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SYNTHESIS, OPTICAL AND ELECTROCHEMICAL PROPERTIES OF SUBSTITUTED 2-CINNAMOYL-1,3-INDANDIONE O-METHYL ETHERS

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Abstract

Seven new 2-cinnamoyl-1,3-indandione (2CID) O-methyl ethers with different substituents (R= -H, -CH₃, -OCH₃, -N(C₆H₅)₂, -N(CH₂CH₂CN)₂, julolidyl, -N(CH₃)₂) in 4-position of the cinnamoyl moiety were synthesized. The methylation with dimethylsulfate occurred at the oxygen atom of the exocyclic enol group with high selectivity.

The synthesized compounds were characterized by ¹H-, ¹³C-NMR, IR, UV-Vis and luminescence spectroscopy, their electrochemical properties were investigated by cyclic voltammetry. The obtained results indicates that introducing an electron donating substituents in the 4-position of cinnamoyl moiety facilitates electrochemical oxidation, remarkably shifts absorption and emission bands to longer wavelengths, simultaneously increases extinction coefficient (ϵ). O-methyl ethers with strong electron donating groups (R= -N(C₆H₅)₂, -N(CH₂CH₂CN)₂, julolidyl, -N(CH₃)₂) in molecule are characterized by luminescence with maximum in range from 547 to 647 nm and absolute photoluminescence quantum yields from 0.02 to 0.32. Quantum yield (QY) of chromophore containing julolidyl fragment is solvent dependent. It was 0.32 in chloroform and decreased in other polar (ethanol, acetone) solvents.

Keywords: O-methyl ethers; 2-cinnamoyl-1,3-indandione; methylation; optical properties

1. Introduction

1,3-Indandione and its derivatives have been intensively studied over years due to their wide range of potential applications. First studies were devoted to investigate biological activity for derivatives of 1,3-indandione. Rat-extermination [1], anti-inflammatory [2,3] and other properties were discovered for several 1,3-indandione compounds. But in the last few decades 1,3-indandione moiety has been used as structural element in synthesis of new chromophores and luminophores with non-linear optical (NLO) properties [4-10]. 1,3-Indandione is well known as strong electron acceptor moiety and, when it is bounded with electron donating substituents, the molecules with potential applications as photoactive organic materials can be obtained [5].

The most studied derivative of 1,3-indandione is 4-*N*,*N*-dimethylaminobenzylidene-1,3-indandione (DMABI) whose crystals and films are characterized with efficient photoconductivity [11] and non-linear luminescence [7].

In recent years particular interest has been focused to 2-acyl- derivatives of 1,3-indandione. Due to the β , β '-triketone fragment, which has strong intramolecular

hydrogen bond in the enol form, some compounds from this class are characterized with high stability upon UV-irradiation [12], large Stokes shift [13] and complexation ability with transition [14-16] and rare earth metal ions [17, 18]. As a result compounds with excellent emission and thermal properties can be obtained, for example, 2-benzoyl-1,3-indandione complex with europium(III) ion has been proposed as potential molecular light converter material for new organic light emitting diodes (OLED) [18]. Whereas 2-acetyl-1,3-indandione complexes with transition metal ions such as silver(I) ion has shown proper thermal decomposition temperature and it can be used as precursor for silver films [16]. Only few studies have been devoted to 2-acyl derivatives of 1,3-indandione with prolonged π -conjugate system in molecule - 2-cinnamoyl-1,3-indandiones (2CID). 2CID similar as 2-acyl-1,3-indandiones exist in exocyclic enolic form, which is stabilized by intramolecular hydrogen bond. If the benzene ring of cinnamoyl part contains strong electron donating substituent in *para*- position, push-pull type molecules on the basis of 2CID can be obtained with excellent electronic and optical properties. Ahmedova et al. [19-22] have investigated optical and complexation properties of some 2CID and their analogues. The authors characterized obtained compounds as chromophores with high molar absorptivity, large Stokes shift, good photostability upon UV-irradiance, however due to low solubility in organic solvents transition metal ion complexes with 2CID ligands does not have practical application.

Due to relatively low number of the studies devoted to 2CID and their analogues, our work was directed towards investigation of new chromophores derived from 2CID – their O-methyl ethers. In some papers also O-methylation of $\beta_1\beta_2$ triketone fragment containing compounds were discussed [23-25], although the properties of O-methyl ethers up till now have not been reported. We are presenting here the synthesis of new chromophores, which contains 1,3-indandione moiety as electron acceptor and with different electron donating substituents derived methylated cinnamoyl fragment. These easily obtainable organic chromophores - 2CID O-methyl ethers consisting of π -conjugated system between electron donor and acceptor could possess pronounced emission characteristics and therefore could find an application in optoelectronic devices, for example in OLED. Newly synthesized 2CID O-methyl ethers are characterized by ¹H-, ¹³C-NMR, FT-IR, UV-Vis and luminescence spectroscopy methods and electrochemical measurement. Furthermore, to investigate the structure modifying effects on the electrochemical and optical properties, 2cinnamoyl-1,3-indandione O-methyl ether with -N(CH₃)₂ substituent is compared with the well investigated "push-pull" chromophore 4-*N*.*N*dimethylaminobenzylidene-1,3-indandione (DMABI).

2. Experimental Procedures

2.1. General

The FT-IR spectra in the range from 4000 to 650 cm⁻¹ were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer using KBr pellets.

The ¹H- and ¹³C-NMR spectra were recorded in $CDCl_3$ or $DMSO-d_6$ solutions on a Brucker Avance 300 MHz spectrometer at 300 MHz for ¹H- and 75 MHz for ¹³Cnuclei. Chemical shifts were expressed in parts per million (ppm) relative to solvent signal.

Diffraction data were collected on a Bruker-Nonius Kappa CCD diffractometer using graphite monochromated Mo-K α radiation (λ =0.71073 Å). The crystal structure was solved by direct methods [26, 27] and refined by full-matrix least

squares [28]. The crystal data, details of data collection and refinement are given in Table 1.

The purity of prepared organic compounds was established on Waters 2695 HPLC using Waters 2996 Photodiode array UV-Vis detector. The chromatographic analyses were performed using XTerra® MS C18 (5μ m 2.1×100 mm) column, 50% Acetonitrile/0,1% formic acid solution as mobile phase and flow rate 0.2 ml/min. MS spectra were acquired on a Waters EMD 1000MS mass detector. Mass spectra were obtained in ESI+ mode, voltage 30 V.

