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## LETTERS TO THE EDITOR

# 2-(2'-Hydroxyphenyl)-5-(4''-nonylphenyl)-1,3,4-oxadiazole and Its Beryllium Complex

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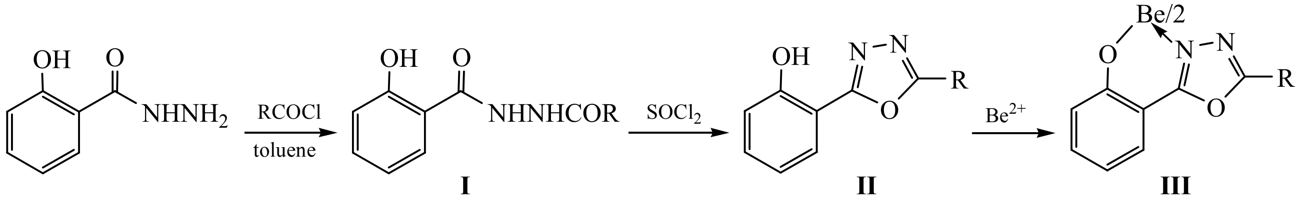
Metal chelates with 2-hydroxyphenyloxadiazole are widely used in development of organic light emitting diodes (OLEDs) as photo- and electroluminescent materials [1, 2]. However, most of them are poorly soluble in organic and aqueous-organic media, banning the modern high-performance and low-cost technologies such as spin-coating or ink-jet printing in the OLEDs production [3]. In order to obtain highly soluble metal complex luminophors, we prepared 2-(2'-hydroxyphenyl)-5-(4''-nonylphenyl)-1,3,4-oxadiazole **II**, containing long-chain alkyl substituent in the 5-aryl fragment that increased solubility of the product in organic medium; its beryllium complex **III** was prepared as well. *N*-Aroylhydrazide **I** obtained via benzoylation of salicylhydrazide was cyclized with thionyl chloride to form oxadiazole **II**. The latter reacted with $BeSO_4 \cdot 4H_2O$ in the presence of alkali to give the complex **III** in good yield.



R = 4-$C_9H_{19}C_6H_4$.

Compounds **II** and **III** containing hydrophilic chelate moiety (**II**) or metal center (**III**) and hydrophobic nonyl substituent can be used to produce mono- and polymolecular nanoscale Langmuir–Blodgett films.

Composition and structure of compounds **I–III** were confirmed by elemental analysis, IR, UV, and $^1$H NMR spectroscopy. In the absorption spectra of compounds **II** and **III** registered in toluene, acetonitrile or DMSO, the maximum of long-wave absorption band was observed in the range of 319–368 nm, indicating the presence of benzoid structures in solutions. The luminescence spectrum of **II** pointed at formation of quinoid structure via photoinitiated proton transfer (ESIPT process [4, 5]) from the phenolic hydroxyl to the nitrogen atom of oxadiazole in the excited state. The spectrum contained short-wave (toluene, $\lambda^{fl}$ 355 nm; $CH_3CN$, $\lambda^{fl}$ 350 nm; DMSO, $\lambda^{fl}$ 376 nm) and long-wave bands (toluene, $\lambda^{fl}$ 493 nm; $CH_3CN$, $\lambda^{fl}$ 487 nm; DMSO, $\lambda^{fl}$ 503 nm) with unusually high Stokes shift (11064–11467 cm$^{-1}$) assigned to the presence of the quinoid form. The low quantum yield of oxadiazole **II** luminescence ($\Phi$ = 0.008–0.012) was due to radiationless deactivation of its excited state via the ESIPTmechanism [5]. Unlike oxadiazole **II**, the beryllium complex **III** luminescence was fairly intense ($\Phi$ = 0.13–0.28). Emission spectrum of **III** contained the only band (toluene, $\lambda^{fl}$ 411 nm; $CH_3CN$, $\lambda^{fl}$ 409 nm) in between the spectral ranges typical of benzenoid and quinoid structures. In the case of DMSO solution spectrum, bathochromic shift was observed ($\lambda^{fl}$ 454 nm) as compared with the quinoid form.

To conclude, we obtained new oxadiazole ligand system and converted it into the organosoluble metal complex luminophor, which can be used to produce various photo- and electroluminescence devices.

