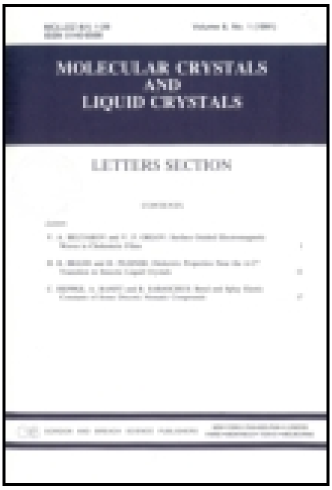
This article was downloaded by: [Xian Jiaotong University]
On: 11 December 2014, At: 13:22
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Properties of 1,3-Indandione-Disubstituted Derivatives of Carbazole, Phenothiazine, and Phenoxazine

Vita Zilinskaite [a], Dalius Gudeika [a], Juozas V. Grazulevicius [a] & Jonas Sidaravicius [b]

[a] Department of Organic Technology, Kaunas University of Technology, Radvilenu Pl. 19, LT- 50254, Kaunas, Lithuania

[b] Department of Polygraphic Machines, Vilnius Gediminas Technical University, J. Basanavičiaus Str. 28, LT-03224, Vilnius, Lithuania

Published online: 28 Mar 2014.

To cite this article: Vita Zilinskaite, Dalius Gudeika, Juozas V. Grazulevicius & Jonas Sidaravicius (2014) Synthesis and Properties of 1,3-Indandione-Disubstituted Derivatives of Carbazole, Phenothiazine, and Phenoxazine, Molecular Crystals and Liquid Crystals, 590:1, 80-89, DOI: 10.1080/15421406.2013.873851

To link to this article: http://dx.doi.org/10.1080/15421406.2013.873851

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Molecular Crystals and Liquid Crystals, Vol. 590: pp. 80–89, 2014
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.873851

Synthesis and Properties of 1,3-Indandione-Disubstituted Derivatives of Carbazole, Phenothiazine, and Phenoxazine

VITA ZILINSKAITE,[1] DALIUS GUDEIKA,[1] JUOZAS V. GRAZULEVICIUS,[1,*] AND JONAS SIDARAVICIUS[2]

[1]Department of Organic Technology, Kaunas University of Technology,
Radvilenu Pl. 19 LT- 50254, Kaunas, Lithuania
[2]Department of Polygraphic Machines, Vilnius Gediminas Technical University,
J. Basanavičiaus Str. 28 LT-03224, Vilnius, Lithuania

Donor-acceptor type 1,3-indandione derivatives were synthesized and their thermal, optical, photophysical, electrochemical, and photoelectrical properties were studied. They form glasses with the glass transition temperatures ranging from 164 to 249°C. 3,6-di(1,3-indandionyl)-10-methyl-phenothiazine showed the lowest energy emission bands in all the investigated solvents, as well as the largest Stokes shifts. Cyclic voltammograms of the synthesized compounds showed one reversible oxidation couple and quasi-reversible reduction waves. The ionization potentials of the solid samples of the synthesized materials were found to be in the range of 5.52–6.01 eV.

Keywords 1, 3-indandione; donor-acceptor; solvatochromic shift; cyclic voltammogram.

1. Introduction

Compounds possessing donor and accepror moieties represent an important class of compounds used for elucidating the relationships between push-pull chromophores and their optical properties [1]. Although the donor and acceptor strengths and the influence of a π-conjugated bridge have been experimentally addressed in detail, it is necessary to get deeper insight into the relationship between the donor-acceptor strengths and the spectral properties. In the last few decades, the interest in 1,3-indandione derivatives has moved from pure synthetic chemistry to the field of materials science [2]. Indandiones are already well-established materials in photophysics [3]. As a strong electron acceptor, 1,3-indandione moiety was studied as a part of bipolar molecules exhibiting interesting optical properties [4,5–6]. In this work, we designed and synthesized three compounds, in which the electron-accepting 1,3-indandione moieties are linked to electron-rich carbazole, phenothiazine, and phenoxazine cores, and studied their thermal, optical, photophysical, electrochemical, and photoelectrical properties.

The electron-rich carbazole molecular moiety is widely used in the synthesis of organic electroactive materials. Carbazole-based derivatives possess good chemical, environmental, and electrochemical stability and the versatility in functionalization [7,8]. Phenothiazine

---

[*] Corresponding author, Juozas V. Grazulevicius. E-mail: juogra@ktu.lt

and phenoxazine moieties are also used in the synthesis of organic electroactive materials [9,10].

2. Experimental

2.1. Materials and Instrumentation

1,3-indandione, 10-methyl-10*H*-phenothiazine, 10*H*-phenoxazine, 9*H*-carbazole, piperidine, 1-iodomethane were purchased from Aldrich Chemical Co and used as received.

