Inorganic Chemistry Communications 12 (2009) 758–760

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

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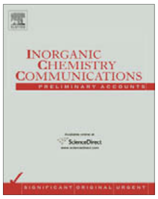

Cyclometallated iridium(III) complexes with dicyanamide or tricyanomethanide

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ARTICLE INFO

Article history:
Received 8 May 2009
Accepted 8 June 2009
Available online 10 June 2009

Keywords:
Dicyanamide
Luminescence
Iridium
2-Phenylpyridine
Tricyanomethanide

ABSTRACT

Reaction of cyclometallated iridium(III) complex $Ir(ppy)_2(PPh_3)Cl$ (**2**, ppy = 2-phenylpyridine) with dicyanamide or tricyanomethanide gave neutral mononuclear complexes $Ir(ppy)_2(PPh_3)N(CN)_2$ (**3a**) or $Ir(ppy)_2(PPh_3)C(CN)_3$ (**3b**), and dicyanamide/tricyanomethanide-linked binuclear iridium(III) complexes $[\{Ir(ppy)_2(PPh_3)\}_2N(CN)_2]^+$ (**4a**) or $[\{Ir(ppy)_2(PPh_3)\}_2C(CN)_3]^+$ (**4b**). Substitution of coordinated chloride in the precursor **2** with dicyanamide or tricyanomethanide improved significantly the luminescence properties of **3a**–**4b**. Compared with that in the precursor **2** (1.6%), 2.2 to 9.3-fold enhancement of emission quantum yields was detected in **3a**–**4b**.

In recent decades, organic light-emitting diodes (OLEDs) have been under active investigations because of the enormous potential applications in flat panel display (FPD) and general lighting [1]. The relevant studies are started from coordination complexes of aluminium(III), iridium(III), and platinum(II) etc. [2], which have been used as the light-emitting dopants in OLEDs with high quantum efficiency. In particular, cyclometallated iridium(III) complexes are intensively studied because they exhibit high emission quantum efficiency in the visible spectral region [3,4]. The mixing of the ^{1}MLCT and ^{3}MLCT states is formed due to strong spin-orbit coupling of heavy metal ions in these complexes so that the ^{3}MLCT emission is enhanced by borrowing the intensity from the ^{1}MLCT state and leads to high phosphorescence efficiencies [5].

Metal complexes of dicyanamide $[N(CN)_2^-]$ and tricyanomethanide $[C(CN)_3^-]$ have attracted much attention because of their intriguing optical, magnetic and electronic properties [6], where the quasi-π-conjugated dicyanamide or tricyanomethanide serves as an effective mediator to transmitting magnetic and electronic interactions. We report herein the preparation and photophysical properties of dicyanamide/tricyanomethanide-containing cyclometallated iridium(III) complexes with ppy (ppy = 2-phenylpyridine). Our research is aimed at exploring the influence on the luminescence properties by substitution of the coordinated chloride in the precursor $Ir(ppy)_2(PPh_3)Cl$ (**2**) with a dicyanamide or tricyanomethanide ligand.

The synthetic routes to complexes **2**–**4b** are depicted in Scheme 1. The precursor $Ir(ppy)_2(PPh_3)Cl$ (**2**) [7] was prepared by reaction of chloride-bridged iridium(III) dimer $Ir_2(ppy)_4(\mu\text{-}Cl)_2$ (**1**) [8] with triphenylphosphine (PPh_3) according to the literature procedure. Reaction of sodium dicyanamide with 1 or 2 equiv. of **2** in methanol-dichloromethane (v/v = 1:1) solution gave rise to isolation of neutral mononuclear complex $Ir(ppy)_2(PPh_3)\{N(CN)_2\}$ (**3a**) or dicyanamide-bridged binuclear iridium(III) complex $[\{Ir(ppy)_2(PPh_3)\}_2\{\mu\text{-}N(CN)_2\}]^+$ (**4a**). Complex **4a** was also accessed by reaction of **3a** with equimolar **2** in a stepwise synthetic approach. Similarly, tricyanomethanide-containing complexes $Ir(ppy)_2(PPh_3)\{C(CN)_3\}$ (**4b**) and $[\{Ir(ppy)_2(PPh_3)\}_2\{\mu\text{-}C(CN)_3\}]^+$ (**4b**) were accessed using potassium tricyanomethanide instead of sodium dicyanamide.