The UV-Vis absorption spectra in CHCl₃ solutions were acquired using Perkin-Elmer 35 UV/Vis spectrometer with a 1 cm path length quartz cell.

Emission spectra in CHCl₃ solutions were measured on Quanta Master 40 steady state spectrofluorometer (Photon Technology International, Inc.) using 1 cm path length quartz cuvettes. Absolute photoluminescence quantum yields in CHCl₃ solutions were determined using QuantaMaster 40 steady state spectrofluorometer (Photon Technology International, Inc.) equipped with 6 inch integrating sphere by LabSphere.

The cyclic voltammograms were recorded using a computer controlled electrochemical system PARSAT 2273. The measurements were carried out using a three-electrode cell configuration. Stationary glassy carbon disk (Ø 0.5 cm) was used as a working electrode, Pt wire - as an auxiliary electrode. Potentials were measured vs saturated calomel electrode (SCE) and recalculated vs normal hydrogen electrode (NHE). The potential scan rate was 100 mV/sec. Electrochemical redox reactions were studied in 0,1 M tetrabutyl-ammonium tetrafluorophosphate (TBAPF₆) acetonitrile solution under Ar atmosphere. Acetonitrile (Merck, puriss. grade) was distilled over phosphorus pentoxide, stored over calcium hydride and distilled just before use.

Melting points were determined using Stuart SMP101 apparatus and are uncorrected. TLC analyses were performed on MERCK silica gel plates and were detected with EURO-BST-203LS UV detector.

All solvents were purchased from Acros Organics with purity of $\geq 99\%$. Dimethylsulphate was purchased from Sigma-Aldrich with purity of $\geq 99\%$. Acetone was dried and distilled over K₂CO₃. Piperidine was purified by distillation before use. 2-Acetyl-1,3-indandione was synthesized as described in the literature [17] and 4-*N*,*N*-dimethylaminobenzylidene-1,3-indandione as in the study [29]. The synthetic route of compounds **3a-g** and **4a-g** are shown in Scheme 1.

Scheme 1

2.2. Synthesis of compounds **3a-g**

2-Acetyl-1,3-indandione **1** (0,010 mol), derivative of benzaldehyde **2a-g** (0,010 mol) and piperidine (0,005 mol) was refluxed at 110 °C for 2 hours. Then reaction mixture was cooled to 80 °C and 8 ml of ethanol was added. Solution was boiled for 30 minutes, and after cooling, the formed crystals were filtered off and washed with ethanol. Products were recrystallized from CH_2Cl_2 and EtOH mixture.

(*E*)-2-(1-hydroxy-3-phenylallylidene)-2*H*-indene-1,3-dione (**3a**), Yield 32%, M.P.=186-187 °C. ¹H-NMR (CDCl₃), δ, [ppm]: 13.20 (s, 1H), 8.04 (d, *J*=15.0 Hz, 1H), 7.92 (d, *J*=15.0 Hz, 1H), 7.89 (m, 2H), 7.74 (m, 4H), 7.46 (m, 3H). ¹³C-NMR (CDCl₃), δ, [ppm]: 197.59, 188.60, 173.25, 145.04, 138.65, 134.25, 134.25, 134.00,

133.50, 131.00, 129.03, 122.94, 122.50, 118.14, 108.02. IR, (KBr), v, [cm⁻¹]: 3400-3200 (v_{OH}), 3027 (v_{CH}), 1704 (v_{C=O}), 1620 (v_{C=O}, c_{=C}), 1579, 1564 (v_{C=C(Ph)}). MS (ES+) m/z: 277.00 (M⁺ requires 277.08), (ES-) m/z: 275.20 (M⁻ requires 275.08).

(*E*)-2-(1-hydroxy-3-(p-tolyl)allylidene)-2*H*-indene-1,3-dione (**3b**), Yield 43%, M.P.=184-185 °C. ¹H-NMR (CDCl₃), δ , [ppm]: 13.30 (s, 1H), 7.97 (d, *J*=13.5 Hz, 1H), 7.89 (m, 3H), 7.73 (m, 2H), 7.62 (d, *J*=6.0 Hz, 2H), 7.27 (d, *J*=6.0 Hz, 2H), 2.43 (s, 3H). ¹³C-NMR (CDCl₃), δ , [ppm]: 197.81, 188.60, 173.68, 145.27, 142.25, 141.13, 138.64, 134.90, 134.70, 132.14, 129.90, 128.98, 122.50, 122.23, 116.79, 107.57. IR, (KBr), v, [cm⁻¹]: 3200-3000 (v_{OH}), 2962, 2917 (v_{CH}), 1699 (v_{C=O}), 1646, 1625 (v_{C=O}, v_{C=C}), 1583 (v_{C=C(Ph})). MS (ES+) *m*/*z*: 291.10 (M⁺ requires 291.09), (ES-) *m*/*z*: 289.30 (M⁻ requires 289.09).

(*E*)-2-(*1*-hydroxy-3-(4-methoxyphenyl)allylidene)-2-*H*-indene-1,3-dione (**3c**), Yield 39%, M.P.=193-194 °C. ¹H-NMR (CDCl₃), δ , [ppm]: 13.30 (s, 1H), 7.93 (d, *J*=15.0 Hz, 1H), 7.88 (m, 3H), 7.82 (m, 2H), 7.69 (d, *J*=9.0 Hz, 2H), 6.98 (d, *J*=9.0 Hz, 2H), 3.90 (s, 3H). ¹³C-NMR (CDCl₃), δ , [ppm]: 197.51, 188.80, 173.66, 162.30, 145.04, 140.82, 138.70, 134.74, 133.98, 131.03, 127.67, 122.64, 122.15, 115.33, 114.53, 107.17, 55.42. IR, (KBr), v, [cm⁻¹]: 3100-2600 (v_{OH}), 3070, 2942, 2845 (v_{CH}), 1698 (v_{C=0}), 1624 (v_{C=0}, c_{=C}), 1565 (v_{C=C(Ph})), 1258, 1210 (v_{COC}). MS (ES+) *m/z*: 307.13 (M⁺ requires 307.09), (ES-) *m/z*: 305.28 (M⁻ requires 305.09).

