

Synthesis and electronic spectra of new low-molecular weight compounds with possible application in electroluminescent layers

Research Article

Georgi H. Dobrikov¹, Georgi M. Dobrikov^{2*}, Mariya Aleksandrova¹

¹Department of Microelectronics,
Technical University of Sofia, Sofia 1000, Bulgaria

²Institute of Organic Chemistry with Centre of Phytochemistry,
Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

Received 24 June 2011; Accepted 14 August 2011

Abstract: Two new low-molecular weight compounds – (Z)-4-(4-(dimethylamino)benzylidene)-1-(9-ethyl-9H-carbazol-3-yl)-2-phenyl-1H-imidazol-5(4H)-one and 2-(6-hydroxyhexyl)-6-(pyrrolidin-1-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione – with possible application in organic light-emitting devices were synthesized. Their photophysical properties in solution and in polymer films were investigated. The determined relative fluorescence quantum yields in solution for both compounds were 0.003 and 0.51, while those in poly(methyl methacrylate) films were around 0.10 and 1.0, respectively. For 1H-imidazol-5(4H)-one derivative, single-layer organic displays with one emitting layer were prepared by spin-coating technology. The applied voltage was 40 V (AC) with 1-3 KHz frequency. The emission maximum of the experimental AC display structures was at 600-630 nm. For displays with 2-(6-hydroxyhexyl)-6-(pyrrolidin-1-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione the applied voltage was 60 V (AC) with 6-9 KHz frequency, but its future success will require more appropriate binding polymers. Based on the obtained experimental results, it is concluded that the investigated compounds could be applied for preparation of color electroluminescent structures.

Keywords: Low-molecular weight compounds • 1,8-naphthalimides • Imidazolones • Fluorescence • Electroluminescent layers

© Versita Sp. z o.o.

1. Introduction

Over the past few years, an increasing interest has been directed toward the preparation and the characterization of organic materials with possible application in display techniques and in optoelectronic devices [1]. Currently existing organic light-emitting materials are divided into two main classes: i) high-molecular weight compounds (conjugated polymers) and ii) low molecular weight materials (LMWC) [2,3]. The main problem arising during preparation of organic electroluminescent (EL) devices with conjugated polymers is the formation of a high energy barrier at the electrode/polymer interfaces [4]. The light emission of such EL structures is dependent on the work function of the electrodes. In contrast with conjugated polymers, the light emission of LMWC is a result of intramolecular n- π^* charge transfer excited states caused by applied voltage with frequencies up to 1 kHz [5]. A significant problem in the development of LMWC is their low chemical stability against extreme

local conditions during the work of the device (high temperatures, electric fields, etc.).

An important prerequisite for the application of these materials in optoelectronic devices is the determination of their fluorescence quantum yields in solution and the study of their photoluminescent (PL) properties in solid state.

In the present paper, the synthesis and the main photophysical characteristics of two new LMWC are reported and their experimental electroluminescent structures were prepared.

2. Experimental procedure

2.1. General

Flash column chromatography was carried out using silica gel 60 (0.040–0.063 mm, 230-400 mesh ASTM, Merck). Commercially available solvents for reactions, flash column chromatography and film preparation

