Russian Journal of General Chemistry, Vol. 75, No. 5, 2005, pp. 665–671. Translated from Zhurnal Obshchei Khimii, Vol. 75, No. 5, 2005, pp. 705–711.
Original Russian Text Copyright © 2005 by Kulikova, McClenaghan, Balashev.

Preparation and Photophysical Properties of Mixed-Ligand Cyclometallated Complexes of Ir(III) with a Dendritic Bipyridine Ligand

M. V. Kulikova*, N. McClenaghan, and K. P. Balashev***

** Herzen Russian State Pedagogical University, St. Petersburg, Russia*
*** University of Messina, Messina, Italy*

Received January 15, 2004

Abstract—Complexes [Ir(C^N)$_2$(G1-bpy)]PF$_6$, where C^N is a cyclometallating ligand derived from 2-(2'-thienyl)pyridine and 2-phenylpyridine, and G1-bpy is a dendritic bipyridine ligand of the first generation, 4,4'-bis[3",5"-bis(benzyloxy)phenylethyl]-2,2'-bipyridine, were prepared and characterized by ^{1}H NMR, electronic absorption, and emission spectroscopy. The polyether dendritic substituents exert a "soft" effect on the spectral and luminescence properties of the complexes, manifested as slight destabilization of the electronically excited charge-transfer state involving the bipyridine ligand, as compared to the model complexes [Ir(C^N)$_2$(bpy)]PF$_6$.

Bis- and triscyclometallated Ir(III) complexes attract increased researchers' attention owing to the possibility of using them as phosphorescing materials in organic light-emitting devices (OLEDs) [1–3]. In these devices, singlet and triplet excited states arising from charge recombination are "trapped" with a chromophore in which fast intercombination conversion results in room-temperature electrophosphorescence. One of the factors governing the performance of phosphorescing OLEDs is the spin–orbital coupling causing the singlet–triplet mixing of the excited states of the chromophore. As compared to Ru(II) and Os(II) complexes, Ir(III) complexes (d^6) are characterized by higher quantum yields of the luminescence in liquid solutions at room temperature {for example [4], φ_{phos} of (*fac*-[Ir(ppy)$_3$] is 0.4, where ppy is 2-phenylpyridinate). This is due to efficient intercombination conversion between the singlet and triplet excited states, caused by spin–orbital coupling in the Ir(III) ion.

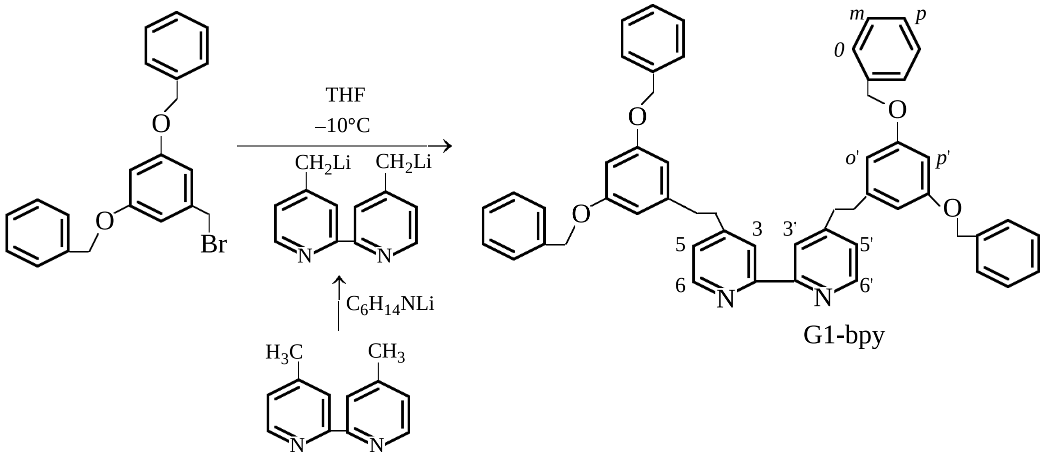
In mixed-ligand biscyclometallated complexes of the type [Ir(C^N)$_2$(bpy)]PF$_6$ [here C^N is 2-(2'-thienyl)pyridinate (tpy) or 2-phenylpyridinate (ppy); bpy is 2,2'-bipyridine], studied in [5, 6], the orbital nature of the luminescing state strongly depends on the solvent polarity and matrix hardness. Colombo *et al.* [5, 6] believe that this effect, especially in the case of the phenylpyridinate complex, is due to the fact that the intraligand excited state and the charge-transfer state involving, respectively, the cyclometallating and bipyridine ligands have close energies. Therefore, it is interesting to study the spectral and luminescence properties of the related mixed-ligand biscyclometallated complexes of Ir(III) containing a 4,4'-substituted dendritic bipyridine ligand. The choice of polyether dendritic substituents is governed, on the one hand, by their donor power and, on the other hand, by the possibility of specific solvation of the bipyridine moiety. Both these factors can affect the energy of the excited charge-transfer state involving the bipyridine ligand.