Nuclear magnetic resonance (^{1}H NMR) spectra were obtained using a Varrian Unity Inova (300 MHz (^{1}H). All the data are given as chemical shifts in δ (ppm), multiplicity, integration downfield from $(CH_3)_4Si$. Infrared (IR) spectra were recorded using a Perkin Elmer Spectrum GX spectrometer. Mass (MS) spectra were obtained on a Waters ZQ 2000 (Milford, USA). UV spectra were recorded with a Perkin Elmer Lambda 35 spectrometer. DSC measurements were carried out using a Q100 TA DSC series thermal analyzer at a heating rate of 10°C/min under nitrogen flow. Fluorescence (FL) spectra were recorded with a Perkin Elmer LS 55. Melting points were measured on an electrothermal MEL-TEMP melting point apparatus. The cyclic voltammetry (CV) measurements were carried out by a three-electrode assembly cell from Bio-Logic SAS and a micro-AUTOLAB Type III potentiostat-galvanostat. The working electrode was a glassy carbon, the reference electrode and the counter electrode were Ag/Ag^+ 0.01 M and Pt wire, respectively. Argon-purged dichloromethane with tetrabulthylammonium perchlorate ($TBAHFP_6$) 0.1M were used as an electrolyte. The ionization potentials were measured by the method of electron photoemission in air [11]. The samples for ionization potential measurements were prepared, as described previously [12].

2.2. Synthesis

9-Methyl-9*H*-carbazole [13] (MCz, m.p. = 117–119°C, lit. [14] 120.5–121°C), was synthesized by the known procedure of alkylation. 3,6-Diformyl-9-methyl-9*H*-carbazole (MCzF) was synthesized by the method of Vilsmeier as described in the literature [15, 16].

*10-Methyl-10*H*-phenoxazine (MPx).* 1-Iodomethane (1.42 g, 10 mmol) and potassium hydroxide (3.39 g, 60.54 mmol) were added to a solution of 10*H*-phenoxazine (1.85 g, 10.11 mmol) in 20 ml of DMSO under stirring. The reaction mixture was stirred for 24 h at room temperature. Then it was concentrated using a rotary evaporator. The crude product was purified using silica gel column chromatography. A mixture of ethylacetate and hexane (1/8) was used as an eluent. 0.85 g of white crystals (43%) was obtained. M.p.: 158–159°C. ^{1}H BMR (300 MHz, DMSO, δ, ppm): 7.12 (dd, 1H, $J_1 = 7.71$ Hz, $J_2 = 7.37$ Hz, Ar), 7.11 (dd, 1H, $J_1 = 7.71$ Hz, $J_2 = 7.41$ Hz, Ar), 6.99 (dd, 1H, $J_1 = 7.88$ Hz, $J_2 = 2.75$ Hz, Ar), 6.98 (dd, 1H, $J_1 = 7.91$ Hz, $J_2 = 3.01$ Hz, Ar), 6.97 (dd, 1H, $J_1 = 8.42$ Hz, $J_2 = 7.39$ Hz, Ar), 6.96 (dd, 1H, $J_1 = 8.45$ Hz, $J_2 = 7.12$ Hz, Ar), 6.71 (dd, 1H, $J_1 = 8.24$ Hz, $J_2 = 3.87$ Hz, Ar), 6.70 (dd, 1H, $J_1 = 8.85$ Hz, $J_2 = 2.89$ Hz, Ar), 3.52 (s, 3H, $-CH_3$).

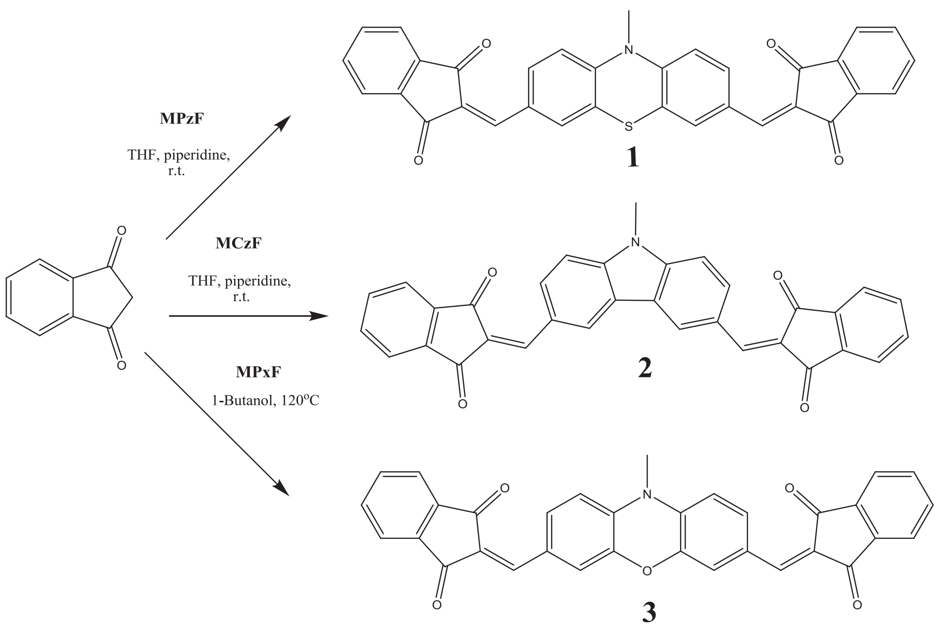
*3,6-Diformyl-10-methyl-10*H*-phenothiazine (MPzF).* 10-Methyl-10*H*-phenothiazine (6 g, 30.46 mmol) was dissolved in 25 ml of dimethylformimide (DMF) and the reaction mixture was cooled down to 0°C. Phosphorus oxychloride (43.08 g, 280.96 mmol) was then added dropwise to the reaction mixture at 0–5°C. When all the required phosphorus oxychloride was added, the temperature of the reaction mixture was increased up to 90°C, and it was stirred for 24 h at this temperature. Then the reaction mixture was cooled down to room temperature and was poured into a cold aqueous potasium hydroxide solution. The reaction mixture was extracted with dichloromethane and distilled water. The organic layer was separated and dried with anhydrous magnesium sulfate. The crude product was purified by column chromatography using ethylacetate and hexane (1/2) as the eluent. The product was recrystallized from the eluent mixture of solvents. The yield was 54% (4.16 g). M.p.: 188–189°C. ^{1}H BMR (300 MHz, DMSO, δ, ppm): 9.83 (s, 2H, $-$CHO), 7.79 (d, 1H, $J =$ 1.29 Hz, Ar), 7.76 (d, 1H, $J =$ 1.78 Hz, Ar), 7.63 (d, 2H, $J =$ 1.23 Hz, Ar), 7.17 (d, 2H, $J =$ 8.47 Hz, Ar), 3.46 (s, 3H, $-CH_3$).

