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SHORT COMMUNICATIONS

New Thiophene- and Phenothiazine-Containing Chalcones: Synthesis, and Electrochemical Properties

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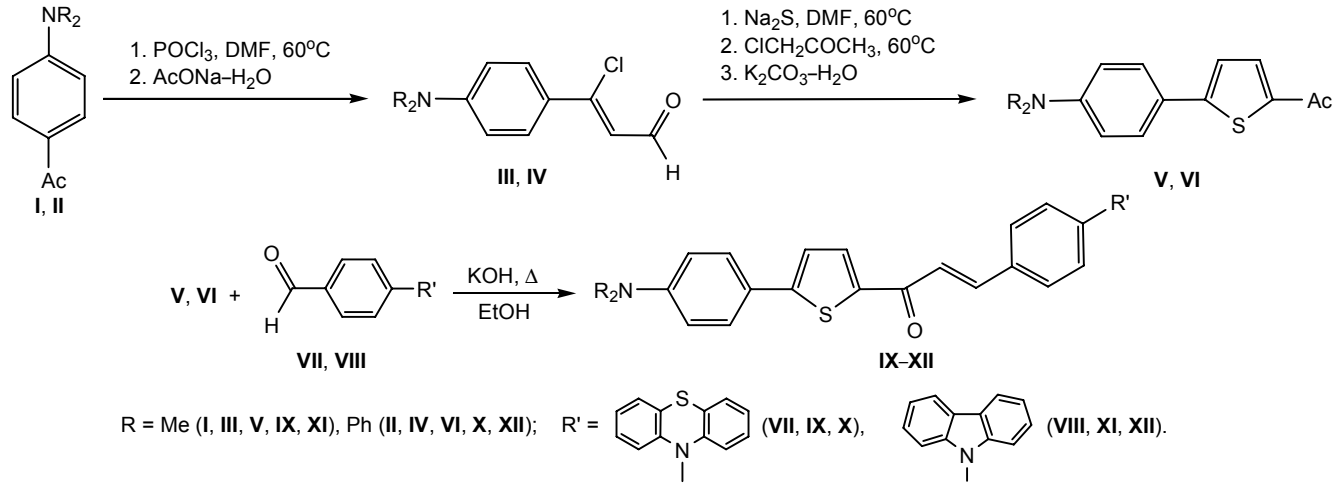
Among the conjugated systems used in design of electronic devices based on organic materials the derivatives of carbazole and phenothiazine occupy are of key importance due to their high thermal stability, hole conductivity and light emission in various spectral regions when used in OLEDs and electrochromic devices, and to hole conductivity [1–4]. Phenothiazine contains electron-rich atoms N and S atoms, possesses a low oxidation potential, and is capable to form stable cation-radicals. The unique electronic and optical characteristics of phenothiazine proceed from its nonplanar geometry providing thereby the possibility to obtain π-packed aggregates and intermolecular excimers [5]. It has been established in our previous research that chalcones prepared on the base of carbazole, phenothiazine, and their substituted derivatives appeared to be good for creation of electrochromic polymer films [6–8]. It is also known that chalcones containing various aromatic fragments in their structure possess nonlinear optical properties indispensable for creation of optoelectronic devices, like electro-optic modulators, optical switches, light-emitting sources, etc. [9, 10]. Therefore it is expedient to synthesize new chalcone series including in their structure various carbo- and heterocyclic fragments and to examine their physicochemical properties, first, from the viewpoint of using them for preparation of polymer compounds, and second from the standpoint of tuning their electronic and optical characteristics by modifying the chemical structure.

In this study there is presented the synthesis and the investigation of physicochemical properties of chalcones **IX–XII** (see the scheme) containing conjugation chains formed by combinations of various carbo- and heterocyclic fragments. For preparation of these chalcones we have initially synthesized two already known methyl ketones **I** [11] and **II** [12], after that a thiophene fragment was introduced into their structure. At the first stage of the synthesis the Vilsmeier–Haak–Arnold reaction was carried out to prepare compounds **III** and **IV**, their cyclization with chloroacetone in the presence of Na_2S afforded methyl ketones **V** and **VI** used further as methylene components in the synthesis of chalcones [11, 13, 14].