The dendritic bipyridine ligand was prepared according to [7] (Scheme 1).

In the first step, 4,4'-dimethyl-2,2'-bipyridine reacts with excess lithium diisopropylamide in anhydrous THF at –10°C. The resulting 4,4'-bis(lithiomethyl)-2,2'-bipyridine reacts with dendritic benzyl bromide in THF. The disubstituted dendritic bipyridine ligand and the monosubstituted product can be subsequently separated by column chromatography.

The ^{1}H NMR spectrum of the resulting dendritic bipyridine ligand confirms its symmetrical structure (see Experimental). In particular, the bipyridine moiety gives three proton signals, the integral intensity of each of them corresponding to 2H, i.e., the related hydrogen atoms of the two pyridine rings are equivalent. At the same time, in the monosubstituted derivative, the protons in positions 3 and 3', and in positions 5 and 5' are nonequivalent and give separate signals. The protons in positions 6 and 6', more remote from the dendritic substituent, are less sensitive to the substitution.

Scheme 1.



In the ^{1}H NMR spectrum of the dendritic bipyridine, the proton signals are shifted upfield as compared to unsubstituted 2,2'-bipyridine (by 0.16 ppm on the average), which reflects the donor power of the dendritic substituent.

The starting compounds for preparing mixed-ligand cyclometallated complexes $[Ir(C\text{^}N)_2(G1\text{-}bpy)]^+$ are the dimeric complexes $[Ir(C\text{^}N)_2Cl]_2$ prepared by the published procedure (Scheme 2).

With a CH_2Cl_2–CH_3OH mixture as solvent, the chloride ligands in the dimeric complex can be readily substituted by the dendritic N^N bipyridine ligand under mild conditions and with a high product yield (62–67%). This route was used previously for preparing $[Rh(ppy)_2(bpy)]^+$ [8]. The reaction course and the purity of the target product were monitored by thin-layer chromatography on Al_2O_3 plates with CH_2Cl_2–CH_3OH, 20 : 1, as eluent.

Scheme 2.

