

Dinuclear Copper(I) Complexes with Substituted Benzimidazole Ligands. Synthesis and Photo- and Electroluminescent Properties

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Abstract—New dinuclear copper(I) complexes with bridging bis-diimine ligands were synthesized on the basis of benzimidazole derivatives. The obtained complexes showed photo- and electroluminescent properties. Copper-containing emitters exhibited yellow, orange, and yellow–green electroluminescence with a maximum brightness of 1166 cd/m².

Keywords: copper, dinuclear complexes, benzimidazole, photoluminescence, electroluminescence

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Among electroluminescent copper(I) compounds, mononuclear complexes with diimine and diphosphine ligands have been studied most thoroughly [1]. Dinuclear copper(I) complexes possessing photo- and electroluminescent properties have been studied to a considerably lesser extent. A distinctive feature of such compounds is the possibility of mutual excitation energy transfer between the metal centers, which could result in enhanced luminescence efficiency. Development of studies in this line seems to be promising.

Mononuclear copper(I) complex with 2-(pyridin-2-yl)benzimidazole ligand and tetrafluoroborate as counterion is one of the most efficient copper-containing

electroluminescent compounds [2]. Introduction of other substituents into the benzimidazole fragment, e.g., quinoline [3] or thiazole [4], changes the electroluminescence color to orange or green.

In this work we have synthesized new symmetrical and unsymmetrical dinuclear ionic copper(I) complexes on the basis of benzimidazole derivatives and studied their photophysical properties. The following ligands were used to obtain dinuclear copper(I) complexes: 1,1'-(butane-1,4-diyl)bis[2-(pyridin-2-yl)-1*H*-benzimidazole] (**L1**) [5], 1,1'-(butane-1,4-diyl)bis-[2-

Scheme 1.

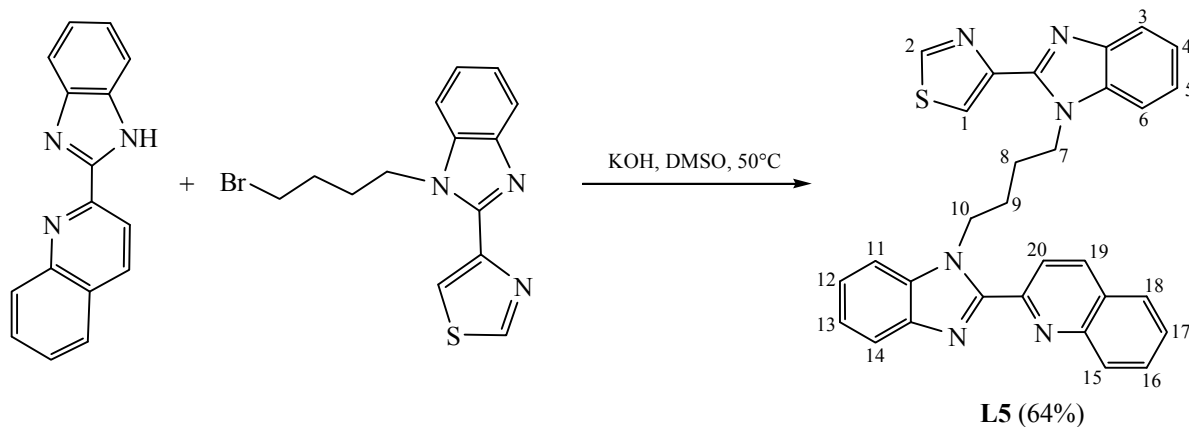
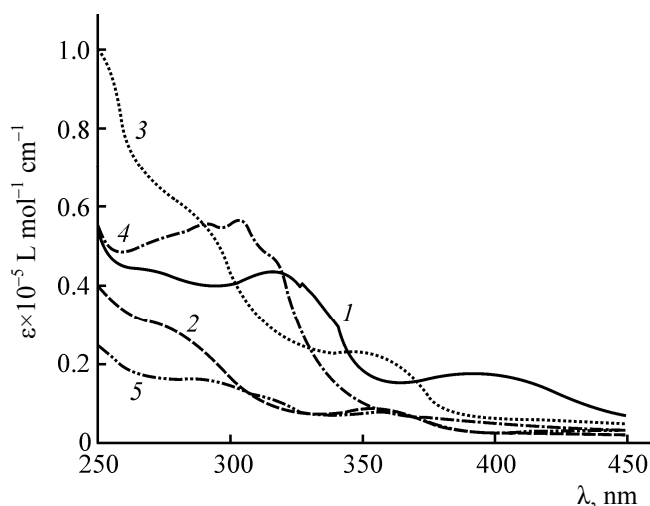


Table 1. Photophysical characteristics of copper(I) complexes 1–5

Complex	$\lambda_{\max}^{\text{abs}}$ (CH ₂ Cl ₂), nm ($\epsilon \times 10^{-5}$ L mol ⁻¹ cm ⁻¹)	$\lambda_{\max}^{\text{em}}$, nm (film)
1	272 (0.44), 317 (0.44), 393 (0.18)	534
2	272 (0.30), 355 (0.23), 410 (0.07)	400, 572
3	272 (0.66), 359 (0.08), 410 (0.06)	400, 574
4	285 sh (0.54), 305 sh (0.57), 320 sh (0.42), 400 (0.05)	532
5	290 (0.16), 355 (0.08), 400 (0.03)	400, 577

