ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 5, pp. 1140–1145. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © A.I. Ilicheva, L.N. Bochkarev, V.A. Ilichev, Yu.D. Semchikov, 2015, published in Zhurnal Obshchei Khimii, 2015, Vol. 85, No. 5, pp. 846–851.

Copolymers Based on Norbornene-Containing Pyridinylbenzimidazole Copper(I) Complex. Synthesis, Photoluminescence, and Electroluminescence

A. I. Ilicheva[a,b], L. N. Bochkarev[a,b], V. A. Ilichev[a,b], and Yu. D. Semchikov[a]

[a] *N.I. Lobachevsky State University of Nizhni Novgorod, pr. Gagarina 23, Nizhni Novgorod, 603950 Russia e-mail: lnb@iomc.ras.ru*

[b] *G.A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, ul. Tropinina 49, Nizhni Novgorod, 603950 Russia*

Received January 12, 2015

Abstract—New carbon-chain polymers containing carbazole and copper(I) pyridinylbenzimidazole complexes side groups have been prepared via metathesis polymerization. Photo- and electroluminescent properties of the prepared polymer materials have been studied. Polymer emitters exhibit yellow electroluminescence with the highest luminance of 13.8 cd/m^2.

Keywords: copper-containing polymer, metathesis polymerization, photoluminescence, electroluminescence

DOI: 10.1134/S1070363215050230

Luminescent metal-containing polymers are promising emitting materials for development of full-color displays and large-area illuminating devices based on organic light-emitting diodes (OLEDs). Incorporation of different luminescent complexes of transition and nontransition metals allows for control of color and efficiency of the polymer electroluminescence [1, 2]. The best electroluminescent properties have been revealed for platinum- and iridium-containing polymer emitters [3–5]; the known copper-containing polymers are less efficient [6, 7]. Nevertheless, development of novel more efficient copper-containing polymer emitters is of indubitable interest due to cheapness and low toxicity of copper compounds. One of the reasons for low luminescence efficiency of copper-containing polymers is likely the nonoptimal ratio of charge-transporting and luminescent metal-containing units.

In this work we prepared copolymers with different content of charge-transporting and luminescent groups with via ring-opening metathesis polymerization.