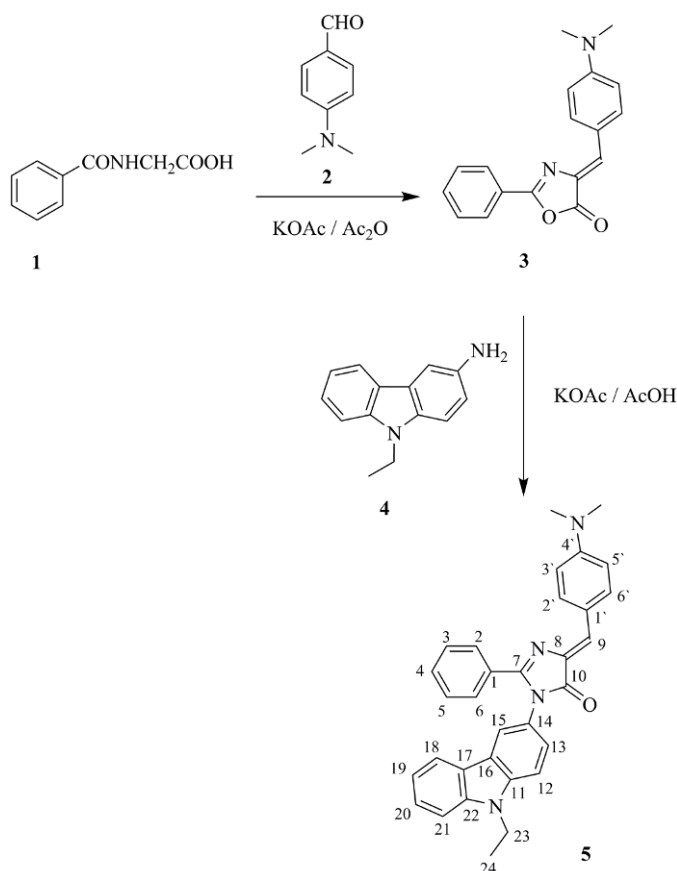
* E-mail: gmdob@orgchem.bas.bg

were used after distillation – hexane, glacial acetic acid (AcOH), dichloromethane (DCM), methanol (MeOH), ethanol (EtOH), diethyl ether (Et₂O), triethylamine (Et₃N). Commercially available reagents for synthesis were purchased from Sigma-Aldrich - anhydrous potassium acetate (KOAc), acetic anhydride (Ac₂O), hippuric acid, 4-(dimethylamino)-benzaldehyde, 9-ethyl-9*H*-carbazol-3-amine, citric acid, pyrrolidine, dimethylformamide (DMF). Melting points were determined in capillary tubes on an Electrothermal MEL-TEMP 1102D-230 VAC apparatus without corrections. NMR spectra were recorded at 300 K on a Bruker Avance DRX-250 (250.13 for ¹H and 62.90 MHz for ¹³C) and at 293 K on a Bruker Avance II+ 600 (600.13 for ¹H and 150.92 MHz and for ¹³C NMR) spectrometers with TMS as internal standard for chemical shifts (δ , ppm). ¹H spectra were calibrated to the signal of TMS (δ =0.0000). ¹³C spectra were calibrated to the signal of the solvent (CDCl₃, δ =77.0000). The following additional NMR techniques were used: Distortionless Enhancement by Polarization Transfer at 135 degree of impulse flip angle (DEPT135), Two-dimensional Correlation Spectroscopy (COSY), Heteronuclear Single Quantum Coherence (HSQC) and Heteronuclear Multiple Bond Correlation (HMBC).

¹H and ¹³C NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), integration, identification, and coupling constants (in Hz). For numbering of the atoms see Figs. 1 and 2. Mass spectra (MS) were measured with a Thermo Scientific High Resolution Magnetic Sector MS DFS by electron ionization (EI), and were reported as fragmentation in m/z with relative intensities (%). Elemental analysis was performed by the Microanalytical Laboratory for Elemental Analysis of the Institute of Organic Chemistry, Bulgarian Academy of Sciences.

2.2. Synthesis of compound 5

Compound **5** was obtained in two steps (Scheme 1). The first step was the preparation of the intermediate (Z)-4-(4-(dimethylamino)benzylidene)-2-phenyloxazol-5(4*H*)-one (**3**) by implementation of the classical Erlenmeyer condensation [6] – a reaction between hippuric acid (**1**) and 4-(dimethylamino)-benzaldehyde (**2**) in refluxing acetic anhydride (Ac₂O) in the presence of anhydrous potassium acetate (KOAc). At the second step, the purified intermediate **3** was refluxed with 9-ethyl-9*H*-carbazol-3-amine (**4**) and anhydrous KOAc



Scheme 1. Two-step synthesis of compound **5**.

in acetic acid (AcOH) in order to obtain the desired compound **5** as pure *Z* isomer [7].