Complexes **2**–**4b** ware characterized by ESI-MS spectrometry, ^{1}H NMR, and IR spectroscopy (Experimental section, ESI), and by X-ray crystallography for **3a** and **4b** [9]. In the IR spectra of **3a**–**4b**, characteristic stretching vibration bands of dicyanamide or tricyanomethanide were detected. Relative to $\nu(N(CN)_2)$ in the free dicyanamide (2287, 2229, and 2181 cm^{-1}), those in mononuclear complex **3a** (2266, 2225, and 2161 cm^{-1}) showed a lower frequency shift due to the σ donation from dicyanamide to the metal center upon coordination. The $\nu(N(CN)_2)$ in dicyanamide-bridged binuclear complex **4a** (2301, 2199 cm^{-1}), however, exhibited higher frequency shifts compared with those in terminal dicyanamide-bound species **3a**, arising probably from the integrated electronic effects of σ donation from the bridging ligand to the organometallic centers as well as π back-donation from the organometallic centers to the ligand. Likewise, compared with the $\nu(C(CN)_3)$ in the free tricyanomethanide (2179 cm^{-1}), a lower frequency shift occurred in terminal tricyanomethanide-bound **3b** (2176 cm^{-1}), whereas a higher frequency shift was detected in tricyanomethanide-bridged binuclear species **4b** (2192 cm^{-1}).

The ORTEP drawings of **3a** and **4b** are depicted in Figs. 1 and 2, respectively. The iridium(III) atom is located at a distorted octahedral environment composed of C_2N_3P donors. The two ppy ligands

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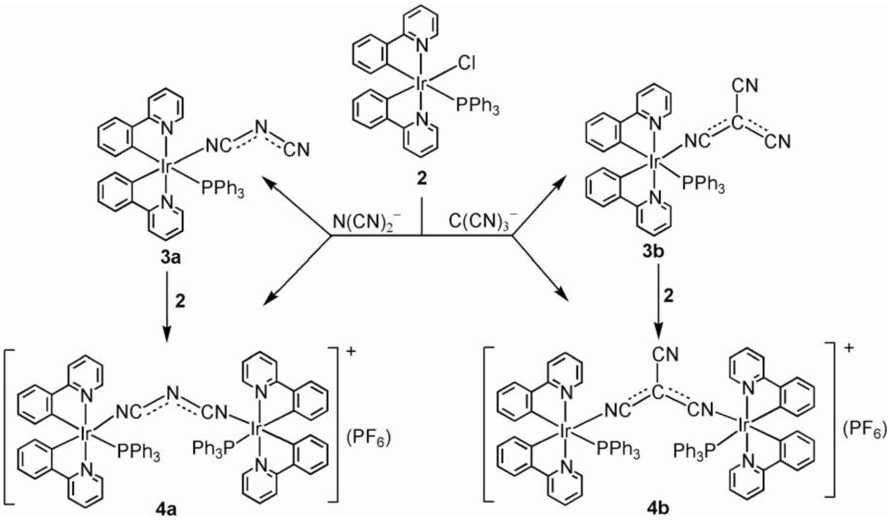
doi:10.1016/j.inoche.2009.06.008



Scheme 1. Synthetic routes to complexes **2**–**4b**.

are cis-arranged with the two C donors in cis-position and the two N donors in trans-orientation. The Ir–C_{ppy} and Ir–N_{ppy} distances are comparable to those in other cyclometallated iridium(III) complexes of ppy [4]. For **3a**, the dicyanamide is terminally bound to the iridium(III) ion with Ir1–N3 distance of 2.128(7) Å. The Ir–N$\equiv$C–N array is quasi-linear with the Ir1–N3–C4 and N3–C4–N4 angles of 167.3(7) and 172.8(11)°, respectively. The C41–N4–C42 angle of dicyanamide is 122.8(11)° due to sp^2 hybridized character of N4 atom. For **4b**, the binuclear iridium(III) centers are linked by a bridging tricyanomethanide with Ir1···Ir2 separation of 8.1 Å. Of the three C$\equiv$N groups in $C(CN)_3^-$, two C$\equiv$N (1.151(5) and 1.155 (6) Å) bound to the iridium(III) centers are appreciably elongated relative to that of the uncoordinated C$\equiv$N (1.102(7) Å). The relevant bonding distances and angles of dicyanamide or tricyanomethanide in **3a** or **4b** are similar to those in other metal complexes with dicyanamide or tricyanomethanide [6].