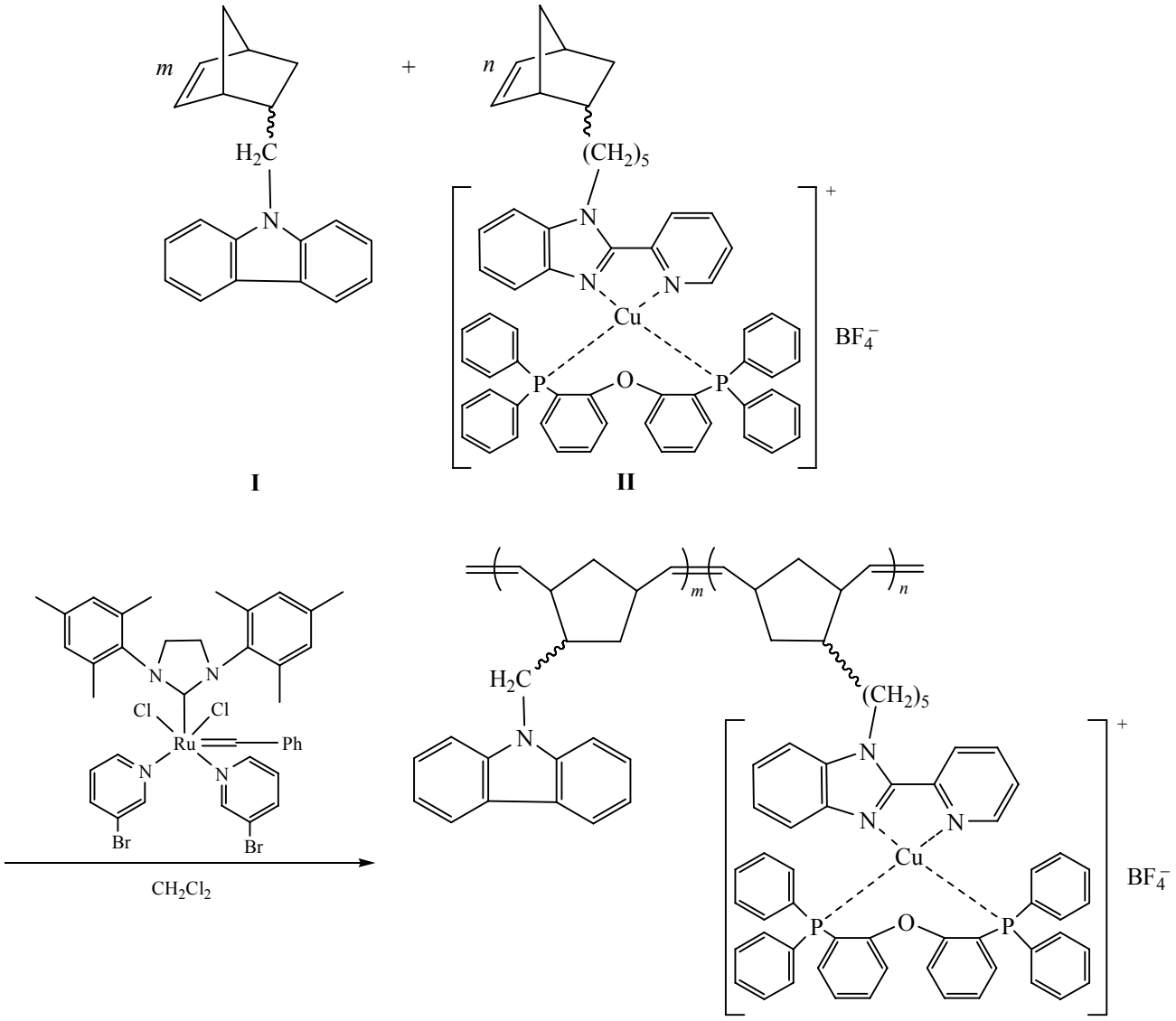
The copper-containing copolymers were prepared from monomer **I** [8] containing charge-transporting carbazole group and monomer **II** [7] containing luminescent copper(I) complex with pyridinylbenzimidazole ligand. Metathesis polymerization was performed in the presence of the III generation Grubbs' catalyst at room temperature (Scheme 1).

In all the cases the amount of the catalyst was of 1 mol % with respect to the total monomers content. TLC monitoring revealed that the highest polymerization conversion was attained after 6 h. The prepared polymers P1–P3 were solid yellow materials stable in air, readily soluble in THF, CH_2Cl_2, and $CHCl_3$. The copolymers composition was confirmed by elemental analysis and ^{1}H NMR spectroscopy data.

Absorption spectra of the copolymers (Fig. 1 and Table 1) contained strong bands at 250–325 nm (assigned to the $\pi\rightarrow\pi^*$ transitions in aromatic systems of carbazole fragments, phosphine groups, and substituted benzimidazole ligands) and weaker bands at 325–400 nm {typical of the metal-to-ligand charge-transfer MLCT transition in pyridinylbenzimidazole copper(I) complexes [9, 10]}.

Photoluminescence spectra of thin film of polymers P1–P3 (Fig. 2a and Table 1) contained strong broad bands with maximum at 530–535 nm assigned to MLCT transitions in the copper(I) complexes and weaker bands at 350–415 nm, typical of carbazole groups emission [11]. Photoluminescence of the copolymers in CH_2Cl_2 solutions exhibited majorly the

Scheme 1.



$m : n$ = 1 : 1 (P1), 8 : 1 (P2), 16 : 1 (P3).

emission bands of the carbazole fragments (Fig. 2b). Likely, transfer of excitation energy from carbazole groups to the copper complexes via the Förster mechanism [12] in the dilute solution was less efficient, and emission bands of the copper-containing fragments were weak.

