Synthesis and Photophysical Properties of Iridium(III) Bisterpyridine and Its Homologues: a Family of Complexes with a Long-Lived Excited State

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Received September 21, 1998

Abstract: A new synthetic procedure has been developed which makes possible the preparation of IrLL′$^{3+}$ complexes (L, L′ = terpyridine derivative) in good yields. In a first step, IrLCl$_3$ is obtained under relatively mild conditions as an intermediate. Subsequent reaction with L′ (a few minutes in refluxing ethylene glycol) affords IrLL′$^{3+}$. The electrochemical behavior and ground- and excited-state spectroscopic properties of four IrLL′$^{3+}$ complexes in nitrile solvents are reported. The X-ray structure of one of these complexes is also described. The complexes have been designed keeping in mind their incorporation in linearly arranged multicomponent arrays, according to a templating strategy based on the assembly of tpy-type ligands by the Ir(III) center. The complexes feature a high-lying level for the luminescent excited state (>2.5 eV), with a satisfactory room-temperature luminescence intensity ($\phi_{em} \approx 10^{-2}$) and lifetime on the microsecond time scale. These favorable properties indicate that the Ir(III)-tpy center will not be the final recipient of the energy-harvesting processes in multipartite systems built around them. Temperature-dependent studies of the luminescence properties in the 95−298 K range indicate that the higher-lying levels of these complexes are not efficient pathways for deactivation of the luminescent states. For these reasons, it is concluded that the studied Ir-tpy-type complexes are well suited (i) to play the role of photoactive center and to gather photo- and electroactive units or (ii) to act as electron relays in linearly arranged multicomponent arrays.

Introduction

To study photoinduced charge separation in multicomponent systems, two available approaches are based on the assembly of the active components via covalent bonds[2a−c] or via weak interactions.[2d,e] The former approach looks appealing because it offers the opportunity to gain a convenient control of the geometric and electronic factors, a theme treated by many research groups.[2,3] Various types of multicomponent arrays have been prepared in the past, and a frequently employed scheme is based on the assembly of a central photoactive core (P) and donor (D) and acceptor (A) electroactive units located on opposite sides.[4] In such systems, and provided the implied energetic requirements are fulfilled, light absorption by P starts

a sequence of elementary electron-transfer events which result in the production of the D$^+$−P−A$^-$ species.

The template strategy is ideally suited to the building up of large-scale assemblies. According to this approach, a transition metal cation, for instance Ru(II),[5] Pt(II),[6] or others,[7] can act as a templating center via coordination of suitable fragments appended to the photo- and electroactive units.[7,8] For instance, Ru(II) coordination of 2,2′:6′,2″-terpyridine (tpy) derivative fragments attached to porphyrins led to assemblies of the type shown in Chart 1.[8,9] The substitution at the 4′-position of the tpy enables the construction of linearly arranged systems and also has the advantage of avoiding the coexistence of geometrical and stereoisomers (present in the case of asymmetrical bidentate ligands). Furthermore, suitable aromatic or aliphatic

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(1) (a) Université Louis Pasteur, Laboratoire de Chimie Organo-Minérale. (b) Istituto FRAE-CNR.

(2) (a) Nishitani, S.; Kurata, N.; Sakata, Y.; Misumi, S.; Karen, A.; Okada, T.; Mataga, N. *J. Am. Chem. Soc.* **1983**, *105*, 7771. (b) Moore, T. A.; Gust, D.; Mathis, P.; Mialocq, J.-C.; Chachaty, C.; Bensasson, R. V.; Land, E. J.; Doizi, D.; Liddell, P. A.; Lehmann, W. R.; Nemeth, G. A.; Moore, A. L. *Nature* **1984**, *307*, 630. (c) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 1080. (d) Sessler, J. L.; Wang, B.; Harriman, A. *J. Am. Chem. Soc.* **1992**, *114*, 388. (e) Deng, Y.; Roberts, J. A.; Peng, S.-M.; Chang, C. K.; Nocera, D. G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2124.

(3) (a) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759. (b) Scandola, F.; Indelli, M. T.; Chiorboli, C.; Bignozzi, C. A. *Top. Curr. Chem.* **1990**, *158*, 63.

