

Investigation of the Fluorescent Quantum Efficiency of New Low-Molecular Weight Compounds

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Abstract - The purpose of this work is an investigation the absorption and the fluorescent properties of two novel examples of low-molecular weight compounds – 2-phenyl-1H-imidazol-5(4H)-ones and para substituted 1,8-naphthalimides (1H-benzo[de]isoquinoline-1,3(2H)-diones). The compounds were synthesized and purified by column chromatography to achieve the high purity required for investigation of its photophysical properties. The fluorescent spectra of the solutions of compounds were detected at different wavelengths of excitation light. The measurements were performed by spectrofluorometric measurements. The obtained high quantum yields suggest that the investigated compounds can be used as promising candidates for electroluminescent layers.

Keywords – Low-molecular weight compounds, Naphthalimides, Imidazolones, Quantum yields, Fluorescence.

I. INTRODUCTION

Recently, the efforts of researchers are directed to investigation and application of organic materials in display technique and optoelectronic devices [1]. However, at the moment the main application possesses the conjugated polymers [2]. The main problem of preparation of organic electroluminescent (EL) display with conjugated polymers is the formation of the energy barrier between electrode/polymer/electrode interfaces [3]. The light emission of this EL device is independent of work function of electrodes. In contrast to conjugated polymers the light emission in low-molecular weight compounds (LMWC) is a result of inner-molecular excitation states with definite lifetimes through $n-\pi^*$ electron transfers leading to singlet and triplet excitons [4].

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The low-molecular weight compounds are poorly investigated for use in organic light-emitting diodes (OLED's). For application in optoelectronic devices of these materials is necessary first to study their quantum yields in solvents and photoluminescent response in solid state. The films of low-molecular weight compounds will be the subject of both academic research and industrial development in the future.

II. EXPERIMENTAL

A. Preparation of compound 5

Step 1: Preparation of intermediate - (Z)-4-(4-(dimethylamino)benzylidene)-2-phenyloxazol-5(4H)-one (3) (Figure 1):

A mixture of hippuric acid (1) (2.00 g, 11.2 mmol), 4-(dimethylamino)-benzaldehyde (2) (1.67 g, 11.2 mmol) and anhydrous KOAc (1.10 g, 11.2 mmol) was refluxed in 15 ml acetic anhydride for 1 h. After cooling the volatile was evaporated at 60°C in vacuo to obtain the crude solid intermediate 3. This solid was washed with 15 ml hexane in ultrasound bath and recrystallized from EtOH:water = 1:1. After recrystallization and drying in vacuo the purity of the oxazolone 3 was checked by TLC and used as starting material for the next step without characterization. Yield 55% (purple crystals).

Step 2: Preparation of target product: (Z)-4-(4-(dimethylamino)benzylidene)-1-(9-ethyl-9H-carbazol-3-yl)-2-phenyl-1H-imidazol-5(4H)-one (5) (Figure 1):

A mixture of oxazolone (3) (1.46 g, 5.0 mmol, 1.0 eq.), 9-ethyl-9H-carbazol-3-amine (4) (4.21 g, 20.0 mmol, 4.0 eq.) and KOAc (0.49 g, 5.0 mmol, 1.0 eq.) was refluxed in glacial acetic acid (20 ml) for 7 h. After cooling the volatile was evaporated at 60°C in vacuo. Residue was washed with 50 ml hexane in ultrasound bath and dried in vacuo to obtain the crude product 5. After twofold column chromatography (190 g silica gel, phase CH₂Cl₂ and CH₂Cl₂:Et₂O = 20:1) 1.07 g (44 % yield) of pure 5 was obtained as orange crystals. m.p. 285-286 °C; ¹H-NMR (CDCl₃, 250 MHz) δ 8.27 (d, 2H, J = 8.9 Hz), 8.03 (dt, 1H, J = 7.8, 1.0 Hz), 7.98 (m, 1H), 7.63-7.65 (m, 1H), 7.59-7.62 (m, 1H), 7.39-7.55 (overlapping m, 3H), 7.36 (s, 1H), 7.31 (m, 1H), 7.19-7.27 (overlapping m, 4H), 6.77 (d, 2H, 3'-H, 5'-H, J = 8.9 Hz), 4.39 (q, 2H, 23-H, J = 7.2 Hz), 3.10 (s, 6H, NMe₂), 1.45 (t, 3H, 24-H, J = 7.2 Hz). ¹³C-NMR (CDCl₃, 63 MHz) δ 171.41 (s, 1C, C-imidazolone),