Electroluminescent properties of the prepared copolymers were studied using model OLED devices of the ITO/Cu-polymer/BATH/Alq_3/Yb configuration: the ITO (indium oxide doped with tin oxide) layer acted as the anode; the polymers P1–P3 were used as the emission layer; 4,7-diphenyl-1,10-phenanthroline (BATH) and aluminum tris(8-oxyquinolinate) (Alq_3) were used as the hole-blocking and the electron-transporting layers, respectively; finally, ytterbium metal was used as the cathode. Electroluminescence spectra of the OLEDs are given in Figs. 3 and 4 along with the current-voltage and brightness-voltage characteristics. The performance parameters of the devices are collected in Table 2.

The electroluminescence spectra of the diodes based on copolymers P1–P3 were similar and contained broad bands with maximum at 575 nm assigned to the MLCT transitions in the copper

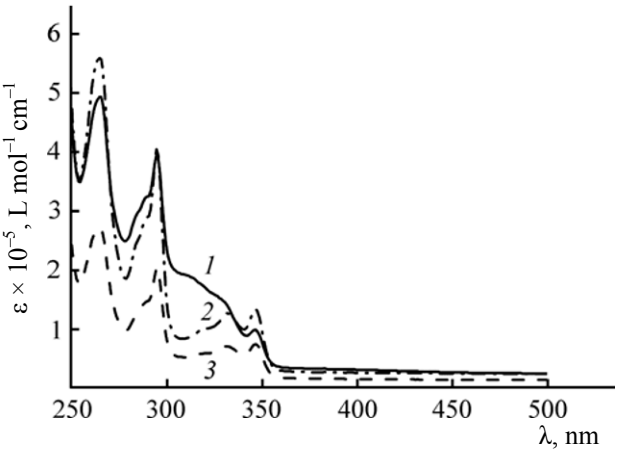


Fig. 1. Absorption spectra of polymers (*1*) P1, (*2*) P2, and (*3*) P3 in CH_2Cl_2 ($c = 2 \times 10^{-6}$ mol/L).

complexes. Coordinates of the emission in the CIE (Commision Internationale de l'Eclairage) diagram (Table 2) corresponded to yellow color. The highest luminance efficiency was observed in the case of copolymer P1 containing equimolar amounts of the carbazole groups and the copper complex units. The electroluminescence efficiency was decreased with the increasing ratio of the carbazole fragments in the copolymer (P2 and P3; Fig. 4 and Table 2). That was likely due to the imbalance of the charge (electrons and holes) carriers.

To conclude, metathesis polymerization yielded new carbon-chain copolymers with the varied ratio of carbazole- and copper-containing units. The non-optimized OLED devices based on polymeric emitters genereted yellow light with the luminance 13.8 cd/m^2. The efficiency of electroluminescence was decreased with the increasing content of the carbazole fragments in the copolymers.

EXPERIMENTAL

All operations with easily oxidized and hydrolyzed compounds were performed in vacuum or in the argon atmosphere using the standard Schlenk technique. 9-(Bicyclo[2.2.1]hept-5-en-2-yl-methyl)-9*H*-carbazole (**I**) [8], 1-{5-(bicyclo[2.2.1]-hept-5-en-2-ylpentyl)}-1*H*-2-pyridinylbenzimidazolo-[bis(2-diphenyl-phosphino)phenyl ether]copper tetrafluoroborate (**II**) [7], and $(H_2IMes)(3\text{-Br-py})_2(Cl)_2Ru{=}CHPh$ (generation III Grubbs' catalyst) [13, 14] were prepared according to the literature procedures. Aluminum tris(8-oxy-quinolinate) (Alq_3) and 4,7-di-phenyl-1,10-phenan-throline (BATH) (both from Aldrich) were used as received.

^{1}H NMR spectra were recorded using a Bruker DPX-200 (200 MHz) spectrometer with TMS as internal reference. IR spectra were registered using a FSM Fourier spectrometer. The copolymers samples were prepared as thin films between KBr plates.

