; Zhou, H.; Zhang, X.; Xu, T.; Liu, X.; Zhao, Y. *Tetrahedron Lett.* **2007**, *48*, 7582; (g) Yang, L. Y.; Li, L. Q.; Wang, C.; Zhu, F. J.; Lu, Y.; Janietz, S.; Wedel, A.; Hua, Y. L.; Yin, S. G. *J. Lumin.* **2007**, *122/123*, 714; (h) Choi, D. H.; Han, K. I.; Chang, I.-H.; Choi, S.-H.; Zhang, X.-H.; Ahn, K.-H.; Lee, Y. K.; Jang, J. *Synth. Met.* **2007**, *157*, 332.
14. (a) Simokaitiene, J.; Danilevicius, A.; Grigalevicius, S.; Grazulevicius, J. V.; Getautis, V.; Jankauskas, V. *Synth. Met.* **2006**, *156*, 926; (b) Danilevicius, A.; Ostrauskaite, J.; Grazulevicius, J. V.; Gaidelis, V.; Jankauskas, V.; Tokarski, Z.; Jubran, N.; Sidaravicius, J.; Grevys, S.; Dzena, A. *J. Photochem. Photobiol., A* **2004**, *163*, 523.
15. (a) Weiss, D. S.; Abkowitz, M. *Chem. Rev.* **2010**, *110*, 479; (b) Lygaitis, R.; Getautis, V.; Grazulevicius, V. J. *Chem. Soc. Rev.* **2008**, *37*, 770.
16. (a) Sailer, M.; Gropeanu, R.-A.; Müller, T. J. J. *J. Org. Chem.* **2003**, *68*, 7509; (b) Lin, H.-H.; Chang, C.-C. *Dyes Pigm.* **2009**, *83*, 230; (c) Doskocz, J.; Soloducho, J.; Cabaj, J.; Lapkowski, M.; Golba, S.; Palewska, K. *Electroanalysis* **2007**, *19*, 1394; (d) Cho, M. J.; Kim, J. Y.; Kim, J. H.; Lee, S. H.; Dalton, L. R.; Choi, D. H. *Bull. Korean Chem. Soc.* **2005**, *26*, 77.
17. (a) Bodea, C.; Terdic, M. *Acad. Repub. Pop. Rom. Fil. Cluj. Stud. Cercet. Chim.* **1962**, *13*, 81; (b) Biehl, E. R.; Daniel, T.; Reeves, P. C.; Lapis, S. *J. Heterocycl. Chem.* **1974**, *11*, 247; (c) Ebdrup, S. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1147; (d) Radu, C.; Vlassa, M.; Silberg, I. A.; Shöke, M.; Färcaş, S. I.; Culea, M. *Heterocycl. Commun.* **1997**, *3*, 317.
18. Turdean, R.; Bogdan, E.; Terec, A.; Petran, A.; Vlase, L.; Turcu, I.; Grosu, I. *Cent. Eur. J. Chem.* **2009**, *7*, 111.
19. Hwang, D.-H.; Kim, S.-K.; Park, M.-J.; Lee, J.-H.; Koo, B.-W.; Kang, I.-N.; Kim, S.-H.; Zyung, T. *Chem. Mater.* **2004**, *16*, 1298.
20. Braun, S.; Kalinowski, H.-O.; Berger, S. *150 and More Basic NMR Experiments*; Wiley-VCH: Weinheim, 1998.
21. (a) Yang, L.; Feng, J.-K.; Ren, A.-M. *J. Org. Chem.* **2005**, *70*, 5987; (b) Kamtekar, K. T.; Dahms, K.; Batsanov, A. S.; Jankus, V.; Vaughan, H. L.; Monkman, A. P.; Bryce, M. R. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 1129.
22. Vaezi-Nejad, S. M. *Int. J. Electron.* **1987**, *62*, 361.
23. Jovanovic, M. J.; Biehl, E. R. *Org. Magn. Reson.* **1984**, *22*, 491.