Accepted Manuscript

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PII: S0143-7208(16)31074-9

DOI: 10.1016/j.dyepig.2017.01.017

Reference: DYPI 5716

To appear in: Dyes and Pigments

Received Date: 27 October 2016

Revised Date: 5 January 2017

Accepted Date: 9 January 2017

Please cite this article as: Malina I, Kampars V, Turovska B, Belyakov S, Novel green-yellow-orange-red light emitting Donor-π-Acceptor type dyes based on 1,3-indandione and dimedone moieties, *Dyes and Pigments* (2017), doi: 10.1016/j.dyepig.2017.01.017.

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Graphical Abstract



Novel Green-Yellow-Orange-Red Light Emitting Donor-π-Acceptor Type Dyes Based on 1,3-Indandione and Dimedone moieties

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9 Abstract

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Ten novel luminescent dyes containing 1,3-indandione or dimedone as 10 11 electron acceptors, amino derivatives (dimethylamino, diphenylamino, julolidine and dibiphenylamino) as electron donor units and different length olefinic linkers (1-12 hydroxyallylidene or 1-hydroxypenta-2,4-dien-1-ylidene) are reported in this study. 13 Newly synthesized compound structures are proven with X-ray analysis, ¹H-, ¹³C-14 NMR spectroscopy and elemental analysis. The UV-Vis absorption, emission, 15 solvatochromism, solvatofluorochromism, redox properties, as well as thermal 16 17 stabilities and quantum chemical calculations of these dyes were systematically investigated to outline relation between structure and properties. These dyes exhibit 18 moderate thermal decomposition temperatures above 200 °C, insignificant 19 solvatochromism and positive, significant solvatofluorochromism, large Stokes shifts 20 and green, yellow, orange and red light emission with quantum yields in range from 21 22 0.03-0.93 in non-polar solvents and in thin films.

Quantum-chemical calculations (DFT) shows, that all dyes exhibit small
HOMO/LUMO gaps from 2.77 to 3.22 eV, which is in agreement with experimental
data.

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29 Keywords: D-π-A dyes; 2-cinnamoyl-1,3-indandione, 2-cinnamoyldimedone,
30 fluorescent dyes, amino donors, positive solvatofluorochromism.

31 **1. Introduction**

32 Among many types of fluorescent organic materials, compounds with π conjugated system between electron donor (D) and electron acceptor (A) have been 33 intensively investigated and found applications in several fields, including medicine 34 35 for fluorescent markers [1], photovoltaic technologies for dye-sensitized solar cells [2] and optoelectronic devices for example, in organic light emitting diodes (OLEDs) [3-36 6], which can be utilized in full-color flat-panel displays for mobile phones and 37 television. The main advantage for compounds with D- π -A structure is the variety of 38 donor, acceptor and π -bridge groups, which allows to adjust the fluorescent material 39 desirable properties, for example emission color. The commonly investigated D- π -A 40 compounds consist of N,N-dialkyl, N,N-diphenyl substituted anilines [3-9], N-41 substituted carbazoles [8] as D parts and dicyanomethylene pyran [3,6,10], 42 43 dicyanomethylene furan [11], pyridine [8,12] and benzothiadiazole [13] as electron A groups. As for the π -bridge, it is possible to use olefinic linkers, such as vinyl or 44 butadienyl fragments [8,10] or different cyclic linkers as thiophene bridge [14]. 45 However, there are not a sufficient data in the literature about comprehension of 46 organic compound structure-luminescence property relationship, which would 47 facilitate new suitable material derivation. Some studies deals with the comparison of 48 different donor [3,4,9], acceptor [14] group or π -linker length [14,15] effect on 49 luminescence properties, however continuous work to understand structure-property 50 51 relationships is necessary.

52 2-Acyl-β-diketones, for example, 2-acetyl-1,3-indandione or 253 acetyldimedone containing three electron withdrawing carbonyl groups are excellent

54 starting materials for D- π -A luminophores. These compounds easily react in aldol 55 condensation reactions with electrophiles, thus forming compounds with extending conjugation system. The most interesting are the 2-acetyl-β-diketone condensation 56 with aromatic aldehydes, which results in 2-cinnamoyl- β -diketone compounds, but 57 only a few studies deal with the investigation of their physical and chemical properties 58 [16-21]. Continuing our previous research work about derivatives of 2-cinnamoyl-1,3-59 indandione O-methyl ethers [22], we investigate new luminophores on the basis of 60 61 two well-known cyclic β -diketones - 1,3-indandione and dimedone. These acceptor units are linked to various amino donors -N,N-dimethyl (N(Me)₂) and N,N-diphenyl 62 63 (N(Ph)₂), *N*,*N*-dibiphenyl (N(BPh)₂) and julolidine through different length of olefinic linkers, such as 1-hydroxyallylidene or 1-hydroxypenta-2,4-dien-1-ylidene. Our goal 64 is to examine structure-property relationship of these luminophores to gain clearer 65 understanding of how π -bridge length, different donor and acceptor units influences 66 67 the thermal, electrochemical, absorption and fluorescent properties. DFT calculations were performed to gain understanding about electronic structures of newly 68 synthesized compounds. 69

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72 2.1. Materials and instrument

2. Experimental

All chemicals used in synthesis and analysis are commercially available and are used without further purification unless otherwise stated. The ¹H- and ¹³C-NMR spectra were recorded in CDCl₃ solutions on a Bruker Avance 300 MHz spectrometer at 300 MHz for ¹H- and 75 MHz for ¹³C- nuclei. Chemical shifts were expressed in parts per million (ppm) relative to solvent signal. The IR spectra in the range from 4000 to 650 cm⁻¹ were recorded on a Perkin-Elmer Spectrum 100 FTIR spectrometer using KBr pellets. Elemental analyses were performed on Euro Vector EA 3000

80 analyzer. Thermal properties were determinated on a Perkin Elmer STA 6000 instrument. Each sample was heated from 30-550 °C with heating rate 10 °C/min in 81 nitrogen atmosphere. The purity of prepared organic compounds was established on 82 Waters 2695 HPLC using Waters 2996 Photodiode array UV-Vis detector. The 83 chromatographic analyses were performed using XTerra® MS C18 (5µm 2.1×100 84 mm) column, 50% Acetonitrile/0,1% formic acid solution as mobile phase and flow 85 86 rate 0.2 ml/min. Low resolution mass spectra were acquired on a Waters EMD 1000MS mass detector (ESI+ mode, voltage 30 V). The UV-Vis absorption spectra of 87 all compounds in solutions and in thin films were acquired using Perkin-Elmer 35 88 UV/Vis spectrometer. Emission spectra in solutions and in thin films were measured 89 on QuantaMaster 40 steady state spectrofluorometer (Photon Technology 90 International, Inc.). Absolute photoluminescence quantum yields in solutions and in 91 thin films were determined using QuantaMaster 40 steady state spectrofluorometer 92 (Photon Technology International, Inc.) equipped with 6 inch integrating sphere by 93 The cyclic voltammograms were recorded using a computer 94 LabSphere. controlled electrochemical system PARSAT 2273. The measurements were carried 95 out using a three-electrode cell configuration. Stationary glassy carbon disk (Ø 0.5 96 97 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 98 99 hydrogen electrode (NHE). The potential scan rate was 100 mV/sec. Electrochemical redox reactions were studied in 0,1 M tetra butylammonium tetrafluorophosphate 100 (TBAPF₆) solution in acetonitrile under Ar atmosphere. Density functional theory 101 (DFT) has been performed using ORCA program [23] and Gaussian 09 [24] package. 102 For auxiliary tasks Avogadro program [25] was used. The geometry optimization of 103 all compounds were obtained using non-local functional B3LYP with 6-311G** [26] 104

105	basis set. Diffraction data was collected on a Bruker-Nonius KappaCCD
106	diffractometer using graphite monochromated Mo-Ka radiation (λ =0.71073 Å). The
107	crystal structure was solved by direct methods [27] and refined by full-matrix least
108	squares [28] using maXus complex of programs [29]. Crystal data or compound 16:
109	monoclinic, $a=12.6089(2)$, $b=10.5952(2)$, $c=25.3021(5)$ Å; $\beta=104.0991(8)$ °;
110	$V=3278.33$ (10) Å ³ ; Z=8, $\mu=0.09 \text{ mm}^{-1}$; $d_{\text{calc}}=1.270 \text{ g/cm}^3$; space group $-P2_1/a$. For
111	structure refinement 5716 independent reflections with $I > 2\sigma(I)$ were used; the final <i>R</i> -
112	factor is 0.137.

113

114 **2.2. Synthesis**

115 2-Acetyl-1,3-indandione (8) was synthesized as described in the literature 116 [30], 2-acetyldimedone (9) as in [31], 4-(bis(4-iodophenyl)amino)benzaldehyde (5) 117 and 4-(di([1,1'-biphenyl]-4-yl)amino)benzaldehyde (7) as in [32]. Synthesis of starting 118 materials 3, 7 are shown in Scheme 1 and in Scheme 2 the synthesis of D- π -A 119 compounds 11-20 are depicted.