Molecular mass distribution of the polymers was determined using gel permeation chromatography

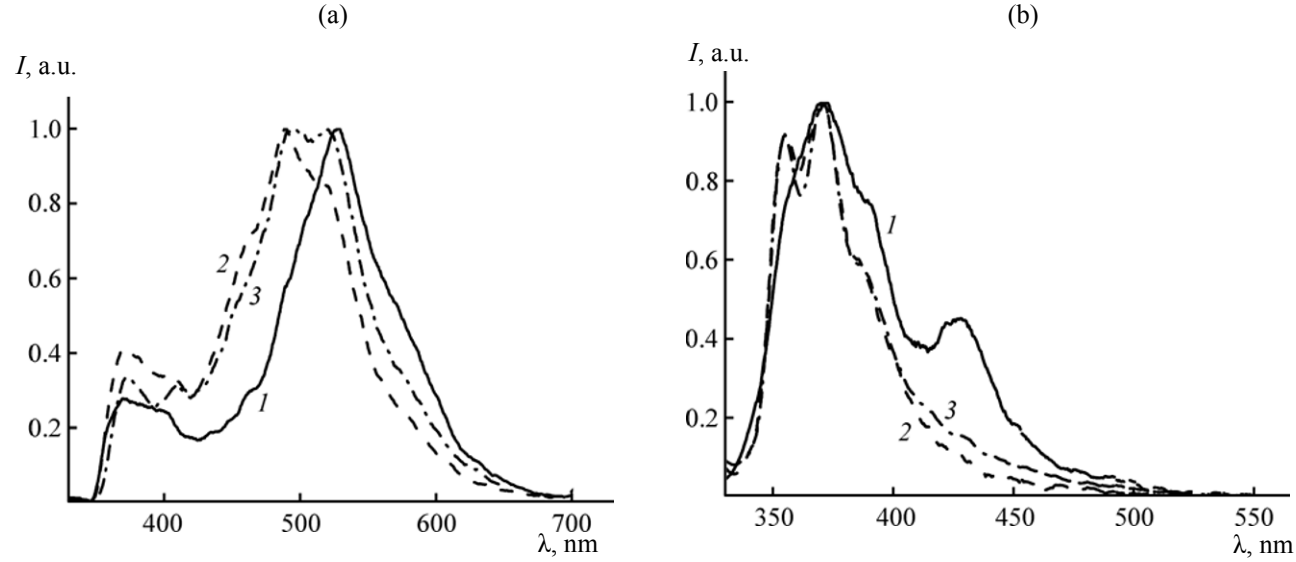


Fig. 2. Normalized photoluminescence spectra of polymers (*1*) P1, (*2*) P2, and (*3*) P3 in (a) thin film and (b) in CH_2Cl_2 solution. λ_{ex} = 320 nm.

Table 1. Photophysical parameters of polymers P1–P3

Compound	λ_{max}^{abs}, nm ($\varepsilon \times 10^{-5}$, L mol^{-1} cm^{-1}), CH_2Cl_2	λ_{max}^{em}, nm	
		film	in CH_2Cl_2
P1	265 (4.92), 279 (2.48), 295 (3.95), 320 sh (1.71), 332 (1.40), 347 (0.98)	380, 540	372, 428
P2	265 (2.71), 279 (0.97), 295 (2.02), 320 sh (0.58), 332 (0.7), 347 (0.74)	380, 530	354, 371
P3	265 (5.58), 279 (1.84), 295 (4.04), 320 sh (0.99), 332 (1.26), 347 (1.33)	380, 530	355, 370

Table 2. Performance[a] of organic light-emitting diodes based on copolymers P1–P3

Copolymer	λ_{max}^{em}, nm	Maximum luminance, cd/m^2	Turn-on voltage[b], V	Highest efficiency		Color coordinates in CIE (x/y)
				current, cd/A	power, lm/W	
P1	575	13.8 (14)	7	0.96 (8)	0.38 (8)	0.48/0.46
P2	575	8.5 (22)	12	0.33 (14)	0.08 (12)	0.46/0.46
P3	575	8 (30)	18	0.02 (24)	0.003 (18)	0.43/0.47

[a] The voltage corresponding to the reported performance characteristics is given in parentheses. [b] At luminance of 1 cd/m^2.

eluting with 2 mL/min of THF at 40°C. A Knauer chromatograph was equipped with two Phenomenex columns filled with Phenogel (10^4 and 10^5 Å) sorbents and a Smartline RID 2300 differential refractometer as detector. The columns were calibrated with 13 polystyrene reference samples.

