Polyhedron 95 (2015) 14–23

Contents lists available at ScienceDirect

Polyhedron

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

Cyclometalated mono and dinuclear rhodium(III) and iridium(III) complexes with imidazolyl phenanthrolines: Synthesis and, photophysical and electrochemical characterization

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ARTICLE INFO

Article history:
Received 5 February 2015
Accepted 9 April 2015
Available online 18 April 2015

Keywords:
Cyclometalation
Iridium
Rhodium
Fluorescence
Electrochemistry

ABSTRACT

Cyclometalated rhodium(III) and iridium(III) complexes were synthesized with imidazolyl modified phenanthroline ligands (**1**–**2**) of general formula [M(ppy)$_2$(**1**)]Cl [M = Rh/Ir] and [{M(ppy)$_2$}$_2$(**2**)]Cl$_2$ [M = Rh/Ir] (**3**–**9**). All the compounds **1**–**9**, have been characterized spectroscopically to reveal their dependence on the solvent polarity and proticity of the environment. The photophysical details show that the ligands as well as the cyclometalated complexes have spectrum of variations depending on the immediate solvent environment and pH of the medium. Electrochemical studies show variation in the electrochemical behaviour due to the change of the metal centres.

1. Introduction

Cyclometalated iridium(III) complexes with polypyridyl based ancillary ligands exhibit rich photophysical properties. They are well addressed for their application as sensors [1–5], in biological imaging [6], light-emitting electrochemical cells [7–11], organic light-emitting diodes [12–20], catalysts for water splitting [21–23], dye-sensitized solar cells (DSSCs) [24–28] and organic transformations [29–35]. In contrast, reports on photophysical properties of the cyclometalated rhodium(III) analogues are limited in literature [4,29,30,36–47]. Spectroscopic transitions in these systems are usually metal centered (MC) and ligand centered (LC), or through charge transfer (either metal-to-ligand, MLCT, or ligand-to-metal, LMCT) and corresponding oxidation and reduction processes are either metal or ligand centered. Ligand-field stabilization in these complexes depends on the oxidation state, nature of the cyclometalating ligand and d-orbitals. However, dissimilarity in photophysical behaviour between the cyclometalated iridium(III) and rhodium(III) complexes originates from the large difference in spin–orbit coupling (ξIr = 3909 cm^{-1} and ξRh = 1259 cm^{-1}) between these two metals. As a result, intersystem crossing from first excited singlet state to triplet state occurs efficiently in the iridium complexes. Hence, cyclometalated iridium(III) complexes are generally characterized by their long-lived triplet excited states. Iridium(III) complexes with strong-field cyclometalating ligands, such as phenylpyridine, usually emit from the admixture of spin-allowed metal-to-ligand charge-transfer, (^{1}MLCT) and π(ppy)–π^*(phen) ligand-to-ligand (^{1}LLCT) processes, whereas, the emission of rhodium(III) complexes are mainly ligand-based [8,29,30,36–51]. Cyclometalated rhodium complexes of phenylpyridines were recently explored for their catalytic properties [52–55]. Polynuclear transition metal complexes bridged through polypyridyl ligands are always interesting for their through-bridge electronic communication. Choice of the bridging ligand is crucial to design such systems. This is important from the structural viewpoint as well as for electronic coupling between the separated subunits [56–75]. Transition metal complexes containing polypyridyls are largely employed as energy donor or acceptor for fast and efficient energy transfer due to their rich photophysics and long-lived triplet excited states. Bis(imidazo[4,5-f][1,10]phenanthroline)s are well suited bridging ligands for this purpose [76–82]. They are fully conjugated, have two N∩N-bidentate coordination sites, and possess protic sites (N–H) that induce pH-dependence. In addition, the photophysical properties can be modulated by incorporating two different cyclometalated subunits into the structure of this tetradentate system. The photoactive characteristic of one subunit can be coupled with the redox active centre in the other. Combined use of cyclometalated iridium(III) complexes and rhodium polypyridyl systems in homogeneous and heterogeneous photocatalytic processes have already been

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http://dx.doi.org/10.1016/j.poly.2015.04.011
0277-5387/

reported [83–85]. The former acts as photosensitizer, and the latter serves as catalyst for proton induced reduction. The photophysical properties of a wide range of cyclometalated heteroleptic iridium(III) complexes with imidazolyl based phenanthroline as ancillary ligand have already been explored [86–95].

In the present work, we have synthesized mononuclear, homo and hetero-dinuclear coordination complexes comprising of cyclometalated iridium and rhodium cores with polypyridyl ligands. In all the complexes the imidazolyl and bis-imidazolyl phenanthrolines bind to cyclometalated iridium and rhodium units as ancillary bidentate ligands. Photophysical characterization of the complexes was done to understand the electronic communication between the metal centres in homodinuclear and heterodinuclear complexes. Cyclic voltammetric measurements for the complexes were done to understand the electrochemical behaviour of the complexes and to understand the potential of heterodinuclear system in the catalytic processes.