*3,6-Diformyl-10-methyl-10*H*-phenoxazine (MPxF).* Was synthesized from 10-methyl-10*H*-phenoxazine (1.2 g, 5.63 mmol) by the procedure similar to that of the synthesis of MPzF. The product was purified by column chromatography using ethylacetate and hexane (1/2) as the eluent. M.p.: 203–204°C. ^{1}H BMR (300 MHz, DMSO, δ, ppm): 9.73 (s, 2H, $-$CHO), 7.51 (dd, 2H, $J_1 = 2.08$ Hz, $J_2 = 8.02$ Hz, Ar), 7.12 (d, 2H, $J = 1.26$ Hz, Ar), 8.34 (d, 2H, $J = 8.34$ Hz, Ar), 3.20 (s, 3H, $-CH_3$).

3,6-di(1,3-indandionyl)-10-methyl-phenothiazine (1). Was synthesized by the method similar to that described in the literature [17]. 3,6-Diformyl-10-methyl-10*H*-phenothiazine (1 g, 3.7 mmol), 1,3-indandione (1.08 g, 7.2 mmol) and piperidine (0.5 ml) were dissolved in toluene (40 ml). The mixture was refluxed for 12 h. The solvent was then evaporated in vacuum. The residue was purified by column chromatography (ethylacetate/hexane, 2/1) and recrystallized from the eluent mixture of solvents to give 1.7 g of red crystals (43% yield). M.p.: 269–270°C, $C_{33}H_{29}NS$, MW = 527.6 g/mol. ^{1}H BMR (300 MHz, DMSO, δ, ppm): 9.86 (s, 2H), 8,63 (d, 1H, $J = 1.93$ Hz, Ar), 8.41 (dd, 1H, $J_1 = 6.74$ Hz, $J_2 =$ 9.14 Hz, Ar), 8,05–7,92 (m, 3H, Ar), 7.86–7.67 (m, 4H, Ar), 7.41 (t, 2H, Ar), 7.31–7.18 (m, 3H, Ar), 1.28 (t, 3H, -CH_3). IR (KBr), ν, cm^{-1}: 3059 (C$-$H$_{ar}$), 2922, 2822 (C$-$H$_{aliph}$), 1722, 1681 (C$=$O), 1568, 1468 (C$=$C), 1292, 1262, 1201, 1155 (C-O-C); 731 (CH$_{ar}$); MS (APCI$^+$, 20 V), m/z: 529 ($[M + H]^+$).

3,6-di(1,3-indandionyl)-10-methyl-phenoxazine (2). Was synthesized by the procedure similar to that described in the literature [18]. 1,3-Indandione (0.65 g, 4.5 mmol) and 6-diformyl-10-methyl-10H-phenoxazine (0.5 g, 2 mmol) were dissolved in 1-butanol (140 ml) and refluxed at 120°C for 12 h. Then the reaction mixture was cooled down to the room temperature. The solid precipitate was collected and recrystallized from 1-butanol to give 0.54 g of deep red crystals (54% yield). M.p.: 299–301°C, $C_{33}H_{19}NO_5$, MW = 509.52 g/mol. ^{1}H BMR (300 MHz, DMSO, δ, m.d.): 9.75 (d, 2H, $J = 4.63$ Hz, Ar), 8.39 (d, 1H, $J = 2.03$ Hz, Ar), 8.01–7.95 (m, 4H, Ar), 7.68 (s, 1H, Ar), 7.53 (d, 2H, $J = 8.57$ Hz, Ar), 7.21–7.16 (m, 3H, Ar), 7.05–7.00 (m, 3H, Ar), 1.92 (t, 3H, -CH_3). IR (KBr), ν, cm^{-1}: 3065 (C-H$_{ar}$), 2920, 2817, 2730 (C$-$H$_{aliph}$), 1719, 1679 (C$=$O), 1588, 1577, 1492 (C$=$C), 1219, 1109, 1087, 1021 (C$-$O$-$C); 737 (CH$_{ar}$); MS (APCI$^+$, 20 V), m/z: 511 ($[M+H]^+$).