Electronic absorption spectra were recorded using a Perkin Elmer Lambda 25 UV/VIS spectrometer. Photoluminescence spectra were registered using a Perkin Elmer LS 55 fluorescence spectrometer.

Electroluminescence spectra, current-voltage and brightness-voltage parameters were detected using a model OLED devices without sealing. The automated PC-attached measuring complex contained a GWINSTEKPPE-3323 power source, GWINSTEKGDM-8246 digital multimeter, and Ocean Optics USB 2000 spectrofluorimeter was used.

Copolymer P1. A solution of 0.0018 g (0.0021 mol) of generation III Grubbs' catalyst (in 1 mL of CH_2Cl_2) was added to a mixture of monomers **I** (0.03 g, 0.11 mmol) and **II** (0.11 g, 0.11 mmol) in 5 mL of CH_2Cl_2. The mixture was stirred at room temperature monitoring the process by TLC. After the polymerization was complete (6 h), several drops of ethyl vinyl ether was added for the catalyst decomposition, and the mixture was stirred during further 30 min. The formed polymer was precipitated with hexane, reprecipitated with hexane from CH_2Cl_2, and dried in vacuum at room temperature to constant weight. Yield 0.11 g (75%) of copolymer P1, pale yellow solid. IR spectrum, ν, cm^{-1}: 2933 s, 2856 m (C_{arom}–H), 1627 w, 1595 m, 1565 w, 1482 s, 1462 s, 1435 s, 1329 s (C_{arom}–C_{arom} and C=N), 1261 m, 1216 m, 1156 m, 1121 m,

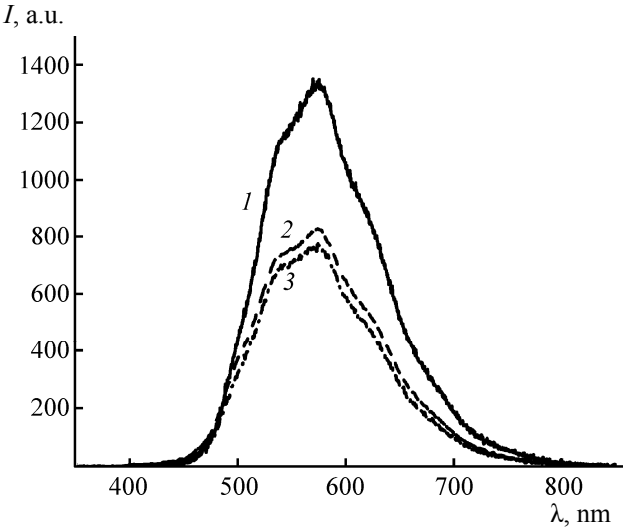


Fig. 3. Electroluminescence spectra of OLEDs based on polymers *(1–3)* P1–P3 at the highest luminance.