The preparation of compound **5** includes the following steps (Scheme 1):

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

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* and the crude intermediate **3** was obtained. This solid was washed with 15 mL hexane in ultrasonic bath and recrystallized from EtOH:water = 1:1. After drying *in vacuo*, the oxazolone **3** was used as starting material for the next synthetic step without characterization.

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

A mixture of oxazolone (**3**) (1.46 g, 5.0 mmol), 9-ethyl-9*H*-carbazol-3-amine (**4**) (4.21 g, 20.0 mmol) and KOAc (0.49 g, 5.0 mmol) was refluxed in glacial acetic acid (20 mL) for 7 h. After cooling, the volatile was evaporated at 60°C *in vacuo*. The residue was washed with 50 mL hexane in ultrasonic bath and dried *in vacuo* to obtain the crude product **5**. After twofold flash column chromatography (190 g silica gel, phase: DCM and DCM:Et₂O = 20:1), 1.07 g of pure compound **5** was obtained as orange crystals (44% yield). 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, 62.9 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 (Mw = 376.24): 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).

2.3. Synthesis of compound 10

Compound **10** was synthesized in two steps, as well (Scheme 2). The first step included preparation by a known procedure [8] of the intermediate **8**, which does not possess fluorescent properties. The reaction takes place in refluxing absolute ethanol and does not affect the bromine atom. In the second step the desired compound **10** was obtained with excellent yield through non-catalytic N-arylation of pyrrolidine with compound **8** in boiling DMF [9].

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

A mixture of **6** (1.50 g, 5.41 mmol) and **7** (0.70 g, 5.95 mmol) 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 the crude product **8** was filtered, washed with water and dried *in vacuo*. After purification with flash 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, 600.13 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). ¹³C-NMR (CDCl₃, 150.92 MHz): δ 163.63 (s, 1C, C=O), 163.61 (s, 1C, C=O), 133.24 (d, 1C, 8-C), 132.02 (d, 1C, 10-C), 131.21 (d, 1C, 4-C), 131.07 (d, 1C, 5-C), 130.58 (s, 1C, 7-C), 130.23 (s, 1C, 6-C), 128.95 (s, 1C, 7a-C), 128.06 (d, 1C, 9-C), 123.05 (s, 1C, 11-C), 122.19 (s, 1C, 3-C), 62.74 (t, 1C, 17-C), 40.33 (t, 1C, 12-C), 32.56 (t, 1C, 16-C), 27.93 (t, 1C, 13-C), 26.64* (t, 1C, 14-C or 15-C), 25.24* (t, 1C, 14-C or 15-C). Anal. calcd. for C₁₈H₁₈BrNO₃ (Mw = 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 (EI) *m/z* (rel. int.): 376.47 (M⁺, 90), 346.27 (16), 304.08 (10), 302.92 (15), 302.06 (11), 290.98 (62), 290.12 (87), 289.04 (78), 277.91 (75), 277.10 (100), 276.04 (99), 260.04 (39), 259.03 (56), 257.98 (30), 232.84 (36), 232.06 (38), 230.04 (17), 197.05 (9), 151.08 (10), 126.04 (15).

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

A mixture of **8** (0.554 g, 1.47 mmol) and pyrrolidine (**9**) (1.22 mL, 14.72 mmol) was refluxed for 1.5 h in 25 mL dry DMF. The orange solution was cooled, poured into 200 mL saturated aqueous citric acid and stirred overnight. The obtained orange precipitate of the crude product **10** was filtered, washed with water and dried *in vacuo*. After purification with column

chromatography (40 g silica gel; phase A: DCM, phase B: Et₂O:MeOH:Et₃N = 50:1:1), the pure compound **10** was obtained as orange-yellow crystals (0.57 g, 96% yield). M.p. 133–134°C. ¹H-NMR (CDCl₃, 600.13 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, 150.92 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 (Mw = 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 (EI) m/z (rel. int.): 366.28 (M⁺, 73), 349.25 (24), 279.22 (34), 266.18 (100), 223.14 (10).