120 2.2.1. Synthesis of (E)-3-(4-(N,N-dimethylamino)phenyl)acrylaldehyde (3)

A mixture of 4-N,N-dimethylaminobenzaldehyde (1) (5.00 g, 34 mmol) and 25 121 ml concentrated sulfuric acid was cooled to 0 °C. Then 1 ml distilled water was added 122 slowly. The solution was cooled to 0 °C and acetaldehyde (2) (5.6 ml, 102 mmol) was 123 added dropwise. During the addition temperature of reaction mixture was not allowed 124 to exceed 2 °C. After that dark colored reaction mixture was stirred at 0 °C for 0.5 h 125 and then poured into ice water and neutralized with 10% NaOH solution until pH 7. 126 The obtained brown solution was filtered and crude product was washed with distilled 127 water, crystallized from ethanol twice to give orange solid. Yield: 56%, m.p.=134-136 128 °C. FT-IR (KBr, cm⁻¹): 2921, 2801, 2738, 1662, 1599, 1527, 1456, 1373. ¹H-NMR 129

130 (300 MHz, CDCl₃, ppm): δ = 9.62 (1H, d, *J*=7.5 Hz), 7.48 (2H, d, *J*=7.5 Hz), 7.41 131 (1H, d, *J*=13.1 Hz), 6.71 (2H, d, *J*=7.5 Hz), 6.57 (1H, dd, *J*=7.5 Hz, 13.1 Hz), 3.08 132 (6H, s). MS (C₁₁H₁₃NO), *m/z*: 176.2 (M⁺).

133



135Scheme 1. Reagents and conditions: (a) - concentrated H_2SO_4 , 0 °C, 0.5 h; 10% NaOH. (b)136KI, KIO₃, (CH₃COO)₂O, 80 °C, 4 h. (c) - 2M Na₂CO₃, Pd(PPh₃)₄, dry toluene, 80 °C, 24 h.

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138 2.2.2. Synthesis of derivatives of 2-cinnamoyl-1,3-indandiones (11-15)

To 2-acetyl-1,3-indandione **8** (1.88 g, 10 mmol) and corresponding derivative of benzaldehyde **1,3,4,7,10** (10 mmol) piperidine (5 mmol) was added. Reaction mixture was refluxed at 110 °C for 4 hours, then it 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 CH₂Cl₂ and EtOH mixture.

145 (E)-2-(3-(4-(N,N-dimethylamino)phenyl)-1-hydroxyallylidene)-1H-indene-1,3(2H)-

146 dione (11), purple crystals, Yield 67%, m.p.=210-211 °C. FT-IR, (KBr, cm⁻¹): 3019,

147 2904, 1698, 1631, 1588, 1567, 1523. ¹H-NMR (300 MHz, CDCl₃, ppm): δ=13.30

148 (1H, s), 7.93 (1H, d, J=15.0 Hz), 7.88-7.78 (2H, m), 7.80 (1H, d, J=15.0 Hz), 7.73-

149	7.67 (2H, m), 7.65 (2H, d, <i>J</i> =7.5 Hz), 6.81 (2H, d, <i>J</i> =7.5 Hz), 3.10 (6H, s). ¹³ C-NMR
150	(75 MHz, CDCl ₃ , ppm): δ=197.31, 189.01, 174.35, 152.52, 146.30, 140.95, 138.76,
151	134.31, 133.51, 131.40, 122.67, 122.07, 111.83, 106.49, 40.23. MS, <i>m/z</i> : 320.2 (M ⁺),
152	318.2 (M ⁻). Anal. Calcd. (%) for C ₂₀ H ₁₇ NO ₃ : C, 75.22; H, 5.37; N, 4.39; found: C,
153	75.22; H 5.33; N, 4.31.
154	(E) - 2 - (3 - (4 - (N, N - diphenylamino)phenyl) - 1 - hydroxyallylidene) - 1 H - indene - 1, 3 (2H) - 1 - hydroxyallylidene) - 1 H - indene - 1, 3 (2H) - 1 - hydroxyallylidene) - 1 H - indene - 1, 3 (2H) - 1 - hydroxyallylidene) - 1 H - indene - 1, 3 (2H) - 1 - hydroxyallylidene) - 1 H - indene - 1, 3 (2H) - 1 - hydroxyallylidene) - 1 H - indene - 1, 3 (2H) - 1 - hydroxyallylidene) - 1 H - indene - 1, 3 (2H) - 1 - hydroxyallylidene) - 1 H - indene - 1, 3 (2H) - 1 - hydroxyallylidene) - 1 H - indene - 1, 3 (2H) - 1 - hydroxyallylidene) - 1 H - indene - 1, 3 (2H) - 1 - hydroxyallylidene) - 1 H - indene - 1, 3 (2H) - 1 - hydroxyallylidene) - 1 H - indene - 1, 3 (2H) - 1 - hydroxyallylidene) - hydroxyallylidene) - hydroxyallylidene) - hydroxyallylidene) - hydroxyallylidene) - hydroxyal
155	dione (12), purple crystals, Yield 60%, m.p.=220-222 °C. FT-IR, (KBr, cm ⁻¹): 3049,
156	3033, 1696, 1632, 1617, 1548, 1504, 1489. ¹ H-NMR (300MHz, CDCl ₃ , ppm):
157	δ=13.25 (1H, s), 7.90 (1H, d, <i>J</i> =13.5 Hz), 7.85-7.80 (3H, m), 7.75-7.66 (2H, m), 7.55
158	(2H, d, <i>J</i> =7.5 Hz), 7.37-7.32 (4H, m), 7.20-7.13 (6H, m), 7.04 (2H, d, <i>J</i> =7.5 Hz). ¹³ C-
159	NMR (75 MHz, CDCl ₃ , ppm): δ=197.59, 188.83, 173.92, 151.01, 145.30, 145.00,
160	139.10, 138.85, 133.80, 133.50, 130.30, 129.61, 126.00, 124.58, 122.50, 122.06,
161	120.90, 114.73, 107.33. MS, m/z: 444.2 (M ⁺), 442.3 (M ⁻). Anal. Calcd. (%) for
162	C ₃₀ H ₂₁ NO ₃ : C, 81.25; H, 4.77; N, 3.16; found: C 81.64; H, 4.82; N, 3.54.
163	(E) - 2 - (3 - (1, 2, 3, 5, 6, 7 - hexahydropyrido [3, 2, 1 - ij] quinolin - 9 - yl) - 1 - hydroxyallylidene) - (1, 2, 3, 5, 6, 7 - hexahydropyrido [3, 2, 1 - ij] quinolin - 9 - yl) - 1 - hydroxyallylidene) - (1, 2, 3, 5, 6, 7 - hexahydropyrido [3, 2, 1 - ij] quinolin - 9 - yl) - 1 - hydroxyallylidene) - (1, 2, 3, 5, 6, 7 - hexahydropyrido [3, 2, 1 - ij] quinolin - 9 - yl) - 1 - hydroxyallylidene) - (1, 2, 3, 5, 6, 7 - hexahydropyrido [3, 2, 1 - ij] quinolin - 9 - yl) - 1 - hydroxyallylidene) - (1, 2, 3, 5, 6, 7 - hexahydropyrido [3, 2, 1 - ij] quinolin - 9 - yl) - 1 - hydroxyallylidene) - (1, 2, 3, 5, 6, 7 - hexahydropyrido [3, 2, 1 - ij] quinolin - 9 - yl) - 1 - hydroxyallylidene) - (1, 2, 3, 5, 6, 7 - hexahydropyrido [3, 2, 1 - ij] quinolin - 9 - yl) - 1 - hydroxyallylidene) - (1, 2, 3, 5, 6, 7 - hexahydropyrido [3, 2, 1 - ij] quinolin - 9 - yl) - 1 - hydroxyallylidene) - (1, 2, 3, 5, 6, 7 - hexahydropyrido [3, 2, 1 - ij] quinolin - 9 - yl) - 1 - hydroxyallylidene) - (1, 2, 3, 5, 6, 7 - hexahydropyrido [3, 2, 1 - ij] quinolin - 9 - yl) - 1 - hydroxyallylidene) - (1, 2, 3, 5, 6, 7 - hexahydropyrido [3, 2, 1 - ij] quinolin - 9 - yl) - 1 - hydroxyallylidene) - (1, 2, 3, 5, 6, 7 - hexahydropyrido [3, 2, 1 - ij] quinolin - 9 - yl) - 1 - hydroxyallylidene) - (1, 2, 3, 5, 6, 7 - hexahydropyrido [3, 2, 1 - ij] quinolin - 9 - yl) - 1 - hydroxyallylidene) - (1, 2, 3, 5, 6, 7 - hexahydropyrido [3, 2, 1 - ij] quinolin - 9 - yl) - (1 - hydroxyallylidene) - (1, 2, 3, 5, 6, 7 - hexahydropyrido [3, 2, 1 - ij] quinolin - 9 - yl) - (1 - hydroxyallylidene) - (1 - hy
164	1H-indene-1,3(2H)-dione (13), dark green crystals, Yield 50%, m.p.=225-226 °C. FT-
165	IR, (KBr, cm ⁻¹): 3014, 2939, 2843, 1693, 1627, 1567, 1543, 1513, 1463. ¹ H-NMR
166	(300MHz, CDCl ₃ , ppm): δ=13.25 (1H, s), 7.84 (1H, d, <i>J</i> =14.3 Hz), 7.82-7.76 (2H, m),
167	7.69 (1H, d, J=14.3 Hz), 7.67-7.61 (2H, m), 7.20 (2H, s), 3.31 (4H, t, J=2.6 Hz), 2.78
168	(4H, t, J=2.6 Hz), 1.99 (4H, quint, J=2.6 Hz). ¹³ C-NMR (75 MHz, CDCl ₃ , ppm):
169	δ=197.51, 189.00, 174.58, 147.30, 147.00, 140.80, 139.00, 133.93, 133.54, 129.70,
170	122.30, 122.20, 122.00, 121.95, 110.00, 106.30, 50.00, 27.10, 21.35. MS, <i>m/z</i> : 372.4
171	(M ⁺). Anal. Calcd. (%) for C ₂₄ H ₂₁ NO ₃ : C, 77.61; H, 5.70; N, 3.77; found: C, 77.62; H,

172 5.72; N, 3.99.