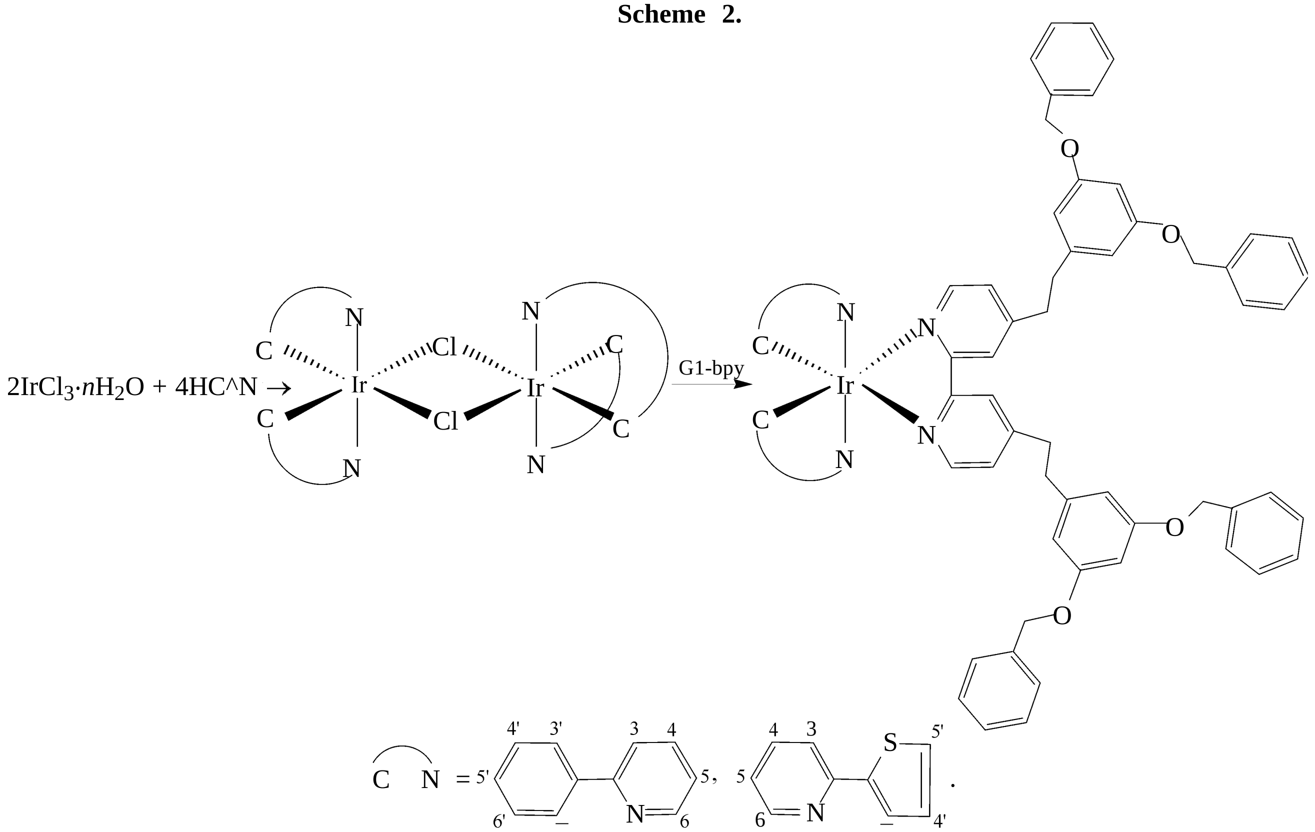


Table 1. ^1H chemical shifts (δ, ppm, relative to TMS) and ^1H–^1H coupling constants (*J*, Hz) in the ^1H NMR spectra of the complexes $[Ir(C\wedge N)_2(G1\text{-}bpy)]^+$ in CD_2Cl_2

Compound	Atom in $(C\wedge N)_2Ir$ fragment							
	3	4	5	6	3'	4'	5'	6'
$[Ir(ppy)_2Cl]_2$	7.94 (^3J 7.5)	7.80 (^3J 7.5, 8.1, ^4J 1.5)	6.83 (^3J 6.0, 7.4, ^4J 1.5)	9.25 (^3J 5.1, ^4J 1.5)	5.87 (^3J 7.8, ^4J 0.9)	6.82 (^3J 7.8, 7.2)	6.61 (^3J 7.8, 7.2)	7.56 (^3J 7.7)
$[Ir(ppy)_2\cdot(bpy)]^{+a}$	7.95 (^3J 8.2)	7.78 (^3J 8.3, 7.4)	6.99 (^3J 7.3, 5.6)	7.51 (^3J 5.5)	6.33 (^3J 7.5)	6.93 (^3J 7.5, 7.4)	7.07 (^3J 7.5, 7.9)	7.74 (^3J 7.8)
$[Ir(ppy)_2\cdot(G1\text{-}bpy)]^+$	7.89 (^3J 7.8)	7.64 (^3J 8.4, 7.4)	6.88 (^3J 7.5, 6.1)	7.41–7.27 m	6.28 (^3J 7.7)	7.06 (^3J 7.6)	6.93 (^3J 8.1, 7.5)	7.71 (^3J 7.8)
$[Ir(tpy)_2Cl]_2$	7.56 (^3J 8.0, ^4J 1.5)	7.68 (^3J 8.4, 6.9)	6.67 (^3J 7.4, 5.9)	9.00 (^3J 5.9)	5.89^b (^3J 4.8)		7.12^c (^3J 4.8)	
$[Ir(tpy)_2\cdot(G1\text{-}bpy)]^+$	7.52	7.40–7.28 m	6.72–6.67 m	7.52	6.28 (^3J 4.8)		7.44 (^3J 4.8)	

Compound	bpy			G1		
	3,3'	5,5'	6,6^'	Ph	CH_2O	CH_2–CH_2
$[Ir(ppy)_2(bpy)]^{+a}$	9.29 (^3J 7.8)	7.45 (^3J 7.3, 5.6)	7.97 (^3J 5.7)	–	–	–
$[Ir(ppy)_2(G1\text{-}bpy)]^+$	8.25 s	7.12 (^3J 5.4)	7.81 (^3J 5.7)	7.41–7.27 m, 6.48–6.45 m	4.99	3.14–3.11 m, 2.98–2.93 m
$[Ir(tpy)_2(G1\text{-}bpy)]^+$	8.26 s	7.16 (^3J 5.7)	7.76 (^3J 5.7)	7.40–7.28 m, 6.49–6.47 m	4.99	3.18–3.12 m, 2.99–2.94 m

[a] Data from [9]. [b] 4'-H. [c] 5'-H.