(*E*)-2-(3-(4-*N*,*N*-(*diphenylamino*)*phenyl*)-1-*hydroxyallylidene*)-2*H*-*indene*-1,3-*dione* (**3d**), Yield 60%, M.P.=220-222 °C. ¹H-NMR (CDCl₃), δ , [ppm]: 13.25 (s, 1H), 7.90 (d, *J*=13.5 Hz, 1H), 7.82 (m, 3H), 7.70 (m, 2H), 7.55 (d, *J*=7.5 Hz, 2H), 7.33 (m, 4H), 7.17 (m, 6H), 7.04 (d, *J*=7.5 Hz, 2H). ¹³C-NMR (CDCl₃), δ , [ppm]: 197.59, 188.83, 173.92, 151.01, 145.30, 145.00, 139.10, 138.85, 133.80, 133.50, 130.30, 129.61, 126.00, 124.58, 122.50, 122.06, 120.90, 114.73, 107.33. IR, (KBr), v, [cm⁻¹]: broad 3200-2800 (v_{OH}), 3049, 3033 (v_{CH}), 1696 (v_{C=O}), 1632, 1617, 1548 (v_{C=O}, v_{C=C}, v_{C=C(Ph})), 1504, 1489 (v_{C=C(Ph})). MS (ES+) *m/z*: 444.20 (M⁺ requires 444.15), (ES-) *m/z*: 442.30 (M⁻ requires 442.15).

(*E*)-2-(3-(4-*N*,*N*-(*bis*-(2-*cyanoethyl*))-*amino*)-*phenyl*)-1-*hydroxy*-allylidene)-2*H*-indene-1,3-dione (**3e**), Yield 32%, M.P.=219-220 °C. ¹H-NMR (DMSO), δ, [ppm]: 13.30 (s, 1H), 7.91 (d, *J*=15.0 Hz, 1H), 7.85 (m, 3H), 7.72 (m, 2H), 7.70 (d, *J*=7.5 Hz, 2H), 6.73 (d, *J*=7.5 Hz, 2H), 3.93 (t, *J*=4.6 Hz, 4H), 2.74 (t, *J*=4.6 Hz, 4H).¹³C-NMR (DMSO), δ, [ppm]: 197.23, 188.30, 173.08, 149.87, 146.17, 141.50, 141.00, 133.77, 133.63, 132.15, 124.30, 124.15, 123.51, 122.46, 119.78, 113.36, 106.64, 45.98, 15.75. IR, (KBr), ν, [cm⁻¹]: 3200-2600 (v_{OH}), 3072, 3020, 2965 (v_{CH}), 2935 (v_{CN}), 1698 (v_{C=O}), 1625 (v_{C=O}, c_{=C}), 1587, 1560, 1547 (v_{C=C(Ph})). MS (ES+) *m/z*: 398.13 (M⁺ requires 398.14), (ES-) *m/z*: 396.21 (M⁻ requires 396.14).

(*E*)-2-(3-(1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinolin-9-yl)-1-hydroxyallylidene)-2*H*-indene-1,3-dione (**3f**), Yield 50%, M.P.=225-226 °C. ¹H-NMR (CDCl₃), δ, [ppm]: 13.25 (s, 1H), 7.84 (d, *J*=14.3 Hz, 1H), 7.79 (m, 2H), 7.69 (d, *J*=14.3 Hz, 1H), 7.66 (m, 2H), 7.20 (m, 2H), 3.31 (t, *J*=2.6 Hz, 4H), 2.78 (4H, t, *J*=2.6 Hz, 4H), 1.99 (t, *J*=2.6 Hz, 4H). ¹³C-NMR (CDCl₃), δ , [ppm]: 197.51, 189.00, 174.58, 147.30, 147.00, 140.80, 139.00, 133.93, 133.54, 129.70, 122.30, 122.20, 122.00, 121.95, 110.00, 106.30, 50.00, 27.10, 21.35. IR, (KBr), v, [cm⁻¹]: broad 3200-2600 (v_{OH}), 3014, 2939, 2843 (v_{CH}), 1693 (v_{C=O}), 1627, 1567, 1543 (v_{C=O}, v_{C=C}, v_{C=C(Ph})), 1513, 1463 (v_{C=C(Ph})). MS (ES+) *m/z*: 372.40 (M⁺ requires 372.43).

(*E*)-2-(3-(4-*N*,*N*-(dimethylamino)phenyl)-1-hydroxyallylidene)-2H-indene-1,3-dione (**3g**), Yield 67%, M.P.=210-211 °C. ¹H-NMR (CDCl₃), δ , [ppm]: 13.30 (s, 1H), 7.93 (d, *J*=15.0 Hz, 1H), 7.82 (m, 2H), 7.80 (d, *J*=15.0 Hz, 1H), 7.70 (m, 2H), 7.65 (d, *J*=7.5 Hz, 2H), 6.81 (d, *J*=7.5 Hz, 2H), 3.10 (s, 6H). ¹³C-NMR (CDCl₃), δ , [ppm]: 197.31, 189.01, 174.35, 152.52, 146.30, 140.95, 138.76, 134.31, 133.51, 131.40, 122.67, 122.07, 111.83, 106.49, 40.23. IR, (KBr), v, [cm⁻¹]: broad 3200-2600 (v_{OH}), 3019, 2904 (v_{CH}), 1698 (v_{C=O}), 1631, 1588, 1567 (v_{C=O}, v_{C=C}, v_{C=C(Ph})), 1523 (v_{C=C(Ph})). MS (ES+) *m/z*: 320.20 (M⁺ requires 320.12), (ES-) *m/z*: 318.20 (M⁻ requires 318.12).

2.3. Synthesis of compounds **4a-g**

Under an argon atmosphere to a stirred solution of compounds **3a-g** (0,001 mol) and K_2CO_3 (0,015 mol) in 25 ml anhydrous acetone was added dimethylsulphate (0,015 mol) and the resulting mixture was heated at reflux for 4 hours. After cooling at room temperature, K_2CO_3 was filtered off and washed with acetone. Filtrate was cooled at 5 °C, and formed precipitate was filtered off. After drying the precipitate was purified with column chromatography (mobile phase ethyl acetate: CH_2Cl_2 1:2).

(*E*)-2-(*1-metoxy-3-phenylallylidene*)-2*H-indene-1,3-dione* (4a), Yield 49%, M.P.=151-152 °C. ¹H-NMR (CDCl₃), δ , [ppm]: 8.18 (d, *J*=13.8 Hz, 1H), 7.90 (m, 2H), 7.76 (d, *J*=13.8 Hz, 1H), 7.71 (m, 4H), 7.44 (m, 3H). 4.35 (s, 3H). ¹³C-NMR (CDCl₃), δ , [ppm]: 191.65, 188.84, 173.91, 145.02, 144.60, 140.45, 134.15, 132.00, 128.52, 122.31, 121.58, 112.39, 65.34. IR, (KBr), v, [cm⁻¹]: 3028, 2941, 2855 (v_{CH}), 1705 (v_{C=O}), 1664, 1614, 1593 (v_{C=O}, v_{C=C}, v_{C=C(Ph})), 1525, 1450 (v_{C=C(Ph})). MS (ES+) *m/z*: 291.20 (M⁺ requires 290.31).