173	(<i>E</i>)-2-(3-(4-(<i>N</i> , <i>N</i> -di([1,1'-biphenyl]-4-yl)amino)phenyl)-1-hydroxyallylidene)-1H-
174	indene-1,3(2H)-dione (14), dark red solid, Yield: 40%, m.p.=202-203 °C. FT-IR
175	(KBr, cm ⁻¹): 3063, 3027, 1700, 1622, 1584, 1558, 1505, 1483. ¹ H-NMR (300 MHz,
176	CDCl ₃ , ppm): δ=13.28 (1H, s), 7.96-7.83 (4H, m), 7.73-7.66 (3H, m), 7.73-7.69 (2H,
177	m), 7.64-7.58 (10H, m), 7.50-7.45 (4H, m), 7.37 (2H, d, J=6.0 Hz), 7.30-7.27 (4H,
178	m), 7.16 (2H, d, <i>J</i> =6.0 Hz). ¹³ C-NMR (75 MHz, CDCl ₃ , ppm): δ=197.39, 188.73,
179	173.65, 150.57, 145.69, 144.83, 141.05, 140.33, 138.81, 137.38, 134.65, 133.81,
180	130.66, 128.85, 128.23, 127.95, 127.23, 126.84, 122.45, 122.08, 121.58, 114.96,
181	107.26. MS, m/z : 596.3 (M ⁺), 594.6 (M ⁻). Anal. Calcd. (%) for C ₄₂ H ₂₉ NO ₃ : C, 84.68;
182	H, 4.91; N, 2.35; found: C, 84.23; H, 4.92; N, 2.52.
183	2-((2E,4E)-5-(4-(N,N-dimethylamino)phenyl)-1-hydroxypenta-2,4-dien-1-ylidene)-
184	1H-indene-1,3(2H)-dione (15), purple solid, Yield: 30%, m.p.=230-231 °C. FT-IR
185	(KBr, cm ⁻¹): 3017, 2913, 2903, 2821, 1690, 1634, 1618, 1572, 1572, 1554, 1522. ¹ H-

- 186 NMR (300MHz, CDCl₃, ppm): δ =13.19 (1H, s), 7.85-7.78 (2H, m), 7.73-7.66 (3H, 187 m), 7.45 (2H, d, *J*=7.5 Hz), 7.40 (1H, d, *J*=13.5 Hz), 7.06-6.92 (2H, m), 6.70 (2H, d, 188 *J*=7.5 Hz) 3.09 (6H, s). ¹³C-NMR (75 MHz, CDCl₃, ppm): δ =197.41, 188.82, 173.72, 189 151.51, 147.30, 144.83, 140.93, 138.82, 134.43, 133.61, 129.61, 124.02, 122.98, 190 122.34, 121.88, 118.01, 112.01, 106.63, 40.15. MS, *m/z*: 346.3 (M⁺), 344.3 (M⁻). 191 Anal. Calcd. (%) for C₂₂H₁₉NO₃: C, 76.50; H, 5.54; N, 4.06; found: C, 76.45; H, 5.54;
- 192 N, 4.20.

193 2.2.3. Synthesis of derivatives of 2-cinnamoyl-1,3-dimedones (16-20)

Compounds 16-20 were synthesized by same procedure as for compounds 1115, except 2-acetyldimedone (9) was used instead of 2-acetyl-1,3-indandione (8).

196 (*E*)-2-(3-(4-(*N*,*N*-dimethylamino)phenyl)-1-hydroxyallylidene)-5,5-

dimethylcyclohexane-1,3-dione (16), pink crystals, Yield 56%, m.p.=154-155 °C. FT-

- IR, (KBr, cm⁻¹): 3093, 2957, 2923, 2866, 2807, 1647, 1612, 1580, 1532, 1280, 1160. 198 ¹H-NMR (300 MHz, CDCl₃, ppm): δ =8.17 (1H, d, J=15.0 Hz), 8.00 (1H, d, J=15.0 199 Hz), 7.60 (2H, d, J=6.4 Hz), 6.69 (2H, d, J=6.4 Hz), 3.08 (6H, s), 2.56 (2H, s), 2.44 200 (2H, s), 1.11 (6H, s). ¹³C-NMR (75 MHz, CDCl₃, ppm): δ=201.85, 196.08, 186.76, 201 152.51, 147.93, 131.50, 122.94, 116.34, 111.75, 53.37, 49.27, 40.09, 30.42, 202 28.27.MS, *m/z*: 314.5 (M⁺), 312.4 (M⁻). Anal. Calcd. (%) for C₁₉H₂₃NO₃: C, 72.82; H, 203 204 7.40; N, 4.47; found: C, 72.90; H, 7.38; N, 4.41. (E)-2-(3-(4-(N,N-diphenylamino)phenyl)-1-hydroxyallylidene)-5,5-205 dimethylcyclohexane-1,3-dione (17), orange crystals, Yield 45%, m.p.=162-164 °C. 206 FT-IR, (KBr, cm⁻¹): 3099, 3033, 2960, 2949, 2869, 1653, 1602, 1582, 1554, 1266, 207 1173. ¹H-NMR (300 MHz, CDCl₃, ppm): δ=8.20 (1H, d, J=13.7 Hz), 7.95 (1H, d, 208 J=13.7 Hz), 7.52 (2H, d, J=6.7 Hz), 7.35-7.30 (4H, m), 7.18-7.11 (6H, m), 7.01 (2H, 209 d, J=6.9 Hz), 2.58 (2H, s), 2.44 (2H, s), 1.12 (6H, s). ¹³C-NMR (75 MHz, CDCl₃, 210 ppm): δ=201.83, 195.97, 187.12, 150.67, 146.64, 146.31 130.56, 129.55, 127.89, 211 125.70, 124.38, 121.08, 119.49, 110.67, 53.27, 49.01, 30.45, 28.27. MS, m/z: 438.4 212 (M^+) , 436.6 (M^-) . Anal. Calcd. (%) for $C_{29}H_{27}NO_3$: C, 79.61; H, 6.22; N, 3.20; found: 213 C, 79.44; H, 6.27; N, 3.29. 214
- 215 (E)-2-(3-(1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinolin-9-yl)-1-hydroxyallylidene)-

216 5,5-dimethylcyclohexane-1,3-dione (18), purple solid, Yield 52%, m.p.=186-187 °C

- 217 FT-IR, (KBr, cm⁻¹): 3105, 2940, 2888, 2862, 2837, 1647, 1577, 1523, 1509, 1273,
- 218 1137. ¹H-NMR (300 MHz, CDCl₃, ppm): δ=8.10 (1H, d, J=13.3 Hz), 7.93 (1H, d,
- 219 J=13.3 Hz), 7.16 (2H, s), 3.28 (4H, t, J=1.8 Hz), 2.75 (4H, t, J=3.5 Hz), 2.54 (2H, s),
- 220 2.43 (2H, s), 1.97 (4H, quint, J=1.8 Hz, 3.5 Hz), 1.10 (6H, s). ¹³C-NMR (75 MHz,
- 221 CDCl₃, ppm): δ=201.97, 196.15, 185.95, 148.67, 146.09, 129.24, 122.11, 121.06,
- 222 114.74, 110.09, 53.31, 50.16, 49.46, 30.49, 28.36, 27.58, 21.29. MS, *m/z*: 366.3 (M⁺),

