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Synthesis, Structure, Optical, and Electrochemical Properties of Iridium(III) Complexes with 2-Arylphenantroimidazoles and Dibenzoylmethane

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Abstract—New cyclometalated neutral iridium(III) complexes $[Ir(L)_2(dbm)]$ have been synthesized, where L is 2-arylphenanthroimidazoles with various electron-donor or acceptor substituents, dbm is dibenzoylmethane. The compositions and structures of the ligands and complexes have been studied by X-ray diffraction and high-resolution mass spectrometry. In the absorption spectra of the complexes, a bathochromic shift of the absorption maxima is observed with an increase in the electron donor properties of the ligands. All the complexes show the reversible redox behavior; redox potentials fall in the range of 0.8-1.6 V. The combination of the obtained results allows us to consider the synthesized compounds as potential photosensitizers in solar cells.

Keywords: cyclometalated iridium complexes, absorption spectra

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In the past two decades, cyclometalated iridium(III) complexes are widely used first as stable and brightly luminescent components of organic lightemitting diodes [1-4]. The unique photophysical properties of these compounds attract an increased interest for their use as photocatalysts for the generation of hydrogen [5, 6] and photosensitizers in solar cells [7–11]. In the latter case, the dye complex should have a noticeable light absorption in the visible region of the spectrum and the reversible redox behavior [12]. The synthesis and comprehensive study of Ir(III) complexes with "antenna" 2-arylbenzimidazole ligands containing electron-donor or acceptor substituents together with the analysis of the literature data allowed us to determine general rules of the effect of the nature of "antenna" ligands on the electronic structure of iridium complexes and their optical and electrochemical properties [13-16]. It was shown that the properties of the complexes can be varied within wide limits; however, it seems that a pronounced effect can be achieved only by replacing the ordinary "anchor" ligand, namely 4,4'-dicarboxy-2,2'-bipyridine. In this connection, aromatic β -diketones [17] seem promising, since they act as negatively charged ligands, which can lead to a noticeable decrease in the redox potentials of the iridium complexes.

In the present work, 2-arylphenanthroimidazoles as "antenna" ligands and dibenzoylmethane as a model β -diketone were used for the synthesis of the target compounds. 2-Arylphenanthroimidazoles were used because their conjugated system is significantly expanded as compared to 2-arylbenzimidazoles; as a result, we can expect an increase in the extinction coefficients in absorption spectra [18, 19].

EXPERIMENTAL

We used commercially available reagents of pure for analysis grade (Russian State Standard) or higher, which is used without additional purification. Aniline was distilled before using in the ligand synthesis. Dibenzoylmethane (dbm) was recrystallized from benzene. The solvents were distilled and dried by routine procedures. Ligands 1,2-diphenylphenanthroimidazole (LH), 1-phenyl-2-(4-chlorophenyl)phenanthroimidazole (LCl), 1-phenyl-2-(4-methoxyphenyl)phenanthroimidazole (LOMe), and 1-phenyl-2-(3,4-dimethoxyphenyl)phenanthroimidazole (LOMe₂) were prepared according to Scheme 1 [19].



Scheme 1. Synthesis of 2-arylphenanthroimidazoles and interpretation of ligand abbreviations.

1,2-Diphenylphenanthroimidazole (LH). A mixture of phenanthrenquinone (0.515 g, 2.5 mmol), benzaldehyde (0.25 mL, 2.5 mmol), ammonium acetate (0.783 g, 10.2 mmol), and aniline (1 mL, 11.0 mmol) was boiled under argon atmosphere in glacial acetic acid (15 mL) for 3 h. After cooling, cold water was added to the solution. The dark green precipitate was filtered off and washed with water until neutral pH was obtained. The filter residue was dissolved in a minimum amount of acetone and heated. A small amount of water was added to the boiling solution, and the resulting white precipitate was filtered off and washed with a mixture of water and ethyl alcohol (1:1 v/v). The substance was purified using column chromatography $(SiO_2, CH_2Cl_2 : petroleum ether (1 : 1 v/v) \rightarrow CH_2Cl_2)$ to form a white powder. Yield, 64%. ¹H NMR spectrum, δ , ppm (CDCl₃): 7.19 (d, J = 7.8 Hz, 1H), 7.25– 7.35 (m, 4H), 7.49–7.55 (m, 3H), 7.57–7.69 (m, 6H), 7.75 (t, J = 8.1 Hz, 1H), 8.72 (d, J = 8.2 Hz, 1H), 8.78 (d, J = 8.2 Hz, 1H), 8.89 (d, J = 8.3 Hz, 1H).