(quinolin-2-yl)-1*H*-benzimidazole] (**L2**) [6], 2-(1-{4-[2-(pyridin-2-yl)-1*H*-benzimidazol-1-yl]butyl}-1*H*-benzimidazol-2-yl)quinoline (**L3**) [7], 4-(1-{4-[2-(pyridin-2-yl)-1*H*-benzimidazol-1-yl]butyl}-1*H*-benzimidazol-2-yl)-1,3-thiazole (**L4**) [7], and 4-(1-{4-[2-(quinolin-2-yl)-1*H*-benzimidazol-1-yl]butyl}-1*H*-benzimidazol-2-yl)-1,3-thiazole (**L5**). Ligand **L5** was synthesized as shown in Scheme 1 and was identified by elemental analysis and IR and NMR spectroscopy. The ¹H NMR spectrum of **L5** showed triplets at δ 5.09 and 4.83 ppm and a multiplet at δ 2.15 ppm due to protons of the CH₂N and CH₂CH₂ groups.

Reactions of ligands **L1–L5** with [Cu(MeCN)₄]BF₄ in the presence of (oxydi-2,1-phenylene)bis(diphenylphosphine) (DPEPhos) afforded dinuclear copper(I) complexes **1–5** (Scheme 2) which showed strong photo- and electroluminescence. Complexes **1–5** were isolated as yellow (**1**, **4**) or orange (**2**, **3**, **5**) solids which were stable in air. The purity of **1–5** was checked by HPLC,

**Fig. 1.** Electronic absorption spectra of copper(I) complexes 1–5 (1–5) in methylene chloride ($c = 2 \times 10^{-5}$ M).

and their structure was confirmed by elemental analysis and IR and NMR spectra.

In the ³¹P NMR spectra of symmetrical complexes **1** and **2** we observed only one singlet at δ_p –11.52 and –11.08 ppm, respectively (equivalent phosphorus atoms). Unsymmetrical complexes **3–5** with non-equivalent phosphorus atoms displayed in the ³¹P NMR spectra two signals at δ_p –11.79 and –10.58, –12.30 and –11.48, and –12.30 and –10.93 ppm, respectively.

The absorption spectra of complexes **1–5** showed broad low-intense absorption bands in the region λ 325–400 nm; by analogy with the spectra of known copper complexes [8, 9], these bands may be assigned to metal-to-ligand charge transfer (MLCT) (Fig. 1, Table 1). Absorption bands in the region λ 250–325 nm correspond to π – π^* transitions in the aromatic rings of the phosphine and substituted benzimidazole ligands.