The main ^1H NMR parameters (chemical shifts and coupling constants J_{HH}) of the complexes $[Ir(C\wedge N)_2\cdot(G1\text{-}bpy)]PF_6$ are given in Table 1. For comparison we also give data for the corresponding (μ-Cl)-dimeric complexes and published data for $[Ir(ppy)_2(bpy)]^+$ [9]. The ^1H NMR data for $[Ir(tpy)_2(bpy)]^+$ are not given in Table 1, because Colombo and Güdel [5] gave only the general view of the spectrum. According to the ^1H NMR spectrum (Fig. 1), the related protons of the two cyclometallating ligands in the complexes $[Ir(C\wedge N)_2(G1\text{-}bpy)]^+$ are equivalent, which indicates that the complex is highly symmetrical. The starting dimeric complexes $[Ir(C\wedge N)_2Cl]_2$ also give first-order ^1H NMR spectra. Taking into account the crystallographic data available for $[Ir(ppy)_2Cl]_2$ [10] and $[Ir(ppy)_2(acac)]$ (here acac is acetylacetonate) [2] and mild conditions of the synthesis of the complexes $[Ir(C\wedge N)_2(G1\text{-}bpy)]PF_6$, we can conclude that the pyridine rings of the two cyclometallating ligands in $[Ir(ppy)_2(G1\text{-}bpy)]PF_6$ and $[Ir(tpy)_2(G1\text{-}bpy)]PF_6$ are arreanged *trans* to each other. As compared to the (μ-Cl)-dimeric complexes, in the corresponding mononuclear complexes $[Ir(C\wedge N)_2(G1\text{-}bpy)]PF_6$ the H^6 protons of the C^N ligand are appreciably shielded, which is due to the anisotropic effect of the pyridine rings of the bipyridine ligand. On the other hand, the $H^{3'}$ protons of the ppy ligand and $H^{4'}$ protons of the tpy ligand in $[Ir(C\wedge N)_2(G1\text{-}bpy)]PF_6$ are less shielded than the corresponding protons in the dimeric complexes because of the absence of π-donor chloride ligands in the *trans* position. The coordination shifts $\Delta\delta = \delta_{comp} - \delta_{lig}$ for the $H^{3,3'}$ and $H^{5,5'}$ protons of the bipyridine moiety of the dendritic ligand in the complexes $[Ir(C\wedge N)_2(G1\text{-}bpy)]PF_6$ are close to zero, whereas for $H^{6,6'}$ this shift is about −0.8 ppm. Such a shielding is due to the anisotropic effect of the ring current in the pyridine ring of the cyclometallating ligand. On the whole, the coordination shifts Δδ in the complexes $[Ir(C\wedge N)_2(G1\text{-}bpy)]PF_6$ are smaller than in the related complexes with unsubstituted 2,2'-bipyridine. The largest difference in Δδ is observed for the $H^{3,3'}$ protons in the bipyridine moiety of the complexes $[Ir(ppy)_2(G1\text{-}bpy)]^+$ and $[Ir(ppy)_2(bpy)]^+$ (Δδ −0.07 and 0.86 ppm, respectively). This may be due to the van der Waals interaction of the H^3 and $H^{3'}$ protons, enhanced by dendritic substituents. It is

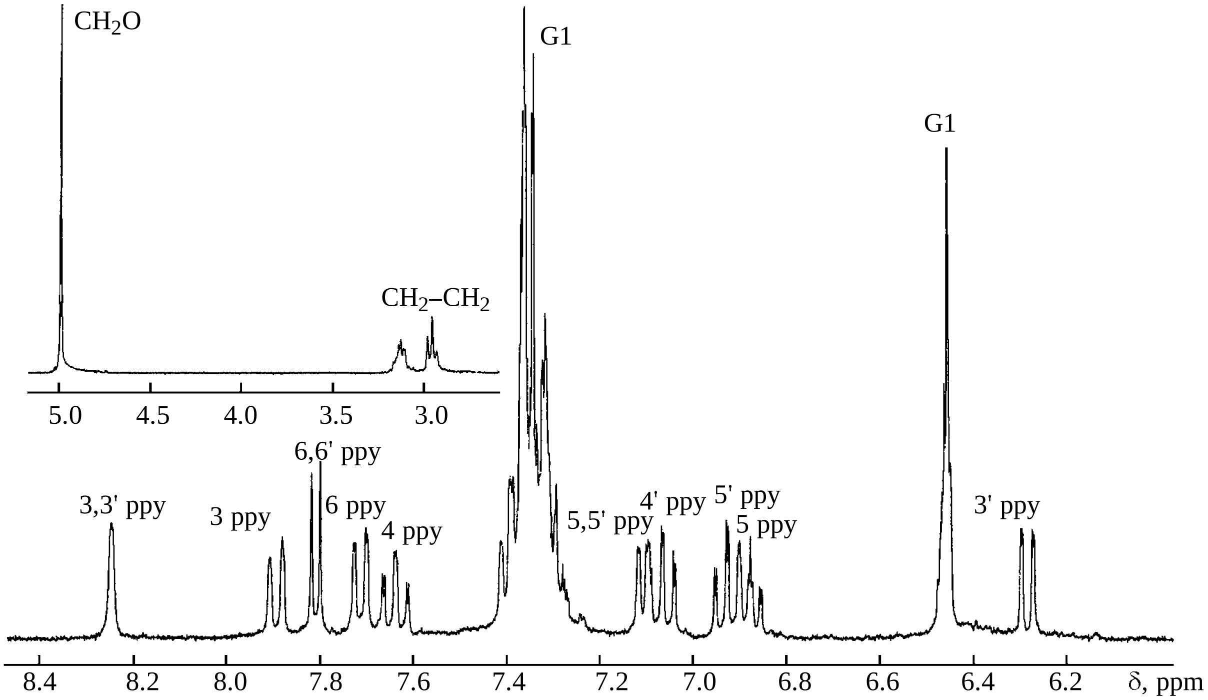


Fig. 1. ^1H NMR spectrum of $[Ir(ppy)_2(G1\text{-}bpy)]PF_6$ in CD_2Cl_2.

interesting that, in the related tpy complexes, the difference in Δδ of the H^3 and $H^{3'}$ protons is considerably smaller (–0.06 and 0.06 ppm).

