A new norbornene-containing copper complex 2 was synthesized via functionalization of the pyridinylbenzimidazole ligand contained in the known copper derivative 1 possessing effective luminescent properties (Scheme 1).

Compound 2 is a pale yellow solid substance that is stable in air.

It was found that monomer 2 enters into a ROMP reaction in the presence of a third-generation Grubbs
catalyst to give a polymer P1 (Scheme 2).

The homopolymer P1 is a pale yellow solid substance that is stable in air and well soluble in THF, CH₂Cl₂, and CHCl₃. The polymeric materials used to fabricate emission layers in OLED devices should be well soluble and stable in air. These requirements are fully satisfied by the polymer P1 we obtained.

It is known that introduction of charge-transporting carbazole groups into polymeric emitters improves their electroluminescent efficiency [4]. Therefore, we used carbazole-containing derivatives 9-{5-(bicycle[2.2.1]hept-5-en-2-yl-pentyl)}-9H-carbazole [NBE(CH₂)₅carb] and bicycle[2.2.1]hept-5-en-2-yl-(9H-carbazol-9-yl)methanone [NBEC(O)carb] to obtain copper-containing copolymers. Similarly to the homopolymerization, the copolymerization occurs in the presence of a third-generation Grubbs catalyst to give target polymeric products in high yield (Scheme 3).

It has been reported previously that the luminescent properties of metal-containing copolymers strongly depend on the ratio between charge-transporting organic and metal-containing emitting units [5–8]. To obtain copper-containing copolymers, we used in the present study the equimolar ratio between the carbazole- and copper-containing comonomers. The copolymers P2 and P3 we obtained are pale yellow solid substances that are stable in air. As evidenced by the results of an elemental analysis and NMR spectroscopic data, the ratio n : m between the carbazole- and copper-containing units was 1 : 1. Their solubility is similar to that of homopolymer P1. The molecular-mass characteristics of the polymeric products P1–P3 are listed in Table 1.
A study of the photophysical properties of the compounds obtained demonstrated that the absorption spectrum of monomer 2 (Fig. 1, Table 2) contains a set of bands in the range 250–325 nm, associated with $\pi \rightarrow \pi^*$ transition in the aromatic systems of the phosphine and substituted benzimidazole ligands. The broad lower intensity band at 350–450 nm, similarly to the analogous band in the spectrum of the known copper complex $1$ with an unsubstituted pyridinylbenzimidazole ligand, may be due to the metal-to-ligand charge transfer (MLCT) [11].

The absorption spectrum of the homopolymer P1 (Fig. 1, Table 2) is similar to that of monomer 2. The spectra of the copolymers P2 and P3 contain, together with the absorption bands of copper complexes, additional bands at 285–305 nm, due to the absorption by

**Table 1.** Molecular-mass characteristics of copper-containing polymers

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>$M_w$</th>
<th>$M_n$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>20800</td>
<td>17000</td>
<td>1.22</td>
</tr>
<tr>
<td>P2</td>
<td>17500</td>
<td>12700</td>
<td>1.38</td>
</tr>
<tr>
<td>P3</td>
<td>15900</td>
<td>10000</td>
<td>1.59</td>
</tr>
</tbody>
</table>

**Fig. 1.** Absorption spectra of compounds 2 (1) and (2–4) P1–P3 in CH$_2$Cl$_2$ ($c = 23 \times 10^{-5}$ M). (ε) Extinction coefficient and (λ) wavelength.
carbazole groups bonded to the polymer chain [14].

The photoluminescence (PL) from complex 2 and the polymeric compounds P1–P3 (Fig. 2, Table 2) appears in a thin film as a broad band peaked at 532 nm, associated with MLCT transitions in copper complexes. The fact that the spectra of the copolymers P2 and P3 contain no emission bands associated with carbazole groups is indicative of an effective excitation energy transfer from the polymeric matrix to copper(I) complexes.