3,6-Di(1,3-indandionyl)-9-methyl-carbazole (3). The synthesis of **3** was carried out by the similar procedure as described for **1** using 3,6-diformyl-9-methyl-9H-carbazole (0.8 g, 3.4 mmol) as the starting compound. The crude product was purified by column chromatography (ethylacetate/hexane, 2/1) to give 1.08 g of brownish powder (74% yield). $C_{33}H_{21}NO_4$, MW = 493.52 g/mol. ^{1}H BMR (300 MHz, DMSO, δ, ppm): 10.05 (s, 2H, Ar),



Scheme 1. Synthetic route to **1–3.**

9. 53 (d, 1H, $J = 3.85$ Hz, Ar), 8.83–8.64 (m, 3H, Ar), 8.10–8.00 (m, 3H, Ar), 7.81–7.63 (m, 4H, Ar), 7.19–7.01 (t, 3H, Ar), 1.61 (t, 3H, -CH_3). IR (KBr), ν, cm^{-1}: 3074 (C-H_{ar}), 2929, 2724 (C-H_{aliph}), 1717, 1673 (C=O), 1559, 1478 (C=C), 1246, 1200, 1151, 1055 (C—O—C); 736 (CH_{ar}); MS ($APCI^+$, 20 V), m/z: 495 ($[M+H]^+$).

3. Results and Discussion

Compounds having electron-rich phenothiazine, carbazole, and phenoxazine moieties disubstituted with electron-deficient 1,3-indandione moieties (**1–3**) were synthesized by the **Knoevenagel** condensation of 1,3-indandione with 3,6-diformyl-10-methyl-10*H*-phenothiazine (**MPzF**), 3,6-diformyl-9-methyl-9*H*-carbazole (**MCzF**) and 3,6-diformyl-10-methyl-10*H*-phenoxazine (**MPxF**), respectively (Scheme 1). The key starting compounds **MCzF** and **MPxF** were obtained by the two-step synthetic routes involving the alkylation of 9*H*-carbazole and 10*H*-phenoxazine, respectively, with 1-iodomethane, followed by formylation of 9-methyl-9H-carbazole (CzF), 10-methyl-10*H*-phenoxazine (**PxF**) by the method of Vilsmeier [15]. **MPzF** was obtained by the formylation of commercially available 10-methyl-10*H*-phenothiazine with phosphorus oxychloride. The synthesized compounds were purified by column chromatography and characterized by IR-, ^{1}H NMR- and mass spectrometries. They are soluble in common organic solvents such as toluene, dioxane, dichloromethane (DCM), and dimethylsulfoxide (DMSO).

The behavior under heating of compounds **1–3** was studied by DSC and TGA. The thermal characteristics of the compounds are summarized in Table 1. All the synthesized compounds (**1–3**) demonstrate the high thermal stability. The temperatures of the onsets of their thermal degradation (T_{ID}) are 354°C and higher, as confirmed by TGA with a heating rate of 20°C/min. The thermal stability of compound **3** is considerably higher than that of **1** and **2**. Compunds **1** and **2** containing phenothiazine and phenoxazine cores were

Table 1. Thermal characteristics of **1–3**

Compound	T_m, (°C)	T_g, (°C)	T_{ID}, (°C)
1	272	164	358
2	—	249	398
3	309	184	354

Scan rate 10°C/min, N_2 atmosphere.

isolated after the synthesis as crystalline materials and their first DSC heating scans revealed endothermal melting signals. No crystallization signals were observed during the cooling scans. In the second DSC heating scans, **1** and **2** exhibited glass transitions at 164 and 184°C, respectively. For the illustration of the above stated, the DSC curves of compound **1** are shown in Fig. 1. Compound **3** with carbazole core showed different behavior in the DSC experiments. Only the glass transition at 249°C was observed in the repeated DSC scans, and no peaks due to crystallization and melting appeared. It is evident that the glass transition temperature of compound **3** with carbazole core is higher compared to those of **1** and **2**. This observation can apparently be explained by an enhanced rigidity of carbazole moiety as compared with those of phenotiazine and phenoxazine.

Optical and photophysical properties of the synthesized derivatives were studied by UV and fluorescence spectrometries. The wavelengths of absorption and emission intensity maxima, Stokes shifts of the solutions of compounds **1–3** in different organic solvents are listed in Table 2. UV spectra of dilute solutions of compounds **1–3** are given in Fig. 2.