- 223 364.5 (M⁻). Anal. Calcd. (%) for C₂₃H₂₇NO₃: C, 75.59; H, 7.45; N, 3.83; found: C,
- 224 75.48; H, 7.50; N, 3.93.
- 225 (E)-2-(3-(4-(N,N-di([1,1'-biphenyl]-4-yl)amino)phenyl)-1-hydroxyallylidene)-5,5-
- dimethylcyclohexane-1,3-dione (19), red solid, Yield 31%, m.p.= 221-222 °C. FT-IR,
- 227 (KBr, cm⁻¹): 3032, 2952, 2869, 1655, 1584, 1486, 1170. ¹H-NMR (300 MHz, CDCl₃,
- 228 ppm): δ=8.23 (1H, d, J=13.9 Hz), 7.98 (1H, d, J=13.9 Hz), 7.64-7.57 (10H, m), 7.49-
- 229 7.44 (4H, m), 7.38 (2H, d, *J*=6.2 Hz), 7.28-7.26 (4H, m), 7.14 (2H, d, *J*=6.2 Hz), 2.58
- 230 (2H, s), 2.45 (2H, s), 1.12 (6H, s). ¹³C-NMR (75 MHz, CDCl₃, ppm): δ=201.91,
- 231 196.04, 187.13, 150.32, 146.20, 145.81, 140.36, 137.08, 128.83, 128.35, 128.18,
- 232 127.18, 126.83, 125.69, 121.73, 119.75, 110.63, 53.27, 49.01, 30.48, 28.28. MS, *m/z*:
- 233 590.6 (M⁺), 588.9 (M⁻). Anal. Calcd. (%) for C₄₁H₃₅NO₃: C, 83.50; H, 5.98; N, 2.38;
- 234 found: C, 83.15; H, 5.98; N, 2.43.
- 235 2-((2E,4E)-5-(4-(N,N-dimethylamino)phenyl)-1-hydroxypenta-2,4-dien-1-ylidene)-
- 5,5-dimethylcyclohexane-1,3-dione (20), purple crystals, Yield 52%, m.p.= 166-167
- ^oC. FT-IR, (KBr, cm⁻¹): 3089, 2963, 2944, 2825, 1655, 1584, 1548, 1415, 1400, 1146.
- ¹H-NMR (300 MHz, CDCl₃, ppm): δ=7.88-7.71 (2H, m), 7.42 (2H, d, *J*=6.5 Hz),
- 239 7.03-6.88 (2H, m), 6.69 (2H, d, J=6.5 Hz), 3.05 (6H, s), 2.55 (2H, s), 2.43 (2H, s),
- 240 1.10 (6H, s). ¹³C-NMR (75 MHz, CDCl₃, ppm): δ=202.06, 195.96, 186.35, 151.38,
- 241 148.74, 148.69, 144.47, 129.43, 124.10, 123.30, 122.61, 112.01, 110.37, 53.28, 49.26,
 242 40.19, 30.42, 28.27.MS, *m/z*: 340.3 (M⁺), 338.5 (M⁻). Anal. Calcd. (%) for
- 243 C₂₁H₂₅NO₃: C, 74.31; H, 7.42; N, 4.13; found: C, 73.98; H, 7.51; N, 4.23.
- 244

245 **3. Results and Discussion**

246 3.1. Synthesis and characterization of luminophores

Schemes 1 and 2 show synthetic routes of luminophores 11-20. (*E*)-3-(4-(*N*,*N*dimethylamino)phenyl)acrylaldehyde (3) was obtained with moderate yield in a single

249 step acid catalyzed aldol condensation between acetaldehyde (2) and 4-N,Ndimethylaminobenzaldehyde (1). It is worth to point out, that other methods for 250 synthesis of cinnamaladehyde with N,N-dimethylamino donor in para position of 251 phenyl ring includes multiple steps (for example, Wittig reaction between 252 benzaldehyde derivative and Wittig reagent, which is followed by Vilsmeir reaction 253 between obtained alkene and Vilsmeir reagent) or expensive reagents (for example, 254 1,3-dioxan-2-yl-tributylphosponium bromide, which is necessary in Wittig 255 oxopropenylation reaction). ¹H-NMR spectra of compounds **3** characterizes with large 256 trans constant (J=13.1 Hz) for double bond protons of cinnamoyl moiety. 257



258
259 Scheme 2. Reagents and conditions: (a) – piperidine, 100 °C, 4 h; ethanol, 80 °C, 0,5 h.
260

Aldehyde 7 was obtained in two-step synthesis from 4-*N*,*N*-diphenylaminobenzaldehyde (4). In the first stage the compound was iodinated with KIO₃/KI mixture and the 4-(bis(4-iodophenyl)amino)benzaldehyde (5) was obtained. Afterwards in Pd(0) catalyzed Suzuki coupling reaction between compound 5 and phenylboronic acid (6), aldehyde 7 with 61 % yield was synthesized.

All luminophores **11-20** were synthesized through Claisen-Schmidt condensation reaction between 2-acetyl-1,3-indandione **8** or 2-acetyldimedone **9** and aldehydes **1,3,4,7,10** in the presence of 5 mmol piperidine. ¹H-, ¹³C-NMR, FT-IR characteristics as well as X-Ray analysis data for 2-cinnamoyl-1,3-indandiones **11-13** were reported in our previous work [22].

271 2-Cinnamoyldimedones **16-20** showed similar characteristics to compounds 272 **11-15**. In ¹H-NMR spectra large coupling constants (J=13.3-15.0 Hz) were found for 273 double bond protons of cinnamoyl fragment, indicating *trans* configuration for these 274 compounds. However, to get unquestionable evidence, that compounds **16-20** similar 275 to cinnamoyl-1,3-indandiones exist in exocyclic enol form, a single crystal of 276 compound **16** was obtained by slow evaporation from saturated ethanol solution for 277 X-ray analysis.

278 279 Table 1

Principal bond lengths in t	he structure 16.	
	Bond	Bond length, Å
	C1-O1	1.276(7)
	C1-C2	1.427(7)
	C2–C3	1.478(7)
	C2–C9	1.433(7)
	C3–O2	1.218(6)
	C9–O9	1.309(7)

280 281

In accordance with the X-ray diffraction data the asymmetric unit of **16** contains two independent molecules, one of them is illustrated in Fig. 1. Table 1 lists

284 the principal bond lengths in molecular structure 16. Due to the fact that bond lengths in two independent molecules are identical within the errors the arithmetical mean 285 values are given in the Table 1. X-ray diffraction data confirms, that derivative of 2-286 287 cinamoyldimedone 16 in solid state exist in exocyclic enol form, which is stabilized by very strong intramolecular hydrogen bond between carbonyl group oxygen atom 288 (O1) from dimedone fragment and hydroxyl group (O9-H9) from allylidene fragment. 289 The hydrogen bond (O1^{...}H9–O9) is characterized with very short bond length, which 290 is equal 2.386(7) Å (O1"H9=1.59 Å, O1"H9-O9=138°) for one of independent 291 molecules and 2.401(7) Å (O1^{...}H9=1.48 Å, O1^{...}H9–O9=149°) for the second. Due to 292 intramolecular hydrogen bond following structural parameters are presented in the 293 294 molecule – bond lengths for C3–C2 are longer than for C1–C2, meaning that bond C3-C2 has less double bond order. Moreover, comparing carbonyl groups bond 295 lengths C3–O2 and C1–O1, the latter ones are significantly longer, showing more 296 single bond character. These data lead to conclusion, that there is extended resonance 297 system between atoms O1-C1-C2-C9-O9 stabilized by the intramolecular hydrogen 298 bond presented in the molecule, similarly that it was reported to the 2-cinnamoyl-1,3-299 indandione 13 [22]. Unfortunately, a bad quality of the crystals 16 does not permit to 300 301 provide a detailed analysis of the molecular geometry.





Fig. 1. ORTEP drawing of compound **16** with the atom numbering scheme. All nonhydrogen atoms are drawn as 50% probability ellipsoids.

305

Interestingly, compound **16** does not show any intermolecular hydrogen bonds between molecules, like it was observed for compound **13** [22]. Dihedral angles between least-squares planes of dimedone and 4-*N*,*N*-dimethylaminophenyl moiety are 7.4 and 13.2° for two independent molecules. These values indicate that molecule **16** are almost planar.

311

312 **3.2. Thermal properties**

In order to investigate thermal behavior of luminophores 11-20, 313 thermogravimetric (TG) analysis were carried out between 30 and 550 °C in nitrogen 314 atmosphere. Table 2 displays decomposition temperatures $(T_{5\%})$ of investigated 315 compounds and TG curves of some luminophores are depicted in Fig. 2. Obtained 316 results from TG analysis indicate, that all 10 dyes are thermally stable up to 200 °C. 317 Identical order in the decrease of thermal stability depending on donor group was 318 319 found for both 2-cinnamoyl derivatives 11-14 and 16-19 and can be arranged in the 320 following order: N(BPh)₂>N(Ph)₂>N(Me)₂>Julolidyl. This sequence indicates that the thermal destruction of compounds begins with the destruction of the donor part. 321

322

323 Thermal and electrochemical properties of compounds **11-20**.

Table 2

	Code	T _{5%} ^a , °C	E _{ox} , V	E _{red} , V
	11	218	0.80	-1.17
	12	283	1.05	-1.07
	13	216	0.60	-1.21
	14	290	0.98	-1.04
	15	238	0.66	-1.04
	16	233	0.81	-1.32
	17	271	1.07	-1.19
	18	219	0.61	-1.36
	19	288	0.96	-1.18
_	20	234	0.67	-1.15

324

^a- $T_{5\%}$ is temperature of 5% weight loss, respectively.