To study the electroluminescent properties of the copper-containing polymers, we fabricated model ITO/Cu-polymer/BATH/Alq3/Yb OLED devices in which the layer of indium oxide doped with tin oxide (ITO) served as the anode. The role of the emission layer was played by P1–P3 polymers. 4,7-Diphenyl-1,10-phenanthroline (BATH) and aluminum tris(8-oxyquinolinate) (Alq3) were used as the hole-blocking and electron-transporting layers, respectively. The layer of metallic ytterbium served as the cathode. The EL spectra and the current–voltage and brightness–voltage characteristics of the LEDs are shown in Figs. 3 and 4, respectively. The basic working parameters are listed in Table 3.

The EL spectra of the homopolymer P1 and copolymers P2 and P3 contain a broad band peaked at 575 nm, associated with MLCT transitions in copper complexes. The fact that the spectra of the copolymers P2 and P3 contain no emission bands associated with carbazole groups is indicative of an effective excitation energy transfer from the polymeric matrix to copper(I) complexes.

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Table 2. Photophysical characteristics of compounds 2 and P1–P3

| Compound | \(\lambda_{\text{max}, \text{abs}}\), nm \((\varepsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1})\), in CH\(_2\)Cl\(_2\) | \(\lambda_{\text{max}, \text{em}}\), nm (film) |
|----------|-------------------------------------------------------------------------------------------------|
| 2        | 274 (2.07), 315 (2.28), 338 (pl 1.83), 395 (0.43)                                               | 532                                      |
| P1       | 271 (1.53), 315 (1.67), 338 (pl 1.06), 395 (0.22)                                               | 532                                      |
| P2       | 265 (1.40), 289 (pl 1.34), 295 (1.35), 319 (1.52), 341 (pl 0.81), 395 (0.20)                      | 532                                      |
| P3       | 268 (4.73), 285 (pl 3.85), 304 (3.18), 315 (3.33), 339 (pl 1.33), 395 (0.23)                      | 532                                      |

Table 3. Characteristics of OLEDs based on polymers P1–P3

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>(\lambda_{\text{max}, \text{em}}), nm</th>
<th>Maximum brightness, Cd m(^{-2}) (voltage, V)</th>
<th>Turn-on voltage, V</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>575</td>
<td>12.5 (27.5)</td>
<td>24.5</td>
</tr>
<tr>
<td>P2</td>
<td>575</td>
<td>37.5 (24.5)</td>
<td>14.5</td>
</tr>
<tr>
<td>P3</td>
<td>575</td>
<td>8.6 (14)</td>
<td>10.0</td>
</tr>
</tbody>
</table>
shifted to longer wavelengths by 43 nm. A similar red shift of the EL emission band relative to the PL band has been observed previously for complexes of copper(I) halides with phosphine ligands [16]. The authors of [16] provided an explanation according to which the EL emission occurs from a lower lying excited state having a planar configuration, whereas the PL emission involves a higher lying state having a distorted tetrahedral configuration. It can be assumed that the bathochromic shift of the emission band in the EL spectra of the polymers P1–P3 is also due to the change in the configuration of the excited state of the copper complexes bonded to the polymer chain. It can be seen in Table 3 that the LED based on the homopolymer P1 has a low emission brightness and high turn-on voltage. Introduction of carbazole-containing units into the polymer chain (co-polymers P2 and P3) leads to a noticeable decrease in the current density and turn-on voltage (Fig. 4, Table 3). However, the maximum emission brightness noticeably increases only for the LED based on the copolymer P2, which contains carbazole groups bound to the polymer backbone via a hydrocarbon bridge –(CH₂)₅–. It can be assumed that the less rigid structure of the copolymer P2, compared with the copolymer P3, leads to weaker deactivation of excited states due to the triplet–triplet annihilation.

EXPERIMENTAL

All procedures with easily oxidized and hydrolyzed substances were performed in a vacuum or in argon by the standard Schlenk technique. The starting reagents were used: complex (1) [11], [Cu(MeCN)₄]BF₄ [17], bicycle[2.2.1]hept-5-en-2-yl-pentyl bromide [NBE(CH₂)₅Br] [18], 9-{5-(bicycle[2.2.1]hept-5-en-2-yl-pentyl)}-9H-carbazole [NBE(CH₂)₅carb (85 : 15 mixture of endo- and exo-isomers) [19], bicycle[2.2.1]hept-5-en-2-yl-(9H-carbazol-9-yl)methanone [NBEC(O)carb] (75 : 25 mixture of endo- and exo-isomers), and (H₂IMes)(3-Br-py)₂(Cl)₂Ru=CPh (third-generation Grubbs catalyst) [20, 21], were synthesized as described in the literature. Aluminum tris(8-oxyquinolinate) (Alq₃) and 4,7-diphenyl-1,10-phenanthroline (BATH) (Aldrich) were used without additional purification.