2. Experimental

2.1. Chemicals and materials

The starting materials, $RhCl_3{\cdot}3H_2O$, $IrCl_3{\cdot}3H_2O$, 2-phenylpyridine, 8-aminoquinoline, 1-naphthylamine and 1-methyl-2-imidazole carboxaldehyde were purchased from Sigma–Aldrich and used without further purification. All the solvents were dried by usual methods prior to use. The cyclometalated iridium(III) and rhodium(III) chloro bridged dimer $[Ir(ppy)_2Cl]_2$ [96] and $[Rh(ppy)_2Cl]_2$ [97], 1,10-phenanthroline-5,6-dione [39], 2-(4-formylphenyl)imidazo[4,5-f][1,10] phenanthroline (**1**) [78], and 2,2-p-Phenylene(imidazo[4,5-f][1,10] phenanthroline (**2**) [78] were synthesized according to the literature methods.

2.2. Synthesis of complexes

2.2.1. Synthesis of [Rh(ppy)$_2$(**1**)]Cl (**3**)

A mixture of $[Rh(ppy)_2Cl]_2$ (0.1 mmol), **1** (0.235 mmol), methanol (15 mL), dichloromethane (15 mL) and acetonitrile (15 mL) was refluxed for 5 h at 90 °C that yielded a reddish orange solution. The product was purified by column chromatography with 5–10% (v/v) methanol in dichloromethane as eluent. A reddish orange compound was obtained after the eluent was dried. Yield: 72%. ESI-MS (*m*/*z*): $[M-Cl]^+$: 735.137 (Calc. 735.13). Elemental Analysis: Calc. C, 65.42; H, 3.66; N, 10.90; Expt. C, 65.79; H, 3.87; N, 11.02; ^{1}H NMR [$CDCl_3$]: δ 10.03 (s, 1H), 9.50 (d, 2H), 8.77 (d, 2H), 8.07 (d, 2H), 7.98 (d, 2H), 7.92 (d, 2H), 7.75 (m, 4H), 7.66 (q, 2H), 7.37 (d, 2H), 7.13 (t, 2H), 7.02 (t, 2H), 6.85 (t, 2H), 6.42 (d, 2H) (for more details see Fig. S8). $\bar{\nu}_{max}$/cm^{-1}: 3423s (br), 2924m, 2360w, 1697s, 1605s, 1580s, 1480s, 1210m, 1118m, 758m, 732m.

2.2.2. Synthesis of [Ir(ppy)$_2$(**1**)]Cl (**4**)

The synthetic procedure is similar to that of **3**. A reddish orange compound was obtained on drying the eluent. Yield: 69%. ESI-MS (*m*/*z*): $[M-Cl]^+$: 825.173 (Calc. 825.19). Elemental Analysis: Calc. C, 58.63; H, 3.28; N, 9.77; Expt. C, 59.10; H, 3.45; N, 9.23; ^{1}H NMR [$CDCl_3$]: δ 10.06 (s, 1H), 9.59 (br, 2H), 8.79 (d, 2H), 8.13 (d, 2H), 8.02 (d, 2H), 7.94 (d, 2H), 7.73 (m, 6H), 7.38 (d, 2H), 7.10 (t, 2H), 6.99 (t, 2H), 6.85 (t, 2H), 6.42 (d, 2H) (for more details see Fig. S9). $\bar{\nu}_{max}$/cm^{-1}: 3430m, 3043m, 2920m, 2850m, 1698s, 1607vs, 1582s, 1478s, 1383m, 757m, 730m.

2.2.3. Synthesis of [Rh(ppy)$_2$(**2**)]Cl (**5**)

A mixture of [Rh(ppy)$_2$(**1**)]Cl (0.0581 mmol), 1,10-phenanthroline-5,6-dione (0.0762 mmol), glacial acetic acid (12 mL) and ammonium acetate (1.01 g, 13.12 mmol) was refluxed for 4 h at 110 °C followed by cooling down to room temperature and dilution with distilled water. A precipitate appeared on neutralizing the solution with aqueous ammonia in a cooling bath. The resulting precipitate was filtered, washed first with water for several times and then with dichloromethane producing a brown coloured compound. Yield: 64%. ESI-MS (*m*/*z*): $[M-Cl]^+$: 925.205 (Calc. 925.20). Elemental Analysis: Calc. C, 67.47; H, 3.57; N, 14.57; Expt. C, 66.96; H, 3.13; N, 14.89; ^{1}H NMR [DMSO-d_6]: δ 9.09 (d, 2H), 9.03 (d, 2H), 8.98 (d, 2H), 8.59 (d, 2H), 8.37 (d, 2H), 8.28 (d, 2H), 8.01 (m, 4H), 7.95 (t, 2H), 7.87 (m, 4H), 7.47 (d, 2H), 7.12 (t, 2H), 7.08 (t, 2H), 7.03 (t, 2H), 6.34 (d, 2H) (for more details see Fig. S10). $\bar{\nu}_{max}$/cm^{-1}: 3403m (br), 2924m, 1605s, 1479m, 1449s, 1351s, 1121s, 810m, 757m, 740m.