Compounds **5** and **10** were carefully purified by column chromatography and were unambiguously characterized by 1D and 2D nuclear magnetic resonance (NMR) experiments, mass spectroscopy (MS), elemental analysis and melting points. Analytical data show that both compounds possess satisfactory purity (over 99.5%), permitting investigation of their fluorescent properties.

2.4. Steady state UV-Vis absorbance, fluorescence measurements and film's preparation

Absorbance spectra and corrected fluorescence spectra were acquired separately on a Perkin Elmer Lambda 25 UV-VIS spectrophotometer and a Perkin Elmer LS

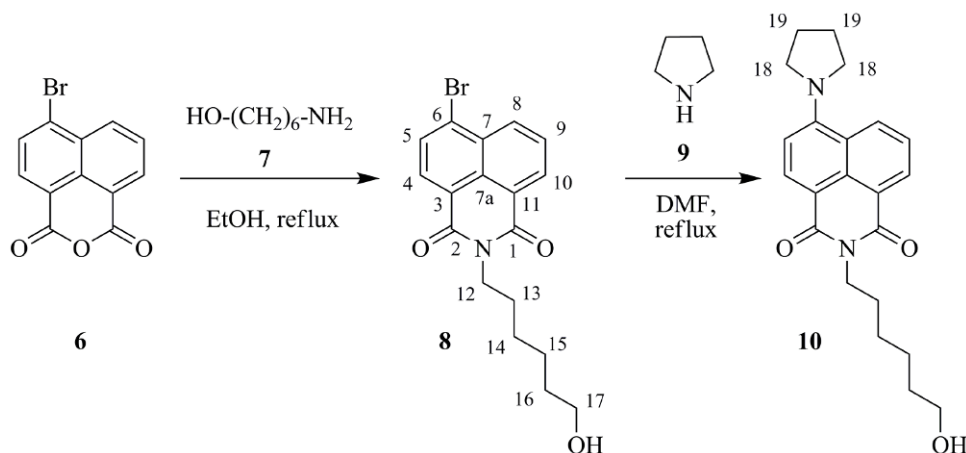
55 spectrofluorimeter, respectively. The brightness of the light emissions of the EL structures was measured by an LS-110-Konica Minolta luminance meter. The fluorescence quantum yield (Q_F) was determined relative to that of 3-p-methoxyphenylmethylene-1(3H) isobenzofuranone (Q_F = 0.12 in ethanol) [10]. Detailed information about quantum yields' determination may be found elsewhere [11]. The emission spectra in polymer films were measured in reflection mode. The solvents used were of fluorescence grade.

The poly(methyl methacrylate) (PMMA) films were prepared as follows: 300 mg PMMA was dissolved in 10⁻⁴ M dichloromethane solution of the investigated compound **5**. The solution was poured in Petri dishes and the solvent was evaporated in air for about 36 hours. The thickness of the resulting films was uniform and the concentration of **5** was about 0.5 – 0.7% weight. The role of PMMA is to increase the adhesion of films on the glass substrates and to promote linear orientation of LMWC molecules. PMMA also decreases the threshold voltage of the emitting layer.

For the preparation of electroluminescent structures, the above described homogeneous mixture of compound **5** and PMMA in dichloromethane was deposited over cleaned glass substrates through a spin-coating method. For deposition of the electrodes of EL structures, the vacuum installation A-400 VL was used. The aluminum electrodes were deposited by vacuum evaporation and the indium-tin oxide (ITO) transparent electrode was deposited by RF sputtering.

3. Results and Discussion

The new structures selected for synthesis are representatives of two classes of fluorescent organic compounds, namely 1H-imidazol-5(4H)-ones and 1,8-naphthalimides. Their preparation allows the usage of



Scheme 2. Two-step synthesis of compound **10**.