'H and 'C{H} NMR spectra were obtained on Bruker DPX-200 (1H NMR at 200 MHz and 13C NMR at 50 MHz) and Bruker Avance III-400 (1H NMR at 400 MHz and 13C NMR at 100 MHz) spectrometers. The chemical shifts are given in ppm relative to tetramethylsilane as internal standard.

IR spectra were measured with an FSM 1201 IR Fourier spectrometer. A sample of monomer 2 was prepared by compaction of pellets at a substance : KBr ratio of 1 : 200. Samples of the copolymers were prepared as thin films sandwiched between KBr plates.

The molecular-mass distribution of the polymers was determined by gel-permeating chromatography (GPC) on a Knauer chromatograph with a Smartline RID 2300 differential refractometer as detector and a set of two Phenomenex columns packed with Phenogel sorbent having pore sizes of 10⁴ and 10⁵ Å (THF as eluent, 2 mL min⁻¹, 40°C). The columns were calibrated against
Electronic absorption spectra were recorded with a Perkin Elmer Lambda 25 UV/VIS spectrometer, and PL spectra, on a Perkin Elmer LS 55 fluorescent spectrometer.

The melting point of monomer 2 (given without corrections) was determined in a sealed evacuated capillary.

EL spectra and current–voltage and brightness–voltage characteristics were measured on model OLED devices without encapsulation on an automated computer-connected complex including a GW INSTEK PPE-3323 power source, GW INSTEK GDM-8246 digital multimeter, and Ocean Optics USB 2000 spectroradiometer.

1-{5-(Bicyclo[2.2.1]hept-5-en-2-yl-pentyl)}-1-H-2-pyrindinylbenzimidazolocis(2-diphenylphosphino phenyl ether) copper tetrafluoroborate (2). Complex 1 (0.45 g, 0.50 mmol) was dissolved in 10 mL of DMF and NaH was added (0.012 g, 0.50 mmol) to the solution in small portions. The reaction mixture was stirred for 2 h at room temperature. Then, NBE(CH2)3Br (0.121 g, 0.50 mmol) in 5 mL of DMF was added to the resulting solution and the mixture was stirred for 18 h at room temperature. After the NaBr precipitate was separated by centrifugation, the solvent was separated by evaporation in a vacuum, and the residue was washed with hexane and dried in a vacuum at 50°C for 3 h. Complex 2 was obtained in an amount of 0.45 g (86%) as a finely crystalline yellow substance well soluble in DMF, THF, CH2Cl2, and CHCl3 and insoluble in hexane; mp (decomp.) 225–230°C. IR spectrum, ν, cm−1: 2960, 2930, 2858 (C arom–H), 1598, 1588 (C–N), 1462, 1436 (C arom–C arom), 1260, 1215, 1158, 1096, 875, 847, 802, 744, 699. 1H NMR spectrum (CDCl3), δ, ppm: 8.54 s (1 H), 8.15 d (1 H), 7.83 d (2 H), 7.12–6.98 m (32 H), 5.36–5.18 m (2 H), 3.40 t (2 H), 2.74 m (2 H), 1.85 m (3 H), 1.41–1.04 m (10 H). Found (%): C 68.75, H 5.36. C60H52BCuF4N3OP2. Calculated (%): C 68.83, H 5.26.

