Inorganica Chimica Acta 415 (2014) 22-30

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

# Tuning the photophysical and electrochemical properties of iridium(III) 2-aryl-1-phenylbenzimidazole complexes



Inorganica Chimica Acta

Stanislav I. Bezzubov\*, Vladimir D. Doljenko, Sergey I. Troyanov, Yuri M. Kiselev

Department of Chemistry, Lomonosov Moscow State University, Moscow 119991, Russian Federation

## ARTICLE INFO

Article history: Received 9 December 2013 Accepted 11 February 2014 Available online 27 February 2014

Keywords: Iridium(III) complexes Benzimidazole Cyclometalation Electrochemical studies DFT calculation Absorption spectra

# ABSTRACT

A series of heteroleptic bis-cyclometalated iridium(III) complexes,  $[Ir(cpbi)_2(H_2dcbpy)][PF_6]$  (1),  $[Ir(pbi)_2(H_2dcbpy)][PF_6]$  (2), and  $[Ir(mpbi)_2(H_2dcbpy)][PF_6]$  (3), where pbi = 1,2-diphenylbenzimidazole, cpbi = 2-(4-chlorophenyl)-1-phenylbenzimidazole, mpbi = 2-(3,4-dimethoxyphenyl)-1-phenylbenzimidazole, and H<sub>2</sub>dcbpy = 2,2'-bipyridine-4,4'-dicarboxylic acid has been synthesized and characterized by elemental analysis, <sup>1</sup>H, <sup>31</sup>P NMR, and high resolution mass-spectra. Molecular structure of complex **3** has been determined from single-crystal X-ray analysis. The complexes exhibit absorption up to 550 nm with molar absorptivities of  $2500 \text{ M}^{-1} \text{ cm}^{-1}$ . They have strong luminescence in broad yellow-to-red region in solutions at room temperature. While chloro-substituent (complex **1**) causes a little hypsochromic shift of the absorption maxima compared to unsubstituted **2**, introduction of two methoxy-groups (complex **3**) gives rise to a bathochromic shift of about 100 nm. Alternating current voltammetry studies of the complexes indicates reversible oxidation and reduction potentials. Calculated excited state oxidation potentials for **1–3** are negative enough to efficiently inject electrons into the conduction band of TiO<sub>2</sub> ( $E_F \approx -0.5 \text{ V}$ ). Thus, from the electrochemical point of view, all the complexes, especially **3**, are good candidates for operation in DSSC as dyes.

© 2014 Elsevier B.V. All rights reserved.

# 1. Introduction

Cyclometalated iridium(III) complexes are of great interest for application in OLEDs [1–6], chemosensors [7–9], photocatalytic hydrogen systems [10,11], and biomarkers [12,13] because of their high thermal and chemical stability, long excited-state lifetimes, and emission colour tunability by cyclometalated ligands variations. Recently, some of these complexes have been demonstrated to be suitable for solar energy harvesting [14–16].

In dye-sensitized solar cells (DSSCs) [17] a photosensitizer (dye) acts as light absorber and charge separator, along with a semiconductor. The photosensitizer choice is strictly controlled by several requirements [17c]: the absorption spectrum of the sensitizer should cover visible light region as much as possible with high extinction coefficients. The LUMO level of the dye should be higher in energy than Fermi level of the semiconductor used (-0.5 V for TiO<sub>2</sub>); for efficient dye regeneration, the HOMO level must be at more positive potential than that of the redox pair (for  $I_3^-/I^- \approx 0.4$  V versus NHE). Anchoring groups (-COOH,  $-H_2PO_3$ ,  $-SO_3H$ , etc.) in the sensitizer structure are essential for strong binding the dye

onto the semiconductor surface. Photochemical and thermal stability of the dye as well as its ability to sustain repeated oxidation/reduction cycles are also required. The most widely used sensitizers are ruthenium(II) polypyridine complexes. For example, N3 ( $[Ru(H_2dcbpy)_2(NCS)_2]$ , where  $H_2dcbpy = 2,2'$ -bipyridine-4,4'dicarboxylic acid; Fig. 1) absorbs a great part of solar spectrum due to intense red-shifted metal-to-ligand charge transfer band (MLCT) centered at ca. 530 nm with molar absorptivity of ca. 15000 M<sup>-1</sup> cm<sup>-1</sup> [15] and gives rise to 10% efficiency ( $\eta$ ) at air mass (AM) 1.5 irradiance [18]. Still, the main drawback of sensitizers like **N3** is the presence of two labile isothiocyanate-groups, which possess poor long-term stability [19]. Cyclometalated ruthenium(II) complexes are considered to be more stable, and they are intensively studied in recent years [17b], but the efficiencies of the devices based on these dyes are less than 10%. In contrast, iridium(III) complexes usually contain two or three cyclometalated ligands and possess high thermal stability and light-harvesting properties [16]. Surprisingly, there are just several reports on application of iridium dyes in DSSC. 1-Phenylpyrazole [20], 2-phenylpyridine (ppy), 2-phenylquinoline (pq) (Fig. 1). benzo[h]quinoline [21,22] as cyclometalated ligands and H<sub>2</sub>dcbpy,  $H_2$ dcbg (dcbg = 2,2'-biguinoline-4,4'-dicarboxylic acid), and pyridine-2,5-dicarboxylic acid as auxiliary ligand have been used to produce simple sensitizers with efficiencies less than 1%.



<sup>\*</sup> Corresponding author. Tel.: +7 (495) 9394549. *E-mail address:* Stas.Bezzubov@gmail.com (S.I. Bezzubov).



Fig. 1. Ruthenium(II) and iridium(III) dyes.

Sophisticated derivatives of ppy and H<sub>2</sub>dcbpy have been applied but efficiencies of the dyes of about 1% have been achieved [23]. The same authors have developed neutral sensitizers bearing acetylacetone (acac) and carboxylate-functionalized ppy and pq ligands, that has increased the efficiency to 2.2% [24]. Tridentate iridium(III) complexes with 2,6-diphenylpyridine derivatives have been reported to have high molar absorptivities ( $\varepsilon \approx 9000 \, \text{M}^{-1}$  $cm^{-1}$  at 515 nm) but low DSSC efficiencies (2.2%) which have been explained by poor cell construction ( $\eta$  = 3.3% for N3) [25]. A series of CF<sub>3</sub>-substituted benzothiazoles have been also used but again the maximal  $\eta$  of 1.4% have been achieved [14]. The main disadvantages of the above iridium sensitizers are narrow absorption spectra and low molar absorptivities in visible light range [23]. Recently, two panchromic iridium(III) complexes bearing bis(arylimino)acenaphtene ligands and absorbing light up to 800 nm with  $\varepsilon$  = 2500 at 630 nm have been reported [15]. Unfortunately, these dyes have no anchoring groups and are not suitable for DSSC operation from the energetic point of view.

In contrast to other N^C aromatic donors used in iridium(III) chemistry, 2-aryl-1-phenylbenzimidazole ligands can be easily modified by conventional chemical reactions, that affects immediately the electronic environment of iridium through highly conjugated heteroaromatic system [26,27]. Thus, we present the synthesis, photophysical, and electrochemical studies of a series of iridium(III) complexes with 2-aryl-1-phenylbenzimidazoles, where the aryl units are phenyl ring substituted with electron-withdrawing (Cl) or electron-donating (OMe) groups at their *para*- (and *meta*-) positions.