325 Investigation of TG curves also confirms conclusion, that thermal degradation pattern is influenced by amino donor group. Compounds with amino donors 326 containing alkyl chains, julolidine shows lower $T_{5\%}$ values than those with phenyl or 327 328 biphenyl groups. Compounds 11,13,15 as well as 16,18,20 starts to decompose at ~215-230° C and the first possible volatile fragments are the alkyl chains on the 329 nitrogen atom. The alkyl chain replacement with phenyl rings leads to increased $T_{5\%}$ 330 (270-290 °C), similar observations was reported for tricyanovinyldihydrofuran D- π -A 331 dyes with different amino donors [33]. 332



Fig. 2. TG curves of compounds 13,14,18,19 (a) and compounds 11,15,16,20 (b). 334 335 2-Cinnamoyl-1,3-indandione 14 and 2-cinnamoyl-dimedone 19 with bulky $N(BPh)_2$ substituent exhibit the highest $T_{5\%}$ over 280 °C, which can be explained with 336 their higher molecular mass, and additional π - π stackings. Prolonging the π -bridge by 337 one more double bond between donor and acceptor $(11\rightarrow 15 \text{ and } 16\rightarrow 20)$ leads to 338 slight increase in $T_{5\%}$, for example compound **11** $T_{5\%}$ is 218 °C, but for its analogue 339 15 decomposition temperature is increased to 238 °C. As it can be seen from Fig. 2 340 (a) compounds with julolidine donor (13 and 18) as well as ones with N(BPh)₂ group 341 (14 and 19) shows two-step weight loss TG curves. On the other hand TG curves of 342

dyes with N(Me)₂ donor group (11,15,16,20) can be characterized with one-step
decomposition. The acceptor group shows no influence on the form of TG curve. The
TG analysis results show, that all compounds have good enough thermal stability for
the application in optoelectronic devices.

347

348 3.3. Electrochemical properties

349 Cyclic voltammetry was employed for all synthesized compounds to 350 investigate their redox behavior. The results are summarized in Table 2 and some 351 compounds cyclic voltammograms in acetonitrile are shown in Fig. 3. For all studied 352 compounds both electrode processes - cathodic reduction as well as anodic oxidation 353 are electrochemically irreversible in acetonitrile.

The structure of the electron acceptor moieties (1,3-indandione or dimedone) 354 has a negligible influence (10-20 mV) on the oxidation potentials of the dyes (11/16;355 12/17; 13/18; 14/19), while prolongation of the olefinic linker facilitates anodic 356 oxidation for 140 mV (11/15; 16/20). Similar effects on oxidation properties caused 357 by elongation of planar π -bridge were reported for imidazole moiety containing dyes 358 The oxidation potentials of the luminophores are affected mainly by the 359 [34]. substituents attached directly to the nitrogen atom. Independently from acceptor 360 moiety (1,3-indandione or dimedone) electron-rich julolidine fragment undergoes 361 oxidation at 0.60 V. Furthermore, dyes 11 and 16 with two electron-donating methyl 362 groups at the nitrogen atom undergo oxidation 200 mV more anodically. For the 363 luminophores 12, 17, 14 and 19 conjugation between the nitrogen lone electron pair 364 365 and the π -electron system of the aromatic rings results in the highest oxidation potential values. 366



367 368

Fig. 3. Cyclic voltammograms of compounds **12,13,16** in acetonitrile solutions.

The electrochemical reduction process of compounds **11-20** are localized on their acceptor moieties. Cathodic peak potentials of the compounds **16-20** are 110-150 mV more negative than those of **11-15**, confirming that 1,3-indandione possesses stronger electron-acceptor strength than dimedone moiety.

374

375 **3.4. Absorption properties**

In order to gain information about compounds structure-property relationship, 376 UV-Vis absorption spectra ($c \sim 1.5 \cdot 10^{-5}$ M) in a series of solvents with different 377 dielectric constants and thin films were investigated. The data of absorption band 378 maxima (λ_{abs}) are summarized in Table 3 and some compounds absorption spectra are 379 depicted in Fig. 4. All compounds 11-20 in chloroform show intense visible light 380 absorption with band maxima from 466 to 540 nm. The absorption bands are wide and 381 correspond to intramolecular charge transfer (ICT) transitions $\pi(D) \rightarrow \pi^*(A)$ between 382 383 donor and acceptor groups in the molecule. For compounds 14 and 19 with N(BPh)₂ 384 substituent in cinnamoyl fragment second absorption band around 341 nm are observed and can be attributed to $\pi \rightarrow \pi^*$ transitions of the aminodibiphenylamino 385 386 moiety. Due to the difference in acceptor groups the ICT band occurrs in the different

387 spectral range - from 466 to 509 nm for dimedone derivatives and from 502 to 540 388 nm for 1,3-indandione derivatives. Amino donor groups based on their structure and strength also shows some effect on ICT band position. By varying the donor moiety 389 390 on 1,3-indandione and dimedone derivatives, ICT band is red shifted in the order: 391 N(Me)₂~N(Ph)₂<N(BPh)₂<Juloidyl. N(Me)₂ and N(Ph)₂ shows similar donor strength based on absorption data. However, it is known, that N(Ph)₂ could have stronger 392 donor character than N(Me)₂ group [9], but due to nitrogen atom lone pair conjugation 393 with π -electrons of phenyl rings, the donor strength is reduced and λ_{abs} does not show 394 the expected red shift. Furthermore, change of the donor unit from N(Ph)₂ to N(BPh)₂ 395 results in bathochromic shift of λ_{abs} (+10 nm) for both dimedone and 1,3-indandione 396 397 compounds. This fact could be explained with nitrogen atom lone pair weaker 398 conjugation with biphenyl than phenyl group, which results in enhanced donor character for N(BPh)₂ group. This assumption was confirmed by theoretical chemical 399 400 calculations (Section 3.6). Among all investigated amino groups julolidyl moiety shows the most red shift of λ_{abs} , which can be explained with its rigid character and 401 402 probably, more effective p- π conjugation, which ensures stronger electron-donating effect than other amino substituents. Furthermore, prolongation of the π -bridge 403 between D and A moieties (11 \rightarrow 15 and 16 \rightarrow 20) also shows some effect on ICT bands 404 position in the spectra. As expected red shift of the λ_{abs} was observed in the 405 absorption spectra - 1,3-indandione derivative (15) shows +17 nm shift, but dimedone 406 derivative (20) +20 nm bathochromic shift. It was concluded, that the strongest 407 impact on absorption spectra position is due to the acceptor unit and π -bridge length 408 between A and D moieties and amino donor group strength shows lesser effect. 409





414

412 Fig. 4. Absorption spectra of compounds 12,14,17,19 in chloroform (c~1.5·10⁻⁵ M) solutions 413 (a) and in thin films (b)

Only four luminophores (12,14,17,19) with N(Ph)₂ and N(BPh)₂ donor groups
formed thin films from chloroform solutions. As it can be seen from Fig. 4 (b) in solid
state compounds 12,14,17,19 absorption bands are wider and slight effect on
absorption band maxima are observed compared to data obtained from solution
samples.

The investigation of solvatochromic behavior of the newly synthesized dyes was also conducted, λ_{abs} in different solvents are summarized in Table 3. Unfortunately, some compounds were insoluble in polar solvents (MeCN and MeOH) and full solvatochromic outlook was not obtained. From the data depicted in Table 3 it was concluded, that these dyes did not show notable solvatochromism and upon changing the solvents polarity from non-polar toluene to polar MeCN, only small λ_{abs} shifts (1-12 nm) were observed.

- 428 **3.5. Emission properties**
- Emission properties of synthesized compounds were examined in series of solvents solutions ($c\sim 1.5 \cdot 10^{-5}$ M) and in thin films. The data of emission band maxima

(λ_{em}) , Stokes shifts (λ_{sts}) , and absolute photoluminescence quantum yields (Φ) are 431

summarized in Table 3. 432

433

Table 3 434 Absorption and emission characteristics of compounds 11-20 in a series in solutions and thin films. 435

minist										
Solvent	Dye	λ _{abs} , nm	λ _{em} , nm	$\lambda_{\rm sts}^{\ a},$ cm ⁻¹	$\Phi^{ extsf{b}}$	Dye	λ _{abs} , nm	λ _{em} , nm	$\lambda_{sts}^{a},$ cm ⁻¹	$\Phi^{\mathfrak{b}}$
Toluene		499	548	1762	0.12		499	568	2434	0.52
THF		499	575	2649	< 0.01		492	624	4300	0.49
CHCl ₃	11	503	566	2212	0.03	12	502	621	3817	0.76
MeCN		500	-	-	-		- ^c			-
MeOH		501	582	2779	< 0.01		_c			-
Thin film		-	-	-	-		501	643	4407	0.07
Toluene		532	577	1466	0.15		506	586	2698	0.93
THF		536	601	2018	< 0.01		502	662	4815	0.10
CHCl ₃	13	540	595	1712	< 0.01	14	512	663	4448	0.21
MeCN		540	-	-	-		494	-	-	-
MeOH		537	-	-	-		499	-	-	-
Thin film		-	-	-	-		500	667	5008	0.13
Toluene		511	613	3256	0.12		454	528	3087	0.05
THF		517	664	4282	0.31		456	546	3615	0.19
CHCl ₃	15	520	647	3775	0.25	16	467	548	3165	0.15
MeCN		514	-		-		459	571	4273	0.02
MeOH		518	680	4599	< 0.01		466	570	3915	0.01
Thin film		-	<u> </u>	-	-		-	-	-	-
Toluene		456	549	3715	0.40		497	552	2005	0.31
THF		452	624	6098	0.56		496	575	2770	0.32
CHCl ₃	17	466	612	5119	0.78	18	509	577	2315	0.36
MeCN		449	675	7457	< 0.01		503	593	3017	< 0.01
MeOH		451	643	6621	< 0.01		510	600	2941	< 0.01
Thin film		466	600	4793	0.17		-	-	-	-
Toluene		465	572	4023	0.79		478	593	4057	0.05
THF		460	636	6016	0.16		476	635	5260	0.22
CHCl ₃	19	476	654	5718	0.16	20	487	624	4508	0.15
MeCN		453	666	7060	< 0.01		475	662	5947	0.13
MeOH		- ^c	-	-	-		483	666	5689	0.05
Thin film		478	626	4946	0.13		-	-	-	-