The parameters of the electronic absorption spectra of the complexes $[Ir(C^\wedge N)_2(G1\text{-}bpy)]PF_6$ in dichloromethane at room temperature are given in Table 2 together with published data for some other cyclometallated Ir(III) complexes. The electronic absorption spectra of the related complexes $[Ir(C^\wedge N)_2\cdot(G1\text{-}bpy)]PF_6$ and $[Ir(C^\wedge N)_2(bpy)]PF_6$ are similar. In the UV range of the spectra, there is a strong band with a vibronic structure at 277–345 nm for the tpy complex and 260–340 nm for the ppy complex, originating from the spin-allowed intraligand transitions involving the cyclometallating and bipyridine ligands. The spin-allowed metal-to-ligand charge-transfer (MLCT) transitions are observed at 380–430 nm. Taking into account the electrochemical data for the complexes $[Ir(C^\wedge N)_2(bpy)]^+$ [8] and the assignment of the related absorption bands for the complexes $[Pt(C^\wedge N)(bpy)]^+$ [12], we can expect lower energy of the MLCT transition involving the bipyridine ligand. The spectrum of $[Ir(ppy)_2(G1\text{-}bpy)]$ contains also the bands of spin-forbidden transitions at 437 (ε 1200) and 469 nm (ε 580). Relatively high intensity of these transitions is due to strong spin–orbital coupling caused by the Ir(III) ion. These low-energy transitions are not manifested in the absorption spectrum of the corresponding tpy complex, probably because of lower molar extinction coefficients. A similar pattern was observed previously [13] with Pt(II) tpy complexes compared to the ppy complexes. As seen from Table 2, the position of the low-energy spin-forbidden transition is sensitive to the structure of the noncyclometallating ligand. An increase in the ligand donor power causes a bathochromic shift of this band from 463 to 492 nm. This fact suggests that the low-energy spin-forbidden transition involving the cyclometallating ligand is essentially an MLCT transition.

Similarly to the previously studied complexes $[Ir(C^\wedge N)_2(bpy)]^+$, the luminescence behavior of the complexes $[Ir(C^\wedge N)_2(G1\text{-}bpy)]^+$ strongly depends on the matrix [dichloromethane or poly(methyl methacrylate)] and temperature (298 or 77 K) (Table 3, Fig. 2). Such a dependence was not observed with mixed-ligand Ir(III) phenylpyridinate complexes with N^N,C-coordinated ligands derived from 6-phenyl-2,2'-bipyridine [14]. Therefore, as a basis for interpretation of the luminescence data we chose a model suggested by Colombo *et al.* [5, 6] for Ir(III) complexes with unsubstituted bipyridine. According to this model, the close energies of the two low-lying excited states and the “purer” MLCT character of the electronically excited state involving the bipyridine ligand allow the stability of this excited state to be varied in a wide range by varying the polarity or hardness of the matrix. Depending on the conditions, the lowest excited state is either the ^{3}(IL/MLCT) (IL is intraligand transition) state involving the cyclometallating

Table 2. Electronic absorption spectra of mixed-ligand cyclometallating complexes of Ir(III) in dichloromethane

Compound	λ_{max}, nm ($\varepsilon \times 10^{-3}$)
$[Ir(tpy)_2(G1\text{-}bpy)]^+$	277 (48.8), 308 sh (34.2), 331 sh (15.1), 417 (9.3)
$[Ir(tpy)_2(bpy)]^{+a}$	279 (46.3), 310 sh (30.6), 417 (8.9)
$[Ir(tpy)_2Cl]_2$	290 (47.9), 403 (10.8), 454 (8.6)
$[Ir(tpy)_2(acac)]^b$	302 (25.1), 336 (12.6), 387 (6.3), 453 (3.2)
$[Ir(ppy)_2(G1\text{-}bpy)]^+$	262 (48.1), 309 sh (20.1), 338 sh (9.2), 357 (6.9), 381 (5.7), 413 sh (3.1), 437 (1.2), 469 (0.58)
$[Ir(ppy)_2(bpy)]^{+c}$	265 (36.1), 310 (16.1), 335 sh, 375 (4.7), 410 (2.8), 465 (0.58)
$(Bu_4N)[Ir(ppy)_2 \cdot (CN)_2]^d$	260 (41.7), 337 (8.5), 384 (5.8), 433 sh (0.43), 463 (0.21)
$(Bu_4N)[Ir(ppy)_2 \cdot (NCS)_2]^d$	266 (38.9), 335 (6.7), 355 (5.3), 400 (3.4), 437 (2.3), 476 (0.65)
$[Ir(ppy)_2(acac)]^e$	260 (49.0), 356 (8.2), 403 (4.7), 450 (3.2), 492 (1.0)
$[Ir(ppy)_2Cl]_2$	260 (68.0), 335 (13.0), 355 sh (11.0), 400 (6.3), 434 (4.2), 484 (1.1)

[a] Data from [5]. [b] Data from [1], 2-methyltetrahydrofuran. [c] Data from [8]. [d] Data from [11]. [e] Data from [2].