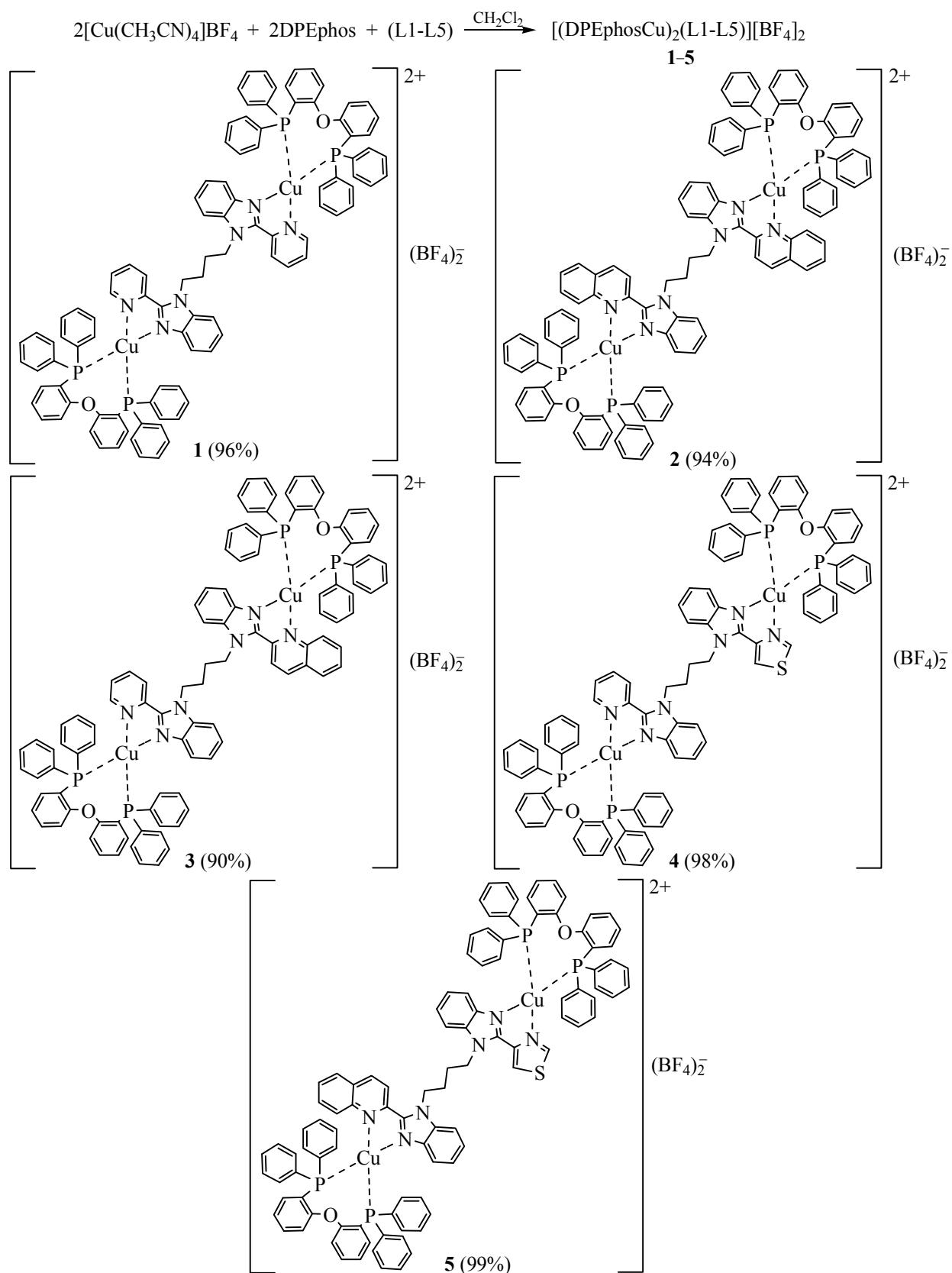
The photoluminescence spectra of **1–5** (Fig. 2, Table 1), recorded from thin films, displayed broad MLCT bands in the region λ 532–577 nm. Introduction of a quinoline fragment into the bis-diimine ligand (complexes **2**, **3**, **5**) induces red shift of the emission band. Presumably, this is the result of extension of the conjugation system in 2-(quinolin-2-yl)benzimidazole ligands, which reduces the energy of the emission level. Analogous red shift of the emission band was observed for the mononuclear copper(I) complex with 2-(quinolin-2-yl)benzimidazole ligand compared to the copper(I) complex with 2-(pyridin-2-yl)benzimidazole ligand [3, 10].

The photoluminescence spectra of **2**, **3**, and **5** contained two bands (Fig. 2, Table 1). Taking into account published data on the photoluminescence of dinuclear copper(I) complexes with phenanthroline ligands [11], the band with its maximum at about λ 400 nm may be assigned to intramolecular charge transfer from one ligand to another, and the band at λ_{\max} 572–577 nm, to MLCT.

The electroluminescent properties of complexes **1–5** were studied using model three-layer organic light emitting diodes (OLED) with the configuration ITO/Cu(I) complex (5–20 wt %): PVK/BATH/Alq₃/Yb. The emitting layer was a PVK matrix doped with 5, 10, or 20 wt % of complex **1–5**.

Figures 3 and 4 show, respectively, the electroluminescence spectra and current–voltage and brightness–voltage curves of the prepared OLEDs. The main

Scheme 2.



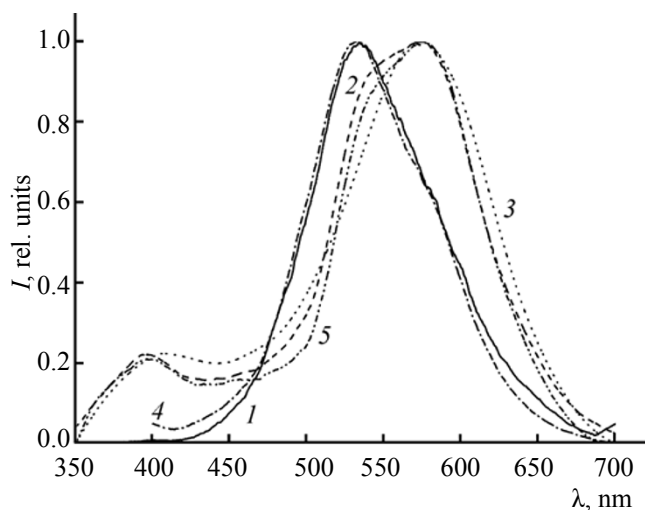


Fig. 2. Normalized photoluminescence spectra of copper(I) complexes **1–5** (*I–5*) in films; λ_{excit} 320 nm.