1-Phenyl-2-(4-chlorophenyl)phenanthroimidazole (LCl). A mixture of phenanthrenequinone (0.517 g, 2.5 mmol), 4-chlorobenzaldehyde (0.337 g, 2.4 mmol), ammonium acetate (0.783 g, 10.2 mmol), and aniline (1 mL, 11.0 mmol) was boiled in glacial acetic acid (15 mL) in an argon atmosphere for 3 h. The resulting red solution was cooled and cold water was added. The dark green precipitate was filtered off, washed with water, and recrystallized several times from acetone: water (2 : 1 v/v) to form a white powder. Yield, 70%. ¹H NMR spectrum, δ , ppm (CDCl₃): 7.17 (d, *J* = 8.0 Hz, 1H), 7.24–7.31 (m, 3H), 7.48–7.55 (m, 5H), 7.59–7.68 (m, 4H), 7.75 (t, *J* = 8.2 Hz, 1H), 8.71 (d, *J* = 8.0 Hz, 1H), 8.77 (d, *J* = 8.2 Hz, 1H), 8.85 (d, *J* = 8.1 Hz, 1H).

1-Phenyl-2-(4-methoxyphenyl)phenanthroimidazole (LOMe). A mixture of phenanthrene quinone (0.513 g, 2.5 mmol), 3,4-dimethoxybenzaldehyde (0.395 g, 2.4 mmol), ammonium acetate (0.782 g, 10.1 mmol), and aniline (1 mL, 11.0 mmol) was boiled in glacial acetic acid (15 mL) in an argon atmosphere for 3 h. In the following, the synthesis was carried out similarly to LCl to prepare colorless crystals. Yield, 65%. ¹H NMR spectrum, δ , ppm (CDCl₃): 3.80 (s, 3H), 6.82 (d, J = 8.0 Hz, 1H), 7.17 (m, 1H), 7.25 (m, 1H), 7.48–7.67 (m, 9H), 7.74 (t, J = 8.0 Hz, 1H), 8.71 (d, J = 8.3 Hz, 1H), 8.77 (d, J = 8.2 Hz, 1H), 8.87 (d, J = 8.0 Hz, 1H).

1-Phenyl-2-(3,4-dimethoxyphenyl)phenanthroimidazole (LOMe₂). A mixture of phenanthrenequinone (0.513 g, 2.5 mmol), 3,4-dimethoxybenzaldehyde (0.395 g, 2.4 mmol), ammonium acetate (0.782 g, 10.1 mmol), and aniline (1 mL, 11.0 mmol) was boiled in glacial acetic acid (15 mL) in an argon atmosphere for 3 h. In the following, the synthesis was carried out similarly to LCl to prepare a white powder. Yield, 75%. ¹H NMR spectrum, δ , ppm (CDCl₃): 3.73 (s, 3H), 3.88 (s, 3H), 6.79 (d, J = 7.9 Hz, 1H), 7.14 (m, 1H), 7.16–7.21 (m, 2H), 7.27 (m, 1H), 7.48–7.57 (m, 3H), 7.60–7.69 (m, 4H), 7.75 (t, J = 7.8 Hz, 1H), 8.72 (d, J = 8.3 Hz, 1H), 8.78 (d, J = 8.4 Hz, 1H), 8.89 (d, J = 8.3 Hz, 1H).

Complexes [Ir(L)₂(dbm)] (1–4) were synthesized in two stages. In the first stage, $IrCl_3 \cdot 3H_2O(0.050 \text{ g}, 0.14 \text{ mmol})$ and an excess of 2-arylphenanthroimidazole L (0.50 mmol) were boiled in a mixture of 2ethoxyethanol : water (3 : 1 vol/vol) for 24 h under argon ($T = 135^{\circ}C$). Then distilled water was added to the hot solution; the precipitate was filtered off and washed with H₂O and ethanol. The product was extracted with dichloromethane, the solvent was evaporated, and the residue was dried in vacuum at 50°C for 12 h. The obtained dimeric complexes [Ir(L)₂Cl]₂ were not characterized and used without further purification.