Table 3. Luminescence characteristics of the complexes $[Ir(C\text{^}N)_2(N\text{^}N)]^+$

Compound	λ_{max}, nm (τ, μs)		
	CH_2Cl_2, 298 K	poly(methyl methacrylate), 298 K	$C_2H_5OH–CH_3OH–CH_2Cl_2$, 77 K
$[Ir(ppy)_2(G1\text{-}bpy)]^+$	562 (<1)	480 sh, 523 (1.7)[a]	470, 524 sh (4.3)[a]
$[Ir(ppy)_2(bpy)]^{+b}$	585	532	524 (4.8)
$[Ir(tpy)_2(G1\text{-}bpy)]^+$	544 sh, 585 (5.1)[a]	540 (10.1)	535 (17.3)
$[Ir(tpy)_2(bpy)]^{+c}$	600	541	532 (17)[d]

[a] Nonexponential luminescence decay; the long-lived component of the luminescence signal is indicated. [b] Data from [6, 8]. [c] Data from [5]. [d] $[Rh(ppy)_2(bpy)]PF_6$ matrix.

ligand or the ^{3}MLCT ($d\pi$ Ir → $\pi^*_{N\text{^}N}$) state. However, nonuniform distribution of complex species in solution can lead to a boundary situation, superposition of two types of luminescence. In particular, in a dichloromethane solution at room temperature, the lowest electronically excited state of $[Ir(ppy)_2(G1\text{-}bpy)]^+$ responsible for the luminescence can be assigned to the ^{3}($d\pi$ Ir → $\pi^*_{N\text{^}N}$) type. The position of the maximum and the shape of the luminescence band are similar to those characteristic of other Ir(III) phenylpyridinate complexes with polypyridine ligands. Introduction of dendritic substituents led to a hypsochromic shift of the maximum of the charge-transfer luminescence band compared to $[Ir(ppy)_2(bpy)]^+$, which is consistent with the donor nature of the substituents. Furthermore, the effect of dendritic substituents is manifested in going to hard matrices. Whereas in the luminescence spectrum of $[Ir(ppy)_2(bpy)]^+$ the superposition of two types of luminescence bands in poly(methyl methacrylate) was observed only at 10 K, in the spectrum of $[Ir(ppy)_2(G1\text{-}bpy)]^+$ the second luminescence component at 480 nm is detected even at room temperature. Another evidence is the nonexponential decay of the luminescence. Similar behavior is observed in glassy matrices at 77 K; the short-wave maximum (470 nm) of the arising luminescence band overlaps with the low-energy band in the absorption

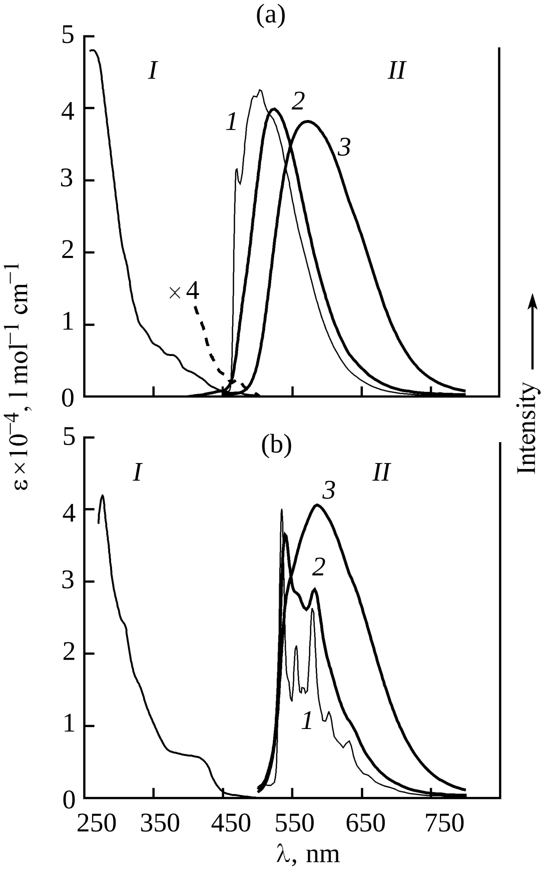


Fig. 2. (*I*) Absorption spectra in dichloromethane and (*II*) luminescence spectra of (a) $[Ir(ppy)_2(G1\text{-}bpy)]PF_6$ and (b) $[Ir(tpy)_2(G1\text{-}bpy)]PF_6$. Solvent (matrix): (*1*) $C_2H_5OH–CH_3OH–CH_2Cl_2$, 4 : 1 : 1, 77 K; (*2*) poly(methyl methacrylate), 298 K; and (*3*) CH_2Cl_2, 298 K.

spectrum. The range 470–515 nm and the lifetime (~1–5 μs) are typical of the luminescence from the electronically excited state of the ^{3}(IL/MLCT) type involving the ppy ligand in phenylpyridinate complexes of both Ir(III) [2, 11] and Pt(II), containing no polypyridine ligand N^N.