436 ^aStokes shifts;

^bAbsolute photoluminescence quantum yield; 437

^c-insoluble 438

440 The emission color of solutions of 11-20 covers a very wide spectral range 441 from bright green to red light region. In non-polar toluene emission color varies from green to red light region, but in polar solvents it shifts from yellow to red region. 442 443 Emission spectra of dyes 11-20 are characterized with wide emission bands (Fig. 5), and emission band maxima λ_{em} is influenced by many factors, including dyes 444 structure. Due to the difference in acceptor groups the λ_{em} position in chloroform 445 solutions shifts - from 548 to 654 nm for dimedone compounds and from 566 to 663 446 nm for 1,3-indandione derivatives. This red shift of λ_{em} for 1,3-indandione derivatives 447 448 compared to the same analogues with dimedone cycle (11/16; 12/17; 13/18 etc) can be explained with additional phenyl ring of 1,3-indandione moiety, which ensures more 449 extend π -conjugation in the molecules. Moreover, amino donor group structure and 450 strength show major impact on λ_{em} position in the spectra. By varying the donor 451 moiety λ_{em} is red shifted in the following order: N(Me)₂<Juloidyl< N(Ph)₂<N(BPh)₂. 452 N(Me)₂ group having the weakest donor character from all amino substituents shows 453 the λ_{em} at 566 nm (dye 11) and at 548 nm (dye 16), while dyes containing N(BPh)₂ 454 substituent shows ~100 nm red shift and emits red light at 663 nm (dye 14) and 654 455 nm (dye 19) in chloroform solutions. All investigated compounds based on their 456 457 amino donor structures can be divided into two groups - compounds containing amino donors with alkyl chains (Julolidyl, N(Me)₂) and phenyl groups (N(BPh)₂, N(Ph)₂). 458 There is essential difference in the Stokes shifts for these groups – first group show 459 smaller λ_{sts} (in the range from 1466-2779 cm⁻¹ for 1,3-indandione derivatives, and 460 2005-4273 cm⁻¹ for dimedone derivatives) than second group. Smallest λ_{sts} was 461 462 obtained for julolidyl group containing compounds and can be explained with similar dipole moment from ground and excited state for these dyes. Similar observations 463 were found for other D- π -A dyes [15]. Observed relatively large Stokes shifts (λ_{sts}) for 464

465 compounds 12,14,15 as well as for 17,19,20 indicates, that after excitation these 466 molecules undergo some structural reorientation, for example, excited state 467 intramolecular proton transfer (ESIPT), which is common for compounds with strong 468 intramolecular hydrogen bond in the molecules [35]. Large Stokes shifts are a huge 469 advantage for dyes for OLED application, because it decreases the possibility of self-470 absorption, which can reduce the total emission efficiency.

The extension of the π -linker between D and A parts (11 \rightarrow 15 and 16 \rightarrow 20) also has an impact on λ_{em} position in the spectra. As expected longer conjugation bridge leads to bathochromic shift of λ_{em} , for example, λ_{em} 11 \rightarrow 15 is red shifted for 81 nm in chloroform solutions.

Another factor, which greatly influences the λ_{em} position in the spectra, is the 475 solvents polarity. Strong positive solvatofluorochromism was observed by all 476 investigated compounds. Upon changing the solvents polarity from non-polar 477 (toluene) to polar (MeOH), λ_{em} shifts in range from 24 to 126 nm. Among the 478 479 compounds investigated dyes with the diphenyl and dibiphenyl substituents exhibit 480 largest emission shifts due to considerably stronger donor groups in the molecules, for example, dye 17 shows the maximum λ_{em} shift +126 nm going from toluene to 481 MeCN. It is common for D- π -A dyes, which exhibit ICT, to have bathochromic shift 482 of λ_{em} [8,9] in polar solvents and can be explained with excited state more polar 483 character than ground state. Therefore, λ_{em} shows larger shifts with solvents polarity 484 change, than λ_{abs} . 485

Also the absolute fluorescence quantum yields (Φ) are largely dependent on the solvents polarity. With the increase in solvents polarity (MeOH, MeCN) the decrease in Φ was observed and almost all dyes except **16** and **20** were non-emissive in polar environment. In non-polar toluene dyes with N(BPh)₂ donor group (**14**, **19**)

shows high Φ values (0.93 and 0.79), dyes **11-13,15,17,18** - moderate Φ ranging from 490 0.12 to 0.52, however remaining compounds 16,20 exhibit relatively low quantum 491 yields (0.05). Moreover, moderate to high quantum yields (0.10-0.78) were obtained 492 in THF and CHCl₃ solvents. Obtained quantum yield data in different solvents 493 demonstrates that emission properties of investigated dyes are affected more by the 494 solvents polarity than nature of the donor group. Low emission intensity in polar 495 media can be explained with interactions between dyes and polar solvent in polar 496 497 excited state, which leads to pronounced non-radiative deactivation [9,36].



499 Fig. 5. (a) - Emission spectra of compounds 11-20 in chloroform (c~1.5·10⁻⁵ M) solutions;
500 (b) - solvatofluorochromism of dye 20
501

498

Photoluminescence spectra of thin films for compounds 12,14,17 and 19 can 502 be characterized as wide emission bands with maximum λ_{em} in the range of 600-667 503 504 nm and with quantum yields Φ from 0.07 to 0.17. Decrease in Φ could be explained with concentration quenching, due to intermolecular interactions in solid state. In the 505 future to increase Φ values in thin films, these dyes need to be doped in polymer 506 matrix. However, still acquired Φ values in thin films are notable, indicating, that 507 compounds 12,14,17 and 19 might be the promising red light emitting optical 508 509 materials for optoelectronic devices.

510 From all synthesized compounds, dye 17 with dimedone cycle as acceptor, $N(Ph)_2$ as donor and 1-hydroxyallylidene as π -bridge shows the most promising 511 optical properties for application in OLED. Intense visible light absorption at ~455 512 nm, large Stokes shifts (3715-6098 cm⁻¹) and bright yellow or orange-light emission 513 in non-polar solvents as well as in thin film with moderate to high quantum yields 514 (0.17-0.78) is characteristic for these dye. However, due to the demand for intense 515 516 red-light emitting organic materials dye 14 with 1,3-indandione as acceptor unit, $N(BPh)_2$ as donor and 1-hydroxyallylidene as π -bridge show some potential 517 application, due to its emission profile (λ_{em} ~663 nm with Φ =0.13-0.21) in THF, 518 519 CHCl₃ and in thin film.

520

521 **3.6.** Quantum-Chemical calculation of Electronic structures

To better understand the effect of the electronic structure on different 522 photophysical properties of synthesized dyes, the density functional theory (DFT) was 523 performed using ORCA program and Gaussian 09 ab initio quantum chemical 524 software package. The calculated HOMO and LUMO energy levels of all dyes are 525 depicted in Table 4. The obtained optimized geometries reveal that compounds with 526 alkyl amino substituents (11,13,15 and 16,18,20) have nearly planar structure. 527 528 However, dyes with phenyl amino groups (N(Ph)₂, N(BPh)₂) shows out of plane 529 twisting. In compounds 12, 14 as well as in 17, 19 phenyl and biphenyl groups are twisted out of the plane of the cinnamoyl fragment with dihedral angles of -30.3, -530 31.2, -30.1 and -32.1 °, respectively. Comparison of these dihedral angles of 531 luminophores with N(Ph)₂ and ones with N(BPh)₂ donor group (12/14, 17/19), leads 532 to the fact, that latter ones have less planar donor moiety, and nitrogen atom lone pair 533 conjugation with biphenyl group is weaker, which results in enhanced donor character 534

for N(BPh)₂. This conclusion is in agreement with absorption data of these luminophores. Moreover, such twisting out of the plane for these four compounds could lead to lowered absorption maxima, which was observed in CHCl₃ solutions (see paragraph 3.4.) and disarranged the order of donor strength based on absorption maxima. Similar observations were reported for different amino donor containing 4pyridylbutadienes [8].