157.55 (s, 1C, C-imidazolone), 151.68 (d, 1C, 4'-C), 140.43 (s, 1C, C-N from carbazole), 139.29 (s, 1C, C-N from carbazole), 134.78 (d, 2C), 130.63 (d, 1C), 130.43 (d, 1C), 129.60 (s, 1C, C-N from carbazole), 129.04 (d, 2C), 128.13 (d, 2C), 126.47 (s, 1C), 126.20 (d, 1C), 125.14 (d, 1C), 123.44 (s, 1C), 122.67 (s, 1C), 122.56 (s, 1C), 120.84 (d, 1C), 119.84 (d, 1C), 119.14 (d, 1C), 111.76 (d, 2C), 109.00 (d, 1C), 108.68 (d, 1C), 40.07 (q, 2C, NMe₂), 37.71 (t, 1C, 23-C), 13.84 (q, 1C, 24-C). Anal. calcd. for C₃₂H₂₈N₄O: C, 79.31; H, 5.82; N, 11.56; O, 3.30 %. Found: C, 79.38; H, 5.80; N, 11.49 %. MS (EI) m/z (rel. int.): 485 (47), 484 (M⁺•, 100), 298 (15), 297 (56), 242 (15), 194 (16), 179 (40), 159 (49), 105 (24).

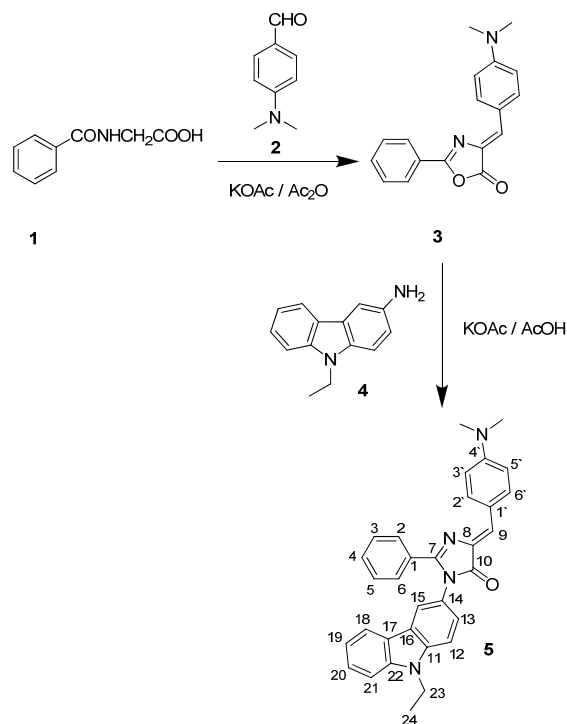


FIGURE 1. SYNTHESIS OF COMPOUND 5 IN TWO STEPS.

B. Preparation of compound 10

Step 1: Preparation of intermediate - 6-bromo-2-(6-hydroxyhexyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (8) (Figure 2):

A mixture of 1.50 g (5.41 mmol, 1.0 eq.) of 6 and 0.70 g (5.95 mmol, 1.1 eq.) of 7 was refluxed for 4 h in 40 ml absolute EtOH. After cooling the reaction mixture was poured into 250 ml 5% aqueous citric acid and stirred overnight. The obtained white precipitate of crude product 8 was filtered, washed with water and dried in vacuo. After purification with column chromatography (60 g silica gel, phase hexane:Et₂O = 1:2) the pure product 8 was obtained as white crystals (1.05 g, 51% yield). m.p. 93-94 °C; ¹H-NMR (CDCl₃, 600 MHz) δ 8.65 (dd, 1H, 10-H), 8.56 (dd, 1H, 8-H), 8.40 (m, 1H, 4-H), 8.04 (m, 1H, 5-H), 7.84 (m, 1H, 9-H), 4.17 (m, 2H, 12-H), 3.65 (q, 2H, 17-H), 1.75 (m, 2H, 13-H), 1.60 (m, 2H, 16-H), 1.41-1.49 (m, 4H, 14-H, 15-H). Anal. calcd. for C₁₈H₁₈BrNO₃ (M_w = 376.24): C, 57.46; H, 4.82; Br, 21.24; N, 3.72; O, 12.76. Found: C, 57.40; H, 4.88; Br, 21.30; N, 3.71. MS (TIC, EI 70 eV,