Refluxing of the obtained methyl ketones **V** and **VI** with 4-(10*N*-phenothiazin-10-yl)- and 4-(9*N*-carbazol-9-yl)benzaldehydes **VII** and **VIII** in the alkaline alcohol solution gave rise to the target chalcones **IX–XII**. Thus prepared chalcones are the dark red or orange crystalline substances, well soluble in common organic solvents, and their solutions in dichloromethane possess a pronounced yellow and yellow-green fluorescence, and in hexane – a blue one. UV absorption and fluorescence spectra of compounds **V**, **VI** and **IX–XII** were recorded for their solutions in chloroform. Stokes shifts were estimated from the data of absorption and emission spectra. On the basis of the value of the longest absorption wavelength (λ_{onset}) the width of the forbidden band gap (E_g^{opt}) was calculated [15]: in chalcone **IX**, including Me_2N groups E_g^{opt} was 2.44 eV, in chalcone containing Ph_2N groups (**X**) E_g^{opt} was 2.40 eV. The corresponding values of E_g^{opt} calculated from the UV spectra of chalcones **XI** and **XII** containing the carbazole fragment instead of the phenothiazine one were equal to 2.67 and 2.50 eV.



Cyclic voltammetry of chalcones **IX** and **X** showed the presence of three oxidation peaks, especially clearly seen in the first cycle of voltammetry. At increasing the number of cycles the smoothing and coalescence of the peaks come about. Practically always two reduction peaks are observed. Basing on the previously published data describing the electrochemical behavior of the chromophores including 4-$Me_2NC_6H_4$ and $Ph_2NC_6H_4$ fragments [16] it is possible to suggest that the first reversible redox peak of chalcones **IX** and **X** corresponds just to the oxidation of these fragments. Thus using C–Si disk as working electrode and Et_4NClO_4 as background electrolyte, we have determined the values of the first oxidation potential and the corresponding reduction potential E_a^I 860, E_c^I 843 mV for compound **IX**, E_a^I 800, E_c^I 824 mV for chalcone **X**. The following peaks correspond to the oxidation of the phenothiazine fragment. The replacement of two methyl groups in the amine fragment of chalcones by phenyls results in the decrease of the redox potentials values. Cyclic voltammograms of chalcone **X** at the use of different working electrodes are presented in Figs. 1, 2. Due to the polymerizations of the phenothiazine moiety there formed darj blue films on the ITO electrode surface. The values of redox potentials are as follows, mV: 840 (E_{ox}^1), 1030 (E_{ox}^2), 1110 (E_{ox}^3), 870 (E_{red}^1), 1100 (E_{red}^2) (**XI**); 977 (E_{ox}^1), 1279 (E_{ox}^2), 1353 (E_{ox}^3), 1862 (E_{ox}^4), 1154 (E_{red}^1), 1915 (E_{red}^2) (**X**).

3-Aryl-3-chloroprop-2-enals III and IV. 17 mL (182 mmol) of $POCl_3$ was slowly added to 20 mL

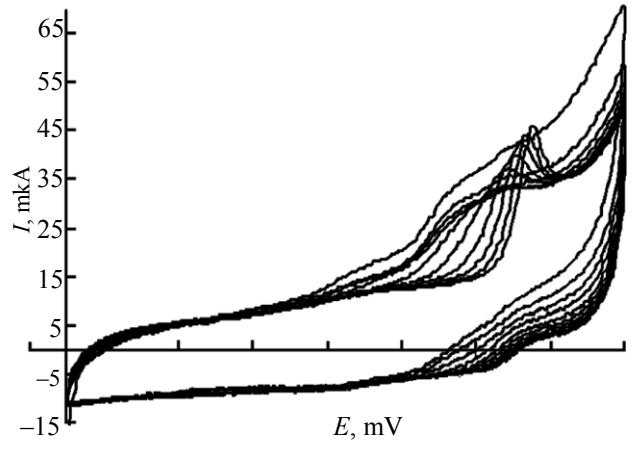


Fig. 1. Cyclic voltammogram of chalcone **X**, C-Si-electrode, 10 cycles, Et_4NClO_4, V_{scan} 50 mV s^{-1}, $CH_3CN–CH_2Cl_2$, 9 : 1.

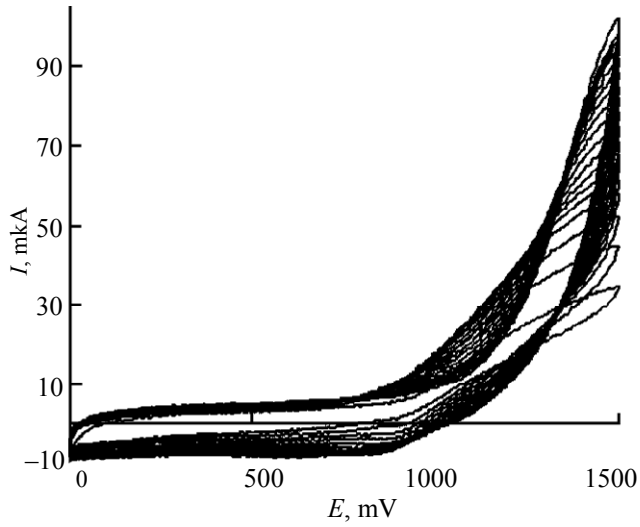


Fig. 2. Cyclic voltammogram of chalcone **X**, ITO-electrode, 20 cycles, Et_4NClO_4, V_{scan} 50 mV s^{-1}, $CH_3CN–CH_2Cl_2$, 9 : 1.