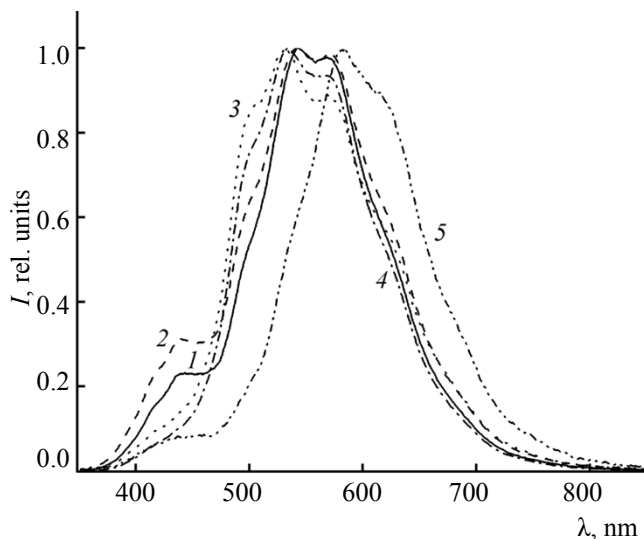


Fig. 3. Electroluminescence spectra of OLEDs based on copper(I) complexes **1–5** (*I–5*).

performance parameters are given in Table 2. The electroluminescence spectra (Fig. 3) displayed low-intense emission bands in the region λ 400–450 nm. These bands belong to the PVK matrix and indicate incomplete excitation energy transfer from the polymer matrix to the copper(I) complex. The bands with their maxima at λ 530–580 nm were assigned to MLCT in the copper-containing luminophore. The maximum brightness of OLEDs (1042–1166 cd/m^2) for each complex was reached at a concentration of 5 wt % in PVK (Fig. 4b, Table 2). Increase of the concentration of copper(I) complexes in the emitting layer resulted in reduced luminescence brightness, presumably due to concentration quenching. The CIE (Commission Internationale de L'Eclairage) chromaticity coordinates

of OLEDs based on complexes **1–5** correspond to orange, yellow, and yellow–green colors (Table 2).

As seen from Fig. 4a, complexes **1–3** are characterized by the best conductivity. Complexes **4** and **5** containing thiabendazole fragments showed considerably lower conductivity. Comparison of the current and power efficiencies of OLEDs based on complexes **1–5** at a concentration of 5 wt % showed that the maximum values were attained with complex **5**, 2.47 cd/A and 0.28 lm/W , respectively (Table 2).

In summary, we have synthesized new dinuclear ionic copper(I) complexes with bis-diimine benzimidazole ligands. The unoptimized OLED devices prepared on the basis of these complexes generate

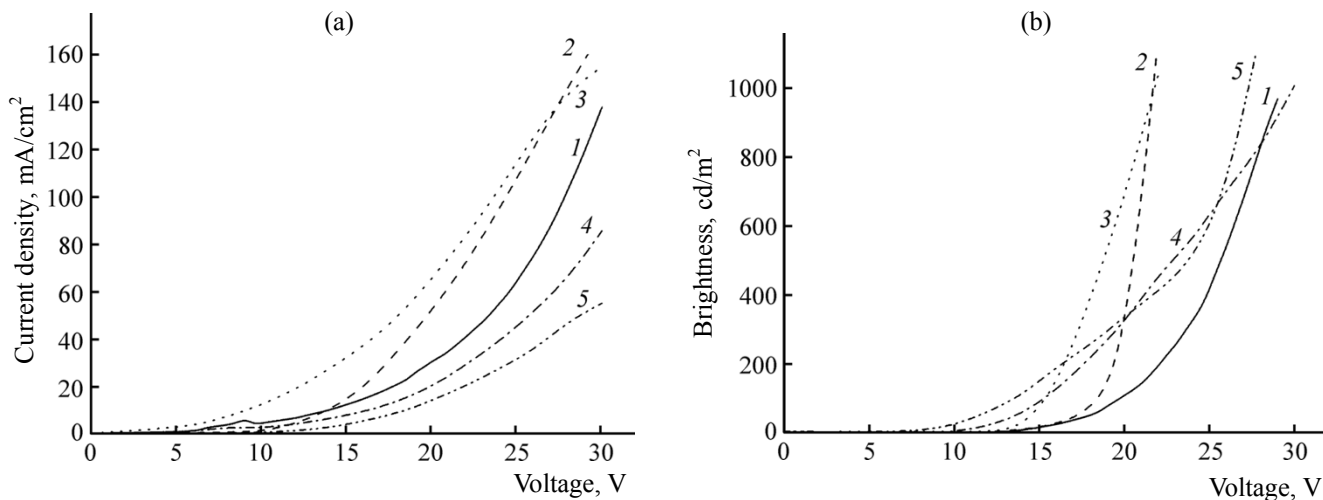


Fig. 4. (a) Current–voltage and (b) brightness–voltage curves for OLEDs based on copper(I) complexes **1–5** (*I–5*).