# 2. Experimental

# 2.1. Materials and methods

All commercially available reagents were at least reagent grade and used without further purification. Solvents were purified and dried according to standard procedures. 2,2'-Bipyridine-4,4'-dicarboxylic acid (H<sub>2</sub>dcbpy) [28], sodium bisulfite adducts of aldehydes [29] were prepared according to published procedures. Preparation of all iridium complexes was carried out under dry argon. Purification and other manipulations with complexes were performed in air.

<sup>1</sup>H. <sup>13</sup>C. and <sup>31</sup>P NMR spectra were acquired at 25 °C on a Bruker Avance 400 instrument and chemical shifts are reported in ppm referenced to residual solvent signals. High resolution mass spectra (HRMS) were measured using electrospray ionization (ESI) and time-of-flight (TOF) mass analyzer. The measurements were done in a positive ion mode (interface capillary voltage -4500 V); mass range from m/z 50 to m/z 3000 Da. Matrix-assisted laser desorption ionization (MALDI) mass spectra were run on a Bruker AutoFlex II apparatus. Electronic absorption spectra were measured on a OKB Spectr SF-2000 spectrophotometer. Luminescence spectra were recorded using a Perkin Elmer LS-55 spectrometer. An Econix-Expert Ltd Ecotest-VA polarograph was used for electrochemical measurements with glassy carbon working electrode, platinum counter electrode, and saturated Ag/AgCl reference electrode. Elemental analyses were performed using an Elementar VarioMicroCube CHN analyzer.

# 2.2. Synthesis of ligands

Benzimidazole derivatives (abbreviated as **bi**) 1,2-diphenylbenzimidazole (**pbi**), 2-(3,4-dimethoxyphenyl)-1-phenylbenzimidazole (**mpbi**), 2-(4-chlorophenyl)-1-phenylbenzimidazole (**cpbi**) were synthesized by reaction of *N*-phenyl-*o*-phenylenediamine with sodium bisulfite adducts of corresponding benzaldehydes following similar procedures [30].

# 2.2.1. Synthesis of **pbi**

*N*-Phenyl-*o*-phenylenediamine (1.56 g, 8.5 mmol) was dissolved in ethanol (25 ml). To this solution benzaldehyde sodium bisulfite adduct (2.23 g, 13.9 mmol) and ethanol (5 ml) were added. The mixture was refluxed for 3 h and cooled. Distilled water (20 ml) was added and the resulting precipitate was filtered and washed sufficiently with water. After two recrystallizations from aqueous ethanol the solid was dried in vacuo at 50 °C during 10 h. Yield: 1.62 g, 70%, colorless needles. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm):  $\delta$  7.79 (d, 1H, *J* = 7.4 Hz), 7.49–7.58 (m, 5H), 7.23–7.42 (m, 7H), 7.17 (d, 1H, *J* = 7.5 Hz). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, ppm): 152.3, 143.0, 137.5, 136.9, 130.5, 130.3, 130.0, 129.6, 129.3, 128.8, 128.0, 123.8, 123.2, 119.9, 110.9. MS (MALDI-TOF): *m/z* = 271.2 (Calc. 271.3 for [M+H]<sup>+</sup>).

## 2.2.2. mpbi

Yield: 66%, colorless plates. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$  7.86 (d, 1H, *J* = 8.0 Hz), 7.42–7.51 (m, 3H), 7.27–7.32 (m, 3H), 7.13–7.23 (m, 3H), 7.09 (dd, 1H, *J*<sub>1</sub> = 8.3 Hz, *J*<sub>2</sub> = 2.0 Hz), 6.73 (d, 1H, *J* = 8.3 Hz), 3.82 (s, 3H), 3.68 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 151.7, 149.7, 148.1, 142.3, 136.9, 136.8, 129.5, 128.2, 127.1, 122.7, 122.6, 122.1, 121.8, 119.0, 111.9, 110.3, 109.9, 55.4, 55.3. MS (MALDI-TOF): *m/z* = 331.2 (Calc. 331.4 for [M+H]<sup>+</sup>).

# 2.2.3. cpbi

Yield: 43%, light brown powder. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): *δ* 8.00 (d, 1H, *J* = 8.0 Hz), 7.54–7.61 (m, 5H), 7.43 (t, 1H, *J* = 7.3 Hz), 7.31–7.37 (m, 5H), 7.27 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 150.7, 142.1, 136.7, 136.2, 135.4, 130.3, 129.6, 128.5, 128.3, 127.8, 127.0, 123.3, 122.9, 119.4, 110.1. MS (MALDI-TOF): *m*/*z* = 305.6 (Calc. 305.8 for [M+H]<sup>+</sup>).

# 2.3. Synthesis of iridium complexes

Cyclometalated  $\mu$ -chloro-bridge iridium dimers  $[(bi)_2Ir(\mu-Cl)_2-Ir(bi)_2]$  were synthesized by Nonoyama's method [31] and used in the next step without purification because of their poor

solubility in most common organic solvents. Cationic complexes [Ir(bi)<sub>2</sub>(H<sub>2</sub>dcbpy)][PF<sub>6</sub>] were prepared by similar procedures.

## 2.3.1. Preparation of $\mu$ -chloro-bridge iridium dimer

To a 25 ml round-bottomed flask containing  $IrCl_3 \cdot 3H_2O$  (80 mg, 0.25 mmol) and mpbi (316 mg, 0.96 mmol) a mixture of 2-ethoxyethanol and water (3:1 v/v, 10 ml) was added. The mixture was refluxed for 20 h under argon atmosphere and cooled to room temperature. Distilled water (3 ml) was added and the precipitate formed was collected by filtration, washed several times with water, ethanol, acetone, and dried in vacuo at 60 °C during 12 h.