(255 mmol) of DMF at 0°C, the mixture was stirred for 10 min at 0°C, then a solution of 148 mmol of an appropriate ketone (**I** or **II**) in 150 mL of DMF was added dropwise. The reaction mixture was then stirred for 3 h at 60°C, cooled, and 10% water solution of sodium acetate was added till pH 4. The precipitate was filtered off and washed with water. For proving structure of 3-aryl-3-chloroprop-2-enals **III** and **IV** samples were purified by column chromatography, in further transformations the products were used without purification.

3-[4-(Dimethylamino)phenyl]-3-chloroprop-2-enal (III). Yield 85%, brown crystals, mp 112°C (114°C [17]). IR spectrum, ν, cm^{-1}: 1657 (CHO). ^1H NMR spectrum, δ, ppm: 3.06 s (6H, $2CH_3$), 6.58 [1H, C(Cl)=CH–CHO, *J* 6.9 Hz], 6.68 d ($2H_{arom}$, *J* 9.3 Hz), 7.68 d ($2H_{arom}$, *J* 8.7 Hz), 10.15 d (1H, CHO, *J* 6.9 Hz). Mass spectrum, *m/z* (I_{rel}, %): 211 (23) $[M + 2H]^+$, 210 (14) $[M + 1H]^+$, 209 (68) $[M]^+$, 174 (59), 173 (11), 146 (100), 145 (39), 144 (58), 131 (14), 130 (12), 129 (16), 128 (13), 102 (12), 101 (14), 75 (10).

3-[4-(Diphenylamino)phenyl]-3-chloroprop-2-enal (IV). Yield 80%, yellow crystals, mp 103–104°C. IR spectrum, *ν,* cm^{-1}: 1662 (CHO). ^1H NMR spectrum, δ, ppm: 6.76 d [1H, C(Cl)=CH–CHO, *J* 6.9 Hz], 6.95–7.35 m ($6H_{arom}$), 7.50 t ($4H_{arom}$, *J* 8.4 Hz), 7.60 d ($2H_{arom}$, *J* 8.7 Hz), 7.87 d ($2H_{arom}$, *J* 8.7 Hz) 10.16 d (1H, CHO, *J* 6.9 Hz). Mass spectrum, *m/z* (I_{rel}, %): 335 (36) $[M + 2H]^+$, 334 (26) $[M + 1H]^+$, 333 (100) $[M]^+$, 299 (14), 298 (58), 270 (44), 269 (33), 268 (24), 267 (21), 245 (12), 191 (25), 190 (12), 168 (11), 167 (23), 166 (15), 165 (21), 77 (15), 51 (11).

1-(5-Arylthiophen-2-yl)ethanones V and VI. 127 Mmol of propenal (**III** or **IV**) was added to a solution of 30.5 g (127 mmol) of sodium sulfide nanohydrate in 200 mL of DMF. The reaction mixture was then stirred for 3 h at 60°C, therafter 10 mL (127 mmol) of chloroacetone was added dropwise, and the mixture was stirred for 2 h at 60°C. Hereon a solution of 17.6 g (127 mmol) of K_2CO_3 in 10 mL of water was added into reaction mixture and the stirring at 60°C was comtinued for 10 min more, the reaction mixture was cooled to room temperature and poured in water. The resulted precipitate was filtered off and purified by recrystallization from ethanol.

1-{5-[4-(Dimethylamino)phenyl]thiophen-2-yl}-ethanone (V). Yield 75%, yellow crystals, solutions in CH_2Cl_2 possess green fluorescence, mp 124–125°C (124–125°C [11]). UV spectrum, λ_{max}, nm: 320, 400. Fluorescence spectrum, λ_{max}, nm: 498. Stokes shift Δλ 98 nm. IR spectrum, ν, cm^{-1}: 1650 (C=O). ^1H NMR spectrum, δ, ppm: 2.53 s (3H, CH_3CO), 3.01 s (6H, $2CH_3$), 6.70 d ($2H_{arom}$, *J* 8.7 Hz), 7.15 d (1H, thiophene, *J* 3.9 Hz), 7.53 d ($2H_{arom}$, *J* 9.0 Hz), 7.61 d (1H, thiophene, *J* 4.2 Hz). Mass spectrum, *m/z* (I_{rel}, %): 246 (17) $[M + 1H]^+$, 245 (100) $[M]^+$, 244 (19), 230 (32), 202 (18), 158 (34), 115 (13).