Table 2. Operation characteristics^a of organic light-emitting diodes based on copper(I) complexes **1–5**

Complex no.	ω (PVK), %	Maximum brightness, cd/m ²	Turn-on voltage, ^b V	Maximum efficiency		CIE chromaticity coordinates (x; y)
				current, cd/A	power, lm/W	
1	5	1123 (30)	15	0.97 (30)	0.11 (21)	0.42; 0.45
	10	548 (30)	14	0.57 (28)	0.05 (14)	0.41; 0.47
	20	430 (30)	14	1.39 (19)	0.88 (16)	0.47; 0.46
2	5	1155 (22)	14	1.61 (22)	0.23 (22)	0.39; 0.41
	10	518 (30)	14	0.94 (21)	0.15 (18)	0.39; 0.42
	20	561 (24)	12	0.44 (20)	0.075 (18)	0.48; 0.41
3	5	1042 (22)	6	1.25 (22)	0.18 (22)	0.53; 0.45
	10	534 (30)	8	3.52 (12)	0.92 (12)	0.55; 0.39
	20	639 (26)	4	2.03 (18)	0.35 (18)	0.52; 0.41
4	5	1134 (29)	8	1.25 (16)	0.26 (14)	0.38; 0.46
	10	1033 (30)	10	1.71 (20)	0.27 (20)	0.37; 0.46
	20	882 (18)	8	0.65 (16)	0.13 (16)	0.35; 0.46
5	5	1166 (28)	4	2.47 (28)	0.28 (28)	0.46; 0.39
	10	500 (20)	6	0.93 (16)	0.18 (16)	0.51; 0.41
	20	618 (28)	6	2.63 (18)	0.46 (18)	0.55; 0.40

^a In parentheses is given the voltage at which the parameter was determined.

^b At a brightness of 1 cd/m².

yellow, orange, and yellow–green luminescence with a maximum brightness of up to 1166 cd/m².

EXPERIMENTAL

All operations with readily oxidizable and hydrolyzable compounds were performed in a vacuum or under argon using standard Schlenk technique. 2-(Quinolin-2-yl)benzimidazole [12], 1,1'-(butane-1,4-diyl)bis[2-(pyridin-2-yl)-1*H*-benzimidazole] (**L1**) [5], 4-[1-(4-bromobutan-1-yl)-1*H*-benzimidazol-2-yl]-1,3-thiazole [7], 2-(1-{4-[2-(pyridin-2-yl)-1*H*-benzimidazol-1-yl]butyl}-1*H*-benzimidazol-2-yl)quinoline (**L3**) [7], 4-(1-{4-[2-(pyridin-2-yl)-1*H*-benzimidazol-1-yl]butyl}-1*H*-benzimidazol-2-yl)-1,3-thiazole (**L4**) [7], and tetrakis(acetonitrile)copper(I) tetrafluoroborate ([Cu(MeCN)₄]BF₄) [13] were synthesized according to known methods. 1,4-Dibromobutane, oxydi(2,1-phenylene)bis(diphenylphosphane) (DPEPhos), poly(vinylcarbazole) (PVK), aluminum tris(quinolin-8-olate) (Alq₃), and 4,7-diphenyl-1,10-phenanthroline (BATH) were commercial products (Aldrich) which were used without additional purification.

The melting points were measured in sealed evacuated capillaries and are uncorrected. The IR spectra were recorded in KBr on an FSM 1201 spectrometer with Fourier transform. The ¹H, ¹³C–{¹H}, and ³¹P–{¹H} NMR spectra were recorded on a Bruker DPX-200 spectrometer using tetramethylsilane (¹H and ¹³C) as internal standard and 85% H₃PO₄ (³¹P) as external standard. The electronic absorption spectra were measured on a Perkin Elmer Lambda 25 UV/Vis spectrophotometer. The photoluminescence spectra were recorded on a Perkin Elmer LS 55 fluorescence spectrometer. The electroluminescence spectra and current–voltage and brightness–voltage curves were obtained from model OLEDs without capsulation using an automated computerized system consisting of a GW INSTEK PPE-3323 power source, GW INSTEK GDM-8246 digital multimeter, and Ocean Optics USB 2000 spectrofluorimeter.

1,1'-(Butane-1,4-diyl)bis[2-(quinolin-2-yl)-1*H*-benzimidazole] (L2). A mixture of 0.2 g (0.82 mmol) of 2-(quinolin-2-yl)-1*H*-benzimidazole and 0.05 g (0.89 mmol) of potassium hydroxide in 5 mL of DMSO was stirred for 1 h at room temperature, 0.09 g

(0.42 mmol) of 1,4-dibromobutane was added, and the mixture was stirred for 5 h at 55°C, cooled to room temperature, and diluted with water. The product was extracted with chloroform (3×10 mL), and the combined extracts were washed with water and dried over MgSO₄. Volatile components were removed under reduced pressure, and the residue was washed with hexane and recrystallized from ethanol. Yield 0.30 g (68%), light brown finely crystalline solid, mp 265–270°C. The IR and NMR spectra of the product were consistent with those given in [6].