**2-Hydroxy-*N*′-(4′-nonylbenzoyl)benzohydrazide (I).** Solution of 2.7 g (0.01 mol) of 4-nonylbenzoic acid in 20 mL of toluene and 20 mL of saturated $Na_2CO_3$ aqueous solution were subsequently added within 10 min to suspension of 1.52 g (0.01 mol) of salicylic acid hydrazide in 15 mL of water upon stirring; pH was maintained at about 8. The reaction mixture was the stirred during 4 h and incubated overnight. The formed precipitate was filtered off, washed with water (2×20 mL), dried in vacuum and recrystallized from ethanol. Yield 3.3 g (85%), colorless crystals, mp 163–165°C. IR spectrum, ν, $cm^{-1}$: 1546, 1607, 1628, 1656 (C=C, C=N), 3042 (NH), 3313 (OH). $^1H$ NMR spectrum (DMSO-$d_6$), $\delta_H$, ppm: 0.92 t (3H, $CH_3$, $^3J_{HH}$ 7.3 Hz), 1.21–1.44 m (12H, $CH_2$), 1.69 q (2H, $CH_2$, $^3J_{HH}$ 7.3 Hz), 2.68 t (2H, $CH_2$, $^3J_{HH}$ 7.5 Hz), 6.92–8.01 m (8H, $H_{Ar}$), 10.50 s (1H, NH), 10.68 s (1H, NH), 12.02 s (1H, OH). Found, %: C 72.60; H 7.40; N 7.60. $C_{23}H_{30}N_2O_3$. Calculated, %: C 72.27; H 7.85; N 7.33.

**2-[5-(4′-Nonylphenyl)-1,3,4-oxadiazol-2-yl]phenol (II).** 7.2 mL of thionyl chloride was added to 3.83 g of hydrazide **I** (0.01 mol). The mixture was refluxed during 4 h, cooled to room temperature, poured into 100 g of crushed ice, and incubated overnight. The formed precipitate was filtered off, washed with water (3×30 mL), dried in vacuum, and twice recrystallized from propan-2-ol (10 mL). Yield 2.44 g (67%), colorless crystals, mp 75–77°C. IR spectrum, ν, $cm^{-1}$: 1542, 1591, 1613, 1624 (C=C, C=N), 3154 (OH). $^1H$ NMR spectrum ($CDCl_3$), $\delta_H$, ppm: 0.86 t (3H, $CH_3$, $^3J_{HH}$ 7.3 Hz), 1.25–1.41 m (12H, $CH_2$), 1.67 q (2H, $CH_2$, $^3J_{HH}$ 7.3 Hz), 2.68 q (2H, $CH_2$, $^3J_{HH}$ 7.5 Hz), 7.02–8.05 m (8H, $H_{Ar}$), 10.20 s (1H, OH). Found, %: C 75.57; H 7.29; N 7.54. $C_{23}H_{28}N_2O_2$. Calculated, %: C 75.84; H 7.69; N 7.69.

**Bis[2-(2′-hydroxyphenyl)-5-(4″-nonylphenyl)-1,3,4-oxadiazolato]beryllium(II) (III).** Solution of 0.056 g (0.001 mol) of KOH in 2 mL of water was added to boiling suspension of 0.36 g (0.001 mol) of oxadiazole **II** in 15 mL of methanol. The mixture was refluxed during 30 min. Then, solution of 0.17 g (0.0005 mol) of $BeSO_4 \cdot 4H_2O$ in 1.5 mL water was added, and the mixture was further refluxed during 7 h. The formed precipitate was filtered off, washed subsequently with methanol (10 mL) and with water (15 mL), dried in vacuum, and recrystallized from toluene (50 mL). Yield 0.41 g (56%), colorless crystals, mp 246–248°C. IR spectrum, ν, $cm^{-1}$: 1503, 1536, 1564, 1589, 1614 (C=C, C=N). $^1H$ NMR spectrum ($CDCl_3$), $\delta_H$, ppm: 0.84 t (6H, $CH_3$, $^3J_{HH}$ 7.3 Hz), 1.18–1.27 m (24H, $CH_2$), 1.59 q (4H, $CH_2$, $^3J_{HH}$ 7.3 Hz), 2.62 t (4H, $CH_2$, $^3J_{HH}$ 7.5 Hz), 6.80–7.92 m (16H, $H_{Ar}$). Found, %: C 75.50; H 6.80; N 8.00; Be 1.60. $C_{46}H_{54}BeN_4O_4$. Calculated, %: C 75.11; H 7.34; N 7.61; Be 1.22.

IR spectra of thin films were registered with Varian Excalibur 3100 FT-IR spectrometer. $^1H$ NMR spectra (250.13 MHz) were recorded with Bruker DPX-250 spectrometer. Absorption and fluorescence spectra were registered with Cary Scan 100 spectrophotometer and Cary Eclipse spectrofluorimeter, respectively. Fluorescence quantum yields were determined relative to acetonitrile solution of anthracene [5, 6].

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