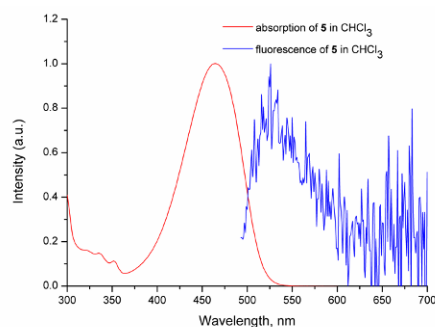


Figure 1. Absorbance and fluorescence spectra of **5** in CHCl_3 .

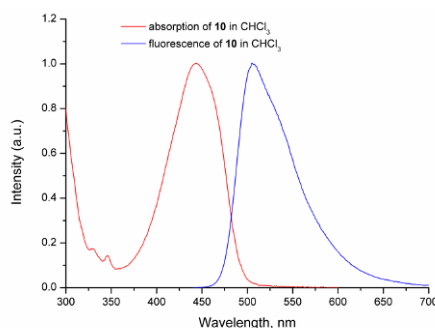


Figure 2. Absorbance and fluorescence spectra of **10** in CHCl_3 .

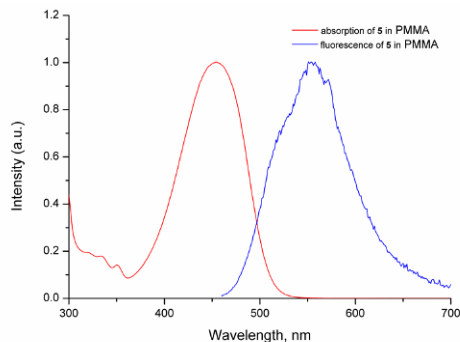


Figure 3. Absorbance and fluorescence spectra of compound **5** deposited in PMMA film.

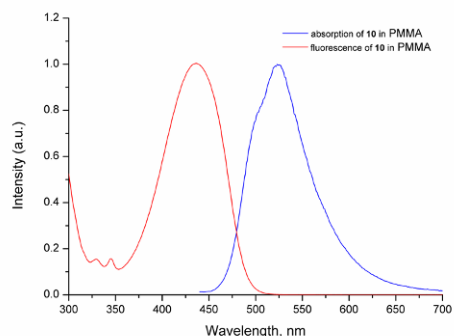


Figure 4. Absorbance and fluorescence spectra of compound **10** deposited in PMMA film.

cheap and commercially available starting materials. Both classes of compounds possess high chemical stability in combination with appropriate fluorescent properties and were a subject of our previous studies [12,13].

The UV-Vis absorbance and fluorescence spectra of compounds **5** and **10** in solution (CHCl_3) at room temperature are shown on Figs. 1 and 2 respectively.

In order to investigate the influence of medium rigidity on the fluorescence quantum yields of **5** and **10**, the compounds of interest were incorporated in PMMA matrix at room temperature. The corresponding absorbance and fluorescence spectra are shown on Figs. 3 and 4.

An increase of the fluorescence intensity was observed in PMMA films. The approximate values of the fluorescence quantum yields of compounds **5** and **10** became 0.1 and 1, respectively (Table 1). The significant increase of the fluorescent quantum yield of **5** in PMMA film (33 fold) encouraged us in our choice to investigate its possible electroluminescent (EL) properties in thin films. Since **5** has a significantly higher melting point, we presumed that it would be more resistant than compound **10** to the expected extreme conditions during the electroluminescent experiments (harsh rise of the temperature, strong electric fields, etc.). We did not observe visible decomposition or crystal structure changes of **5** at temperatures lower than the melting point. These results suggested the viability of compound **5** as a model structure for our electroluminescent experiments.