4-(1-{4-[2-(Quinolin-2-yl)-1H-benzimidazol-1-yl]-butyl}-1H-benzimidazol-2-yl)-1,3-thiazole (L5) was synthesized in a similar way from 0.16 g (0.65 mmol) of 2-(quinolin-2-yl)-1H-benzimidazole and 0.22 g (0.65 mmol) of 4-[1-(4-bromobutyl)-1H-benzimidazol-2-yl]-1,3-thiazole using 0.05 g (0.89 mmol) of KOH. Yield 0.21 g (64%), light brown finely crystalline solid, mp 195–200°C. IR spectrum, ν , cm⁻¹: 3081 m (C–H_{arom}), 2924 m, 2853 m (C–H); 1613 w, 1595 m, 1456 m, 1438 s, 1405 s, 1361 m, 1329 m, 1305 m, 1285 m, 1260 m (C=C_{arom}, C=N, C–C); 1153 m (N–C); 839 m, 757 s, 737 v.s. [δ (C–H_{arom})]. ¹H NMR spectrum (CDCl₃), δ , ppm (*J*, Hz): 8.74 m (1H, 2-H), 8.58 d (1H, *J* = 8.7, 20-H), 8.30 m (2H, 1-H, 19-H), 7.94–7.78 m (4H, 15-H, 16-H, 17-H, 18-H), 7.72–7.55 m (2H, 3-H, 6-H), 7.41–7.29 m (6H, 4-H, 5-H, 11-H, 12-H, 13-H, 14-H), 5.01 t (2H, *J* = 6.0, 10-H), 4.83 t (2H, *J* = 6.9, 7-H), 2.15 m (4H, 8-H, 9-H). ¹³C NMR spectrum (CDCl₃), δ _C, ppm: 152.80, 150.42, 149.54, 147.93, 147.29, 146.62, 143.56, 143.04, 136.87, 136.50, 129.80, 129.53, 127.75, 127.28, 123.73, 123.06, 122.73, 122.63, 121.87, 121.16, 120.44, 119.82, 110.04, 109.89, 45.46, 44.78, 27.67, 27.58. Found, %: C 72.10; H 4.86. C₃₀H₂₄N₆S. Calculated, %: C 72.00; H 4.80.

1,1'-(Butane-1,4-diyl)bis{[2-(pyridin-2-yl)-1H-benzimidazole]bis[oxydi(2,1-phenylene)bis(diphenylphosphane)]dicopper(I) bis(tetrafluoroborate) (1)}. A mixture of 0.14 g (0.44 mmol) of [Cu(MeCN)₄]BF₄ and 0.24 g (0.44 mmol) of DPEPhos in 10 mL of methylene chloride was stirred for 1 h at room temperature. A solution of 0.10 g (0.22 mmol) of 1,1'-(butane-1,4-diyl)bis[2-(pyridin-2-yl)-1H-benzimidazole] (L1) in 10 mL of methylene chloride was added, and the mixture was stirred for 2 h at room temperature. The solvent and volatile compounds were removed under reduced pressure, and the residue was washed with hexane and dried under reduced pressure. Yield 0.53 g (96%), yellow finely crystalline solid, decomposition point 340–343°C. IR spectrum, ν , cm⁻¹:

3057 m (C–H_{arom}); 2959 m, 2856 m (C–H); 1598 w, 1589 m, 1565 m, 1482 m, 1465 s, 1435 v.s., 1334 m, 1302 m, 1261 m, 1216 m (C=C_{arom}, C=N, C–C); 1183 m, 1163 m (C–N); 875 m, 802 v.s. [δ (C–H_{arom})]. ¹H NMR spectrum (CDCl₃), δ _C, ppm: 8.29 br.s (7H), 7.67–7.63 m (3H), 7.24–7.14 m (34H), 7.02–6.91 m (28H), 4.66 br.s (4H, NCH₂), 2.36 br.s (4H, CH₂CH₂). ¹³C NMR spectrum (CDCl₃), δ _C, ppm: 158.57, 150.22, 148.43, 144.36, 139.96, 139.33, 136.68, 134.15, 133.41, 132.42, 131.78, 130.54, 130.10, 128.59, 125.76, 125.45, 124.89, 124.55, 124.06, 120.25, 118.34, 111.61, 45.52, 27.08. ³¹P NMR spectrum (CDCl₃): δ _P –11.52 ppm. Found, %: C 66.03; H 4.52. C₁₀₀H₈₀B₂Cu₂F₈N₆O₂P₄. Calculated, %: C 65.91; H 4.42.

1,1'-(Butane-1,4-diyl)bis{[2-(quinolin-2-yl)-1H-benzimidazole]bis[oxydi(2,1-phenylene)bis(diphenylphosphane)]dicopper(I) bis(tetrafluoroborate) (2)} was synthesized in a similar way. Yield 0.20 g (94%), pale yellow finely crystalline solid. IR spectrum, ν , cm⁻¹: 3057 m (C–H_{arom}); 2962 m, 2853 m (C–H); 1622 w, 1592 m, 1565 m, 1480 m, 1462 s, 1435 v.s., 1334 w, 1260 m, 1219 m (C=C_{arom}, C=N, C–C); 1183 w, 1097 m (C–N, C–O); 875 m, 801 v.s. [δ (C–H_{arom})]. ¹H NMR spectrum (CDCl₃), δ , ppm (*J*, Hz): 8.65 d (2H, *J* = 7.5), 8.34 m (2H), 8.07 m (4H), 7.81 m (2H), 7.58 m (6H), 7.07 m (42H), 6.68 m (18H), 4.83 br.s (4H, NCH₂), 2.47 br.s (4H, CH₂CH₂). ¹³C NMR spectrum (CDCl₃), δ _C, ppm: 157.79, 150.21, 149.24, 147.29, 141.44, 140.13, 134.19, 133.87, 133.71, 133.55, 131.98, 130.71, 130.07, 129.70, 129.33, 129.19, 129.09, 129.00, 128.15, 127.54, 124.87, 123.13, 123.07, 119.64, 111.01, 46.47, 29.69. ³¹P NMR spectrum (CDCl₃): δ _P –11.08 ppm. Found, %: C 67.54; H 4.46. C₁₀₈H₈₄B₂Cu₂F₈N₆O₂P₄. Calculated, %: C 67.43; H 4.37.