In the second stage, the dimer (0.03 mmol), dibenzoylmethane (16.8 mg, 0.075 mmol), and K_2CO_3 (33.1 mg, 0.24 mmol) were mixed in acetonitrile (10 mL) and heated under reflux with stirring in dark under argon for 16 h. After cooling, a precipitate was formed, which contained the target product, a slight excess of diketone and potassium carbonate, and impurities from the starting dimer. The precipitate was filtered off, washed with water, dissolved in CH₂Cl₂,

	LOMe	3
Molecular formula	C ₂₈ H ₂₀ N ₂ O	$C_{71}H_{49}IrN_4O_4 \cdot CH_2Cl_2$
FW	400.46	1299.27
Crystal size, mm	$0.08 \times 0.15 \times 0.50$	$0.35 \times 0.35 \times 0.40$
Crystal system	Orthorhombic	Orthorhombic
Space group	Pbca	Pbca
a, Å	8.5356(6)	21.897(8)
b, Å	18.8806(13)	22.12(2)
<i>c</i> , Å	24.9462(16)	23.090(10)
<i>V</i> , Å ³	4020.3(5)	11184(12)
Ζ	8	8
$\rho_{calc}, g/cm^3$	1.323	1.543
μ , mm ⁻¹	0.081	2.541
<i>F</i> (000)	1680	5232
θ range, deg	2.16-27.00	2.04 - 25.00
Index intervals	$-10 \le h \le 10$	$-3 \le h \le 26$
	$-24 \le k \le 24$	$-3 \le k \le 26$
	$-31 \le l \le 31$	$-3 \le l \le 27$
Number of reflections:		
collected	27214	15449
unique	4390	9813
Completeness of data collection to θ , %	100	99.9
Number of parameters	281	748
GOOF to F^2	1.038	0.973
R_1 for $I > 2\sigma(I)$	0.0406	0.0351
wR_2 (all data)	0.0961	0.0744
$\Delta \rho_{max} / \Delta \rho_{min}, e / Å^3$	0.225/-0.204	0.797/-0.628

 Table 1. Crystallographic data, details of data collection, and characteristics of data refinement for the structures of LOMe and complex 3

and used for chromatography (SiO₂, eluent CH₂Cl₂ : petroleum ether (1 : 1 vol/vol) \rightarrow CH₂Cl₂). The first fraction was an excess of diketone; the second colored fraction is the product; the remaining impurities were retained on the sorbent. The product was dried in a vacuum for 10–12 h.

Complex [Ir(LCl)₂(dbm)] (1). Yield, 34%. ¹H NMR spectrum, δ , ppm (DMSO- d_6): 6.06 s (1H), 6.18 m (4H), 6.59 m (2H), 6.90 m (2H), 7.11 m (2H), 7.21–7.33 m (8H), 7.40 m (2H), 7.52 m (2H), 7.66 d (4H, J = 8.0 Hz), 7.73 d (2H, J = 7.9 Hz), 8.05 m (8H), 8.63 d (2H, J = 8.4 Hz), 8.78 d (2H, J = 8.3 Hz), 9.02 d (2H, J = 8.3 Hz). High resolution mass spectrum (ESI) m/z: [M]⁺ for C₆₉H₄₃IrN₄O₂Cl⁺₂ calcd. 1222.2393, found 1222.2397.

Complex [Ir(LH)₂(dbm)] (2). Yield, 54%. ¹H NMR spectrum, δ , ppm (DMSO- d_6): 5.98 s (1H), 6.34 d (2H, J = 7.7 Hz), 6.53 t (2H, J = 7.8 Hz), 6.58 t (2H, J = 7.6 Hz), 6.79 t (2H, J = 8.0 Hz), 7.06 m (4H), 7.24–7.31 m (8H), 7.38 m (2H), 7.52 d (2H, J = 8.0 Hz), 7.62 d (4H, J = 8.1 Hz), 7.69 d (2H, J = 7.9 Hz), 7.94– 8.05 m (6H), 8.10 m (2H), 8.65 d (2H, J = 8.2 Hz), 8.80 d (2H, J = 8.1 Hz), 9.01 d (2H, J = 8.3 Hz). High resolution mass spectrum (ESI) m/z: $[M]^+$ for $C_{69}H_{45}IrN_4O_2^+$ calcd. 1154.3194, found 1154.3201.