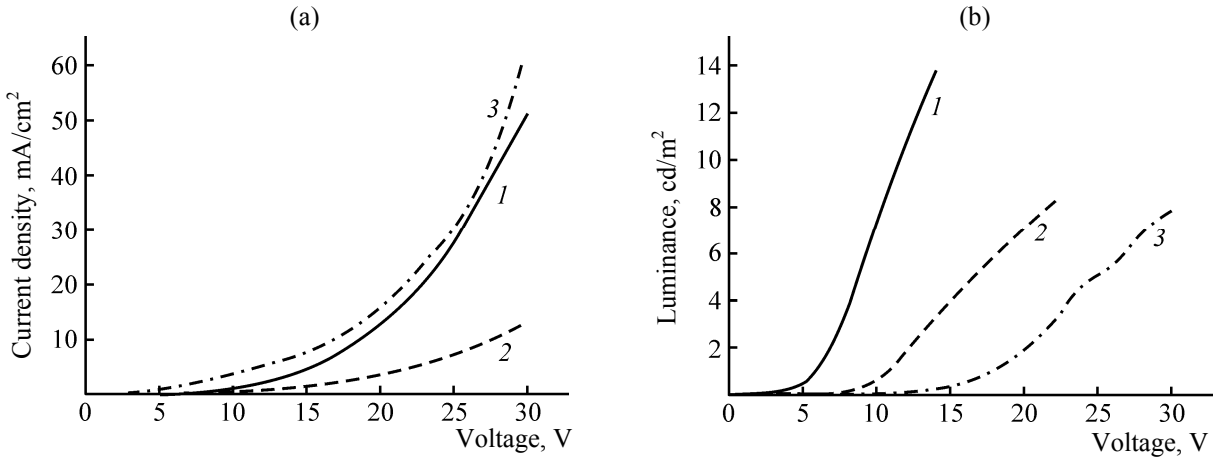


Fig. 4. (a) current-voltage and (b) brightness-voltage parameters of light diodes based on copolymers (*1*) P1, (*2*) P2, and (*3*) P3.

971 w (C–C), 748 s, 725 s, 698 w, 618 w (C_{arom}–H). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.01 s (5H), 7.33–7.12 m (28H), 5.34–5.18 m (4H), 4.1 br.s (2H), 2.62–1.14 m (35H). M_w 5700, M_n 3900, M_w/M_n 1.4. Found, %: C 72.83; H 5.68. $C_{80}H_{74}BCuF_4N_4OP_2$. Calculated, %: C 72.78; H 5.61.

Copolymers P2 and P3 were prepared similarly.

Copolymer P2. Yield 0.14 g (93%). IR spectrum, ν, cm^{-1}: 2932 s, 2865 m (C_{arom}–H), 1627 w, 1595 m, 1482 s, 1462 s, 1452 s, 1349 m, 1326 s (C_{arom}–C_{arom}, C=N), 1261 m, 1231 m, 1216 m, 1154 m, 1121 m, 973 w (C–C), 748 s, 725 s, 648 w, 618 w (C_{arom}–H). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.01 s (25H), 7.34–7.13 m (78H), 5.41–5.14 m (18H), 4.02 br.s (12H), 2.53–1.14 m (74H). M_w 19700, M_n 11900, M_w/M_n 1.6. Found, %: C 81.67; H 6.36. $C_{220}H_{207}BCuF_4N_{11}OP_2$. Calculated, %: C 81.73; H 6.41.

Copolymer P3. Yield 0.15 g (94%). IR spectrum, ν, cm^{-1}: 2933 s, 2865 m (C_{arom}–H), 1627 w, 1595 m, 1482 s, 1462 s, 1453 s, 1349 m, 1326 s (C_{apom}–C_{apom}, C=N), 1261 m, 1231 m, 1213 m, 1154 m, 1121 m, 973 w (C–C), 748 s, 725 s, 648 w, 618 w (C_{apom}–H). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.01 s (45H), 7.34–7.14 m (141H), 5.54–5.12 m (34H), 4.03 br.s (16H), 2.51–1.11 m (123H). M_w 24200, M_n 16300, M_w/M_n 1.5. Found, %: C 84.14; H 6.57. $C_{380}H_{359}BCuF_4N_{19}OP_2$. Calculated, %: C 84.23; H 6.63.

OLED device assembly. Glass plate covered with ITO layer (120 nm, 15 Ω/cm^2, Lumtec) acting as anode was used as a support for the ITO/Cu-copolymer (40 nm)/BATH (30 nm)/Alq_3 (30 nm)/Yb (150 nm) OLED device. The emitting copolymer layer was deposited from its solution in CH_2Cl_2 (5 mg/mL) using a Spincoat G3-8 centrifuge (3000 rpm, 30 s) and dried in vacuum at 70°C during 2 h. The layer thickness was determined using a META-900 ellipsometer. The BATH (hole-blocking), Alq_3 (electron-conductive), and Yb (Aldrich) (cathode) layers were deposited via vaporization in vacuum (10^{-6} mmHg) from the separate thermoresistive evaporators. The layers thickness was determined with a calibrated quartz resonator. The active area of the device was a circle of 5 mm diameter.

ACKNOWLEDGMENTS

This work was financially supported by Ministry of Education and Science of Russian Federation (project no. 02.B.49.21.0003) and Foundation for Competitive Support of students, PhD students, and research fellows of Lobachevsky State University of Nizhni Novgorod.

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