1-{5-[4-(Diphenylamino)phenyl]thiophen-2-yl}-ethanone (VI). Yield 70%, yellow crystals, solutions in CH_2Cl_2 possess yellow-green fluorescence, mp 119–120°C. IR spectrum, ν, cm^{-1}: 1651 (C=O). ^1H NMR spectrum, δ, ppm: 2.54 s (3H, CH_3), 7.01 d (2H, Ph, *J* 8.4 Hz), 7.13–7.18 m (2H, thiophene; 2H, Ph), 7.31–7.34 m ($8H_{arom}$), 7.66 d (2H, Ph, *J* 8.7 Hz). Mass spectrum, *m/z* (I_{rel}, %): 370.1 (27.97) $[M + 1H]^+$, 369.2 (100) $[M]^+$, 326.1 (6.19), 282.05 (24.92), 177 (14.54). UV spectrum, λ_{max}, nm: 234, 284, 355. Fluorescence spectrum: λ_{max} 461 nm. Stokes shift Δλ 106 nm.

1,3-Di(hetarylphenyl)prop-2-en-1-ones IX–XII. General procedure. 25 mL of 10% KOH solution in EtOH was added to a solution of 0.01 mol of aldehyde (**VII** [18] or **VIII**) and 0.01 mol of ketone (**V** or **VI**) in 25 mL of EtOH, then the mixture was refluxed for 12 h, on cooling it was poured in water and extracted with CH_2Cl_2. The extract was evaporated, the residue was chromatographed on a column (silica gel, eluent ethyl acetate–hexane, 1 : 1).

1-{5-[4-(Dimethylamino)phenyl]thiophen-2-yl}-3-[4-(10*H*-phenothiazine-10-yl)phenyl]prop-2-en-1-one (IX). Yield 60%, red crystals, solutions in CH_2Cl_2 possess yellow-green fluorescence, mp 94–96°C. UV spectrum, λ_{max}, nm: 240, 260, 320, 339, 400, 415. Fluorescence spectrum, λ_{max}, nm: 514, 565. Stokes shift Δλ 150 nm. IR spectrum, ν, cm^{-1}: 1642 (C=O). ^1H NMR spectrum, δ, ppm: 3.01 s (6H, 2 CH_3), 6.97–7.08 m (6H, Ph + phenothiazine), 7.00 and 7.50 d [1H, C(O)CH=, *J* 15.3 Hz], 7.15 d (1H, Th, *J* 4.2 Hz), 7.21 d (1H, Th, *J* 4.2 Hz), 7.33–7.40 m (6H, Ph + phenothiazine), 7.52–7.61 m (4H, Ph), 7.76 and 7.81 d (1H, CH=, *J* 15.9 Hz). Found, %: C 74.62; H 4.96; N 5.31; S 12.01. $C_{33}H_{26}N_2OS_2$. Calculated, %: C 74.68; H 4.94; N 5.28; S 12.08.

1-{5-[4-(Diphenylamino)phenyl]thiophen-2-yl}-3-[4-(10*H*-phenothiazine-10-yl)phenyl]prop-2-en-1-one (X). Yield 65%, red crystals, solutions in CH_2Cl_2 possess yellow-green fluorescence, mp 114–115°C. UV spectrum, λ_{max}, nm: 237, 259, 307, 420. Fluorescence spectrum: λ_{max} 560 nm. Stokes shift Δλ 140 nm.

IR spectrum, ν, cm^{-1}: 1643 (C=O). ^1H NMR spectrum, δ, ppm: 6.99–7.18 m (16H, Ph + pheno-thiazine), 7.27–7.36 m (7H, Ph + phenothiazine), 7.07 and 7.18 d [1H, C(O)CH=, *J* 15.0 Hz], 7.50 t ($2H_{arom}$), 7.67 d ($4H_{arom}$), 7.76 and 7.81 d (1H, CH=, *J* 15.9 Hz). Found, %: C 78.78; H 4.65; N 4.24; S 9.71. $C_{43}H_{30}N_2OS_2$. Calculated, %: C 78.87; H 4.62; N 4.28; S 9.79.