Complex [Ir(LOMe)₂(dbm)] (3). Yield, 47%. ¹H NMR spectrum, δ , ppm (DMSO- d_6): 3.31 s (6H), 6.01 s (1H), 6.26 m (4H), 6.49 m (2H), 6.82 t (2H, J =7.9 Hz), 7.06 t (2H, J = 7.9 Hz), 7.22–7.32 m (8H), 7.38 m (2H), 7.51 t (2H, J = 8.0 Hz), 7.63 d (4H, J =8.2 Hz), 7.69 d (2H, J = 7.9 Hz), 7.93–8.07 m (8H), 8.65 d (2H, J = 8.3 Hz), 8.80 d (2H, J = 8.4 Hz), 9.05 d (2H, J = 8.2 Hz). High resolution mass spectrum (ESI) m/z: [M]⁺ for C₇₁H₄₉IrN₄O⁺₄ calcd. 1214.3405, found 1214.3419.

Complex [Ir(LOMe₂)₂(dbm)] (4). Yield, 20%. ¹H NMR spectrum, δ , ppm (DMSO-*d*₆): 3.02 s (6H), 3.19 s (6H), 5.93 s (2H), 6.05 s (1H), 6.51 s (2H), 6.86 t (2H, *J* = 7.8 Hz), 7.15 d (2H, *J* = 7.7 Hz), 7.31 t (6H, *J* = 7.7 Hz), 7.38 m (2H), 7.43–7.53 m (4H), 7.66 d (4H, *J* = 7.9 Hz), 7.76 d (2H, *J* = 7.9 Hz), 7.95 –8.03 m (8H), 8.66 d (2H, *J* = 8.3 Hz), 8.81 d (2H, *J* = 7.9 Hz), 9.10 d (2H, *J* = 8.0 Hz). High resolution mass spectrum (ESI) *m/z*: [M]⁺ for C₇₃H₅₄IrN₄O⁺₆ calcd. 1275.3695, found 1275.3654.



Fig. 1. Molecular structure of 1-phenyl-2-(4-methoxyphenyl)phenanthroimidazole (LOMe). The ellipsoids of thermal vibrations of atoms are shown with a 50% probability.

¹H NMR spectra were recorded at 25°C on a Bruker Avance 400 spectrometer, chemical shifts are given in ppm relative to the signals of the solvent residues. High-resolution mass spectra were measured on a Brukermicro TOF-QTM ESI-TOF mass spectrometer (electrospray ionization) equipped with a timeof-flight detector. Electronic absorption spectra of solutions of complexes in dimethylformamide (DMF) were measured on an SF-2000 spectrophotometer in quartz cells (1 cm) at room temperature. Cyclic voltammograms were measured on an Ecotest-VA polarograph in a three-electrode cell with a carbon glass working electrode, a platinum auxiliary electrode, and a standard silver chloride reference electrode. The complexes were dissolved in a 0.01 M solution of $(n-Bu_4N)ClO_4$ in DMF saturated with argon. The measurements were carried out at a potential sweep of 25 mV/s in the alternating mode (modulation amplitude 30 mV, frequency 20 Hz); ferrocene was used as an external standard.

Single crystals of the LOMe ligand were obtained by its recrystallization from ethanol. The experimental data were collected on a Bruker SMART APEX II diffractom-

eter at a temperature of 100 K using Mo K_{α} radiation ($\lambda =$ 0.71073 Å, graphite monochromator) in the ω -scanning mode. The data were corrected for absorption by measuring the intensities of the equivalent reflections [20]. Single crystals of complex 3 were obtained by slow evaporation of a solution of the complex in methylene chloride. Single-crystal X-ray diffraction analysis of complex 3 was performed on an Enraf-Nonius CAD4 automatic diffractometer at 150 K using MoK_{α} radiation ($\lambda = 0.71073$ Å, graphite monochromator). The experimental data were corrected for the Lorentz factors and polarization. The data were corrected for absorption by measuring the intensities of equivalent reflections [20]. Both structures were determined by a direct method and refined by the full-matrix anisotropic least-squares method for F^2 for all non-hydrogen atoms [21]. Hydrogen atoms were located in calculated positions and refined using the "rider" model. Main crystal data, details of data collection, and characteristics of structure refinement are listed in Table 1. The crystallographic data have been deposited with the Cambridge Structural Database: CCDC nos. 1828295 (LOMe ligand) and 1828296 (complex 3) (http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The compositions and structures of the ligands and complexes 1-4 were determined according to the

¹H NMR and high resolution mass spectroscopy data. Structural formulas of the iridium(III) complexes obtained here are shown in Scheme 2.