exact mass 375.05) m/z (rel. int.): 376.47 (M⁺•, 90.13), 346.27 (16.15), 304.08 (10.03), 302.92 (15.21), 302.06 (10.73), 290.98 (61.56), 290.12 (86.68), 289.04 (77.99), 277.91 (74.97), 277.10 (100), 276.04 (99.21), 260.04 (38.60), 259.03 (56.35), 257.98 (30.14), 232.84 (36.34), 232.06 (38.01), 230.04 (17.22), 197.05 (9.32), 151.08 (10.00), 126.04 (15.33).

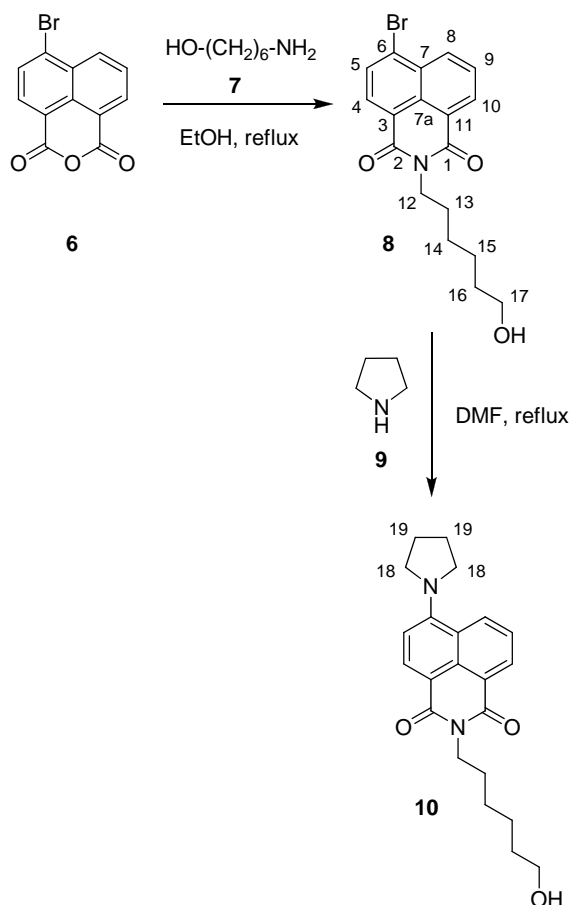
Step 2: Preparation of target product: 2-(6-hydroxyhexyl)-6-(pyrrolidin-1-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (10):