# 2.3.2. Synthesis of complex [Ir(mpbi)<sub>2</sub>(H<sub>2</sub>dcbpy)][PF<sub>6</sub>] (**3**)

The crude µ-chloro-bridge iridium dimer (70 mg. 0.0395 mmol),  $H_2$ dcbpy (19.3 mg, 0.079 mmol) in a mixture of  $CH_2Cl_2$  and methanol (2:1 v/v, 15 ml) were refluxed under Ar atmosphere in dark for 7 h and cooled to room temperature. A solution of NH<sub>4</sub>PF<sub>6</sub> (124 mg, 0.76 mmol) in methanol (3 ml) was added and the mixture was stirred for 30 min. The solid formed was filtered off, and the solution was concentrated to dryness. The dark red solid was extracted with CH<sub>2</sub>Cl<sub>2</sub>, the extract was filtered, and evaporated to dryness. After flash chromatography (SiO<sub>2</sub>, eluent CH<sub>2</sub>Cl<sub>2</sub>/MeOH 3/1), the product was recrystallized from a mixture of chloroform/hexane (3/1) to give dark red powder. Yield: 41.4 mg, 42%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 9.00 (s, 2H), 8.35 (d, 2H, J = 5.4 Hz), 8.06 (d, 2H, J = 5.2 Hz), 7.58-7.72 (m, 6H), 7.53 (d, 2H, J = 7.1 Hz), 7.29 (m, 2H), 7.10 (t, 2H, J = 7.6 Hz), 7.00 (d, 2H, J = 8.0 Hz), 6.89 (t, 2H, J = 7.7 Hz), 6.12 (s, 2H), 5.70 (s, 2H), 5.66 (d, 2H, J = 8.1 Hz), 3.85 (s, 6H), 3.92 (s, 6H). <sup>31</sup>P NMR (CDCl<sub>3</sub>, ppm)  $\delta$  –144.51 (septet, *J* = 712 Hz). HRMS (ESI): Calc. for C<sub>54</sub>H<sub>42</sub>N<sub>6</sub>O<sub>8</sub>Ir (M<sup>+</sup>): 1095.2692. Found: 1095.2701 (M<sup>+</sup>). Anal. Calc. for C<sub>54</sub>H<sub>42</sub>N<sub>6</sub>O<sub>8</sub>F<sub>6</sub>PIr (MW 1240.13): C, 52.30; H, 3.41; N, 6.78. Found: C, 52.47; H, 3.34; N, 6.79%.

## 2.3.3. [Ir(pbi)<sub>2</sub>(H<sub>2</sub>dcbpy)][PF<sub>6</sub>] (**2**)

Yield: 53%, orange red powder. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): δ 9.31 (s, 2H), 8.37 (d, 2H, *J* = 5.6 Hz), 8.21 (d, 2H, *J* = 5.4 Hz), 7.79 (m, 8H), 7.68 (m, 2H), 7.25 (t, 2H, *J* = 7.8 Hz), 7.02–7.12 (m, 4H), 6.85 (t, 2H, *J* = 7.4 Hz), 6.75 (t, 2H, *J* = 7.5 Hz), 6.57 (d, 2H, *J* = 7.8 Hz), 6.39 (d, 2H, *J* = 6.3), 5.75 (d, 2H, *J* = 8.2 Hz). <sup>31</sup>P NMR (DMSO-*d*<sub>6</sub>, ppm) δ –144.24 (septet, *J* = 709 Hz). MS (MALDI-TOF): *m/z* = 975.1 (Calc. 975.1 for [Ir(pbi)<sub>2</sub>(H<sub>2</sub>dcbpy)]<sup>+</sup>), *m/z* = 731.2 (Calc. 730.9 for [Ir(pbi)<sub>2</sub>]<sup>+</sup>). Anal. Calc. for C<sub>50</sub>H<sub>34</sub>N<sub>6</sub>O<sub>4</sub>F<sub>6</sub>PIr (MW 1120.02): C, 53.62; H, 3.06; N, 7.50. Found: C, 53.55; H, 3.09; N, 7.62%.

# 2.3.4. [Ir(cpbi)<sub>2</sub>(H<sub>2</sub>dcbpy)][PF<sub>6</sub>] (**1**)

Yield: 39%, yellow orange powder. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): δ 8.96 (s, 2H), 8.19 (d, 2H, *J* = 5.1 Hz), 8.03 (d, 2H, *J* = 5.4 Hz), 7.79 (br s, 8H), 7.59 (br s, 2H), 7.24 (t, 2H, *J* = 7.0 Hz), 7.10 (d, 2H, *J* = 8.2 Hz), 7.02 (br s, 2H), 6.90 (d, 2H, *J* = 8.4 Hz), 6.56 (d, 2H, *J* = 8.6 Hz), 6.25 (s, 2H), 5.72 (m, 2H). <sup>31</sup>P NMR (DMSO-*d*<sub>6</sub>, ppm)  $\delta$  –144.21 (septet, *J* = 711 Hz). MS (MALDI-TOF): *m/z* = 1043.7 (Calc. 1043.9 for [Ir(cpbi)<sub>2</sub>(H<sub>2</sub>dcbpy)]<sup>+</sup>), *m/z* = 799.2 (Calc. 799.7 for [Ir(cpbi)<sub>2</sub>]<sup>+</sup>). Anal. Calc. for C<sub>50</sub>H<sub>32</sub>N<sub>6</sub>O<sub>4</sub>Cl<sub>2</sub>F<sub>6</sub>PIr (MW 1188.91): C, 50.51; H, 2.71; N, 7.07. Found: C, 50.39; H, 2.54; N, 6.94%.

## 2.4. X-ray crystallography

Data collection for [Ir(mpbi)<sub>2</sub>(Hdcbpy)]-3DMSO-H<sub>2</sub>O (**3** solvate) was performed at 100 K on an IPDS diffractometer (Stoe) using monochromatized Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Numerical absorption correction was applied with  $T_{max}/T_{min}$  = 0.8223/0.7147. The structure was solved and anisotropically refined with SHELX package [32]. All the hydrogen atoms were included into refinement in geometrically calculated positions. In the structure,

one of the methoxy groups is orientationaly disordered. Solvent molecules are also disordered.

## 2.5. Computational details

Density functional theory (**DFT**) calculations were performed with Firefly QC package [33], which is partially based on the GAMESS (US) [34] source code, using the B3LYP functional [35], Stuttgart-Dresden ECP for iridium and 6-31G\* basis sets for all other atoms [36,37]. On the basis of the optimized geometries, the natural bond orbital (NBO) was employed to analyze the molecular orbital compositions (%). Time-dependent DFT (TDDFT) calculations were carried out at the ground state geometries to obtain vertical excitation energies and theoretical absorption spectra. The lowest 30 singlet-singlet excitations were computed.

# 3. Results and discussion

1-Phenylbenzimidazole derivatives were prepared by reaction of *N*-phenyl-o-phenylenediamine with appropriate benzaldehyde sodium bisulfite adducts [30] (Fig. 2a). N-Phenyl substituted ligands have been chosen because of their better solubility in most organic solvents than that of 1-H-benzimidazoles [26]. Cationic bis-cyclometalated iridium(III) complexes were synthesized in two steps: treatment of IrCl<sub>3</sub>·3H<sub>2</sub>O with 3.8-4.0 eq. of benzimidazole ligands gave  $\mu$ -chloro-bridge dimers  $[(bi)_2 Ir(\mu-Cl)_2 Ir(bi)_2]$ (bi - cyclometalated ligand); further reaction of the dimers with bidentate 2,2'-bipyridine-4,4'-dicarboxylic acid (H<sub>2</sub>dcbpy) followed by replacement of Cl<sup>-</sup> with PF<sub>6</sub><sup>-</sup> produced the desired complexes  $[Ir(bi)_2(H_2dcbpy)][PF_6]$  (Fig. 2b). The complexes possessed limited solubility in CHCl<sub>3</sub> and MeOH, and an extended solubility in DMSO. Low yield (40-55%) of the complexes might be due to poor solubility of H<sub>2</sub>dcbpy in CH<sub>2</sub>Cl<sub>2</sub> and MeOH. The use of more soluble diester of H<sub>2</sub>dcbpy [38] would scarecely provide better total yield as additional hydrolysis and protonated complexes purification steps would be required.