Copolymer P2. To a solution of monomer 2 (0.45 g, 0.43 mmol) and NBE(CH2)3carb (0.14 g, 0.43 mmol) in 5 mL of CH2Cl2 was added a solution of the third-generation Grubbs catalyst (0.0075 g, 0.0085 mmol, 1 mol % relative to the total amount of the monomers) in 1 mL of CH2Cl2. The mixture was stirred at room temperature. The polymerization process was monitored by TLC. After the reaction was completed (6 h), several drops of ethyl vinyl ether were added to the reaction mixture to decompose the catalyst and the mixture was additionally stirred for 30 min. The resulting polymer was precipitated with exene, additionally purified by reprecipitation with hexane from CH2Cl2, and dried in a vacuum at room temperature to constant mass. Polymer P1 was obtained in an amount of 0.15 g (75%) as a pale yellow solid substance. IR spectrum, ν, cm−1: 2924, 2855 (C arom–H), 1599, 1588 (C–N), 1479, 1462, 1437 (C arom–C arom), 1261, 1215, 1158, 1096, 971, 744, 698. 1H NMR spectrum (CDC13), δ, ppm: 8.54 s (1H), 8.15 br.s (1H), 7.83 d (2H), 7.12–6.98 m (32H), 5.36–5.18 m (2H), 3.40 t (2H), 2.74 m (2H), 1.85 m (3H), 1.41–1.04 m (10H). Found (%): C 68.75, H 5.36. C60H52BCuF4N3OP2. Calculated (%): C 68.83, H 5.26.

Copolymer P3. The copolymerization of monomer 2 (0.17 g, 0.16 mmol) and NBEC(O)carb (0.05 g, 0.16 mmol) in 5 mL of CH2Cl2 was added a solution of the third-generation Grubbs catalyst (0.0075 g, 0.0085 mmol, 1 mol % relative to the total amount of the monomers) in 1 mL of CH2Cl2. The mixture was stirred at room temperature. The polymerization process was monitored by TLC. After the reaction was completed (6 h), several drops of ethyl vinyl ether were added to the reaction mixture to decompose the catalyst and the mixture was additionally stirred for 30 min. The resulting polymer was precipitated with exene, additionally purified by reprecipitation with hexane from CH2Cl2, and dried in a vacuum at room temperature to constant mass. Polymer P1 was obtained in an amount of 0.17 g (81%) as a pale yellow solid substance. IR spectrum, ν, cm−1: 2924, 2855 (C arom–H), 1686 (C=O),
1599, 1588 (C–N), 1490, 1478, 1435 (Саром–Саром), 1274, 1238, 1212, 1157, 1096, 971, 754, 724, 698.

1H NMR spectrum (CDCl3), δ, ppm: 8.71 br.s (1 Н), 8.25–7.89 m (5 Н), 7.44 m (6 Н), 7.18–6.94 m (22 Н), 5.27 m (4 Н), 4.18–3.18 m (4 Н), 2.24–0.78 m (30 Н).

Found (%): С 71.98, Н 5.48. С80Н72BCuF4N4O2P2.

Calculated (%): С 72.02, H 5.40.

Fabrication of OLED devices. A glass plate with a deposited ITO layer (120 nm, 15 Ω cm–2) (Lum Tec) serving as the anode was used as a carrying support for OLED devices with an ITO/Cu-polymer (40 nm)/BATH (30 nm)/Alq3 (30 nm)/Yb configuration. The emission layer of the copolymer was deposited from its solution in CH2Cl2 (5 mg mL–1) on a Spincoat G3-8 centrifuge (3000 rpm, 30 s) and dried in a vacuum at 70°C for 1 h. The layer thickness was determined with a META-900 ellipsometer. The hole-blocking BATH layer, electron-transporting Alq3 layer, and Yb layer (Aldrich) were deposited by evaporation in a vacuum (residual pressure 10–6 mm Hg) from separate thermoresistive evaporators. The layer thicknesses were monitored with a calibrated quartz resonator. The active area of the devices had the form of a circle 5 mm in diameter.

CONCLUSIONS

(1) A new complex of copper(I) with a norbornene-containing 1-H-2-pyridinylbenzimidazole ligand was synthesized. New copper-containing carbochain homo- and copolymers were produced on the basis of this complex by metathesis polymerization.

(2) The compounds obtained exhibited a noticeable luminescent activity. The photo- and electroluminescence spectra of the polymers synthesized contain broad bands at 532 and 575 nm, respectively, associated with MLCT transitions in copper complexes.

(3) The maximum brightness of unoptimized OLED devices based on copper-containing polymeric materials was 37 Cd m–2 at 25 V. The efficiency of copper-containing polymeric emitters can be improved by changing the ligand environment in copper complexes and optimizing the light-emitting heterostructures.

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REFERENCES