(4) (a) Gust, D.; Moore, T. *Top. Curr. Chem.* **1991**, *159*, 103. (b) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 365.

(5) (a) Odobel, F.; Sauvage, J.-P. *New J. Chem.* **1994**, *18*, 1139. (b) Harriman, A.; Odobel, F.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1995**, *117*, 9461.
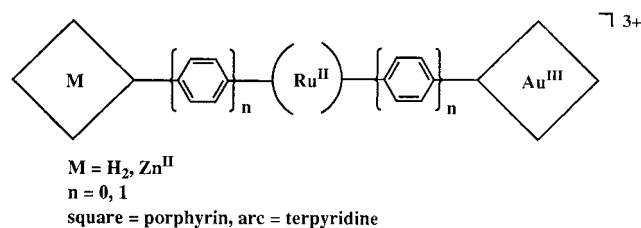
(6) Ziessel, R. *J. Chem. Educ.* **1997**, *74*, 673.

(7) (a) Danielson, E.; Elliott, C. M.; Merkert, J. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 2519. (b) Opperman, K. A.; Mecklenburg, S. L.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 5295. (c) Harriman, A.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1996**, 1707.

(8) Harriman, A.; Sauvage, J.-P. *Chem. Soc. Rev.* **1996**, 41.

(9) (a) Flamigni, L.; Barigelletti, F.; Armaroli, N.; Collin, J.-P.; Sauvage, J.-P.; Williams, J. A. G. *Chem., Eur. J.* **1998**, *4*, 1744. (b) Flamigni, L.; Barigelletti, F.; Armaroli, N.; Ventura, B.; Collin, J.-P.; Sauvage, J.-P.; Williams, J. A. G. submitted to *Inorg. Chem.* (c) Flamigni, L.; Armaroli, N.; Barigelletti, F.; Balzani, V.; Collin, J.-P.; Dalbavie, J.-O.; Heitz, V.; Sauvage, J.-P. *J. Phys. Chem. B* **1997**, *101*, 5936. (d) Collin, J.-P.; Dalbavie, J.-O.; Heitz, V.; Sauvage, J.-P.; Flamigni, L.; Armaroli, N.; Balzani, V.; Barigelletti, F.; Montanari, I. *Bull. Soc. Chim. Fr.* **1996**, *133*, 749.

Chart 1

M = H$_2$, Zn^{II}
n = 0, 1
square = porphyrin, arc = terpyridine

Chart 2

M = H$_2$, Zn^{II}
square = porphyrin, arc = terpyridine

Chart 3

spacers[10,11] can be inserted between the templating center and the active units, leading to systems with a varied intercomponent distance.

In one of these arrays,[9] the Ru-based core was found to be extensively involved in energy-transfer processes, mainly because of the presence of low-lying Ru → tpy charge-transfer levels, located at 2 eV.[9a,b] Indeed, energy transfer from the primary singlet porphyrin excited state to the ^{3}MLCT excited state localized on the complex was found to be competitive with the desired electron-transfer step. There are cases in which the templating center is wished not to take part in the energy-transfer events within the array. In such cases, the metal center should not possess easily accessible excited states so that its role, in addition to a structural one, will likely be restricted to that of an electroactive unit.

An additional pitfall of arrays based on a Ru(tpy)$_2$$^{2+}$ core is the fact that, in this chromophore, the lowest-lying excited state undergoes a fast deactivation, its lifetime being shorter than 1 ns.[12] One undesired consequence is that long-distance intercomponent steps may be scarcely competitive toward the intrinsic deactivation of the templating unit.[9c] Concerning the possible use of the longer-lived Os-based analogues, limitations arise from the low energy level of their MLCT luminescent states (around 1.6 eV[12]). On this basis, Os(tpy)$_2$$^{2+}$ is bound to play a dominant, parasitic role as an energy sinker with respect to the processes taking place in the assembly.