(*E*)-2-(*1-methoxy-3-(p-tolyl)allylidene*)-2*H-indene-1,3-dione* (**4b**), Yield 56%, M.P.=139-140 °C. ¹H-NMR (CDCl₃), δ , [ppm]: 8.10 (d, *J*=13.8 Hz, 1H), 7.85 (m, 2H), 7.72 (m, 3H), 7.57 (d, *J*=5.0 Hz, 2H), 7.21 (d, *J*=5.0 Hz, 2H), 4.35 (s, 3H), 2.38 (s, 3H). ¹³C-NMR (CDCl₃), δ , [ppm]: 192.40, 188.85, 174.19, 144.58, 141.49, 140.68, 134.68, 134.00, 133.14, 126.56, 122.23, 120.73, 112.40, 65.35, 21.63. IR, (KBr), v, [cm⁻¹]: 3023, 2926, 2847 (v_{CH}), 1715 (v_{C=0}), 1670, 1612, 1598 (v_{C=0}, v_{C=C}, v_{C=C(Ph})), 1524 (v_{C=C(Ph})). MS (ES+) *m/z*: 305.30 (M⁺ requires 305.11).

(*E*)-2-(*1-methoxy-3-*(4-*methoxyphenyl*)*allylidene*)-2-*H*-*indene-1,3-dione* (4c), Yield 34%, M.P.=148-151 °C. ¹H-NMR (CDCl₃), δ , [ppm]: 8.05 (d, *J*=15.0 Hz, 1H), 7.87 (m, 2H), 7.78 (d, *J*=15.0 Hz, 1H), 7.73 (m, 2H), 7.67 (d, *J*=8.3 Hz, 2H), 6.97 (d, *J*=8.3

Hz, 2H), 4.36 (s, 3H), 3.89 (s, 3H). ¹³C-NMR (CDCl₃), δ , [ppm]: 192.31, 188.07, 175.00, 162.50, 141.10, 134.90, 134.50, 132.00, 128.00, 122.50, 119.00, 114.00, 112.00, 65.55, 55.55. IR, (KBr), v, [cm⁻¹]: 3029, 2965, 2838 (v_{CH}), 1705 (v_{C=O}), 1663, 1593(v_{C=O}, v_{C=C}, v_{C=C(Ph})), 1524, 1509 (v_{C=C(Ph})). MS (ES+) *m/z*: 321.40 (M⁺ requires 321.34).

(*E*)-2-(3-(4-*N*,*N*-(*diphenylamino*)*phenyl*)-1-*methoxyallylidene*)-2*H*-*indene*-1,3-*dione* (**4d**), Yield 53%, M.P.=186-188 °C. ¹H-NMR (CDCl₃), δ , [ppm]: 8.00 (d, *J*=13.6 Hz, 1H), 7.86 (m, 2H), 7.73 (d, *J*=13.6 Hz, 1H), 7.70 (m, 2H), 7.54 (d, *J*=7.5 Hz, 2H), 7.32 (m, 4H), 7.15 (m, 6H), 7.03 (d, *J*=7.5 Hz, 2H), 4.34 (s, 3H). ¹³C-NMR (CDCl₃), δ , [ppm]: 193.00, 189.03, 174.66, 150.54, 147.89, 144.59, 134.29, 131.59, 130.00, 128.20, 125.51, 124.44, 122.27, 121.15, 119.09, 111.70, 65.13. IR, (KBr), v, [cm⁻¹]: 3027, 2970, 2847 (v_{CH}), 1738 (v_{C=0}), 1662, 1581 (v_{C=0}, v_{C=C}, v_{C=C(Ph})), 1521 (v_{C=C(Ph})). MS (ES+) *m*/*z*: 458.30 (M⁺ requires 458.17).

(*E*)-2-(*3*-(*4*-*N*,*N*-(*bis*-(2-cyanoethyl))-amino)-phenyl)-1-metyoxyallylidene)-2*H*-indene -1,3-dione (**4e**), Yield 54%, M.P.=159-160 °C. ¹H-NMR (CDCl₃), δ , [ppm]: 8.00 (d, *J*=13.1 Hz, 1H), 7.85 (m, 2H), 7.72 (m, 3H), 7.76 (d, *J*=6.9 Hz, 2H), 6.70 (d, *J*=6.9 Hz, 2H), 4.34 (s, 3H), 3.90 (t, *J*=5.0 Hz, 4H), 2.72 (t, *J*=5.0 Hz, 4H). ¹³C-NMR (CDCl₃), δ , [ppm]: 192.03, 188.20, 174.67, 147.07, 144.34, 140.91, 134.21, 131.45, 125.98, 122.27, 118.00, 117.90, 112.44, 111.94, 65.36, 47.68, 15.75. IR, (KBr) v, [cm⁻¹]: 3007, 2851 (v_{CH}), 2949 (v_{CN}), 1737 (v_{C=0}), 1655, 1586 (v_{C=0}, v_{C=C}, v_{C=C(Ph})), 1516, 1465 (v_{C=C(Ph})) 1217 (v_{COC}). MS (ES+) *m/z*: 412.30 (M⁺ requires 412.16.)

(*E*)-2-(*3*-(*1*,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinolin-9-yl)-1-methoxyallylidene)-2*H*-indene-1,3-dione (**4f**), Yield 74%, M.P.=178-180 °C. ¹H-NMR (CDCl₃), δ , [ppm]: 7.85 (d, *J*=15.0 Hz, 1H), 7.82 (m, 2H), 7.73 (d, *J*=15.0 Hz, 1H), 7.66 (m, 2H), 7.18 (s, 2H), 4.28 (s, 3H), 3.30 (t, *J*=3.0 Hz, 4H), 2.76 (t, *J*=3.0 Hz, 4H), 1.97 (dt, *J*=3.0 Hz, 4H). ¹³C-NMR (CDCl₃), δ , [ppm]: 197.22, 188.50, 175.52, 147.34, 146.31, 140.60, 133.72, 129.40, 122.27, 121.65, 121.13, 114.50, 110.27, 54.66, 50.10, 27.60, 21.37. IR, (KBr), v, [cm⁻¹]: 2940, 2842, 2812 (v_{CH}), 1702 (v_{C=0}), 1660, 1578, (v_{C=0}, v_{C=C}, v_{C=C(Ph})), 1501, 1434 (v_{C=C(Ph})), 1195 (v_{COC}). MS (ES+) *m/z*: 386.30 (M⁺ requires 386.16).