Bis[oxydi(2,1-phenylene)bis(diphenylphosphane)]-[2-(1-{4-(2-(pyridin-2-yl)-1H-benzimidazol-1-yl)-butyl}-1H-benzimidazol-2-yl)quinoline]dicopper(I) bis(tetrafluoroborate) (3) was synthesized in a similar way. Yield 0.17 g (90%), pale yellow finely crystalline solid. IR spectrum, ν , cm⁻¹: 3057 m (C–H_{arom}); 2962 m, 2856 m (C–H); 1589 m, 1565 m, 1480 m, 1462 s, 1438 v.s., 1382 w, 1331 w, 1261 m, 1219 m (C=C_{arom}, C=N, C–O); 1183 w, 1163 m (C–N); 875 m, 802 v.s. [δ (C–H_{arom})]. ¹H NMR spectrum (CDCl₃), δ , ppm (*J*, Hz): 8.35 d (2H, *J* = 8.0), 8.07 d (2H, *J* = 7.8), 7.94 d (2H, *J* = 7.6), 7.83–6.78 m (2H), 7.62–7.58 m (2H), 7.41–7.33 m (26H), 7.19–6.76 m (32H), 6.62–6.55 m (6H), 4.56 m (4H, NCH₂), 2.46 m (4H, CH₂CH₂). ¹³C NMR spectrum (CDCl₃), δ _C, ppm: 158.82, 157.62, 153.04, 146.52, 141.44, 140.86, 139.44, 137.02, 134.44,

134.26, 134.11, 133.72, 132.08, 131.69, 130.72, 130.40, 129.79, 129.67, 129.05, 128.70, 128.14, 125.76, 125.19, 125.00, 124.74, 124.20, 120.34, 120.04, 119.68, 119.26, 118.40, 112.40, 45.91, 44.19, 27.23. ^{31}P NMR spectrum (CDCl_3), δ_{P} , ppm: -11.79, -10.58. Found, %: C 66.74; H 4.46. $\text{C}_{104}\text{H}_{82}\text{B}_2\text{Cu}_2\text{F}_8\text{N}_6\text{O}_2\text{P}_4$. Calculated, %: C 66.67; H 4.38.

Bis[oxydi(2,1-phenylene)bis(diphenylphosphane)]-[4-(1-{[2-(pyridin-2-yl)-1H-benzimidazol-1-yl]butyl}-1H-benzimidazol-2-yl)-1,3-thiazole]dicopper(I) bis(tetrafluoroborate) (4) was synthesized in a similar way. Yield 0.38 g (98%), pale yellow finely crystalline solid. IR spectrum, ν , cm^{-1} : 3057 m (C-H_{arom}); 2962 w, 2859 w (C-H); 1589 m, 1565 m, 1480 m, 1462 s, 1432 v.s, 1332 m, 1308 m, 1261 m, 1216 m (C=C_{arom} , C=N , C-C); 1095 m, 1056 s (C-N , C-O); 878 m, 802 v.s [$\delta(\text{C-H}_{\text{arom}})$]. ^1H NMR spectrum (CDCl_3), δ , ppm: 8.56–8.45 m (3H), 8.26 m (2H), 7.69–7.66 m (3H), 7.35 m (12H), 7.14–6.89 m (50H), 4.62 m (4H, NCH_2), 2.29 m (4H, CH_2CH_2). ^{13}C NMR spectrum (CDCl_3), δ_{C} , ppm: 152.7, 148.5, 147.9, 146.6, 142.9, 142.7, 136.8, 136.6, 135.7, 134.3, 133.7, 133.0, 131.7, 131.1, 129.9, 128.7, 124.9, 123.7, 123.4, 123.0, 122.6, 121.3, 120.2, 119.8, 110.0, 109.9, 44.9, 44.5, 27.3. ^{31}P NMR spectrum (CDCl_3), δ_{P} , ppm: -12.30, -11.48. Found, %: C 64.39; H 4.34. $\text{C}_{98}\text{H}_{78}\text{B}_2\text{Cu}_2\text{F}_8\text{N}_6\text{O}_2\text{P}_4\text{S}$. Calculated, %: C 64.33; H 4.27.