The UV–vis absorption spectra of **2**–**4b** (Table 1) in dichloromethane solutions are featured by UV absorptions below 330 nm from ligand centered characters together with low-energy bands with wavelength longer than 330 nm due to d(Ir) → π^*(ppy) MLCT (metal-to-ligand charge transfer) state [10]. Upon irradiation at λ_{ex} > 350 nm, **2**–**4b** exhibit bright cyan emission in both solid states and solutions with sub-microsecond ranges of lifetimes at ambient temperature [11], arising most likely from ^{3}[d(Ir) → π^*(ppy)] ^{3}MLCT triplet excited state. As depicted in Fig. 3, the emission of **3a**–**4b** is obviously blue-shifted compared with that of **2** in both solution and solid state (Table 1), suggesting that substitution of the chloride in **2** with a stronger σ donating and π accepting ligand such as dicyanamide or tricyanomethanide can raise the emission energy in some extent. This can be rationally elucidated by the fact that stronger ligand field would cause larger splitting of the d-orbital and consequently lower the energy of metal-centered HOMO [12]. The emission quantum yields of **3a**–**4b** are in the range 3.7–15% which are much higher than that of the precursor **2**. This reveals that strong-field ligand substitution of the coordinated chloride results in significantly enhanced luminescence efficiency because the stronger Ir–N bonding compared with that of Ir–Cl favors suppressing the non-radiative process due to some Ir-solvent interaction in solutions.

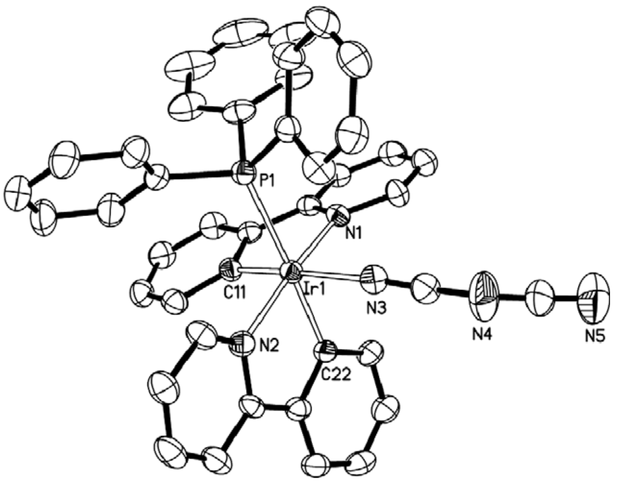


Fig. 1. ORTEP drawing of **3a** with 30% thermal ellipsoids probability. Selected bond lengths (Å) and angles (°): Ir1–N1 2.044(5), Ir1–N2 2.087(6), Ir1–N3 2.128(7), Ir1–C11 2.010(7), Ir1–C22 2.044(7), Ir1–P1 2.441(2), N3–C41 1.137(10), N4–C41 1.311(12), N5–C42 1.158(18) Å; N1–Ir–N2 171.5(2), N1–Ir–C11 80.3(3), N2–Ir–C22 79.6(3), N3–C41–N4 172.8(11), N4–C42–N5 174.1(18), C11–Ir–C22 85.7(3), C41–N3–Ir 167.3(7), C41–N4–C42 122.8(11)°.

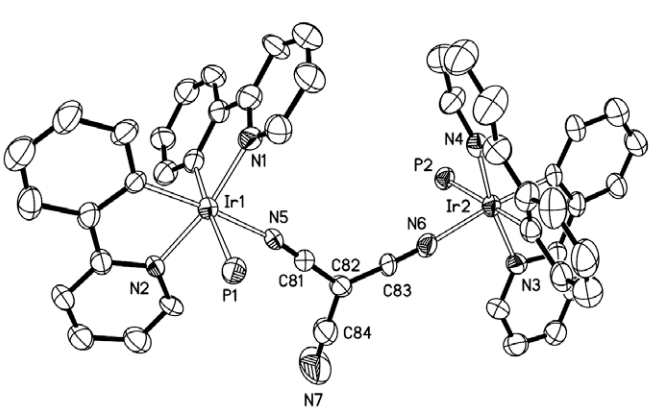


Fig. 2. ORTEP drawing of **4b** with 30% thermal ellipsoids probability. The phenyl groups in P atoms are omitted for clarity. Selected bond lengths (Å) and angles (°):Ir1–C22 1.994(9), Ir1–C11 010(9), Ir–N1 2.050(8), Ir1–N2 2.065(7), Ir1–N5 2.079(7), Ir1–P1 2.419(3), N5–C81 1.160(10), N6–C83 1.134(11), N7–C84 1.118(15); C22–Ir1–C11 89.6(3), C22–Ir1–N1 92.4(3), C11–Ir1–N1 80.0(4), C22–Ir1–N2 80.0(3), C11–Ir1–N2 91.2(3), N1–Ir1–N2 168.5(3), C22–Ir1–N5 173.1(3), C11–Ir1–N5 87.8(3), N1–Ir1–N5 93.4(3), N2–Ir1–N5 93.7(3), C22–Ir1–P1 94.5(2), C11–Ir1–P1 175.6(2), N1–Ir1–P1 98.2(2), N2–Ir1–P1 90.99(19), N5–Ir1–P1 88.3(2).