The experimental EL structure was prepared with an active EL film of compound **5** with mean thickness 300 nm. The film was deposited by a spin-coating method on an ITO covered substrate at 3200 rpm via addition of PMMA in solution for improving film adhesion. A vacuum evaporated aluminum layer with 200 nm mean thickness was used as the top electrode. The structure was supplied by 40 V AC with 1-3 KHz frequency. Fig. 5 shows the scheme of the prepared structure, while Fig. 6 show the obtained EL spectra. The highest intensity of the emitted light was detected at frequencies of the applied voltage between 1.5 and 2 KHz. The electroluminescence maximum of the structure is in the visible region of the spectrum at 600-630 nm. The intensity of the light emission depends on the frequency of the applied voltage. The change of the frequencies from 1 to 3 KHz leads to a bathochromic shift of the maximum by about 30 nm and to a lowering of the emission intensity, as well. The investigated structures produce light emission with a brightness of 150 cd m^{-2} (at frequency 1.5-2 KHz). The measurements were performed at permanent work of the structure for

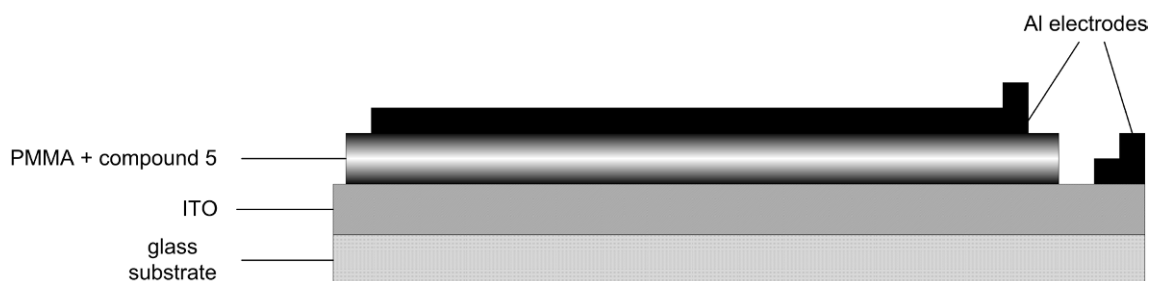


Figure 5. Experimental electroluminescent structure and its layers.

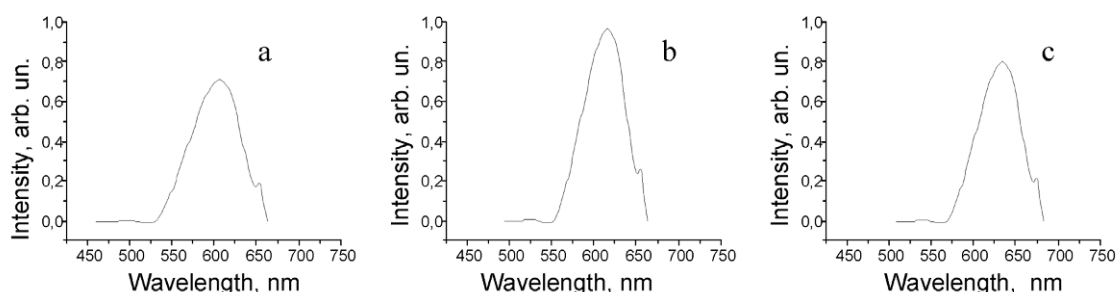


Figure 6. Electroluminescent spectra of EL structure with compound **5** incorporated in light emitting layer at three different AC frequencies: a) at 1 KHz; b) at 1.5-2 KHz; c) at 3 KHz.

Table 1. Absorbance and fluorescence maxima and fluorescence quantum yields of compounds **5** and **10** in CHCl_3 solution and PMMA film.

Compound	Absorbance maximum [nm]	Fluorescence maximum [nm]	Fluorescence quantum yield Q_f
In CHCl_3 solution			
5	465	525	0.003
10	445	505	0.510
In PMMA film			
5	455	555	around 0.10
10	435	525	around 1.00

8 hours. The electroluminescent measurements were repeated at every 30 minutes. The results showed that the parameters of the investigated structures remain stable during the experiment. It should be pointed out that the maximum of electroluminescence of compound **5** is bathochromically shifted in comparison to its fluorescent maximum in PMMA film by about 50 nm. Based on this experimental result, it could be concluded that the energy transitions taking place in the molecules of compound **5** are not the same for both processes.