Fig. 6 shows the HOMO and LUMO orbitals of optimized ground state 541 structures. HOMO orbitals of compounds 11-20 are mainly localized on the donor 542 543 unit and cinnamoyl part of the molecule and the delocalization is not influenced by acceptor moiety. On contrary LUMO orbitals are localized on the acceptor and 544 cinnamoyl moiety. Such a charge distribution leads to conclusion, that there is 545 noticeable intramolecular charge transfer presented in HOMO-JLUMO transition. 546 Similar localization of molecular orbitals and charge distribution was reported for 547 derivatives of cinnamoyl pyrones [17]. 548

Optical (E_{g}^{Opt}) and electrochemical (E_{g}) bandgap, as well as bandgap (E_{g}^{DFT}) 549 calculated from theoretically obtained HUMO/LUMO levels are depicted in Table 4. 550 From the data of electronic levels, it can be seen that, band gap (Eg^{DFT}) calculated with 551 DFT method are in the range from 2.77 to 3.22 eV and reduces with the increase of 552 strength of the donor groups, for example, compound 11 has the largest difference 553 between HOMO-LUMO levels and weakest donor group character. Moreover, there is 554 555 relationship between conjugation length of D- π -A system and band gap – molecules with larger HOMO-LUMO band gap have shorter conjugation length, for example, 556 luminophores 15 and 20 with longer π -spacer between A and D units presents the 557 smallest Eg^{DFT} values. 558

559

2	Calculated HOMO/LUMO energy levels and band gaps of luminophores 11-20.					
	Code	HOMO, eV	LUMO, eV	Eg^{DFT} , eV^{a}	E_g^{Opt} , eV^b	E_g, V^c
	11	-5.37	-2.28	3.09	2.25	1.97
	12	-5.34	-2.47	2.87	2.22	2.12
	13	-5.11	-2.19	2.92	2.11	1.81
	14	-5.27	-2.50	2.77	2.16	2.02
	15	-5.22	-2.43	2.79	2.04	1.70
	16	-5.38	-2.16	3.22	2.37	2.13
	17	-5.33	-2.37	2.96	2.30	2.26
	18	-5.16	-2.11	3.05	2.21	1.97
	19	-5.26	-2.40	2.86	2.26	2.14
	20	-5.21	-2.34	2.87	2.15	1.82

562	Calculated HOMO/LUMO energy	v levels and hand gan	s of luminophores 11-20
J02	Calculated HOMO/LOMO cherg	y icvers and band gap	s of fullinopholes 11-20.

561

^a-Calculated from DFT calculations: Eg^{DFT}=LUMO-HOMO; 563

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^b-Optical band gap E_g^{Opt} calculated from UV-Vis spectra in CHCl₃ solution: $E_g^{Opt}=1240/\lambda_{onset}$ 564 (nm); 565 ^c-Electrochemical band gap E_g calculated from cyclic voltammograms: $E_g=E_{ox}-E_{red}$. 566

567 Optical and electrochemical band gaps are in the range 2.04-2.37 eV and 1.70-568 2.26 eV, respectively. The difference between calculated Eg^{DFT} and experimentally 569 obtained Eg Opt and Eg band gap values can be explained with use of different methods 570 and conditions for experiments. All three method results shows, that compounds with 571 prolonged π -bridge and N(Me)₂ donor (15, 20) has the smallest band gap value and, 572 from the other hand compounds (11, 16) with same donor unit and shorter 573 conjugation length exhibit the largest band gap values. 574

Table 4





Fig. 6. HOMO and LUMO orbitals of optimized ground state structures of compounds 11-20, obtained using B3LYP 6-311G** set.

579 **4. Conclusions**

In summary, the synthesis of ten D- π -A dyes containing different amino 580 substituents as donors (D), 1,3-indandione or dimedone as acceptors (A) and different 581 1-hydroxyallylidene or 1-hydroxypenta-2,4-dien-1-ylidene as π -bridge are reported. 582 Donor, acceptor and π -bridge influence on absorption, emission, electrochemical and 583 thermal properties are investigated. Investigated dyes exhibit high thermal stability 584 585 above 200 °C, negligible solvatochromic behavior and noticeable solvatofluorochromism changing solvents polarity as well as intense green, yellow, 586 orange and red light luminescence with quantum yields from 0.03 to 0.93 in non-polar 587 solvents. Prolongation of π -bridge by one double bond in 2-cinnamoyl-1,3-indandione 588 and dimedone derivatives leads to red shift of absorption and emission, enhanced 589 photoluminescence quantum yield and decomposition temperature, as well as reduced 590 591 oxidation potential. Substitution of a strong, bulky amino donor groups (diphenylamino and dibiphenylamino) in dyes structures leads to higher quantum 592 593 yields, red-shifted emission, and large Stokes shifts.

For practical application in OLED dye 17 with dimedone cycle as acceptor, 594 $N(Ph)_2$ as donor and 1-hydroxyallylidene as π -bridge, and dye 14 with 1,3-indandione 595 as acceptor unit, N(BPh)₂ as donor and 1-hydroxyallylidene as π -bridge shows the 596 597 most promising properties among all investigated compounds. These two dyes showed high thermal stability with $T_{5\%}$ >270 °C, film forming properties and excellent 598 optical properties. Compound 17 is characterized with intense visible light absorption 599 at ~455 nm, large Stokes shifts (3715-6098 cm⁻¹) and bright yellow (~549 nm) or 600 orange-light (~620 nm) emission in non-polar solvents as well as in thin film with 601 moderate to high quantum yields (0.17-0.78). However, due to the demand for intense 602

603	red-light emitting organic materials dye 14 show some potential application, due to its
604	emission profile (λ_{em} ~663 nm with Φ =0.10-0.21) in THF, CHCl ₃ and in thin film.
605	

606 Acknowledgements

This work was supported by the doctoral studies grants of Material Science and Applied Chemistry of Riga Technical University (Grant Nr. 34-14000-DOK.MLĶF) and the National research program of Latvia "IMIS2". The authors thank Ms. Chem. I.Mihailovs for his help with DFT calculations.

611 Supplementary material

The deposition number CCDC 1510493 for compound **16** 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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619 **References**

[1] Bai D, Benniston AC, Clift S, Baisch U, Steyn J, Everitt N, Andras P. Low
molecular weight Neutral Boron Dipyrromethene (Bodipy) dyads for fluorescencebased neural imaging. J Mol Struct 2014;1065-6:10–5.
http://dx.doi.org/10.1016/j.molstruc.2014.02.026

[2] Bobe SR, Gupta A, Rananaware A, Bilic A, Xiang W, Li J, et al. Insertion of a
naphthalenediimide unit in a metal-free donore acceptor organic sensitizer for
efficiency enhancement of a dye-sensitized solar cell. Dyes Pigm 2016;134:83-90.

627 <u>http://dx.doi.org/10.1016/j.dyepig.2016.06.038</u>

- 628 [3] Yao YS, Zhou QX, Wang XS, Wang Y, Zhang BW. A DCM-Type Red-
- 629 Fluorescent Dopant for High-Performance Organic Electroluminescent Devices. Adv

630 Funct Mater 2007:17:93–100. <u>http://doi.wiley.com/10.1002/adfm.200600055</u>

- 631 [4] Yoon JY, Lee JS, Yoon SS, Kim YK. Red Fluorescent Donor- π -Acceptor Type
- 632 Materials based on Chromene Moiety for Organic Light-Emitting Diodes. Bull
- 633 Korean Chem Soc 2014;35:1670-4. <u>http://dx.doi.org/10.5012/bkcs.2014.35.6.1670</u>
- [5] Hwang DH, Lee JD, Lee MJ, Lee C. Organic light-emitting diode using a new
- 635 DCM derivative as an efficient orange-red doping molecule. Curr Appl Phys
- 636 2005;5:244–8. <u>http://dx.doi.org/10.1016/j.cap.2004.02.009</u>
- 637[6] Chang YJ, Chow TJ. Highly efficient red fluorescent dyes for organic light-638emittingdiodes.JMaterChem2011;21:3091–9.
- 639 <u>http://dx.doi.org/10.1039/c0jm03109g</u>
- [7] Yang Y, Bo S, Wang H, Liu F, Liu J, Qiu L, et al. Novel chromophores with
- 641 excellent electro-optic activity based on double-donor chromophores by optimizing
- 642 thiophene bridges. Dyes Pigm 2015;122:139-46.
 643 http://dx.doi.org/10.1016/j.dyepig.2015.06.012
- 644 [8] Agnihotri H, Mahalingavelar P, Mande H, Ghalsasi P, Kanvah S. Amino
- 645 substituted 4-pyridylbutadienes: Synthesis and fluorescence investigations. Dyes
- 646 Pigm 2015;123:341-8. <u>http://dx.doi.org/10.1016/j.dyepig.2015.08.018</u>
- 647 [9] Palakollu V, Kanvah S. α-Cyanostilbene based fluorophores: Aggregation-induced
- enhanced emission, solvatochromism and the pH effect. New J Chem 2014;38:5736-
- 649 46. <u>http://dx.doi.org/10.1039/c4nj01103a</u>
- 650 [10] Zhao P, Tang H, Zhang Q, Pi Y, Xu M, Sun R, Zhu W. The facile synthesis and
- high efficiency of the red electroluminescent dopant DCINB: A promising alternative
- to DCJTB. Dyes Pigm 2009;82:316-21. <u>http://dx.doi.org/10.1016/j.dyepig.2009.01.01</u>