It is known that tpy complexes are characterized by larger (by 3000 cm^{-1} on the average) singlet–triplet splitting than the corresponding ppy complexes [6, 13]. This accounts for the larger energy gap between the electronically excited state involving the cyclometallating ligand and the ^{3}MLCT ($d\pi$ Ir $\rightarrow \pi^*_{\mathrm{N^\wedge N}}$) state. As a result, in hard matrices [e.g., poly(methyl methacrylate)], even at room temperature, only the ^{3}(IL/MLCT) state in $[\mathrm{Ir(tpy)_2(G1\text{-}bpy)}]^+$ and $[\mathrm{Ir(tpy)_2 \cdot (bpy)}]^+$ is luminescing, with a characteristic shape of the luminescence band. Dendritic substituents exert an additional effect in dichloromethane solutions at room temperature. Appearance of a shoulder at 544 nm in the luminescence spectrum of $[\mathrm{Ir(tpy)_2(G1\text{-}bpy)}]^+$, absent in the spectrum of $[\mathrm{Ir(tpy)_2(bpy)}]^+$ taken under the same conditions, and the nonexponential luminescence decay suggest superposition of two types of luminescence bands, as it was recorded for the corresponding ppy complex in a poly(methyl methacrylate) matrix at 298 K.

Thus, the luminescence behavior of mixed-ligand cyclometallated Ir(III) complexes with a dendritic bipyridine ligand strongly depends on the structure of the cyclometallating ligand (effect through the singlet–triplet splitting energy), temperature, and matrix (effect of the hardness and polarity). Introduction of dendritic substituents can be considered as one more influencing factor; polyether dendritic substituents in positions 4 and 4' of the bipyridine ligand exert a “soft” effect on the spectral and luminescence properties of the complexes $[\mathrm{Ir(C^\wedge N)_2(G1\text{-}bpy)}]\mathrm{PF_6}$, manifested in slight destabilization of the electronically excited charge-transfer state involving the bipyridine ligand, compared to the model complexes $[\mathrm{Ir(C^\wedge N)_2 \cdot (bpy)}]\mathrm{PF_6}$.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker Aspect-300 spectrometer at 298 K. The electronic absorption spectra were taken on a Kontron-Uvikon-860 spectrophotometer. Luminescence measurements were performed with a Spex-Jobin Yvon-Fluoromax-2 fluorimeter and a KSVU-1 installation (LGI-21 nitrogen pulse laser, λ_{exc} 337 nm, τ_{pulse} 10 ns).

Syntheses were performed in an inert atmosphere. The starting dimeric complexes $[\mathrm{Ir(C^\wedge N)_2Cl}]_2$ were prepared according to [5].

The dendritic bipyridine ligand G1-bpy was prepared according to [7]. A 2 M solution of lithium diisopropylamide in THF–heptane (1.4 ml) was added at –10°C to a solution of 171 mg of 4,4'-dimethyl-2,2'-bipyridine in anhydrous THF. After stirring for 45 min, a solution of 1 g of 3,5-bis(benzyloxy)benzyl bromide in 30 ml of anhydrous THF was added. The resulting solution was stirred for 12 h at room temperature. When the solution became light yellow, the reaction was considered to be complete. The resulting solution was poured onto ice, and the aqueous layer was extracted with dichloromethane (5 × 50 ml). The extract was dried over $\mathrm{Na_2SO_4}$. The solvent was evaporated on a rotary evaporator, and the residue was chromatographed on $\mathrm{SiO_2}$ (eluent dichloromethane–ethyl acetate, 5 : 1 by volume). Fractions with R_f 0.5 (TLC on $\mathrm{SiO_2}$ plates, eluent dichloromethane–methanol, 20 : 1) were combined, and the solvents were removed on a rotary evaporator. The reaction product was dissolved in diethyl ether, precipitated with ethanol, filtered off, and vacuum-dried. Yield 23%. ^{1}H NMR spectrum ($\mathrm{CDCl_3}$), δ, ppm (J, Hz): 8.59 ($\mathrm{H}^{6,6'}$, $^3J_{\mathrm{HH}}$ 5.0, $^5J_{\mathrm{HH}}$ 0.9), 8.32 ($\mathrm{H}^{3,3'}$, $^5J_{\mathrm{HH}}$ 0.9), 7.46–7.35 m ($\mathrm{H}_{o,m,p}$), 7.12 ($\mathrm{H}^{5,5'}$, $^3J_{\mathrm{HH}}$ 5.1), 6.52 ($\mathrm{H}_{p'}$, $^4J_{\mathrm{HH}}$ 2.1), 6.49 ($\mathrm{H}_{o'}$, $^4J_{\mathrm{HH}}$ 2.1), 3.01–2.97 m ($\mathrm{CH_2}$–$\mathrm{CH_2}$), 5.03 s ($\mathrm{CH_2O}$).