Consideration of our previous attempts[9] has led us to start the design of multicomponent systems based on Ir(III)-tpy-type templating centers,[13–15] where the convenient geometric properties brought about by the tpy ligand[11,12] are combined with the high energy content of the excited states of the Ir(III) centers (see below)[14,15] and a fair ability to accept electrons. Chart 2
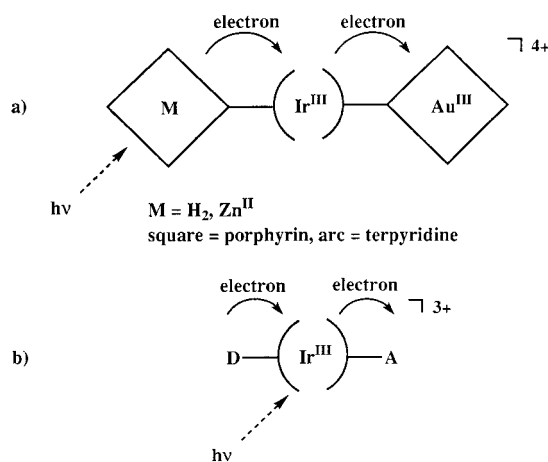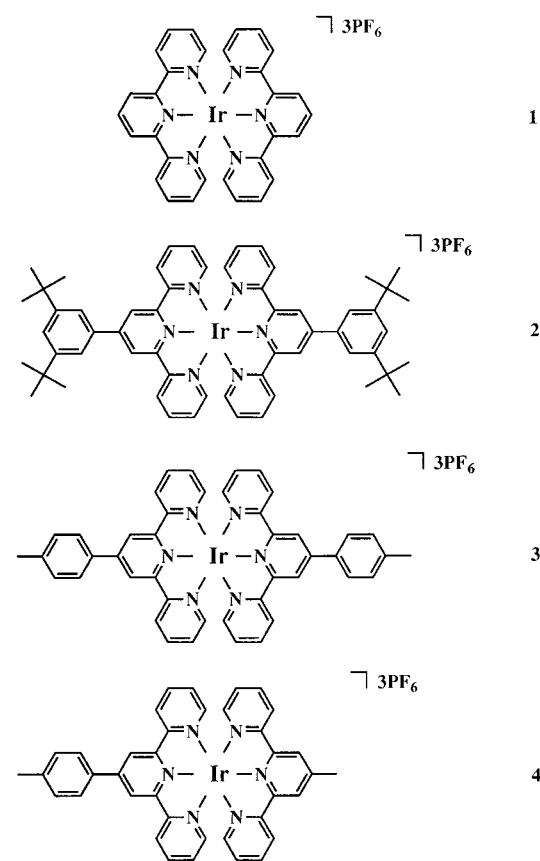
summarizes two possible uses of the Ir(tpy)$_2$$^{3+}$ core, (a) as assembling metal and electron relay or (b) as photoactive center and electron relay.

In this report, we describe the synthesis, the electrochemical behavior, and the spectroscopic and photophysical properties of complexes **1**−**4** (Chart 3) and the X-ray structure of **1**. We performed a detailed investigation of their photophysical properties, particularly with respect to the possible role of high-lying,

(10) Barigelletti, F.; Flamigni, L.; Collin, J.-P.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1997**, 333.

(11) A list of representative papers follows: (a) Boyde, S.; Strouse, G. F.; Jones, W. E., Jr.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 7395. (b) Scandola, F.; Argazzi, R.; Bignozzi, C. A.; Indelli, M. T. *J. Photochem. Photobiol. A: Chem.* **1994**, *82*, 191. (c) Show, J. R.; Webb, R. T.; Schmehel, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 7395. (d) De Cola, L.; Balzani, V.; Barigelletti, F.; Flamigni, L.; Belser, P. Von Zelewsky, A., Franck, M.; Vögtle, F. *Inorg. Chem.* **1993**, *32*, 5228. (e) Vögtle, F.; Franck, M.; Nieger, M.; Belser, P.; Von Zelewsky, A.; Balzani, V.; Barigelletti, F.; De Cola, L.; Flamigni, L. *Angew. Chem. Int. Ed.* **1993**, *32*, 1643. (f) Benniston, A. C.; Grosshenny, V.; Harrimann, A.; Ziessel, R *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1884. (g) Benniston, A. C.; Goulle, V.; Harriman, A.; Lehn, J.-M.; Marczinke, B. *J. Phys. Chem.* **1994**, *98*, 7798. (h) Ho, P. K.-K.; Cheung, K.-K.; Che, C.-M. *J. Chem. Soc., Chem. Commun.* **1996**, 1197. (i) Vogler, L. M.; Brewer, K. J. *Inorg. Chem.* **1996**, *35*, 818. (j) Bolger, J.; Gordon, A.; Ishow, E.; Launay, J.-P. *J. Chem. Soc., Chem. Commun.* **1995**, 1799. (k) Wärnmark, K.; Thomas, J. A.; Heyke, O.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1996**, 701.