Scheme 2. Structures of iridium(III) complexes 1–4 synthesized in this work.

In the ¹H NMR spectra, both the coordinated cyclometalated ligands are chemically identical and give the same set of signals with signals of deprotonated dibenzoylmethane superimposed. In the mass spectra, in addition to the signals of complexes 1-4, peaks corresponding to the $[Ir(L)_2]^+$ fragments are observed, i.e. those of cyclometalized residues of the complexes obtained probably when dibenzoylmethane is released in the course of ionization. This indicates a significantly higher bond strength between the Ir(III) cation and cyclometalated ligands as compared to additional O- or N-donor ligands.

The structures of ligand LOMe and complex **3** were studied by X-ray diffraction. In the ligand molecule (Fig. 1), the phenanthrene and imidazole fragments are in the same plane, while the 4-methoxyphenyl ring is inclined to this plane by an angle of $\sim 23^{\circ}$. In turn, the N-phenyl ring is located almost orthogonal (angle $\sim 88^{\circ}$) to the phenanthroimidazole moiety.

The coordination environment of the iridium atom in complex **3** is a strongly distorted octahedron (Fig. 2, Table 2) formed by the carbon and nitrogen atoms of two 2-arylphenanthroimidazoles and two oxygen atoms of deprotonated dibenzoylmethane. In this structure, the Ir–O bond lengths are significantly



Fig. 2. Molecular structure of complex 3. Hydrogen atoms are omitted for clarity. The ellipsoids of thermal vibrations of atoms are shown with a 50% probability.

shorter (by ~0.04 Å) as compared to those in the previously studied Ir(III) complex with 1,2-diphenylbenzimidazole and dbm [22], while the Ir–N bond lengths, on the contrary, are longer by ~0.03 Å. In addition, the cyclometalated ligands are not completely flat. In one of them the phenanthrene fragment is inclined relative to the imidazole by ~7°, while the latter is inclined by ~6° with respect to the 4-methoxyphenyl ring. In the second ligand coordinated to iridium, the deviations are even more pronounced: the phenanthrene fragment is not flat, and two benzene rings form an angle of ~24°. In turn, the plane most closely corresponding to the phenanthrene fragment (according to the least-squares method) forms an angle of ~12° with the plane of the imidazole ring, which is inclined by ~26° with respect to the 4methoxyphenyl ring. In both the coordinated ligands, the N-phenyl rings are practically orthogonal (the angle is ~85°) to the phenanthroimidazole moieties, as in the free ligands. Unlike the Ir(III) complex with 1,2-diphenylbenzimidazole, where the molecule has C_2 symmetry, complex **3** does not possess symmetry due to the extremely strong geometric differences between the chemically identical cyclometalated ligands. In general, X-ray diffraction studies show that the molecule of complex **3** exists in a tensed state and seems to be less stable than, for example, analogous complexes with 2-arylbenzimidazole derivatives. Since cyclometalated ligands of all synthesized complexes contain a phenanthrene fragment, it can be argued with high probability that the molecules of these compounds are tense and have relatively low stability, which is consistent with the mass spectrometry data obtained.

The crystal packing of complex **3** is formed due to numerous weak directed interactions of the type C– $H \cdots \pi$ and $\pi \cdots \pi$. The solvent molecule of dichloromethane is retained in the structure by weak C– $H \cdots \pi$ contacts with phenanthrene fragments of two neighboring molecules of the complexes.

The dried complexes showed marked solubility only in DMF or DMSO. Electronic absorption spectra of complexes 1–4 were measured in DMF at 25°C (Fig. 3) and interpreted according to the quantum chemical calculations of such complexes [13, 14]. The electronic transitions $\pi \rightarrow \pi^*$ localized on cyclometalated ligands, cause intense absorption of the complexes in the UV region (Table 3). The absorption bands in the range of 350-450 nm are caused by charge transfer from the metal to the ligands and between the phenanthroimidazole ligands and dibenzoylmethane ($\varepsilon \approx 10000-30000 \text{ L mol}^{-1} \text{ cm}^{-1}$). The extinction coefficients are higher as compared to those for the corresponding complexes with 2-arylbenzimidazoles. In this case, the bands undergo a significant bathochromic shift when chlorine is replaced by methoxy groups in the aryl fragment of the ligands. The long-wavelength absorption bands (>450 nm) of the complexes have molar absorption coefficients falling in the range $300-2000 \text{ L mol}^{-1} \text{ cm}^{-1}$, which may be due to the non-planar structure of the ligands and, as a result, the violation of the conjugation and a decrease in the probability of separate electronic transitions with charge transfer.