2.2.4. Synthesis of [Ir(ppy)$_2$(**2**)]Cl (**6**)

The synthetic procedure is similar to that of **5**. A dark brown coloured compound was obtained as the final product. Yield: 61%. ESI-MS (*m*/*z*): $[M-Cl]^+$: 1015.23 (Calc. 1015.26). Elemental Analysis: Calc. C, 61.73; H, 3.26; N, 13.33; Expt. C, 62.94; H, 2.87; N, 13.67; ^{1}H NMR [DMSO-d_6]: δ 9.09 (d, 2H), 9.01 (d, 4H), 8.59 (d, 2H), 8.40 (d, 2H), 8.26 (d, 2H), 7.95 (d, 4H), 7.86 (m, 6H), 7.50 (d, 2H), 7.06–7.00 (m, 4H), 6.95 (t, 2H), 6.32 (d, 2H) (for more details see Fig. S11). $\bar{\nu}_{max}$/cm^{-1}: 3386s (br), 3060s, 1606s, 1581s, 1563s, 1478s, 1449s, 1397s, 758m, 740s.

2.2.5. Synthesis of [{Rh(ppy)$_2$}2(**2**)]Cl$_2$ (**7**)

A mixture of **6** (0.047 mmol), $[Rh(ppy)_2Cl]_2$ (0.035 mmol) and acetonitrile/dichloromethane/methanol (1:1:1, v/v, 30 mL) was refluxed at 90 °C for about 3 h. The resulting yellowish orange coloured solution was cooled down to room temperature. Subsequently, the compound was purified by thin layer chromatography with 10% methanol in dichloromethane mixture. A dark yellow compound was obtained on drying. Yield: 65%. ESI-MS (*m*/*z*): $[M-2Cl]^{2+}$/2: 713.13 (Calc. 713.14), $[M-2Cl-H^+]^+$ = 1425.25 (Calc. $[M-2Cl]^+$ = 1426.29); Elemental Analysis: Calc. C, 62.44; H, 3.45; N, 11.50; Expt. C, 62.76; H, 3.85; N, 11.20; ^{1}H NMR [$CDCl_3$]: 9.74 (br, 4H), 8.77 (s, 4H), 8.15 (d, 2H), 8.12 (d, 2H), 7.95 (d, 4H), 7.79–7.72 (m, 12H), 7.38 (t, 4H), 7.14 (t, 2H), 7.08 (t, 2H), 7.02 (t, 2H), 6.97 (t, 2H), 6.91 (t, 2H), 6.86 (t, 2H), 6.42 (d, 4H) (for more details see Fig. S12). $\bar{\nu}_{max}$/cm^{-1}: 3433s (br), 3043m, 2922m, 1606s, 1581m, 1479s, 1449m, 758m, 731m.

2.2.6. Synthesis of [{Ir(ppy)$_2$(**2**)Rh(ppy)$_2$}](PF$_6$)$_2$ (**8**)

8: was synthesized by refluxing $[Rh(ppy)_2Cl]_2$ (0.25 mmol) with **2** (0.25 mmol) in EtOH/dichloromethane mixture (2:1 v/v, 30 mL) for 4 h. The mixture was heated until the volume was reduced to 8 mL followed by addition of 10 mL water. The desired compound was precipitated by adding an excess of aqueous NH_4PF_6 to the solution. Filtration yielded a yellow coloured compound. Yield: 68%. ESI-MS (*m*/*z*): $[M-2PF_6]^{2+}$/2: 668.09 (Calc. 668.12). $[M-2PF_6-H^+]^+$ = 1335.22; (Calc. $[M-2PF_6]^+$ = 1336.24); Elemental Analysis: Calc. C, 61.59; H, 3.40; N, 11.34; Expt. C, 61.78; H, 3.56; N, 12.02;^{1}H NMR [DMSO-d_6]: δ 9.26 (d, 4H), 8.60 (s, 4H), 8.30 (d, 4H), 8.23 (d, 4H), 8.12 (t, 4H), 8.03 (d, 4H), 7.97 (t, 4H), 7.49 (d, 4H), 7.15 (t, 4H), 7.07–7.02 (m, 8H), 6.32 (d, 4H) (for more details see Fig. S13). $\bar{\nu}_{max}$/cm^{-1}: 3430s (br), 1606s, 1578s, 1480s, 1451m, 846vs, 757s, 733m.

2.2.7. Synthesis of [{Ir(ppy)$_2$}$_2$(**2**)]Cl$_2$ (**9**)

A mixture of $[Ir(ppy)_2Cl]_2$ (0.1 mmol), **2** (0.1 mmol) and acetonitrile/dichloromethane (1:1 v/v, 30 mL) was refluxed for 4 h at 90 °C to obtain an orange coloured mixture. It was cooled down to room temperature and the solvent was evaporated using a rotary evaporator. The residue was purified by column chromatography (5% methanol in dichloromethane was used as eluent) yielding a