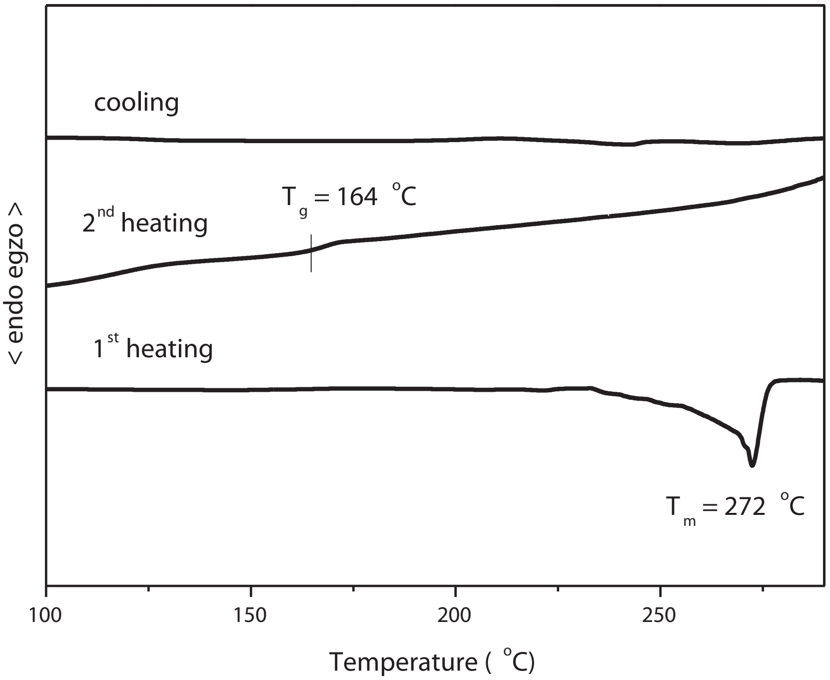


Figure 1. DSK curve of **1** recorded at the heating rate of 10°C/min in N_2 atmosphere.

Table 2. Photophysical data of the solutions of **1-3** in the solvents of different polarities

Solvent (Δf)	**1**			**2**			**3**		
	λ_{abs} /nm	λ_{em} /nm	$\delta\nu$	λ_{abs} /nm	λ_{em} /nm	$\delta\nu$	λ_{abs} /nm	λ_{em} /nm	$\delta\nu$
DCM (0.2171)	458	646	6354	485	521	1424	524	631	3236
Dioxane (0.0200)	454	631	6178	476	508	1323	519	612	2927
Toluene (0.0131)	466	623	5407	490	498	327	522	597	2406
DMSO (0.2637)	459	684	7187	488	534	1765	536	661	3528

λ_{abs} – absorption maximum; λ_{em} – emission maximum; $\delta\nu$ – Stokes shift (cm^{-1}); δf – orientation polarizability of Lippert equation.

UV spectra of dilute solutions of derivatives **1–3** exhibited positive solvatochromic shift changing the solvent from less polar dioxane to more polar DMSO. The shifts of π–π^* absorption bands from 454 to 459 nm for **1**, from 519 to 536 nm for **2**,and from 476 to 488 nm for **3** were observed. The solvatochromic shift for **1** (454–466 nm) was smaller than those of **2** and **3** (Fig. 2). Generally, the positive solvatochromism with increase in the solvent polarity indicates that the dipole moment of a molecule in the excited state (μ_e) is

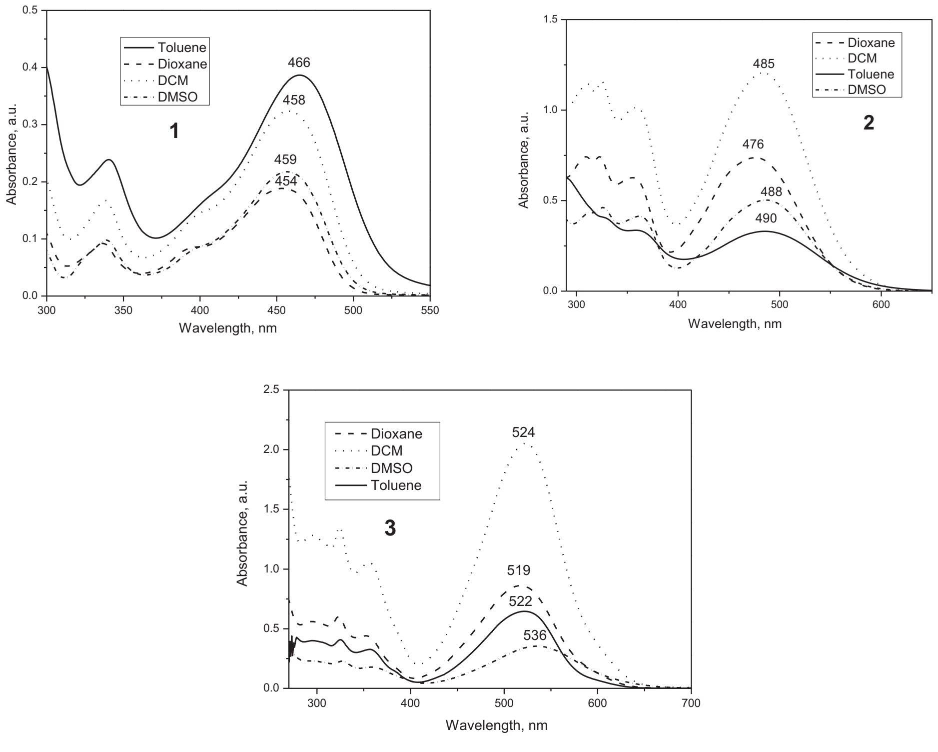


Figure 2. UV absorption spectra of dilute solutions (c = 10^{-5} M) of **1–3** in different solvents.