The dimethoxy complex appeared as pure **3** isomer rather than **3**'. In the aromatic region of <sup>1</sup>H NMR spectrum of the sample two singlets at 5.70 and 6.12 ppm (see Fig. 3) were assigned to protons H<sup>1</sup> and H<sup>2</sup>, while in the case of **3**' two aromatic protons of dimethoxy benzene ring must produce a more complicated AB spectral pattern. Three characteristic low-field signals (singlet and two dublets with small spin–spin coupling constants) that remained nearly unaffected by benzimidazole ligand change were assigned to three protons of 2,2'-bipyridine-4,4'-dicarboxylic acid coordinated to Ir<sup>3+</sup> [39]. All spectral data were consistent with the structures of complexes **1–3** presented in Fig. 2b.

Upon recrystallization of **3** from DMSO/H<sub>2</sub>O by slow cooling the solution from 100 °C to room temperature, X-ray suitable crystals of  $[Ir(mpbi)_2(Hdcbpy)]$ -3DMSO-H<sub>2</sub>O (**3**-solvate) were collected. The molecular structure of the complex is shown in Fig. 4, selected crystallographic data are presented in Tables 1 and 2.



**Fig. 2a.** Preparation of ligands: benzimidazoles (bi) and 2,2'-bipyridine-4,4'-dicarboxylic acid (H<sub>2</sub>dcbpy): (i) ethanol, reflux, 3-5 h; (ii) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, conc. H<sub>2</sub>SO<sub>4</sub>, 75 °C, 1 h; (iii) 50% HNO<sub>3</sub>, reflux, 2 h.



**Fig. 2b.** Two-step synthesis of iridium cationic complexes: (i) 2-ethoxyethanol/H<sub>2</sub>O (3/1, v/v), argon, reflux, 24 h; (ii) H<sub>2</sub>dcbpy, CH<sub>2</sub>Cl<sub>2</sub>/MeOH (2/1, v/v), argon, darkness, reflux, 5–24 h; (iii) NH<sub>4</sub>PF<sub>6</sub>, 30 min.

In complex 3-solvate, iridium ion resides in a distorted octahedral environment of two C and two N atoms from mpbi, and two N atoms from Hdcbpy. N atoms from C^N ligands adopt trans-configuration, which is common for many bis-cyclometalated iridium complexes [38,40]. The average Ir-C and Ir-N (Hdcbpy) distances (2.025 and 2.126 Å, respectively) are in good agreement with those of [Ir(ppy)<sub>2</sub>(Hdcbpy)] (2.019 and 2.125 Å, respectively, ppy = 2-phenylpyridine) [39]. The distances between Ir and N of Hdcbpy (2.118 and 2.134 Å) are larger than those between Ir and N in benzimidazole ligands (2.043 and 2.047 Å) because of trans-effect of the C donor in mpbi [39]. Benzimidazolyl and dimethoxyphenyl rings in cyclometalated ligands are more coplanar than two pyridyl rings of Hdcbpy (average dihedral angles are 3.6 and 0.8° in two mpbi and 8.6° in dcbpy). These values are in good agreement with those of  $[Ir(tpy)_2(Hdcbpy)]$  (tpy = 2-(p-tolyl)pyridine): 3.8 and 0.5° in two tpy and 11.5° in Hdcbpy [38]. The plane of N-phenyl ring of benzimidazole ligand is inclined to the plane of benzimidazolyl at the angle of 80.1°.

Deprotonation of  $H_2$  dcbpy in related iridium(III) compounds leading to neutral complexes has been reported [39]. As no



Fig. 4. Molecular structure of  $[Ir(mpbi)_2(Hdcbpy)]$  (hydrogen atoms and solvate molecules are omitted for clarity).

counterion was found in the structure of **3**-solvate, one of the carboxylic groups of **3** appeared to be deprotonated during crystallization to produce neutral molecule. Indeed, the distances between C and two O in deprotonated carboxylic group of **3**-solvate are very close to each other (1.245 and 1.246 Å), while in protonated –COOH group, C–O (OH) distance (1.311 Å) is notably larger than C=O distance (1.213 Å).

Absorption spectra of ligands and complexes **1–3** are presented in Figs. 5 and 6. All benzimidazoles possess strong absorption band in UV region due to  $\pi$ – $\pi$ \* transition centered at ca. 300 nm with molar absorptivities of 20000 M<sup>-1</sup> cm<sup>-1</sup>. Complexes have greater extinction coefficients ( $\varepsilon$  = 45000–60000 M<sup>-1</sup> cm<sup>-1</sup>) in range 250–300 nm due to  $\pi$ – $\pi$ \* transitions located on benzimidazoles



Fig. 3. Aromatic region of <sup>1</sup>H NMR spectrum of 3 (CDCl<sub>3</sub>).

Table 1 Selected [Ir(mpbi) <sub>2</sub> (Hdcbp	crystallographic y)]*3DMSO*H <sub>2</sub> O.	data	for
Formula		C <sub>60</sub> H <sub>61</sub> IrN <sub>6</sub>	0 <sub>12</sub> S <sub>3</sub>
$M_{ m r}~({ m g~mol^{-1}})$		1346.57	
T (K)		100	
Space group		$P\bar{1}$	
a (Å)		12.4800(3)	1
b (Å)		13.7434(4)	)
c (Å)		18.5908(5)	)
α (°)		99.292(2)	
β(°)		97.331(2)	
γ (°)		111.455(2)	)
V (Å)		2867.63	
D <sub>c</sub> (g cm <sup>-3</sup> )		1.560	
Ζ		2	
$\mu_{ m Mo}~( m mm^{-1})$		2.507	

Table 2	2
---------	---

 $T_{\min, \max}$ 

 $2\theta_{max}$ 

Nref

 $R_1$  $wR_2$ 

S

Selected bond lengths (Å) and angles (°) in the coordination environment of Ir atom in [Ir(mpbi)<sub>2</sub>(Hdcbpy)].

0.715, 0.822

58.36

14188 0.0410

0.0922

1.037

Ir1-C9	2.024(4)	C9-Ir-C30	89.17(16)
Ir1-C30	2.025(4)	N5-Ir1-N6	76.29(13)
Ir1-N2	2.043(3)	C30-Ir1-N2	79.40(15)
Ir1-N4	2.047(3)	C9-Ir1-N4	79.40(16)
Ir1-N5	2.134(4)	N2-Ir1-N4	169.56(13)
Ir1-N6	2.118(3)		

and H<sub>2</sub>dcbpy. The broad bands at 350-425 nm ( $\varepsilon = 15000 27000 \text{ M}^{-1} \text{ cm}^{-1}$ ) in spectra of **1-3** could be assigned to spinallowed metal-to-ligand charge transfer (<sup>1</sup>**MLCT**)  $[d\pi (Ir) - \pi^*$ (H<sub>2</sub>dcbpy)] and, to a greater extent, to ligand-to-ligand charge transfer (<sup>1</sup>**LLCT**) [ $\pi$  (bi) –  $\pi^*$  (H<sub>2</sub>dcbpy)], which are common for iridium(III) compounds [26,27,38–40]. Low energy bands of complexes are likely to have mixed spin-allowed and spin-forbidden <sup>1</sup>MLCT–<sup>3</sup>MLCT and <sup>1</sup>LLCT–<sup>3</sup>LLCT nature due to strong spin-orbital coupling of iridium(III) [26,27] and are very sensitive to electrondonor (withdrawing) properties of substituents in 2-phenyl ring of benzimidazoles: changing chlorine to two methoxy-groups gives rise to nearly 100 nm bathochromic shift of the bands (Fig. 6). Additionally, low energy absorption bands of **1–3** are significantly red shifted compared to related iridium(III) complexes Irppy, Irpq [21], and Irppz [20] (see Table 3). This can be explained by stronger  $\pi$ -donor properties of benzimidazolyl than those of pyridyl, quinolynyl, and pyrazolyl [41].