3-[4-(9*H*-Carbazol-9-yl)phenylprop-2-]-1-{5-[4-(dimethylamino)phenyl]thiophen-2-yl}en-1-one (XI). Yield 70%, red crystals, solutions in CH_2Cl_2 possess yellow-green fluorescence, mp 121–122°C. UV spectrum, λ_{max}, nm: 302, 330, 395. Fluorescence spectrum: λ_{max} 495 nm. Stokes shift Δλ 100 nm. IR spectrum, ν, cm^{-1}: 1647 (C=O). ^1H NMR spectrum, δ, ppm: 3.01 s (6H, 2 CH_3), 6.72 d (2H, Ph, *J* 8.4 Hz), 7.05 and 7.10 d [1H, C(O)CH=, *J* 15.3 Hz], 7.23–7.33 m (2H, carbazole), 7.40–7.47 m (3H, carbazole + thiophene), 7.53 d (2H, carbazole, *J* 7.8 Hz), 7.60 (1H, thiophene, *J* 4.2 Hz), 7.65 d (2H, Ph, *J* 8.7 Hz), 7.83 d (2H, Ph, *J* 8.7 Hz), 7.83 and 7.90 d (1H, CH=, *J* 15.3 Hz), 7.84 d (2H, Ph, *J* 8.4 Hz), 8.15 d (2H, carbazole, *J* 7.8 Hz). Found, %: C 79.42; H 5.28; N 5.66; S 6.35. $C_{33}H_{26}N_2OS$. Calculated, %: C 79.49; H 5.26; N 5.62; S 6.43.

3-[4-(9*H*-Carbazol-9-yl)phenyl]-1-{5-[4-(diphenylamino)phenyl]thiophen-2-yl}prop-2-en-1-one (XII). Yield 65%, orange crystals, solutions in CH_2Cl_2 possess yellow fluorescence, mp 91–93°C. UV spectrum, λ_{max}, nm: 293, 367, 440. Fluorescence spectrum: λ_{max} 554 nm. Stokes shift Δλ 114 nm. IR spectrum, ν, sm^{-1}: 1643 (C=O). ^1H NMR spectrum, δ, ppm: 7.00 d (2H, Ph, *J* 8.7 Hz), 7.03 and 7.08 d [1H, C(O)CH=, *J* 15.3 Hz], 7.10–7.16 m (4H, carbazole), 7.15 d (2H, Ph, *J* 8.4 Hz), 7.20 d (2H, Ph, *J* 8.4 Hz), 7.22–7.27 m (5H, thiophene + 2Ph), 7.31 d (2H, Ph, *J* 8.4 Hz), 7.31–7.37 m (2H, 2Ph), 7.39–7.41 m (2H, carbazole), 7.65 d (2H, Ph, *J* 8.7 Hz), 7.75 and 7.81 d (1H, thiophene; 1H, CH=, *J* 15.0 Hz), 8.05–8.13 m (4H, carbazole + Ph). Found, %: C 82.87; H 4.89; N 4.54; S 5.08. $C_{43}H_{30}N_2OS$. Calculated, %: C 82.93; H 4.86; N 4.50; S 5.15.

^1H NMR spectra were recorded in $CDCl_3$ with a Varian Mercury plus 300 spectrometer, internal reference HMDS. Mass spectra were measured with an Agilent Technologies 6890N/5975B instrument. IR spectra were recorded with a Specord 75IR spectrophotometer from mulls in mineral oil. Elemental analysis was carried out using CHNS-932 LECO Corp analyzer. UV spectra of the solutions in $CHCl_3$ were recorded with the help of SF-2000 spectrophotometer. Fluorescence spectra of the solutions in $CHCl_3$ were recorded with Shimadzu RF-5301 spectrofluorimeter, excitation wavelength 220 nm, cell size 10 × 10 mm. The reaction progress was monitored and the compounds purity was controlled by TLC (Silufol plates). The isolation and purification of reaction products was performed by chromatography (Silica gel 60, 0.06–0.20 mm, Lancaster). The electrochemical measurements were carried for monomer solutions (C = 10^{-3} mol/L) in the acetonitrile–CH_2Cl_2 (9 : 1), mixture at room temperature with $Et_4N^+ClO_4^-$ as background electrolyte (C = 0.1 mol/L) using potentiostat P-8 with electrochemical probe Modul' EM-04 and three electrode electrochemical cell with Si(C)-disk, ITO-plate, or Pt wire as working electrodes, Pt wire as auxiliary electrode, silver chloride electrode as reference electrode. For ITO electrode there were used glass plates covered on one side with indium-tin-oxides layer Rs 8-12 Aldrich. Potential scan rate (V_{scan}) was 50–100 mV/s.

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