(*E*)-2-(*3*-(*4*-*N*,*N*-(*dimethylamino*)*phenyl*)-*1*-*methoxyallylidene*)-2*H*-*indene*-1,*3*-*dione* (**4g**), Yield 34%, M.P.=133-134 °C. ¹H-NMR (CDCl₃), δ , [ppm]: 7.95 (d, *J*=14.1 Hz, 1H), 7.85 (m, 2H), 7.79 (d, *J*=14.1 Hz, 1H), 7.68 (m, 2H), 7.61 (d, *J*=7.1 Hz, 2H), 6.70 (d, *J*=7.1 Hz, 2H), 4.32 (s, 3H), 3.09 (s, 6H). ¹³C-NMR (CDCl₃), δ , [ppm]: 192.09, 188.28, 175.40, 152.31, 146.29, 140.67, 133.71, 131.39, 123.37, 121.85, 116.15, 111.89, 111.06, 64.90, 40.24. IR, (KBr), v, [cm⁻¹]: 3072, 3024, 2959, 2869 (v_{CH}), 1697 (v_{C=O}), 1652, 1576 (v_{C=O}, v_{C=C}, v_{C=C(Ph})), 1531, 1499 (v_{C=C(Ph})) 1278 (v_{COC}). MS (ES+) *m/z*: 334.20 (M⁺ requires 333.14)

3. Results and discussion

3.1. Synthesis and characterization of substituted 2-cinnamoyl-1,3-indandiones

Substituted 2-cinnamoyl-1,3-indandiones (2CID) **3a-g** were obtained in Claisen-Schmidt condensation reaction (Scheme 1) between 2-acetyl-1,3-indandione **1** and derivative of benzaldehyde **2a-g** in the presence of piperidine. The chemical structures of the compounds **3a-g** were identified with ¹H-, ¹³C-NMR and FT-IR spectroscopy, compound **3f** was also characterized by X-ray diffraction data.

¹H-NMR spectra of compounds **3a-g** are characterized with broad singlet near 13.20 ppm, which attributes to proton from enol hydroxyl group. Two doublets appears at ~8.00 and 7.90 ppm, which corresponds to protons from double bound of allylidene fragment and their spin coupling constants are in the range from 13.5 to 15.0 Hz indicating that all substituted 2CID **3a-g** exist in trans form. In the ¹³C-NMR spectra of compounds **3a-g** chemical shifts for 1,3-indandione cycle carbon atoms C(9) and C(8) (see Scheme 1) are not equal, thus meaning that chemical environment are not identical for these atoms. This could be explained with hydrogen bond formation between hydroxyl group and one of the two carbonyl groups of the 1,3-indandione moiety.

FT-IR spectra for compounds **3a-g** shows broad band between 3200 and 3400 cm⁻¹, which is assigned to enol hydroxyl group stretching vibrations. Non-bonded hydroxyl group vibrations usually appears as a sharp absorption band near 3670-3580 cm⁻¹, therefore such shift to lower region of inverse centimeters and band broadening indicate that the intramolecular hydrogen bond exist in 2-cinnamoyl-1,3-indandione molecules.

By slow evaporation of saturated dichloromethane solution good quality single crystals of 2-cinnamoyl-1,3-indandione 3f were obtained for crystallographic analysis. The crystal structure of compound 3f is shown in Fig 1. and selected geometrical parameters are listed in Table 2.

Table 1

X-ray diffraction data confirms, that compound 3f in solid state exist in exocyclic enol form, which is stabilized by intramolecular hydrogen bond between carbonyl group oxygen atom (O11) from 1,3-indandione moiety and hydroxyl group (H13-O13) from allylidene fragment. Hydrogen bond O13-H13-O11 is characterized by bond length of 1.66(8) Å (O11...H13) and 2.606(7) Å (O11...O13), and angle of 160(6)° (O13-H13...O11). Interestingly, comparing bonds C2-C3 (1.432(7) Å) and C1-C2 (1.461(7) Å), the latter ones are longer, showing less double bound character. Moreover, bond C3-O11 (1.252(6) Å) are significantly longer than bond C1-O10 (1.222(6) Å), showing more single bond character. These data indicate that the conjugated π -electron system stabilized by the intramolecular hydrogen bond is present in the molecule of 3f. The angles between atoms O10-C1-C2 (128.7(5)°) are wider than for O11-C3-C2 (125.3(5)°), confirming that hydrogen bond causes carbonyl group (C3-O11) positioning closer to hydroxyl group and therefore pseudoaromatic six-membered system is formed in molecule. Similar data were obtained for other 2-acyl-1,3-indandiones, for examples, 2-acetyl-1,3-indandione [14, 30], 2-(3-thiophen-2-yl-1-hydroxy-allylidene)-2H-inden-1,3-dione [21], 2-(3-furan-2yl-1-hydroxy-allylidene)-2H-inden-1,3-dione [21], 2-(1-hydroxy-3-(p-tolyl)allylidene)-2H-indene-1,3-dione [22].

Fig. 1

Dihedral angle between 1,3-indandione moiety and julolidyl substituent plane is 9.60°, meaning that molecule are almost planar. Interestingly, 2-acyl-1,3indandiones with 2-thiophene or 2-furan rings in the molecule are planar [21], but on the contrary 2-(1-hydroxy-3-(p-tolyl)allylidene)-2H-indene-1,3-dione (compound **3b**) is not planar and has larger dihedral angle (11.34°) than **3f** [22]. Planarity of the 1,3indandione moiety approves dihedral angle (0.96°) between cyclopentane and benzene rings planes.

Compound **3f** also exhibits weak intermolecular hydrogen bonds between carbonyl group oxygen atom (O10) as proton acceptor and CH₂ group (C25-H25) from julolidyl substituent as proton donor. Contrary to the compound **3b** [22] cinnamoyl-1,3-indandione **3f** does not show π - π stacking between aromatic rings.

Table 2

3.2. Synthesis and characterization of substituted 2-cinnamoyl-1,3-indandione Omethyl ethers

Methylation of compounds **3a-g** was carried out in acetone under argon atmosphere with dimethlysulphate as alkylating agent in the presence of potassium carbonate (Scheme 1).