Fig. 5. UV-Vis absorption (left) and emission (right) spectra of ligands in  $CH_2Cl_2$  solution at room temperature.

In DSSC, the absorption spectrum of the dye should cover visible light region as much as possible with high extinction coefficients. While absorption maxima of **1–3** in visible light region can be easily tuned by 2-aryl substituents change, the molar absorptivity is just slightly varied in range 3100–2600 M<sup>-1</sup> cm<sup>-1</sup>. These values are high among other iridium(III) complexes in this spectral range, but are smaller than those of simple ruthenium(II) dyes (for N3,  $\varepsilon = 15000 \text{ M}^{-1} \text{ cm}^{-1}$  at 530 nm [14]). Thus, further modification of the cyclometalated ligands is needed to expand their conjugative system.

Luminescent spectra were measured in  $CH_2Cl_2$  solutions at room temperature. Emission maxima of the ligands are centered at ~365 nm and are slightly influenced by substituents (Fig. 5),

 Table 3

 Photophysical properties of ligands, 1–3, and reference complexes in solutions.

Substance	$\lambda^{\rm abs}$ , nm ( $\epsilon \cdot 10^{-3}$ , M <sup><math>-1</math></sup> cm <sup><math>-1</math></sup> ) <sup>a</sup>	$\lambda^{ex} (nm)^{a}$	$\lambda^{em} (nm)^{a}$
cpbi	297(20)	250	368
pbi	293(18)	296	363
mpbi	304(22)	313	367
1	307(47), 365(15), 462(3.1)	421	556
2	306(44), 369(18), 465(3.5), 490(3.1)	582	680
3	306(58), 373(27), 530(2.6)	506	648
		627	760
Irppy	291(24), 379(6.3) <sup>b</sup>		580 <sup>b</sup>
Irpq	321(14), 346(11), 436(1.9) <sup>b</sup>		553 <sup>b</sup>
Irppz	455(0.7) <sup>c</sup>		604 <sup>c</sup>

<sup>a</sup> Recorded in air-equilibrated CH<sub>2</sub>Cl<sub>2</sub> at room temperature.
 <sup>b</sup> EtOH [21].

<sup>c</sup> [20].



Fig. 6. UV-Vis absorption spectra of 1-3 in CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature.



Fig. 7. Normalized emission spectra of complexes 1-3 in  $CH_2Cl_2$  solutions at room temperature.

while complexes **1–3** exhibit luminescence in broad yellow-to-red region (Fig. 7). Changing the aryl substituents in the complexes causes blue- and red-shifts of emission in the same way as in absorption spectra of **1–3**. Still, the emission maximum for **3** depends on the excitation wavelength (Fig. 1\*). The ratio of the intensities for resulting two emission bands at 648 and 760 nm is as 2:1.

Benzimidazole-based iridium(III) complexes are known to possess intensive phosphorescence [26,27]. The relative contribution of <sup>3</sup>MLCT versus ligand-based <sup>3</sup> $\pi$ - $\pi$ \* transitions to the phosphorescent emission of 1-3 may affect the Stokes shifts between <sup>3</sup>MLCT and emission bands of complexes: ligand-based  ${}^{3}\pi$ - $\pi^{*}$  transitions gives rise to a larger Stokes shift [42]. Since Stokes shifts for 1 (94 nm) and 3 (118 nm, first emission band) are significantly smaller than those for 2 (190 nm) and 3 (230 nm, second emission band), phosphorescence of **1** appears to have predominantly  $^{3}$ MLCT character, while phosphorescence of **2** is likely to result from  ${}^{3}LC$  transitions. Emission of **3** seems to have contribution from both <sup>3</sup>MLCT and <sup>3</sup>LC transitions, with emission maxima being controlled by the excitation wavelength. The values of  $E_{0-0}$  (energy difference between ground and excited states, both taken at their zero vibrational levels [43]) were estimated from the onset of emission spectra at ca. 10% intensity (Table 4). They are decreased by increasing donor properties of the cyclometalated ligands.

Electrochemical behavior of **1–3** was studied by alternating current voltammetry (ACV) in acetonitrile using ferrocene as an external standard at the beginning of the experiment (Fig. 8). The ACV

Table 4	
Electrochemical properties of 1-3 an	d reference complexes in solutions

$E_{1/2}$ , $V^{\rm a}$ vs. NH	IE ( $\Delta E_{\rm p}$ , mV)	$\Delta E, V$	$E_{0-0}$ , eV	$E(S^+/S^*), V^b$
$E_{\rm red}, V$	E <sub>ox</sub> , V			
-0.86(46)	1.68(58)	2.54	2.47	-0.79
-0.88(61)	1.55(50)	2.43	2.09	-0.54
-0.94(44)	1.19(55)	2.13	1.77 <sup>d</sup>	-0.58
	1.59 <sup>°</sup>		2.46 <sup>e</sup>	-0.87
$-0.89^{f}$	1.13 <sup>f</sup>	2.02		
	$\frac{E_{1/2}, V^{a} \text{ vs. NH}}{E_{red}, V}$ $-0.86(46)$ $-0.88(61)$ $-0.94(44)$ $-0.89^{f}$	$\begin{tabular}{ c c c c c c c } \hline $E_{1/2}$, $V^a$ vs. NHE ($\Delta E_p$, $mV$) \\ \hline $E_{red}$, $V$ & $E_{ox}$, $V$ \\ \hline $-0.86(46)$ & $1.68(58)$ \\ $-0.88(61)$ & $1.55(50)$ \\ $-0.89(61)$ & $1.19(55)$ \\ $1.59^c$ \\ $-0.89^f$ & $1.13^f$ \\ \hline \end{tabular}$	$ \begin{array}{c c} \hline E_{1/2}, V^{\rm a}  {\rm vs.}  {\rm NHE}  (\Delta E_{\rm p},  {\rm mV}) \\ \hline \hline E_{\rm red}, V & E_{\rm ox}, V \\ \hline \hline -0.86(46) & 1.68(58) & 2.54 \\ -0.88(61) & 1.55(50) & 2.43 \\ -0.94(44) & 1.19(55) & 2.13 \\ & 1.59^{\rm c} \\ -0.89^{\rm f} & 1.13^{\rm f} & 2.02 \\ \end{array} $	$ \begin{array}{c c} \hline E_{1/2}, V^{\rm s} \mbox{ vs. NHE } (\Delta E_{\rm p}, \mbox{ mV}) \\ \hline E_{\rm red}, V & E_{\rm ox}, V \\ \hline \hline \hline \\ \hline -0.86(46) & 1.68(58) & 2.54 & 2.47 \\ \hline -0.88(61) & 1.55(50) & 2.43 & 2.09 \\ \hline -0.94(44) & 1.19(55) & 2.13 & 1.77^{\rm d} \\ \hline 1.59^{\rm c} & 2.46^{\rm e} \\ \hline \\ -0.89^{\rm f} & 1.13^{\rm f} & 2.02 \end{array} $

<sup>a</sup> Recorded in Ar-saturated acetonitrile with 0.1 M (<sup>*n*</sup>Bu<sub>4</sub>N)ClO<sub>4</sub> at scan rate of 50 mV/s, frequency 25 Hz, and amplitude 30 mV. Ferrocene was used as an external standard prior to measurements. The values are measured against NHE.  $\Delta E = E_{\text{ox}} - E_{\text{red}}$ . Estimated error: ±20 mV for  $E_{\text{ox}}$  and  $E_{\text{red}}$ .