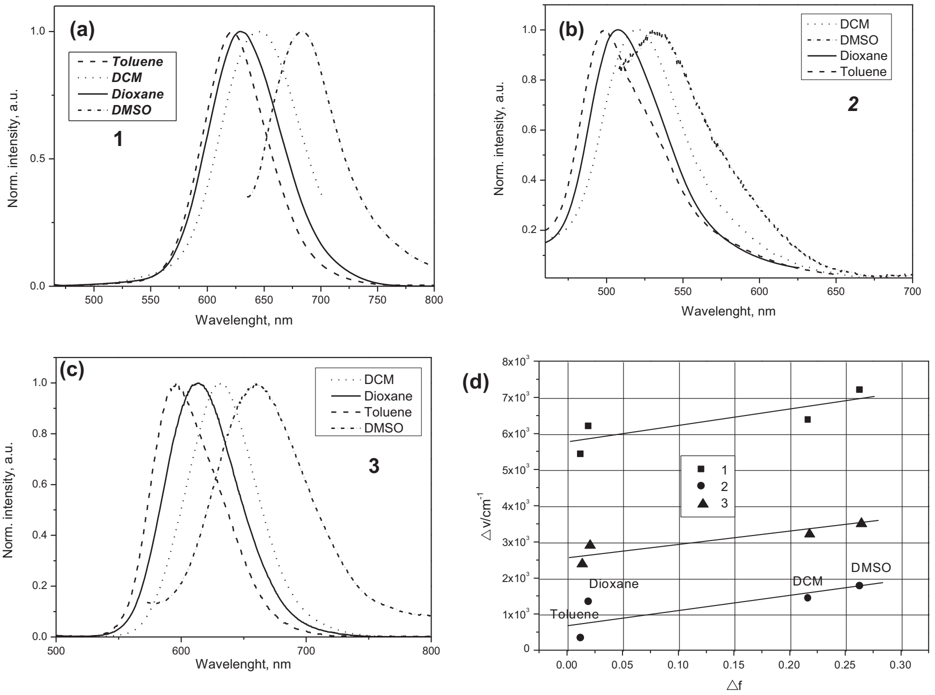


Figure 3. (a—c) normalized fluorescence emission spectra of dilute solutions of **1–3** in different solvents. Excitation wavelengths are absorption maxima. (d) the Lippert-Mataga plot of the Stokes shift $\delta\nu$.

expected to be higher than that in the ground state (μ_g). The value of μ_e for **1–3** for the series of solvents used should be higher than their μ_g. Figure 2 shows that the lowest energy absorption band of compound **2** containing phenoxazine moiety exhibit a certain shift to longer wavelengths with respect to those of compounds **1** and **3,** having phenothiazine and carbazole moieties.

Fluorescence spectra of the dilute toluene, dioxane, DCM, and DMSO solutions of compounds **1–3** are presented in Fig. 3(a–c). The dilute solutions of the materials emit light in the spectral range from green to red, depending on the polarity of a solvent, with the intensity maxima ranging from 498 to 684 nm. Solvatochromic red shifts of the emission spectra were observed for the dilute solutions of compounds **1–3** with increase in the solvent polarity. The maximum red shifts observed in the emission spectra when increasing the polarity were 61, 36, and 64 nm for **1**, **2**, and **3**, respectively. Compound **1** showed the longest emission maxima wavelengths in all investigated solvents, as well as the largest Stokes shifts.

The additional information regarding the solvent sensitivity of the absorption and emission spectra of **1–3** was obtained from the evaluation of the Stokes shifts of **1–3** in terms of Lippert plots [19]:

$$\nu_A - \nu_F = 2/hc \times \Delta\mu^2 \times \Delta f \times a^{-3} + const,$$
$$\Delta f = (\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(2n^2 + 1),\ \ \Delta\mu = \mu_E - \mu_G,$$
$$(\nu_A - \nu_F)/\Delta f = 11307.6\Delta\mu^2 \times a^{-3} + const,$$

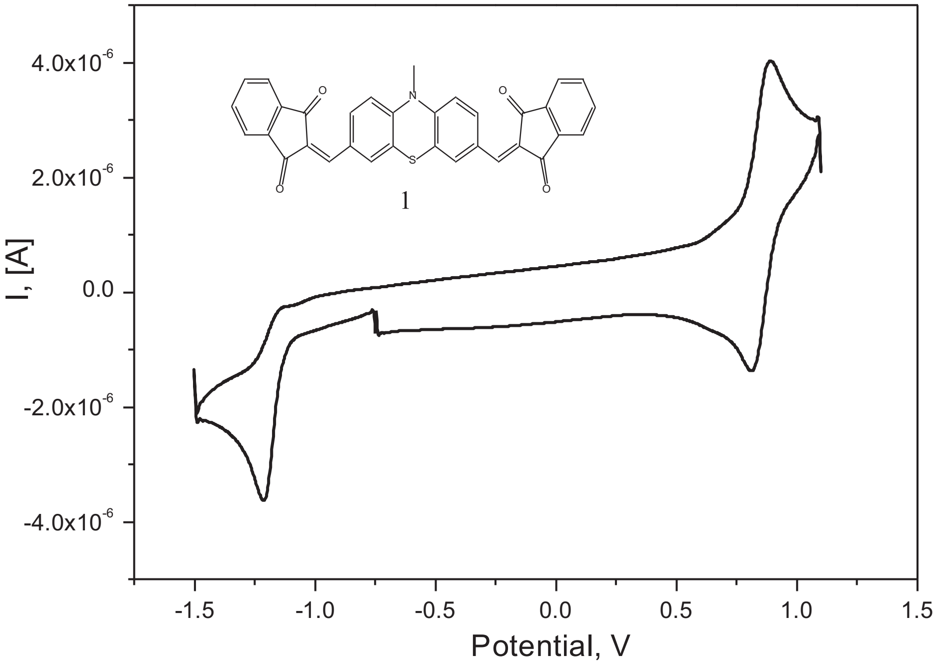


Figure 4. Cyclic voltammogram of **1** registered in an inert atmosphere. Scan rate 100 mV s^{-1}, electrolyte 0.1 M TBAHFP$_6$ in CH$_2$Cl$_2$.