Methylation of β , β '-triketones can lead to two different O-methyl ethers [25]. It is possible to add methyl group to carbonyl group of 1,3-indandione moiety or to enol hydroxyl group of cinnamoyl fragment, and the result mainly depends from the used alkylation agent. In the case of substituted 2-cinnamoyl-1,3-indandiones the theoretically possible methylation products - O-methyl ethers **A** and **B** are shown in Fig. 2. It was confirmed by ¹³C-NMR, that all O-methyl ethers **4a-g** have a structure **A**. In the case of structure **B** the symmetry of 1,3-indandione moiety would be lowered, which would lead to different chemical shifts for carbon atoms C(9) and C(8) near to methoxy group. However obtained compounds **4a-g** showed identical chemical shifts for these atoms in ¹³C-NMR spectra.

Fig. 2

The chemical structures of the compounds **4a-g** were confirmed with ¹H- and ¹³C-NMR spectroscopy, and FT-IR spectroscopy. ¹H-NMR spectra of compounds **4a-g** shows minor changes from **3a-g** spectra – a singlet for methoxy group protons appears at 4.35 ppm and broad singlet for hydroxyl group proton disappears. ¹³C-NMR spectra shows more differences. The comparison of ¹³C-NMR spectra chemical shifts for **3a** and O-methyl ether **4a** are given in Table 3. Firstly chemical shifts of carbon atoms C(8) and C(9) from 1,3-indandione moiety became identical, thus indicating that chemical environment around these two atoms are identical. Secondly chemical shifts for atom pairs C(4) and C(7), as well as C(5) and C(6) are identical, which could be explained with more symmetrical structure for O-methyl ethers **4a-g** than for 2CID **3a-g**. Compounds **3a-g** have a strong hydrogen bond between hydroxyl group and carbonyl group from 1,3-indandione moiety in the molecule, which could

make molecule less symmetrical. Furthermore, in the IR spectra of compounds **4a-g** a broad band around 3200 cm⁻¹, corresponding to hydroxyl group vibrations, was not observed.

Table 3

3.3. Electrochemical properties

Redox properties of the synthesized chromophores **4a-g** were investigated by cyclic voltammetry. Both electrode processes - cathodic reduction as well as anodic oxidation - are electrochemically irreversible (Fig. 3).

Fig. 3

In acetonitrile electrochemical reduction of the investigated compounds proceeds in one step at potentials close to -1 V and are practically unaffected by the substituent R (Table 4). On the contrary, electrochemical oxidation potential E_{ox} values are greatly affected by the substituents and are lowered with an increase of their electron donating properties in the line -H, -CH₃, -OCH₃, -N(CH₂CH₂CN)₂, -N(C₆H₅)₂, -N(CH₃)₂, julolidyl (Table 4). It can be concluded that the peak potentials E_{ox} and E_{red} represents the energies of the frontal molecular orbitals, which are localized on the different parts of chromophore molecules - the oxidation process is localized on the cinnamoyl part of the molecules, while 1,3-indandione moiety undergoes electrochemical reduction.

Table 4

3.4. Optical properties

In order to explore the effect of different substituents in cinnamoyl moiety on the optical properties of compounds **4a-g**, absorption spectra were investigated in $1.5 \cdot 10^{-5}$ M chloroform solution. The absorption bands of the chromophores **4a-g** are presented in the Fig. 4 and the values of its maxima (λ_{abs}) and molar extinction coefficients (ϵ) are summarized in Table 4.

As shown in Fig. 4, unsubstituted O-methyl ether **4a** exhibit a broad absorption band with ε value 22392 cm⁻¹·M⁻¹ and maximum at 389 nm, which could be assigned to an intramolecular charge transfer (ICT) transitions from cinnamoyl fragment to 1,3-indandione moiety. Introduction of the donor groups in the benzene ring of cinnamoyl moiety shifts absorption bands to longer wavelength and increases its molar absorptivity. Red shift of absorption band increases in the following sequence - **4b**, **4c**, **4e**, **4d**, **4g**, and **4f**. Introducing weak electron donor groups (methyl and methoxy) in the benzene ring (chromophores **4b** and **4c**) exhibits the smallest red shift for 11 and 35 nm of absorption band maxima, but their molar absorptivity increases two times compared to unsubstituted O-methyl ethers **4d-g** contains electron rich dialkylamino, diphenylamino or polycyclic amino - julolidine substituents, which possess larger electron donating strength. Therefore large bathochromic shifts of 72-125 nm and higher ε values more

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than two times are observed for compounds **4d,e,g**. Similar observations were reported to analogues of substituted 2-cinnamoyl-1,3-indandiones [22]. Julolidyl donor causes the largest bathochromic shift (173 nm), probably due to nitrogen atom location in the donor group. In julolidyl fragment nitrogen is in fixed position, due to polycyclic structure, which promotes the overlap between p-orbital of the amino group and benzene ring. This structure facilitates nitrogen lone pair electron conjugation with the π -electron system of molecule and increase the electron-donating strength of substituent. Similar observation was reported in the study [31].

Fig. 4

The absorption wavelengths of chromophores **4a-g** (the charge – transfer transition energy) linearly depends on the difference between the electrochemical oxidation and reduction peak potentials (E_{ox} - E_{red}), which indicates that the absorption is connected with charge transfer from cinnamoyl fragment to 1,3-indandione moiety (Fig. 5).

Fig. 5

The emission properties of newly synthesized chromophores **4a-g** were also studied in $1.5 \cdot 10^{-5}$ M chloroform solutions; emission bands maxima (λ_{em}), Stokes shifts ($\Delta \lambda_{sts}$) and absolute photoluminescence quantum yields (QY) are depicted in Table 4.

Unsubstituted and methyl and methoxy group substituted O-methyl ethers 4ac does not show emission properties, probably due to weak donating group presence in molecule. The luminescence are observed only for compounds 4d-g, which have both strong electron acceptor (1,3-indandione) and electron donor $(-N(C_6H_5)_2, -$ N(CH₂CH₂CN)₂, julolidyl, -N(CH₃)₂) groups in molecule. Red shift for emission bands increases in the following sequence - 4e, 4g, 4d, and 4f, respectively. Emission bands are wide with maximum in range from 547 to 647 nm (Fig. 6), but photoluminescence quantum yields (QY) varies from 0.02 and 0.06 for 4g and 4d, to 0.32 for compound **4f**. Interestingly, the replacement of the electron donor $N(CH_3)_2$ by -N(CH₂CH₂CN)₂ leads to decrease in QY value below 0.01. This fact could be explained with cyano group location in the donor substituent in chromophore 4e molecule. Cyano group act as an electron acceptor and therefore decrease the donating strength of diethylamino group to 1,3-indandione. High quantum yield of 4f in chloroform solution cause a great interest. We assumed, that high quantum yield of O-methyl ether 4f could be explained with its rigid donor substituent, which prevents amino group from rotation in excited state. Other luminescent O-methyl ethers 4d.e.g have dialkyl or diphenyl amino groups as donors, which could easily twist in the excited state and therefore lead to the fast non-radiative excited-state deactivation of the whole molecule, likewise it was observed for structurally similar compound -DMABI [32].