Table 1
Absorption and emission data of **2**–**4b**.

	Medium	λ_{abs}/nm (ε/dm^3 mol^{-1} cm^{-1})	298 K			77 K
			λ_{em}/nm[a]	τ/μs	Φ_{em}[b]	λ_{em}/nm
2	Solid		512	0.107		500, 512
	CH_2Cl_2	258 (42,650) 347 (6210) 388 (3490)	480, 510sh	0.018	0.016	452, 481
3a	Solid		498	0.099		490, 519
	CH_2Cl_2	250 (38,590) 302 (13,320) 378 (3010)	472, 496	0.146	0.150	457, 483
3b	Solid		497	0.047		481, 512
	CH_2Cl_2	248 (50,390) 302 (15,260) 378 (4370)	466, 495	0.059	0.061	452, 481
4a	Solid		502	0.055.		509
	CH_2Cl_2	249 (73,950) 302 (24,940) 378 (6580)	469, 496	0.057	0.110	475, 501
4b	Solid		502	0.024		495
	CH_2Cl_2	249 (88,600) 306 (26,010) 376 (6070)	469, 493	0.026	0.037	469, 496

[a] Emission spectra are recorded in 10^{-5} M of dichloromethane solutions at 298 K.
[b] The emission quantum yields are measured using *fac*-Ir(ppy)$_3$ (Φ_{em} = 0.40 [10a]) as the standard.

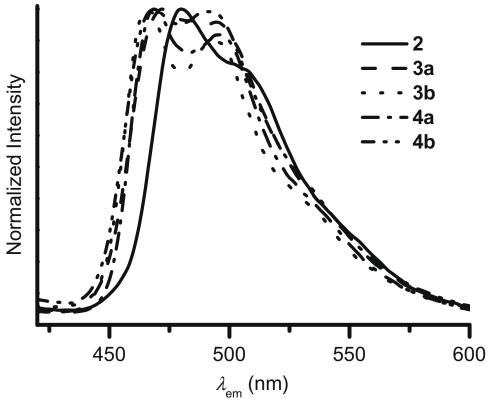


Fig. 3. Emission spectra of **2**–**4b** in dichloromethane solutions at 298 K.

In summary, four mono- and binuclear iridium(III) complexes were prepared by substitution of the chloride in the precursor Ir(p-py)$_2$(PPh$_3$)Cl with dicyanamide or tricyanomethanide. Stronger field ligand substitution gave rise to an obvious blue shift of the emission and 2.2 to 9.3-fold enhancements of the luminescence quantum yields in **3a**–**4b**.

Acknowledgements

We thank financial supports from the NSFC, the 973 project (2007CB815304) from MSTC, and NSF of Fujian Province (2008I0027 and 2008F3117).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2009.06.008.

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[9] Crystal data for **3a**·CH_2Cl_2: $C_{43}H_{33}Cl_2IrN_5P$, $M = 913.81$, monoclinic, space group $P2_1/n$, $a = 17.352(7)$ Å, $b = 9.391(3)$ Å, $c = 24.936(10)$ Å, $\beta = 99.942(7)°$, $V = 4003(3)$ Å^3, $Z = 4$, $T = 293(2)$ K, μ(Mo Kα) = 3.546 mm^{-1}, $D_c = 1.516$ g cm^{-1}, $\lambda = 0.71073$ Å, $2\theta = 55°$. The structure, refined on F^2, converged for 9188 unique reflections ($R_{int} = 0.050$) and 7722 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.0552$ and $wR_2 = 0.1527$ and a goodness-of-fit = 1.140. Crystal data for **4b**·5/2CH_2Cl_2: $C_{86.5}H_{67}Cl_5F_6Ir_2N_7P_3$: $M = 1973.03$, triclinic, space group $P\bar{1}$, $a = 15.693(5)$ Å, $b = 16.502(5)$ Å, $c = 19.029(5)$ Å, $\alpha = 72.358(13)°$ $\beta = 69.636(12)°$, $\gamma = 71.034(11)°$, $V = 4268(2)$ Å^3, $Z = 2$, $T = 293(2)$ K, μ(Mo Kα) = 3.389 mm^{-1}, $D_c = 1.535$ g cm^{-1}, $\lambda = 0.71073$ Å, $2\theta = 55°$. The structure, refined on F^2, converged for 14,611 unique reflections ($R_{int} = 0.0519$) and 9916 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.0578$ and $wR_2 = 0.1283$ and a goodness-of-fit = 1.075.

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