- 653 [11] Kim SH, Lee SY, Gwon SY, Son YA, Bae JS. D-p-A solvatochromic charge 2-cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-654 transfer dyes containing a dihydrofuran acceptor. Pigm 2010;84:169-75. 655 Dyes 656 http://dx.doi.org/10.1016/j.dyepig.2009.07.012
- [12] Li H, Guo Y, Li G, Xiao H, Lei Y, Huang X, Chen J, Wu H, Ding J, Cheng Y.
- 658 Aggregation-Induced Fluorescence Emission Properties of Dicyanomethylene-1,4-
- 659 dihydropyridine Derivatives. J Phys Chem C 2015;119:6737-48.
- 660 http://dx.doi.org/10.1021/jp511060k
- [13] Behramand B, Molin F, Gallardo H. 2,1,3-Benzoxadiazole and 2,1,3benzothiadiazole-based fluorescent compounds: Synthesis, characterization and
 photophysical /electrochemical properties. Dyes Pigm 2012;95:600-5.
 http://dx.doi.org/10.1016/j.dyepig.2012.06.001
- [14] Genin E, Hugues V, Clermont G, Herbivo C, Castro MCR, Comel A, Raposo
 MMM, Blanchard-Desce M. Fluorescence and two-photon absorption of push-pull
 aryl(bi)thiophenes:structure-property relationships. Photochem Photobiol Sci
- 668 2012;11:1756–66. <u>doi: 10.1039/c2pp25258a</u>
- 669 [15] Fulopova A, Magdolen P, Sigmundova I, Zahradnik P, Rakovsky E, Cigan M.
- 670 Benzotristhiazole based chromophores for nonlinear optics. J Mol Struct
- 671 2012;1027:70–80. <u>http://dx.doi.org/10.1016/j.molstruc.2012.06.018</u>
- 672 [16] Mitsuya M, Suzuki T, Koyama T, Shirai H, Taniguchi Y, Satsuki M, Suga S.
- Bright red organic light-emitting diodes doped with a fluorescent dye. Appl Phys Lett
- 674 2000;77:3272-4. http://dx.doi.org/10.1063/1.1326491
- [17] Tykhanov DA, Sanin EV, Serikova II, Yaremenko FG, Roshal AD. Cinnamoyl
- 676 pyrones in proton-donating media: Electronic structure and spectral properties of

- 677 protolytic forms. Spectrochim Acta A Mol Biomol Spectrosc 2011;83:221–30.
- 678 <u>http://dx.doi.org/10.1016/j.saa.2011.08.022</u>
- [18] Zyabrev K, Dekhtyar M, Vlasenko Y, Chernega A, Slominskii Y, Tolmachev A.
- 680 New 2,2-difluoro-1,3,2(2H)oxazaborines and merocyanines derived from them. Dyes
- 681 Pigm 2011;92:749-57. <u>http://dx.doi.org/10.1016/j.dyepig.2011.05.025</u>
- 682 [19] Ahmedova A, Atanasov V, Marinova P, Stoyanov N, Mitewa M. Synthesis,
- 683 characterization and spectroscopic properties of some 2-substituted 1,3-indandiones
- 684 and their metal complexes. Cent Eur J Chem 2009;7:429-38.
- 685 <u>http://dx.doi.org/10.2478/s11532-009-0039-6</u>
- [20] Ahmedova A, Pavlovic G, Zhiryakova D, Šišak D, Stoyanov N, Springborg M,
- 687 Mitewa M. Experimental and theoretical study on the structure and optical properties
- 688 of 2-acyl-1,3-indandiones Conformational effects, J Mol Struct 2010;981:10-20.
- 689 <u>http://dx.doi.org/10.1016/j.molstruc.2010.07.008</u>
- [21] Ahmedova A, Marinova P, Pavlovic G, Guncheva M, Stoyanov N, Mitewa M.
- 691 Structure and properties of a series of 2-cinnamoyl-1,3-indandiones and their metal
- 692 complexes. J Iran chem soc 2012;9:297-06. <u>doi:10.1007/s13738-011-0024-9</u>
- 693 [22] Malina I, Kampars V, Turovska B. Synthesis, optical and electrochemical
- 694 properties of substituted 2-cinnamoyl-1,3-indandione o-methyl ethers. J Mol Struct
- 695 2016;1115:241-9. <u>http://dx.doi.org/10.1016/j.molstruc.2016.02.090</u>
- 696 [23] Nesse F. The ORCA program system. Wiley Interdiscip Rev:Comput Mol Sci
- 697 2011;2:73-8. <u>http://dx.doi.org/10.1002/wcms.81.</u>
- [24] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et
- al. Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2009.

- 700 [25] Hanwell MD, Curtis DE, Lonie DC, Vandermeerschd T, Zurek E, Hutchison GR.
- 701 Avogadro: an advanced semantic chemical editor, visualization, and analysis platform
- 702 J Cheminform 2012;4:17-34. <u>http://dx.doi.org/10.1186/1758-2946-4-17</u>
- 703 [26] Krishnan R, Binkley JS, Seeger R, Pople JA. Self-consistent molecular orbital
- methods. XX. A basis set for correlated wave functions. J Chem Phys 1980;72:650-6.
- 705 <u>http://dx.doi.org/10.1063/1.438955</u>
- 706 [27] Altomare A, Burla M, Cammali M, Cascarano G, Giacovazzo C, Guagliardi A,
- 707 Moliterni A, Spagna R, SIR97: A New Tool for Crystal Structure Determination and
- 708
 Refinement.
 J
 Appl
 Cryst
 1999;32:115-9.

 709
 http://dx.doi:10.1107/S0021889898007717

 <t
- 710 [28] Sheldrick GM. A short history of SHELX. Acta Cryst 2008;A64:112-22.
- 711 <u>http://dx.doi.org/10.1107/S0108767307043930</u>
- [29] Mackay S, Dong W, Edwards C, Henderson A, Gilmore CJ, Stewart N,
 Shankland K, Donald A. maXus, Integrated Crystallography Software, 2003, BrukerNonius and University of Glasgow.
- [30] Teotonio EES, Brito HF, Viertler H, Faustino WM, Malta OL, deSá GF, et al.
 Synthesis and luminescent properties of Eu³⁺-complexes with 2-acyl-1,3indandionates (ACIND) and TPPO ligands: The first X-ray structure of Eu–ACIND
 complex. Polyhedron 2006;25:3488–94. <u>http://dx.doi.org/10.1016/j.poly.2006.06.035</u>
 [31] Akhrem AA, Lakhvich FA, Budai SI, Khlebnicova TS, Petrusevish II. A new
 simple synthesis of 2-acylcyclohexane-1,3-diones. Synthesis1978;12:925-7. <u>DOI:</u>
 10.1055/s-1978-24943
- 722 [32] Heoa J, Oha JW, Ahna HI, Leec SB, Choc SE, Kimc MR, et al. Synthesis and
- characterization of triphenylamine-based organic dyes for dye-sensitized solar cells.
- 724 Synth Met 2010;160:2143–50. <u>http://dx.doi.org/10.1016/j.synthmet.2010.08.001</u>

- 725 [33] Liu F, Yang Y, Wang H, Liu J, Hu C, Huo F et al. Comparative studies on
- structure-nonlinearity relationships in a series of novel second-order nonlinear optical
- chromophores with different aromatic amine donors. Dyes Pigm 2015;120:347-56.
- 728 <u>http://dx.doi.org/10.1016/j.dyepig.2015.05.003</u>
- 729 [34] Kulhánek J, Bures F, Mikysek T, Ludvík J, Pytela O. Imidazole as a central p-
- 730 linkage in Y-shaped push pull chromophores. Dyes Pigm 2011;90:48-55.
- 731 <u>http://dx.doi.org/10.1016/j.dyepig.2010.11.004</u>
- 732 [35] Enchev V, Bakalova S, Ivanova G, Stoyanov N. Excited state intramolecular
- 733 proton transfer an 2-acetylindan-1,3-dione. Chem Phys Lett 1999;314:234-8.
- 734 <u>http://dx.doi.org/10.1016/S0009-2614(99)01160-4</u>

- [36] Gupta VD, Tathe AB, Padalkar VS, Umape PG, Sekar N. Red emitting solid
- state fluorescent triphenylamine dyes: Synthesis, photo-physical property and DFT
- 737 study. Dyes Pigm 2013;97:429-39. <u>http://dx.doi.org/10.1016/j.dyepig.2012.12.024</u>

Highlights

Series of 1,3-indandione and dimedone dyes with amino substituents are synthesized.

Structure-properties relationship is analyzed through different methods.

Dyes emission color and quantum yields are dependent on used amino donor structure.

Dyes with diphenylamino and biphenylamino donors shows high quantum yields.

 π -spacer length has significant impact on optical and electrochemical properties.