Bis[oxydi(2,1-phenylene)bis(diphenylphosphane)]-[4-(1-{4-[2-(quinolin-2-yl)-1H-benzimidazol-1-yl]-butyl}-1H-benzimidazol-2-yl)-1,3-thiazole]dicopper(I) bis(tetrafluoroborate) (5) was synthesized in a similar way. Yield 0.36 g (99%), pale yellow finely crystalline solid. IR spectrum, ν , cm^{-1} : 3057 m (C-H_{arom}); 2959 m, 2853 m (C-H); 1589 m, 1565 m, 1482 m, 1465 s, 1435 v.s, 1332 w, 1260 m, 1219 m (C=C , C=N , C-C); 1183 w, 1161 m (C-N , C-O); 876 m, 805 v.s [$\delta(\text{C-H}_{\text{arom}})$]. ^1H NMR spectrum (CDCl_3), δ , ppm: 8.84 m (1H), 8.63–8.57 m (1H), 8.27–8.08 m (1H), 7.91 m (1H), 7.74–7.61 m (3H), 7.33 m (30H), 7.08–6.84 m (35H), 4.70–4.51 m (4H, NCH_2), 2.35 br.s (4H, CH_2CH_2). ^{13}C NMR spectrum (CDCl_3), δ_{C} , ppm: 158.74, 157.88, 146.61, 145.07, 140.78, 139.54, 134.20, 133.70, 133.05, 131.85, 130.64, 130.09, 128.96, 128.11, 124.89, 120.02, 119.65, 111.92, 45.90, 29.68. ^{31}P NMR spectrum (CDCl_3), δ_{P} , ppm: -12.30, -10.93. Found, %: C 65.27; H 4.29. $\text{C}_{102}\text{H}_{80}\text{B}_2\text{Cu}_2\text{F}_8\text{N}_6\text{O}_2\text{P}_4\text{S}$. Calculated, %: C 65.18; H 4.26.

OLED devices with a configuration ITO/complex 1–5 (5–20 wt %): PVK (40 nm)/BATH (30 nm)/Alq₃

(30 nm)/Yb (150 nm) were prepared using a glass plate (support) coated with an ITO layer (120 nm, $15 \Omega/\text{cm}^2$) (Lum Tec) which acted as anode. The emitting layer was deposited from a solution in methylene chloride on a Spincoat G3-8 centrifuge (3000 rpm, 30 s) and was dried for 2 h under reduced pressure at 70°C. The hole-blocking layer (BATH), electron-transporting layer (Alq₃), and Yb layer (cathode; Aldrich) were prepared by vacuum deposition (10^{-6} mm) from separate thermoresistive evaporators. The layer thickness was controlled with the aid of a calibrated quartz resonator. The active area of OLEDs was 5×5 mm.

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REFERENCES

- Dumur, F., *Org. Electron.*, 2015, vol. 21, p. 27. doi 10.1016/j.orgel.2015.02.026
- Si, Z., Li, J., Li, B., Liu, S., and Li, W., *J. Lumin.*, 2009, vol. 129, p. 181. doi 10.1016/j.jlumin.2008.09.014
- Min, J., Zhang, Q., Sun, W., Cheng, Y., and Wang, L., *Dalton Trans.*, 2011, vol. 40, p. 686. doi 10.1039/c0dt01031f
- Zhang, D., *J. Lumin.*, 2010, vol. 130, p. 1419. doi 10.1016/j.jlumin.2010.03.005
- Liu, H.-Y., Wu, H., Ma, J.-F., Liu, Y.-Y., Liu, B., and Yang, J., *Cryst. Growth Des.*, 2010, vol. 10, p. 4795. doi 10.1021/cg100688z
- Mamedov, V.A., Safina, D.F., Gubaidullin, A.T., Ganieva, V.R., Kadyrova, S.F., Rakov, D.V., Rizvanov, I.K., and Sinyashin, O.G., *Tetrahedron Lett.*, 2010, vol. 51, p. 6503. doi 10.1016/j.tetlet.2010.10.007
- Il'icheva, A.I., Baranov, E.V., Begantsova, Yu.E., Varvarin, A.E., and Bochkarev, L.N., *Russ. J. Coord. Chem.*, 2017, vol. 43, no. 2, p. 106. doi 10.7868/S0132344X17020037
- Si, Z., Li, J., Li, B., Liu, S., and Li, W., *J. Lumin.*, 2008, vol. 128, p. 1303. doi 10.1016/j.jlumin.2007.12.035
- Xu, J., Yun, D., and Lin, B., *Synth. Met.*, 2011, vol. 161, p. 1276. doi 10.1016/j.synthmet.2011.04.023
- Xu, J., *Synth. Met.*, 2011, vol. 161, p. 919. doi 10.1016/j.synthmet.2011.02.025
- Xin, X.-L., Chen, M., Ai, Y.-b., Yang, F.-L., Li, X.-L., and Li, F., *Inorg. Chem.*, 2014, vol. 53, p. 2922. doi 10.1021/ic402685u
- Chen, T.-R., *Mater. Lett.*, 2005, vol. 59, p. 1050. doi 10.1016/j.matlet.2004.12.002
- Kubas, G.J., *Inorg. Synth.*, 1979, vol. 19, p. 90. doi 10.1002/9780470132500.ch18