where ν_A and ν_F are the wavenumbers (cm^{-1}) of the absorption and emission maxima, respectively, $h = 6.6256 \times 10^{-27}$ erg s is Planck's constant; $c = 2.9979 \times 10^{10}$ cm s^{-1} is the speed of light; a is the radius of a cavity in which the fluorophore resides; μ_G and μ_E refer to the ground-state and excited-state dipole moments, respectively; the term Δf is the orientation polarizability. The slope of the Lippert plot reflects the solvent sensitivity of a fluorophore. The plot of $\Delta\nu$ (ν_A–ν_F) *vs* Δf for each solvent is presented in Fig. 3d. Positive solvatochromism was found for all compounds, indicating the involvement of solvent-polarity-dependent intramolecular charge transfer emissive states.

In order to gain information on the charge injection capabilities, the electrochemical behavior of compounds **1–3** was estimated by cyclic voltammetry at room temperature in dichloromethane solutions, using a three-electrode system: the platinum rod as a counter electrode, glassy carbon as the working electrode and Ag/AgNO$_3$ as the reference electrode.

Table 3. Redox potentials, optical and electrochemical band gap energies, HOMO/LUMO energy values of **1–3**

Compound	E^{ox}_{onset} vs Fc/V	E^{red}_{onset} vs Fc/V	IP$_{echem,}$ /eV	EA, /eV	E^{el}_{g}, /eV	E^{opt}_{g}, /eV
1	0.63	−1.44	5.43	−3.36	2.07	2.36
2	0.87	−1.30	5.67	−3.50	2.17	2.08
3	0.55	−1.54	5.35	−3.26	2.09	2.11

IP$_{echem}$ = -(E^{ox}_{onset}+4.8); EA = -(E^{red}_{onset}+4.8) (where, E^{red}_{onset} and E^{ox}_{onset} are onset reduction and oxidation potentials versus the Fc/Fc$^+$); E^{el}_{g} = IP – EA.

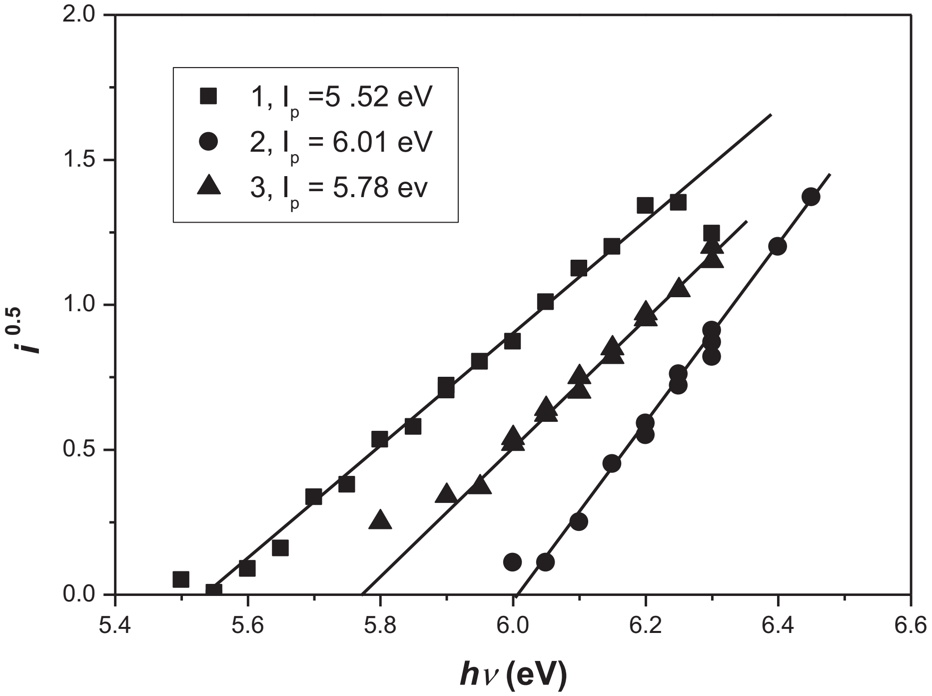


Figure 5. Photoelectron spectra and ionization potentials of thin films of compounds **1–3.**

The cyclic voltammograms of the synthesized compounds in dichloromethane showed reversible oxidation and quasi-reversible reduction couples. For the illustration of this statement, CV curve of **1** is shown in Fig. 4. The redox potentials, electrochemical and optical band gap energies, the values of solid state ionization potentials (IP_{echem}), and electron affinities (EA) are summarized in Table 2. To estimate IP_{echem} and EA, we took $E_{1/2}$ of the first oxidation and $E_{1/2}$ of the first reduction of compounds **1–3** relative to the ferrocenium/ferrocene couple and added the offset in potential to the reported IP of ferrocene (4.8 eV) [20].