Table 2. Selected bond lengths and bond angles in the structure of 3

Bond	<i>d</i> , Å	Bond	$d, \mathrm{\AA}$
Ir(1)–C(1)	1.989(5)	Ir(1)–N(3)	2.091(5)
Ir(1)–C(29)	1.982(5)	Ir(1)–O(3)	2.138(4)
Ir(1)–N(1)	2.061(4)	Ir(1)–O(4)	2.129(4)
Angle	ω, deg	Angle	ω, deg
C(1)Ir(1)C(29)	92.7(2)	N(1)Ir(1)O(3)	99.99(17)
C(1)Ir(1)N(3)	96.8(2)	N(1)Ir(1)O(4)	78.05(15)
C(1)Ir(1)O(4)	88.19(18)	N(1)Ir(1)N(3)	176.02(16)
C(1)Ir(1)O(3)	174.20(18)	N(3)Ir(1)O(3)	83.49(16)
C(29)Ir(1)N(1)	97.80(19)	N(3)Ir(1)O(4)	104.24(16)
C(29)Ir(1)O(3)	93.00(18)	C(29)Ir(1)O(4)	175.52(17)

According to the data of alternating cyclic voltammetry (Fig. 4, Table 3), complexes 1–3 demonstrate the reversible redox behavior, and two oxidationreduction waves are observed for each of these compounds. Both waves undergo a noticeable effect from varying substituents in cyclometalated ligands. Thus, the introduction of a chloride atom into the aryl fragment of ligands leads to a significant increase in redox potentials. In turn, the methoxy group in the same position has only a minor effect on the potentials. It seems that the methoxy group is a mesomeric donor and, at the same time, an inductive acceptor. When the methoxy group is in the meta position to the metalized carbon atom, both its effects become less pronounced decreasing its influence on the molecular orbitals of the complex. On the contrary, the introduction of the second methoxy group into complex 4 (in the *para*-position to the metallic carbon) significantly



Fig. 3. Electronic absorption spectra of complexes 1–4 (DMF, 25°C).

Complex	λ_{abs} , nm ($\epsilon \times 10^{-3}$, mol ⁻¹ cm ⁻¹) ^a	$E_{ m ox}$, ${ m V}^b$
1	313 (64), 362 (31), 405 (12), 490 (0.6)	1.24, 1.60
2	310 (59), 367 (28), 415 (19), 516 (0.3)	1.05, 1.30
3	311 (54), 360 (30), 410 (23), 485 (1.0), 518 (0.5)	1.03, 1.26
4	322 (51), 368 (29), 436 (21), 515 (0.3)	$0.82, 1.05^c, 1.22, 1.34^c$

Table 3. Optical and redox characteristics of complexes 1-4

 \overline{a} Measured in DMF at 25°C.

^b Measured in DMF saturated with argon at 25°C. Electrolyte 0.01 M (n-Bu₄N)ClO₄, potential sweep 25 mV/s, frequency 10 Hz, amplitude 30 mV. Ferrocene was used as an external standard before measuring the complexes. The values of the potentials are given relative to the standard hydrogen electrode.

^c Irreversible oxidation.

Standard error $\pm 1 \text{ nm}$ for λ_{max} , $\pm 10 \text{ mV}$ for E_{ox} .

reduces the redox potential. At the same time, irreversible oxidation-reduction waves appear for complex 4. This is explained by the fact that an increase in the electron donor properties of the ligands leads to a decrease in the fraction of d orbitals of iridium in the occupied boundary molecular orbitals of the complex and the electrons are lost during oxidation by irreversibly oxidizing ligands. We have repeatedly observed this fact and interpreted it on the basis of the quantum chemical calculations [13–15]. Most importantly, the replacement of 4,4'-dicarboxy-2,2'-bipyridine in the iridium complexes with dibenzoylmethane has significantly reduced the redox potential of the complexes.

CONCLUSIONS

Four new cyclometalated Ir(III) complexes with 2-arylphenanthroimidazoles of different nature have been prepared. Due to the expansion of the conjugated ligand system, it has been possible to increase the extinction coefficients of the complexes in the range of 350-450 nm, and dibenzoylmethane used as an auxiliary ligand allowed us to decrease the redox potential of the complexes by ~0.5 V as compared to complexes with ligands based on 2,2'-bipyridine. The resulting complexes show optical and electrochemical charac-



Fig. 4. Alternating current voltammograms of complexes 1–4 (DMF, 25°C).

teristics comparable to those for effective photosensitizers.