In order to compare results for compound **5**, an experimental EL structure was prepared with compound **10**, as well, applying the technology described above. Unfortunately, the experiment with this structure was not successful. Despite its higher quantum yield, the structure demonstrated instability of its electroluminescent parameters after voltage was supplied (the experimental established parameters for causing of EL for this structure were 60 V AC and

6-9 KHz). After about 1 minute work, electrical break occurred, causing mechanical destruction of the glass substrate and visible decomposition of the organic layer. Only for a few seconds before the electrical break, a bright yellow electroluminescence was observed but its duration was insufficient for measurement of EL spectra or brightness of the light emission.

Experiments aimed at improving the technology of layer deposition, especially finding an appropriate binding polymer (with different electrophysical parameters than PMMA), are currently in progress, and results will be the subject of further publications.

4. Conclusions

Two new and stable low-molecular weight compounds (Z)-4-(4-(dimethylamino)benzylidene)-1-(9-ethyl-9H-carbazol-3-yl)-2-phenyl-1H-imidazol-5(4H)-one (**5**) and

2-(6-hydroxyhexyl)-6-(pyrrolidin-1-yl)-1*H*-benzo[de]isoquinoline-1,3(2*H*)-dione (**10**) were synthesized and their main photoluminescence properties were investigated. The prepared experimental EL structure with compound **5** showed encouraging electroluminescent properties (especially stability of the light emission for a long period of time – 8 hours) when high frequency AC voltage was supplied and could be applied as an alternative to OLEDs with polymeric light emitting layers. Compound **10** is of great importance for us because of the demonstrated bright electroluminescence – even for a short period of time – and the efforts for its successful application in EL-layers will be continued.

References

- [1] M.M. Kravtsiv, A.P. Kovalskiy, O.I. Shpotyuk, Adv. Optoelectron. Lasers 2, 194 (2003)
- [2] S.W. Kim, B.H. Hwang, J.H. Lee, J.I. Kang, K.W. Min, W.Y. Kim, Curr. Appl. Phys. 2, 335 (2002)
- [3] J. Davenas, S. Besbes, H. ben Ouada, M. Majdoub, Mater. Sci. Eng. C 21, 259 (2002)
- [4] S. Braun, W. Osikowicz, Y. Wang, W.R. Salaneck, Org. Electron. 8, 14 (2007)
- [5] E.F. Schubert, T. Gessmann, J.K. Kim, In: K. Mullen, U. Scherf (Eds.), Organic Light Emitting Devices. Synthesis, Properties and Applications (WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006)
- [6] A.K. Mukerjee, Heterocycles 26, 1077 (1987)
- [7] V.O. Topuzyan, A.A. Oganessian, G.A. Panosyan, Russ. J. Org. Chem (Eng.) 40, 1644 (2004)
- [8] I. Grabtchev, T. Konstantinov, S. Guittonneau, P. Meallier, Dyes and Pigments 35, 361 (1997)
- [9] J. Gan, H. Tian, Z. Wang, K. Chen, J. Hill, P.A. Lane, M.D. Rahn, A.M. Fox, D.D.C. Bradley, J. Organometal. Chem. 645, 168 (2002)
- [10] P. Nikolov, F. Fratev, St. Minchev, Z. Naturforsch. A 38, 200 (1983)
- [11] A.T.R. Williams, S.A. Winfield, J.N. Miller, Analyst 108, 1067 (1983)
- [12] I. Petkova, G. Dobrikov, N. Banerji, G. Duvanel, R. Perez, V. Dimitrov, P. Nikolov, E. Vauthey, J. Phys. Chem. A 114, 10 (2010)
- [13] P. Angelova, N. Kuchukova, G. Dobrikov, I. Timtcheva, K. Kostova, I. Petkova, E. Vauthey, J. Mol. Struct. 993, 185 (2011)

Acknowledgements

This study was supported by contracts DO-1/377-3, DOO2-358 with the Ministry of Education and Science of Bulgaria.