A mixture of 0.554 g (1.47 mmol, 1.0 eq.) of 8 and 1.047 g (1.22 ml, 14.72 mmol, 10 eq) of pyrrolidine (9) was refluxed for 1.5 h in 25 ml dry DMF. The orange solution was cooled and poured into 200 ml 5% aqueous citric acid and stirred overnight. The obtained orange precipitate of crude product 10 was filtered, washed with water and dried in vacuo. After purification with column chromatography (40 g silica gel; phase A: CH₂Cl₂, phase B: Et₂O:MeOH:Et₃N = 50:1:1) the pure product 10 was obtained as orange-yellow crystals (0.57 g, 96% yield). m.p. 133-134 °C; ¹H-NMR (CDCl₃, 600 MHz) δ 8.57 (m, 2H, 8-H, 10-H), 8.41 (d, 1H, 4-H, J = 8.7 Hz), 7.52 (dd, 1H, 9-H, J = 8.4, 7.5 Hz), 6.80 (d, 1H, 5-H, J = 8.7 Hz), 4.18 (m, 2H, 12-H), 3.78 (m, 4H, 18-H), 3.63 (t, 2H, 17-H, J = 6.5 Hz), 2.10 (m, 4H, 19-H), 1.76 (qt, 2H, 13-H, J = 7.5 Hz), 1.59 (qt, 2H, 16-H, J = 6.9 Hz), 1.41-1.49 (m, 4H, 14-H, 15-H). ¹³C-NMR (CDCl₃, 150 MHz) δ 164.92 (s, 1C, 1-C), 164.14 (s, 1C, 2-C), 152.60 (s, 1C, 6-C), 133.40 (d, 1C, 4-C), 131.89 (d, 1C, 8-C), 131.14 (s, 1C, 7a-C), 131.03 (d, 1C, 10-C), 123.00 (s and d, 2C, 7-C, 9-C), 122.52 (s, 1C, 11-C), 110.65 (s, 1C, 3-C), 108.45 (d, 1C, 5-C), 62.68 (t, 1C, 17-C), 53.14 (t, 2C, 18-C), 39.81 (t, 1C, 12-C), 32.58 (t, 1C, 16-C), 27.99 (t, 1C, 13-C), 26.54* (t, 1C, 14-C or 15-C) 26.06 (t, 2C, 19-C), 25.15* (t, 1C, 14-C or 15-C). Anal. calcd. for C₂₂H₂₆N₂O₃ (M_w = 366.45): C, 72.11; H, 7.15; N, 7.64; O, 13.10. Found: C, 72.16; H, 7.11; N, 7.69. MS (TIC, EI 70 eV, exact mass 366.19) m/z (rel. int.): 366.28 (M⁺•, 72.54), 349.25 (24.01), 279.22 (33.56), 266.18 (100.00), 223.14 (9.65).

III. RESULTS AND DISCUSSIONS

Both classes of compounds - 2-phenyl-1H-imidazol-5(4H)-ones and para substituted 1,8-naphthalimides possess high chemical stability in combination with fluorescent properties [5]. We chose to synthesize two new examples of these classes of compounds using cheap and commercially available starting materials.

Compound 5 was obtained in two steps (Figure 1). The first step includes preparation of intermediate (Z)-4-(4-(dimethylamino)benzylidene)-2-phenyloxazol-5(4H)-one 3 by implementation of the classic Erlenmeyer condensation [6] – reaction between hippuric acid (1) and 4-(dimethylamino)-benzaldehyde (2) in refluxing acetic anhydride (Ac₂O) and presence of anhydrous potassium acetate (KOAc). At the second step the purified intermediate 3 was refluxed with 9-ethyl-9H-carbazol-3-amine (4) and anhydrous KOAc in acetic acid (AcOH) to afford the desired compound 5 as pure Z isomer [7].

FIGURE 2. SYNTHESIS OF COMPOUND **10** IN TWO STEPS.