Fig. 6

However, it was observed, that emission properties for compound **4f** were solvent dependent. QY of **4f** was relatively low in polar solvents, for example, in $1.5 \cdot 10^{-5}$ M ethanol solution QY was only 0.01 and in $1.5 \cdot 10^{-5}$ M acetone solution -

0.03. To explore ethanol influence on the emission properties of 4f, several chloroform-ethanol mixtures with different ethanol volume were prepared, and solutions of 4f with concentration $1.5 \cdot 10^{-5}$ M were prepared and their QY were determined. Obtained data are shown in Fig. 7. As it was expected ethanol has a quenching effect on fluorescence of 4f. QY lowers for 0.1, when ethanol volume is 6% in mixed ethanol-chloroform solution and decreases for half (0.16), when ethanol volume is 15%. Polar solvents probably increase non-radiative processes in the excited state of compound 4f molecules. This could mean that several factors, including structure geometry, interactions of ground and excited states with environment could influence the O-methyl ether 4f emission properties. To explain clearly O-methyl ether 4f emission properties further experimental and theoretical investigations are needed.

Fig. 7

In conclusion for practical application only O-methyl ether **4f** with julolidyl substituent presents valuable red light emission with high QY and therefore should be further investigated for use in the optolectronic materials.

Similarly to 2-cinnamoyl-1,3-indandione analogues with heterocyclic ring in molecule [21] large Stokes shift ($\Delta \lambda_{sts}$) were observed for O-methyl ethers **4d-g**, what can be explained with intramolecular rearrangements in excited state for these molecules.

Absorption and emission spectra of compounds **4a-g** in non-polar (cyclohexane, MTBE), polar aprotic (acetone, DMF) and protic (ethanol) solvents were registered in room temperature, data of λ_{abs} and λ_{em} are depicted in Table 5. Since the dipole moments of the ground and the excited states are different, the change of solvent polarity leads to the different stabilization of these states and cause the solvatochromic effect. For chromophores **4a-c** solvents polarity has an insignificant effect on absorption properties and red shift in DMF compared to cyclohexane by 5-10 nm are observed. Other chromophores **4d-g** shows larger bathochromic shift by 18-47 nm, thus meaning that these chromophores have more polar character than **4a-c**. Impact of solvents polarity on emission properties is similar to those for absorption properties. By changing solvents from cyclohexane to DMF the compounds **4d-g** shows large red shift by 77-99 nm of λ_{em} in DMF compared to one in cyclohexane (or MTBE for **4e**).

Table 5

3.5. Comparison of the characteristics for substituted cinnamoyl-1,3-indandione Omethyl ethers and benzylidene-1,3-indandiones

To gain clearer information about the difference in properties for benzylidene and cinnamoyl derivatives of 1,3-indandione, the compound **4g** with $-N(CH_3)_2$ substituent in cinnamoyl fragment was compared to well-known chromophore 4-*N*,*N*dimethylaminobenzylidene-1,3-indandione (DMABI). The properties of DMABI are given in Table 6. Comparison of absorption properties between DMABI and **4g**, showed that latter one has a red shift of absorption band maximum for 32 nm, due to more extended π -conjugate system in the molecule. Though the DMABI exhibit more intensive absorption band, it is not so wide as absorption band of compound **4g** (89 nm). Furthermore, chromophore 4g relative strongly emits yellow light at 597 nm, whereas DMABI has a weak luminescence with quantum yield <0.01.

Table 6

5. Conclusions

A series of new substituted 2-cinnamoyl-1,3-indandione O-methyl ethers were synthesized in methylation reaction between substituted 2-cinnamoyl-1,3-indandiones and dimethylsulphate. Obtained O-methyl ether structures were confirmed by ¹H-, ¹³C-NMR, FT-IR spectroscopy.

Investigation of electrochemical properties by cyclic voltammetry shows that all obtained compounds are "push-pull" chromophores with a location of highest occupied molecular orbital on cinnamoyl and lowest vacant molecular orbital on 1,3-indandione moieties. All 2-cinnamoyl-1,3-indandione O-methyl ethers exhibit strong absorption in 350-600 nm range with high molar absorptivity (22000-57000 cm⁻¹·M⁻¹). Linear dependence of absorption wavelength on difference between oxidation and reduction peak potentials establishes that absorption is connected with charge transfer from cinnamoyl fragment to 1,3-indandione moiety.

Luminescence for three newly synthesized compounds with no or weak electron donor substituents (R= -H, -CH₃, -OCH₃) were not observed, but other O-methyl ethers with strong electron donor substituents (R= $-N(C_6H_5)_2$, $-N(CH_2CH_2CN)_2$, julolidyl, $-N(CH_3)_2$) in chloroform solutions shows emission with maximum at 647, 547, 634, 597 nm and with absolute photoluminescence quantum yields - 0.06, <0.01, 0.32, 0.02, respectively. High photoluminescence quantum yield in the case of julolidyl derivative is influenced by several factors, including structure geometry and interactions with environment in the ground and excited states. To elucidate emission properties for the compound with julolidyl substituent, further investigations are necessary.

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Supplementary material

The deposition number CCDC 1439051 for compound **3f** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at <u>www.ccdc.cam.ac.uk/data request/cif</u> or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 (0) 1223 336033; email:deposit@ccdc.cam.ac.uk.

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Schemes, Tables and Figures



Scheme 1. Reagents and conditions: (i) Piperidine, 110 $^{\circ}$ C, 2 hours; (ii) dimethylsulphate, K₂CO₃, acetone, 56 $^{\circ}$ C, 4 hours.