$[\mathrm{Ir(ppy)_2(G1\text{-}bpy)}]\mathrm{PF_6}$. To a solution of 30 mg of G1-bpy in $\mathrm{CH_2Cl_2}$–$\mathrm{CH_3OH}$ (5 : 6) we added 20.7 mg of $[\mathrm{Ir(ppy)_2Cl}]_2$. The mixture was refluxed for 12 h. The reaction progress was monitored by TLC ($\mathrm{SiO_2}$, $\mathrm{CH_2Cl_2}$–$\mathrm{CH_3OH}$, 20 : 1). The final solution was cooled to room temperature, and the solvents were removed on a rotary evaporator. The residue was dissolved in a minimal volume of methanol and filtered; a saturated solution of $\mathrm{NH_4PF_6}$ in methanol was added to the filtrate. The resulting yellow precipitate was filtered off, washed with diethyl ether, and vacuum-dried; yield 62%.

$[\mathrm{Ir(tpy)_2(G1\text{-}bpy)}]\mathrm{PF_6}$ was prepared similarly from 30 mg of G1-bpy and 20.9 mg of $[\mathrm{Ir(tpy)_2Cl}]_2$. Yield 67%.

ACKNOWLEDGMENTS

The authors are grateful to staff members of Prof. S. Campagna’s laboratory (University of Messina, Italy) for the assistance in the study.

The study was financially supported by the Ministry of Education of the Russian Federation (grant for young scientists no. PD02-1.3-15).

REFERENCES

1. Lamansky, S., Djurovich, P., Murphy, D., Abdel-Razzag, F., Lee, H.-E., Afachi, C., Burrows, P.E., Forrest, S.R., and Thompson, M.E., *J. Am. Chem. Soc.*, 2001, vol. 123, no. 18, p. 4304.
2. Lamansky, S., Djurovich, P., Murphy, D., Abdel-Razzag, F., Kwong, R., Tsyba, I., Bortz, M., Mui, B., Bau, R., and Thompson, M.E., *Inorg. Chem.*, 2001, vol. 40, no. 7, p. 1704.
3. Grushin, V., Herron, N., LeCloux, D.D., Marshall, W.J., Petrov, V., and Wang, Y., *Chem. Commun.*, 2001, no. 16, p. 1494.
4. Tomayo, A.B., Alleyne, B.D., Djurovich, P., Lamansky, S., Tsyba, I., Ho, N.N., Bau, R., and Thompson, M.E., *J. Am. Chem. Soc.*, 2003, vol. 125, no. 24, p. 7377.
5. Colombo, M.G. and Güdel, H.U., *Inorg. Chem.*, 1993, vol. 32, no. 14, p. 3081.
6. Colombo, M.G., Hauser, A., and Güdel, H.U., *Inorg. Chem.*, 1993, vol. 32, no. 14, p. 3088.
7. Vögtle, F., Plevoets, M., Nieger, M., Azzellini, G., Credi, A., De Cola, L., De Marchis, V., Venturi, M., and Balzani, V., *J. Am. Chem. Soc.*, 1999, vol. 121, no. 26, p. 6290.
8. Ohsawa, Y., Sprouse, S., King, K.A., De Armond, M.K., Hanck, K.W., and Watts, R.J., *J. Phys. Chem.*, 1987, vol. 91, no. 5, p. 1047.
9. Garces, F.O. and Watts, R.J., *Magn. Reson. Chem.*, 1993, vol. 31, no. 5, p. 529.
10. Garces, F.O., King, K.A., and Watts, R.J., *Inorg. Chem.*, 1988, vol. 27, no. 20, p. 3464.
11. Nazeeruddin, Md.K., Humphry-Baker, R., Berner, D., Rivier, S., Zuppiroli, L., and Graetzel, M., *J. Am. Chem. Soc.*, 2003, vol. 125, no. 29, p. 8790.
12. Kwam, P.-I., Puzyk, M.V., Balashev, K.P., and Songstad, J., *Acta Chem. Scand.*, 1995, vol. 49, no. 5, p. 335.
13. Kwam, P.-I., Puzyk, M.V., Cotlyr, V.S., Balashev, K.P., and Songstad, J., *Acta Chem. Scand.*, 1995, vol. 49, no. 9, p. 645.
14. Neve, F., Crispini, A., Campagna, S., and Serroni, S., *Inorg. Chem.*, 1999, vol. 38, no. 10, p. 2250.