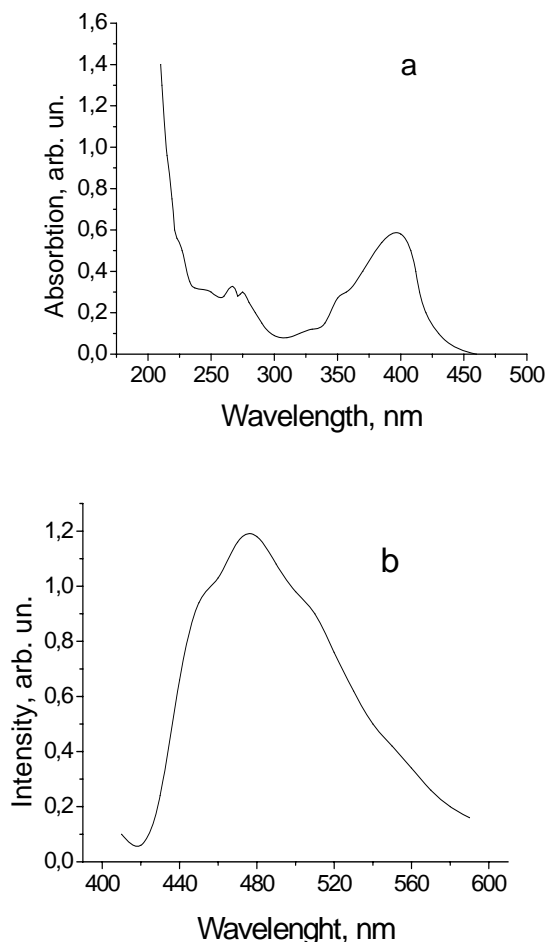
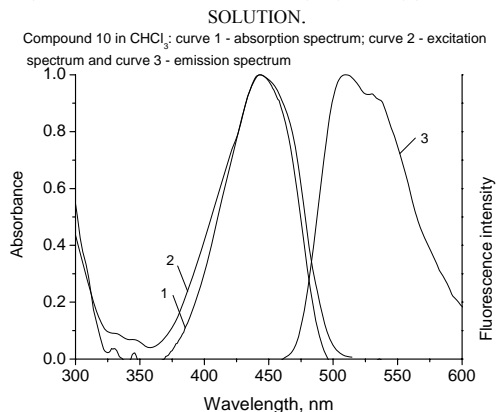
Compound **10** was obtained in two steps, too (Figure 2). The first step includes preparing by known procedure and high yields [8] of the intermediate compound **8**, which doesn't possess fluorescent properties. The reaction takes place regioselectively in refluxing absolute ethanol and doesn't affect bromine atom. In the second step the purified **8** was converted through reaction of N-arylation of pyrrolidine in excellent yields [9] to the desired compound **10** in refluxing dimethylformamide (DMF).

The new target compounds **5** and **10** were purified by column chromatography to achieve the high purity required for investigation of its photophysical properties. The purity of the compounds and its full characterization was determined by several standard methods for organic synthetic chemistry: 1D and 2D NMR experiments, melting points, elemental analysis and mass spectrometry. It was found that the compounds possess purity over 99.5%.

For measurements of absorption and fluorescent properties, and calculation of the fluorescent quantum yields the low-molecular weight compounds were dissolved in chloroform (CHCl₃). For study of maximum of absorption spectra, and excited PL profiles the measurements of solutions of the low-molecular weight compounds were led by use of Perkin-Elmer LS-55-spectrofluorimeter.

The absorption and fluorescent spectra of investigated compounds in CHCl₃ solutions were presented in Figures 3 and 4. The fluorescence quantum yields (Q_F) were determined at room temperature from the area under the fluorescence spectra taking as reference a ethanol solution of 3-p-methoxyphenylmethylene-1(3*H*)-isobenzofuranone

($Q_F = 0.14$) of the same absorbance at the excitation wavelength. At this wavelength, the concentrations were adjusted to an absorbance of 0.1, so that the fluorescence intensities were proportional to the absorbances of the solutions [10]. The calculated quantum yields in CHCl₃ solutions for (Z)-4-(4-(dimethylamino)benzylidene)-1-(9-ethyl-9*H*-carbazol-3-yl)-2-phenyl-1*H*-imidazol-5(4*H*)-one **5** was 0.26 and for 2-(6-hydroxyhexyl)-6-(pyrrolidin-1-yl)-1*H*-benzo[de]isoquinoline-1,3(2*H*)-dione **10** was 0.89, respectively.

FIGURE 3. ABSORPTION (A) AND FLUORESCENT (B) SPECTRA OF (Z)-4-(4-(DIMETHYLAMINO)BENZYLIDENE)-1-(9-ETHYL-9*H*-CARBAZOL-3-YL)-2-PHENYL-1*H*-IMIDAZOL-5(4*H*)-ONE (**5**) IN CHCl₃ SOLUTION.FIGURE 4. ABSORPTION AND FLUORESCENT SPECTRA OF 2-(6-HYDROXYHEXYL)-6-(PYRROLIDIN-1-YL)-1*H*-BENZO[DE]ISOQUINOLINE-1,3(2*H*)-DIONE (**10**) IN CHCl₃ SOLUTION.

IV. CONCLUSIONS

The investigations carried out show that the proposed new stable low-molecular weight compounds exhibit a photoluminescence in the visible range with high quantum yields, (especially compound 10). The results are promising and encourage us for further investigation of the electroluminescent properties of the presented new compounds and its usage in OLED's instead of polymers.

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