The IP_{echem} values of the synthesized compounds range from 5.35 to 5.67 eV. The highest IP_{echem} value was observed for carbazole-based compound **3,** while the values of IP_{echem} **1** and **2** were found to be comparable. The EA range from −3.26 to −3.50 eV. The optical energy band gaps of **1–3**, which were taken as the absorption onsets of the UV spectra of the materials, were estimated to range from 2.08 to 2.36 eV.

Ionization potentials (I_p) of thin solid layers of the synthesized compounds were also estimated by photoelectron spectroscopy. Photoelectron emission spectra and ionization potentials of the layers of **1–3** are shown in Fig. 5. I_p values of the amorphous films of **1–3** range from 5.52 to 6.01 eV. The highest value of ionization energy was again observed for the carbazole-based compound.

4. Conclusions

The derivatives of electron-rich phenothiazine, carbazole, and phenoxazine disubstituted with electron-accepting 1,3-indandione moieties are synthesized, and their thermal, optical, photophysical, electrochemical, and photoelectrical properties are investigated. The synthesized compounds form glasses with the glass transition temperatures ranging from 164 to 249°C. The dilute solutions of the compounds showed red-shift in absorption spectra changing the solvents from less polar dioxane to more polar DMSO. The emission intensity maxima of the dilute solutions of the compounds are solvent-polarity-dependent and ranged from 498 nm to 684 nm. The solutions of 3,6-di(1,3-indandionyl)-10-methylphenothiazine showed longer emission wavelengths in all investigated solvents, as well as the largest Stokes shifts.

Acknowledgments

This research was funded by the **European Social Fund** under the **Global Grant measure**. Habil. dr. V. Gaidelis is thanked for the help in ionization potential measurements.

References

[1] Reichardt, C. (2003). *Solvents and solvent effects in organic chemistry. Chapter 3*. Wiley-VCH: Weinheim.

[2] Kim, D. U., Paik, S. H., Kim, S. H., Tak, Y. H., Han, Y. S., Kim, S. D., Kim, K. B., Ju, H. J., Kim, T. J. (2004). *Mater. Sci. Eng.: C.*, *24*, 147.

[3] Silinsh, E. A., *et al.*. (1996). *NATO ASI series, 3. High Technology*, vol. 9. Kluwer: Dordrecht, 375.

[4] Stiller, B., Saphiannikova, M., Morawetz, K., Ilnytskyi, J., Neher, D., Muzikante, I., Pastors, P., Kampars, V. (2008). *Thin Solid Films*, *516*, 8893.

[5] Jursenas, S., Kurilcik, N., Karpicz, R., Gulbinas, V., Valkunas, L., Rutkis, M., Muzikante, I. (2008). *Thin Solid Films*, *516*, 8909.

[6] Traskovskis, K., Mihailovs, I., Tokmakovs, A., Jurgis, A., Kokars, V., Rutkis, M. (2008). *J. Mater. Chem. 22*, 11268.

[7] Li, J., Grimsdale, A. C. (2010). *Chem. Soc. Rev.*, *39*, 2399.

[8] Blouin, N., Leclerc, M. (2008). *Accounts Chem. Res.*, *41*, 1110.

[9] Yoon, H. S., Lee, W. H., Lee, J. H., Lim, D. G., Hwang, D. H., Kang, I. N. (2009). *Bull. Korean Chem. Soc.*, *30*(10), 2371.

[10] Park, Y., Kim, B., Lee, C., Hyun, A., Jang, S., Lee, J. H., Gal, Y. S., Hyung, K. T., Kim, K. S., Jongwook, P. (2011). *J. Phys. Chem. C*, *115*, 4843.

[11] Miyamoto, E., Yamaguchi, Y., Yokoyama, M. (1989). *Electrophotography*, *28*, 364.

[12] Malinauskas, T., Daskeviciene, M., Kazlauskas, K., Su, H. C., Grazulevicius, J. V., Jursenas, S., Wu, C. C., Getautis, V. (2011). *Tetrahedron*, *67*, 1852.

[13] Jiménez, P., Roux, M. V., Turrión, C. (1990). *J. Chem. Thermodynamics*, *22*, 721.

[14] Campaigne, E., Lake, R. D. (1959). *J. Org. Chem.*, *24*, 478.

[15] Das, G. K., Bijali, Ch., Das, K., Das, B. P. (1999). *J. Chem. Research (S)*, 244.

[16] Vilsmeier, V., Haack, A. (1927). *Berichte Dtsch Chem. Ges.*, *60*, 119.

[17] Wagner, K., Crowe, L. L., Wagner, P., Gambhir, S., Partridge, A. C., Earles, J. C, Clarke, T. M., Gordon, K. C., Officer, D. L. (2010). *Macromolecules*, *43*, 3817.

[18] Li, X., Kim, S. H., Son, Y. A. (2009). *Dyes Pigments*, *82*, 293.

[19] Bangal, P. R., Panja, S., Chakravorti, S. (2001). *J. Photochem. Photobiol. A*, *139*, 5.

[20] Li, Y., Sonar P., Singh S. P., Zeng W., Soh, M. S. (2011). *J. Mater. Chem.*, *21*, 10829.