Compound	3f
Molecular formula	$C_{24}H_{21}NO_3$
Molecular weight	371.42
Crystal system	Monoclinic
Space group	$P 2_1/n$
<i>a</i> (Á)	8.5990 (4)
<i>b</i> (Á)	21.7570 (5)
<i>c</i> (Á)	10.5800 (14)
β (°)	108.692 (3)
V (Å ³)	1875.0 (3)
Ζ	4
$D_{\rm c}~({\rm Mg}{\cdot}{\rm m}^{-3})$	1.316
<i>T</i> (K)	293
μ (mm ⁻¹)	0.09
<i>F</i> (000)	784
2θ _{max} (°)	54.2
h, k, l range	-10 to 10, -27 to 26, -12 to 13
No. measured reflections	11204
No. independent reflections (R_{int})	4089 (0.139)
No. observed reflections ($I > 2\sigma(I)$)	1399
No. refined parameters/restraints	257/0
$R, wR [I > 2\sigma(I)]$	0.0936, 0.2348
R, wR [all data]	0.2702, 0.3341
Goodness of Fit on F ² , S	0.902
Max., Min electron density (e Å ⁻³)	0.23, -0.21
Maximum Δ/σ	0.021

Table 1 Crystal data and refinement parameters for compound **3f**.

Table 2		
Selected geometry of con	npound	3f .

Bond distances					Bond angles		
C1-O10	1.222 (6)	C14-C1	15	1.347 (7)	C1-C2-C3	107.7 (4)	
C1-C2	1.461 (7)	C15-C1	16	1.447 (7)	C1-C2-C12	129.7 (5)	
C1-C8	1.488 (7)	C16-C1	17	1.392 (7)	C2-C12-O13	118.4 (5)	
C2-C3	1.432 (7)	C16-C2	21	1.391 (7)	C3-C2-C12	122.5 (5)	
C2-C12	1.385 (7)	C17-C1	18	1.367 (7)	O10-C1-C2	128.7 (5)	
C3-O11	1.252 (6)	C18-C1	19	1.425 (7)	O10-C1-C8	125.1 (5)	
C3-C9	1.477 (7)	C19-C20		1.407 (7)	O11-C3-C2	125.3 (5)	
C12-O13	1.340 (6)	C20-C21		1.380 (7)	O11-C3-C9	126.3 (5)	
C12-C14	1.414 (7)						
Hydrogen bond geo	ometry				Symmetr	y code	
D-H…A	D-H	Н…А	D····A	∠D-H…A			
O13-H13…O11	0.98 (7)	1.66 (8) 2.606 (7) 160 (6) intramoleo		ecular			
C25-H25-O10	0.96	2.49 3.422 (8) 162) 162	-1/2+x, $1/2-y$, $1/2+z$		

130	δ, ppm			
C atom	3 a	4 a		
C(1)	188.61	188.84		
C(2)	108.02	112.39		
C(3)	197.59	191.65		
C(4)	122.50	132.00		
C(5)	133.50	134.15		
C(6)	134.25	134.15		
C(7)	122.94	132.00		
C(8)	138.65	145.02		
C(9)	134.25	145.02		
= <u>C</u> -OH	173.25	-		
-CH= <u>C</u> H-Ph	145.04	144.60		
1-C-Ph	134.00	140.45		
2,6-C-Ph	131.00	122.31		
3,4,5-C-Ph	129.03	128.52		
- <u>C</u> H=CH-Ph	118.14	121.58		
$=\underline{C}-OCH_3$	-	173.91		
-O <u>C</u> H3	-	65.34		

Table 3

Comparison of ¹³C-NMR chemical shifts for 2-cinnamoyl-1,3-indandione 3a and O-methyl ether 4a.

 Table 4

 Absorption, emission and electrochemical properties of compounds 4a-g.

1.80	-0.98
1.69	-1.00
1.46	-1.05
0.97	-0.97
1.02	-0.97
0.57	-1.14
0.77	-1.11
_	1.80 1.69 1.46 0.97 1.02 0.57 0.77

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Absorption (λ_{abs}) and emission (λ_{em}) band maxima of compounds 4a-g in various solvents.										
	Cyclohe	exane	M	ГВЕ	Ace	etone	Eth	anol	DM	IF
Compound	λ_{abs}, n	λ _{em} ,	λ_{abs} ,	λ _{em} ,	λ _{abs} ,	λ _{em} ,	λ_{abs} ,	λ _{em} ,	λ_{abs} ,	λ _{em} ,
	m	nm	nm	nm	nm	nm	nm	nm	nm	nm
4 a	374	-	375	-	378	-	382	-	382	-
4b	391	-	389	-	391	-	396	-	396	-
4 c	410	-	410	-	413	-	423	-	420	-
4 d	478, 498sh	524, 555	484	597	488	649	506	645	496	654
4e	_ ^a	_ ^a	455	526	474	593	483	608	488	611
4f	500sh, 522	558, 600	529	610	551	651	573	655	564	662
4 g	471, 491sh	545	487	576	505	619	524	628	518	634

^a-insoluble in cyclohexane Sh – shoulder

Table 5

Table 6				
Absorption, e	emission and	electrochemical	properties of	DMAB

on, emission and electrochemical properties of DMABI.	
Characteristics	DMABI
E _{ox} , V	1.00
E _{red} , V	-1.26
$E_{ox} - E_{red}$, V	2.26
λ_{abs} , nm in chloroform	482
λ_{em} , nm in chloroform	531
$\Delta\lambda_{\rm sts}$, nm	49
Photoluminescence quantum yield in chloroform	< 0.01
Solvatochromic shift of absorption band by	27
changing solvent from cyclohexane to DMF, nm	
ϵ , cm ⁻¹ ·M ⁻¹	68900
Half width of absorption band in chloroform, nm	47

ACCEPTED MANUSCRIPT



Fig. 1. ORTEP drawing of compound **3f** with the atom numbering scheme. All non-hydrogen atoms are drawn as 50% probability ellipsoids.



Fig. 2. Structures of possible methylation products of substituted 2-cinnamoyl-1,3-indandiones.



Fig. 3. Cyclic voltammogramms of chromophores 4a-c.



Fig. 4. Absorption spectra of compounds **4a-g** in 1,5·10⁻⁵M chloroform solutions.



Fig. 5. Correlation of the absorption band maxima with the difference of the electrochemical oxidation and reduction peak potentials.



Fig. 6. Emission spectrum of O-methyl ether **4f** in $1.5 \cdot 10^{-5}$ M chloroform solution.



Fig. 7. Stern-Volmer-like plot of quenching of compound **4f** by ethanol.

Highlights:

- 1. Differently substituted 2-cinnamoyl-1,3-indandione O-methyl ethers were synthesized.
- 2. Methylation occurred at the exocyclic enol group of cinnamoyl fragment.
- 3. Some obtained compounds have high molar absorptivity and intensive luminescence.
- 4. Compound with julolidyl substituent showed relatively high quantum yield.