<sup>b</sup> Calculated from  $E(S^*/S^*) = E_{0x} - E_{0-0}$ , where  $E_{0-0}$  is estimated from the onset of the emission spectrum at ca. 10% intensity.

<sup>c</sup> Determined from CV measurements in acetonitrile with 0.1 M (<sup>n</sup>Bu<sub>4</sub>N)PF<sub>6</sub>.

<sup>d</sup> Second emission band for **3** (maximum at 760 nm) was used.

<sup>e</sup> Estimated from the intersection of absorption and emission spectra [20].
 <sup>f</sup> MeOH [40].



**Fig. 8.** AC voltammogramms of **1–3** (V vs. NHE) recorded at room temperature at scan rate of 50 mV/s, frequency 25 Hz, and amplitude 30 mV in Ar-saturated acetonitrile with 0.1 M ( $^{n}$ Bu<sub>4</sub>N)ClO<sub>4</sub> as supporting electrolyte.

method was applied to achieve higher sensitivity and to measure more accurate values of redox potentials. All the complexes have reversible ground state oxidation ( $E_{ox}$ ) and reduction ( $E_{red}$ ) potentials (Table 4). Complexes **1–3** are strong oxidants with  $E_{ox} > 1.1$  V versus NHE, but they are sufficiently stable (due to iridium(III) inertness and high Ir–C bonds strength) to sustain repeated oxidation/reduction cycles, that has been shown by their reversible electrochemical behavior. In addition,  $E_{ox}$  values of **1–3** are positive enough for the oxidized complexes to be spontaneously reduced not only by an I<sub>3</sub>/I<sup>–</sup> but also by a Br<sub>3</sub>/Br<sup>–</sup> redox system ( $E \approx$ 1.1 V versus NHE). The latter redox pair yields a significant increase of open-circuit voltage ( $V_{oc}$ ), that has enhanced DSSC efficiency [44]. So, complexes **1–3** combined with Br<sub>3</sub>/Br<sup>–</sup> pair may produce very stable DSSC with high  $V_{oc}$ .

 $E_{\rm ox}$  values of **1–3** are strongly dependent on the cyclometalated ligand used. Introduction of methoxy-substituents (complex **3**) destabilizes the HOMO level and reduces  $E_{\rm ox}$  compared to the complex of unsubstituted 1,2-diphenylbenzimidazole (**2**), while chloro-substituent (complex **1**) stabilizes HOMO level and increases oxidation potential. Changing the substituents causes a little variation of  $E_{\rm red}$  values. It is more negative for **3** than for **1** and **2** because of strong  $\pi$ -donor properties of **mpbi**. The great  $E_{\rm ox}$  ( $\approx$ 500 mV) and little  $E_{\rm red}$  ( $\approx$ 80 mV) variation is likely to indicate that HOMOs of the complexes are largely localized on the cyclometalated ligands, while LUMOs are mainly localized on the strongly electron-withdrawing auxiliary ligand (H<sub>2</sub>dcbpy).

The  $E_{\text{ox}}$  and  $E_{\text{red}}$  values of **3** are very close to that of **N3** [45] with the electrochemical gap (2.13 V) being slightly larger than  $\Delta E$  for **N3** (2.02 V). Additionally, calculated excited state oxidation potentials for **1–3**,  $E(S^+/S^*)$  are sufficiently negative to efficiently inject



Fig. 9. Energy diagram and plot of the frontier orbitals for 1-3 (hydrogen atoms are omited for clarity).

electrons into the conduction band of TiO<sub>2</sub> ( $E_{\rm F} \approx -0.5$  V). Thus, from the electrochemical point of view, all the complexes, especially **3**, are good candidates for operation in DSSC as dyes.

To further understand electronic and photophysical properties of 1-3 DFT studies were performed. Ground state geometries of 1-3 were optimized in the gas phase at B3LYP level with the Stuttgart-Dresden effective-core potential (ECP) for iridium and 6-31G\* basis sets for all other atoms. For each complex, geometries and

SCF-energies of three possible isomers were computed, and the
isomers with N atoms of C^N ligands adopting trans-configuration
were found to be more stable by approximately 45 kJ/mol (Fig. 2*).
This fact correlates well with results of X-ray crystal structure
analysis of 3. For time-dependent DFT (TDDFT) calculations ground
state geometries of these isomers were used. Plot of the frontier
molecular orbitals is shown in Fig. 9. Molecular orbitals composi-
tions for 1-3 are presented in Table 5. HOMOs of complexes are

Table 5				
Frontier molecular orbitals	com	positions (	(%)	) for <b>1–3</b> .

Complex	Location	HOMO – 2	HOMO – 1	НОМО	LUMO	LUMO+1	LUMO+2
1	Ir	51.0	22.2	49.2	10.0	4.1	3.6
	H <sub>2</sub> dcbpy	4.6	5.0	3.0	83.9	95.0	93.4
	cpbi	44.4	72.8	47.8	6.1	0.9	3.0
2	Ir	50.0	13.0	42.9	9.0	3.7	3.7
	H <sub>2</sub> dcbpy	3.9	2.6	2.4	84.2	95.2	92.5
	pbi	46.1	84.4	54.7	6.8	1.1	3.8
3	Ir	47.2	5.9	20.8	10.2	4.2	3.5
	H <sub>2</sub> dcbpy	3.6	1.9	1.4	83.4	94.8	93.6
	mpbi	49.2	92.2	77.8	6.4	1.0	2.9

mainly localized on Ir atom and benzimidazole ligands. Contribution of iridium orbitals to HOMOs is significantly decreased from **1** to **3**, that seems to increase immediately HOMOs energy levels. Iridium orbitals contribution to HOMOs – 1 is decreased from **1** to **3** producing similar HOMOs – 1 energies change. From HOMOs - 2 to HOMOs – 4, electron density is nearly equally localized both on Ir center and C^N ligands with very small decreasing iridium orbitals contribution from **1** to **3**, that results in close orbital energies for all complexes (purple frames on Fig. 9). Additionally, *N*-phenyl rings of benzimidazoles have very small contribution to occupied orbitals, that reflects their negligible participation in the cojugated system of ligands.