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REFERENCES

- S. Lamansky, P. Djurovich, D. Murphy, et al., J. Am. Chem. Soc. 123, 4304 (2001). https://doi.org/10.1021/ja003693s.
- Iridium(III) in Optoelectronic and Photonics Applications, Ed. by E. Zysman-Colman (Wiley, 2017). https://doi.org/10.1002/9781119007166.
- M. N. Bochkarev, A. G. Vitukhnovskii, and M. A. Katkova, Organic Light-Emitting Diodes (OLEDs) (DEKOM, 2011).
- E. O. Platonova, A. P. Pushkarev, L. N. Bochkarev, et al., Russ. J. Coord. Chem. 43, 491 (2017). https://doi.org/10.1134/S107032841708005X.
- I. N. Mills, J. A. Porras, and S. Bernhard, Acc. Chem. Res. 51, 352 (2018). https://doi.org/ 10.1021/acs.accounts.7b00375.
- C. Lentz, O. Schott, B. Elias, et al., Inorg. Chem. 56, 10875 (2017). https://doi.org/10.1021/acs.inorgchem.7b00684.
- A. Sinopoli, C. J. Wood, E. A. Gibson, and P. I. P. Elliott, Eur. J. Inorg. Chem, No. 18, 2887 (2016). doi 10.1002/ejic.201600242
- J. A. Porras, I. N. Mills, W. J. Transue, and S. Bernhard, J. Am. Chem. Soc. **138** (30), 9460 (2016). https://doi.org/10.1021/jacs.6b03246.
- A. Sinopoli, C. J. Wood, E. A. Gibson, and P. I. P. Elliott, Inorg. Chim. Acta 457, 81 (2017). https://doi.org/10.1016/j.ica.2016.12.003.
- A. Sinopoli, C. J. Wood, E. A. Gibson, and P. I. P. Elliott, Dyes Pigm. **140**, 269 (2017). https://doi.org/10.1016/j.dyepig.2017.01.011.
- 11. I. A. Wright, Polyhedron **140**, 84 (2018). https://doi.org/10.1016/j.poly.2017.11.050.

- Sun et al. Chem Rev. 18 R. Eranc
- A. Hagfeldt, G. Boschloo, L. Sun, et al., Chem. Rev. 110, 6595 (2010). https://doi.org/10.1021/cr900356p.
- S. I. Bezzubov, V. D. Doljenko, S. I. Troyanov, and Yu. M. Kiselev, Inorg. Chim. Acta 415, 22 (2014). https://doi.org/10.1016/j.ica.2014.02.024.
- S. I. Bezzubov, V. D. Dolzhenko, and Yu. M. Kiselev, Russ. J. Inorg. Chem. 59, 571 (2014). https://doi.org/10.1134/S0036023614060047.
- S. I. Bezzubov, V. D. Doljenko, Yu. M. Kiselev, et al., Eur. J. Inorg. Chem. 3, 347 (2016). https://doi.org/10.1002/ejic.201501068.
- S. I. Bezzubov, A. A. Bilyalova, V. D. Dolzhenko, et al., Russ. J. Inorg. Chem. 62, 1085 (2017). https://doi.org/10.1134/S0036023617080046.
- E. Baranoff, M. Grätzel, M. K. Nazeeruddin, et al., Chem. Asian J. 5, 496 (2010). https://doi.org/10.1002/asia.200900429.

- R. Francke and R. D. Little, J. Am. Chem. Soc. 136, 427 (2014). https://doi.org/10.1021/ja410865z.
- Y. Yuan, D. Li, Y. Wang, et al., New J. Chem. 35, 1534 (2011). https://doi.org/10.1039/C1NJ20072K.
- 20. G. M. Sheldrick, SADABS: Program for Scaling and Correction of Area Detector Data (Univ. of Göttingen, Göttingen, 1997).
- 21. G. M. Sheldrick, Acta Crystallogr., Sect. A 64, 112 (2008). https://doi.org/10.1107/S0108767307043930.
- 22. S. I. Bezzubov, V. D. Doljenko, Yu. M. Kiselev, et al., IUCrDATA 1 (12), x161915 (2016). https://doi.org/10.1107/S2414314616019155.

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