LUMOs of 1-3 are largely localized on H<sub>2</sub>dcbpy with small contributions from iridium and C^N ligands orbitals, that well correlates with our conclusions from electrochemical data. LUMOs + 1 and LUMO + 2 are nearly entirely located on H<sub>2</sub>dcbpy, and orbital energies have little variations from **1** to **3**. Our results are in good agreement with the ability of independent tuning HOMO and LUMO energy levels known for many iridium(III) complexes [4-6]. In addition, electron density of lower unoccupied orbitals is significantly resides on carboxy-groups, that is extremely needed for efficient electron injection in DSSC [17c]. HOMO-LUMO gaps correlate well with  $E_{0-0}$  values obtained from spectral data and also reproduce experimental absorption maxima change: bathochromic shift of low-energy bands from 1 to 3. Still, HOMO-LUMO gaps give overestimated, especially for 3, values of transition energies; these transitions were not observed in experimental spectra. To gain insight into the optical properties of the complexes, TDDFT approach was applied.

The most intensive transitions and TDDFT electronic spectra (overlaid with experimental spectra) for 1-3 are summarized in Table 6 and Fig. 10. Calculated absorption spectra are in good agreement with experimental data. Two transitions (at 496 nm for 1 and at 511 nm for 2) are slightly red-shifted compared to experimental bands that may be due to neglecting the solvatation effect. In UV range intensive electronic transitions originate mainly in Ir-bi  $\rightarrow$  bi and bi  $\rightarrow$  bi excitations (MLCT/ILCT), that correlates well with our assignment based on the literature data. Surprisingly, in low-energy region ( $\lambda > 420$  nm) transitions to S<sub>1</sub> state (HOMO  $\rightarrow$  LUMO excitations) have very small oscillator strengths (f < 0.001) for all the complexes. Still, there are two similar intensive transitions, which imply charge transfers from Ir-bi moiety to H<sub>2</sub>dcbpy unit (MLCT/LLCT). Differences between complexes 1, **2**, and **3** appear when the origin of these transitions is analyzed. For **1** and **2**, they result mainly from HOMO  $-1 \rightarrow$  LUMO (496)

Table 6					
TDDFT	singlet	excited	states	for	1–3. <sup>a</sup>



**Fig. 10.** Experimental (red) and calculated TDDFT (blue) electronic spectra of **1–3**. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and 511 nm) and HOMO – 3  $\rightarrow$  LUMO (432 and 456 nm) excitations, while for **3** – from HOMO – 3  $\rightarrow$  LUMO (528 nm) and HOMO – 3  $\rightarrow$  LUMO + 1 (431 nm) excitations. That is, absorption of all the complexes in visible range is mainly described by electronic transitions from occupied orbitals with close energies to the lowest unoccupied orbitals. So, bathochromic shift of the lowest-energy band due to strong electron-donor properties of

Compound	State	$\lambda$ (nm)	f <sup>b</sup>	Dominant monoexcitation	Nature
1					
	S <sub>1</sub>	634	0.001	$H \rightarrow L (0.96)$	Ir-cpbi $\rightarrow$ H <sub>2</sub> dcbpy
	S <sub>2</sub>	496	0.03	$H-1 \rightarrow L (0.98)$	Ir-cpbi $\rightarrow$ H <sub>2</sub> dcbpy
	S <sub>6</sub>	432	0.03	$H-3 \rightarrow L (0.54)$	Ir-cpbi $\rightarrow$ H <sub>2</sub> dcbpy
	S <sub>7</sub>	414	0.02	$H-1 \rightarrow L+1 (0.94)$	Ir-cpbi $\rightarrow$ H <sub>2</sub> dcbpy
2					
	<b>S</b> <sub>1</sub>	681	0.001	$H \rightarrow L(0.98)$	Ir-pbi $\rightarrow$ H <sub>2</sub> dcbpy
	S <sub>3</sub>	511	0.04	$H-1 \rightarrow L (0.98)$	Ir-pbi $\rightarrow$ H <sub>2</sub> dcbpy
	S <sub>5</sub>	456	0.03	$H-3 \rightarrow L(0.88)$	Ir-pbi $\rightarrow$ H <sub>2</sub> dcbpy
	S <sub>8</sub>	420	0.03	$H-1 \rightarrow L+1 (0.60)$	Ir-pbi $\rightarrow$ H <sub>2</sub> dcbpy
3					
	S <sub>1</sub>	930	0.0003	$H \rightarrow L(0.98)$	Ir-mpbi $\rightarrow$ H <sub>2</sub> dcbpy
	S <sub>8</sub>	528	0.05	$H-3 \rightarrow L(0.94)$	Ir-mpbi $\rightarrow$ H <sub>2</sub> dcbpy
	S <sub>15</sub>	431	0.03	$H-3 \rightarrow L+1 \ (0.74)$	Ir-mpbi $\rightarrow$ H <sub>2</sub> dcbpy

<sup>a</sup> Vertical excitation wavelengths ( $\lambda$ ), oscillator strengths (f), dominant monoexcitations (with their contributions within parentheses), and nature of the electronic transitions are presented. H = HOMO, L = LUMO, H-1 = HOMO - 1, L+1 = LUMO + 1, etc.

<sup>b</sup> Only the singlet states with f > 0.02 and  $H \rightarrow L$  excitations have been included.

dimethoxy-groups is significantly smaller than it might be expected from simple analysis of HOMO-LUMO gaps. This conclusion is confirmed by the experimental spectra change from 1 to 3. Hence, the effect of donor substituents in benzimidazole ligands on expanding absorption spectra of the complexes into red region seems to be too small to provide panchromatic properties required for DSSC sensitizer. Extending conjugated system of the ligands is likely to result in enhancing light-harvesting properties of iridium(III) complexes.

## 4. Conclusions

In summary, we have presented the synthesis, crystal structure, spectroscopic and electrochemical properties of three new iridium(III) complexes with 2-arylbenzimidazole-based cyclometalated ligands in which electron-donor/withdrawing properties of the substituents have been varied, and 2,2'-bipyridine-4,4'-dicarboxylic acid as ancillary ligand. The complexes absorb visible light significantly ( $\varepsilon$  = 1000–3000 M<sup>-1</sup> cm<sup>-1</sup>) up to 600 nm. The nature of electronic transitions has been studied by TDDFT approach. Reversible oxidation potentials of 1-3 are high enough ( $E_{ox} > 1.2$  V versus NHE) for the oxidized complexes to be spontaneously reduced not only by a common  $I_3^-/I^-$  redox mediator but also by a  $Br_3^-/Br^-$  redox couple. Thus, all the complexes, especially **3**, are good candidates for operation in DSSC as dyes.

# Acknowledgements

The authors thank the Russian Foundation for Basic Research (project 13-03-00972) for financial support. Dr. Ivan Vatsouro and Dr. Kirill Puchnin are acknowledged for assistance concerning NMR measurements.

#### Appendix A. Supplementary material

CCDC 974801 contains the supplementary crystallographic data for the structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.ica.2014.02.024.

# References

- [1] V. Bulovic, G. Gu, P.E. Burrows, S.R. Forrest, M.E. Thompson, Nature 380 (1996) 29.
- [2] S. Kappaun, C. Slugovc, E.J.W. List, Int. J. Mol. Sci. 9 (2008) 1527.
  [3] E. Holder, B.M.W. Langeveld, U.S. Schubert, Adv. Mater. 17 (2005) 1109.
- [4] K. Műllen, U. Scherf (Eds.), Organic light emitting devices. Synthesis, properties and applications, WILEY-VCH, Weinheim, 2006, p. 410.
- W.-Y. Wong, C.-L. Ho, Coord. Chem. Rev. 253 (2009) 1709.
   R.C. Evans, P. Douglas, C.J. Winscom, Coord. Chem. Rev. 250 (2006) 2093.
- [7] G. Di Marco, M. Lanza, A. Mamo, I. Stefio, C. Di Pietro, G. Romeo, S. Campagna, Anal Chem 70 (1998) 5019
- [8] M.E. Kőse, R.J. Crutchley, M.C. DeRosa, J.R. Reynolds, K.S. Schanze, Langmuir 21 (2005) 8255.

- [9] M.M.-S. Toro, J.F. Fernandez-Sanchez, E. Baranoff, M. Grätzel, M.K. Nazeeruddin, A. Fernandez-Gutierrez, Talanta 82 (2010) 620.
- [10] J.I. Goldsmith, W.R. Hudson, M.S. Lowry, T.H. Anderson, S. Bernhard, J. Am. Chem. Soc. 127 (2005) 7502.
- [11] E.D. Cline, S.E. Adamson, S. Bernhard, Inorg. Chem. 47 (2008) 10378.
- [12] K.K.-W. Lo, W.-K. Hui, C.-K. Chung, K.H.-K. Tsang, T.K.-M. Lee, Coord. Chem. Rev. 250 (2006) 1724.
- [13] K.K.-W. Lo, K.H.-K. Tsang, K.-S. Sze, C.-K. Chung, T.K.-M. Lee, K.Y. Zhang, W.-K. Hui, C.-K. Li, J.S.-Y. Lau, D.C.-M. Ng, N. Zhu, Coord. Chem. Rev. 251 (2007) 2292.
- [14] Y.-J. Yuan, J.-Y. Zhang, Z.-T. Yu, J.-Y. Feng, W.-J. Luo, J.-H. Ye, Z.-G. Zou, Inorg. Chem. 51 (2012) 4123.
- [15] K. Hasan, E. Zysman-Colman, Inorg. Chem. 51 (2012) 12560.
- [16] Y.-J. Yuan, Z.-T. Yu, H.-L. Gao, Z.-G. Zou, C. Zheng, W. Huang, Chem. Eur. J. 19 (2013) 6340.
- [17] For recent reviews on DSSCs, see: (a) C.A. Bignozzi, R. Argazzi, R. Boaretto, E. Busatto, S. Carli, F. Ronconi, S. Caramori, Coord. Chem. Rev. 257 (2013) 1472; (b) P.G. Bomben, K.C.D. Robson, B.D. Koivisto, C.P. Berlinguette, Coord. Chem. Rev. 256 (2012) 1438;
  - (c) A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, Chem. Rev. 110 (2010) 6595;
- (d) P.D. Frischmann, K. Mahata, F. Wurthner, Chem. Soc. Rev. 42 (2013) 1847. [18] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, J. Am. Chem. Soc. 115 (1993) 6382.
- [19] M. Grätzel, Acc. Chem. Res. 42 (2009) 1788.
- [20] E.I. Mayo, K. Kilsa, T. Tirrell, P.J. Djurovich, H.B. Gray, Photochem. Photobiol. Sci. 5 (2006) 871.
- [21] C. Dragonetti, A. Valore, A. Colombo, S. Righetto, V. Trifiletti, Inorg. Chim. Acta 388 (2012) 163.
- [22] Z. Ning, Q. Zhang, W. Wu, H. Tian, J. Organomet. Chem. 694 (2009) 2705.
- [23] E. Baranoff, J.-H. Yum, M. Grätzel, M.K. Nazeeruddin, J. Organomet. Chem. 694 (2009) 2661.
- [24] E. Baranoff, J.-H. Yum, I. Jung, R. Vulcano, M. Grätzel, M.K. Nazeeruddin, Chem. Asian J. 5 (2010) 496.
- [25] Y. Shinpuku, F. Inui, M. Nakai, Y. Nakabayashi, J. Photochem. Photobiol. A: Chem. 222 (2011) 203.
- [26] W.-S. Huang, J.T. Lin, C.-H. Chien, Y.-T. Tao, Sh.-S.h. Sun, Y.-S.h. Wen, Chem. Mater. 16 (2004) 2480.
- [27] G.-G. Shan, H.-B. Li, H.-Z. Sun, H.-T. Cao, D.-X. Zhu, Z.-M. Su, Dalton Trans. 42 (2013) 11056.
- [28] A.M. Oki, R.J. Morgan, Synth. Commun. 25 (1995) 4093.
- [29] A.R. Ronzio, T.D. Waugh, Org. Synth. 3 (1955) 438.
- [30] H.F. Ridley, R.G.W. Spickett, G.M. Timmis, J. Heterocycl. Chem. 2 (1965) 453.
- [31] M. Nonoyama, Bull. Chem. Soc. Jpn. 47 (1974) 767.
- [32] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.
  [33] A.A. Granovsky, Firefly version 7.1.G, http://www.classic.chem.msu.su/gran/ firefly/index.html.
- [34] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, J. Comput. Chem. 14 (1993) 1347.
- [35] P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, J. Phys. Chem. 98 (1994) 11623.
- [36] D. Andrae, U. Haussermann, M. Dolg, H. Stoll, H. Preuss, Theor. Chim. Acta 77 (1990) 123.
- [37] R. Krishnan, J.S. Binkley, R. Seeger, J.A. Pople, J. Chem. Phys. 72 (1980) 650.
- [38] D. Hanss, J.C. Freys, G. Bernardinelli, O.S. Wenger, Eur. J. Inorg. Chem. (2009) 4850.
- [39] W. Jiang, Y. Gao, Y. Sun, F. Ding, Y. Xu, Z. Bian, F. Li, J. Bian, C. Huang, Inorg. Chem. 49 (2010) 3252.
- [40] Q. Zhao, S.J. Liu, M. Shi, C.M. Wang, M.X. Yu, L. Li, F.J. Li, T. Yi, C.H. Huang, Inorg. Chem. 45 (2006) 6152.
- [41] A.R. Katritzky, A.F. Pozharskii (Eds.), Handbook of heterocyclic chemistry, 2nd ed., Pergamon, 2000, p. 748. [42] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H.-E. Lee, C. Adachi, P.E.
- Burrows, S.R. Forrest, M.E. Thompson, J. Am. Chem. Soc. 123 (2001) 4304.
- [43] P. Ceroni (Ed.), The exploration of supramolecular systems and nanostructures by photochemical techniques, Springer, 2012, p. 232.
- [44] C. Teng, X. Yang, S. Li, M. Cheng, A. Hagfeldt, L.-Z. Wu, L. Sun, Chem. Eur. J. 16 (2010) 13127.
- [45] H.C. Zhao, J.P. Harney, Y.-T. Huang, J.-H. Yum, M.K. Nazeeruddin, M. Grätzel, M.-K. Tsai, J. Rochford, Inorg. Chem. 51 (2012) 1.