(12) Sauvage, J.-P.; Collin, J.-P.; Chambron, J.-C.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelletti, F.; De Cola, L.; Flamigni, L. *Chem. Rev.* **1994**, *94*, 993 and references therein.

(13) (a) Ayala, N. P.; Flynn, C. M., Jr.; Sacksteder, L.; Demas, J. N.; DeGraff, B. A. *J. Am. Chem. Soc.* **1990**, *112*, 3837. (b) Mamo, A.; Stefio, I.; Parisi, M. F.; Credi, A.; Venturi, M.; Di Pietro, C.; Campagna, S. *Inorg. Chem.* **1997**, *36*, 5947. For Ir(III) complexes of bidentate ligands, see ref 14. Ir(III) complexes have also been employed for photoinitiated energy collection in polymetallic species; see ref 15.

(14) (a) Watts, R. J.; Crosby, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 3184. (b) Flynn, C. M., Jr.; Demas, J. N. *J. Am. Chem. Soc.* **1974**, *96*, 1959. (c) Schmid, B.; Garces, F. O.; Watts, R. J. *Inorg. Chem.* **1994**, *33*, 9. (d) Ohsawa, Y.; Sprouse, S.; King, K. A.; DeArmond, M. K.; Hanck, K. W.; Watts, R. J. *J. Phys. Chem.* **1987**, *91*, 1047. (e) Didier, P.; Otmans, I.; Kirsch-De Mesmaeker, A.; Watts, R. J. *Inorg. Chem.* **1993**, *32*, 5239.

(15) (a) Molnar, S. M.; Nallas, G.; Bridgewater, J. S. Brewer, K. J. *J. Am. Chem. Soc.* **1994**, *116*, 5206. (b) Nallas, G. N. A.; Jones, S. W.; Brewer, K. J. *Inorg. Chem.* **1996**, *35*, 6980.

but thermally accessible, excited states. Given that, in these arrays, the distance (and the electronic coupling) between the opposite components will be varied by using 1,4-phenylene spacers, the coordinated ligands of **1–4** feature a varying number of aryl substituents.

Experimental Section

General Procedures. The following chemicals were obtained commercially and were used without further purification: KPF_6 (Janssen), NH_4PF_6 (Aldrich), 2-acetylpyridine (Lancaster), ammonium acetate (Prolabo), acetamide (Acros), 2,2′:6′,2″-terpyridine (Aldrich), $IrCl_3$ (Johnson Matthey), and $IrCl_3 \cdot 4H_2O$ (Pressure Chemical). Thin-layer chromatography was performed using plastic sheets coated with silica or neutral alumina (Macherey-Nagel). Column chromatography was carried out on silica gel 60 (Merck, 63–200 μm) or neutral alumina 90 (Merck, 63–200 μm).

Starting Organic Compounds. 3,5-Di-*tert*-butylbenzaldehyde,[16] 4′-tolyl-2,2′:6′,2″-terpyridine (ttpy),[17] and 4′-methyl-2,2′:6′,2″-terpyridine (Metpy)[18] were prepared according to literature procedures.

4′-(3,5-Di-*tert*-butylphenyl)-2,2′:6′,2″-terpyridine (tButpy). 2-Acetylpyridine (5 g, 0.04 mol), 3,5-di-*tert*-butylbenzaldehyde[16] (4.5 g, 0.02 mol), ammonium acetate (23 g, 0.3 mol), and acetamide (35 g, 0.6 mol) were heated to 160 °C for 2 h. After the mixture was cooled to 100 °C, NaOH (20 g in 40 mL of H_2O) was added very slowly, and this mixture was heated to 120 °C for a further 2 h without stirring. The two phases were decanted, and the black supernatant was taken into dichloromethane and washed with water. Chromatography on alumina (hexane/ether from 100/0 to 97/3) gave **tButpy** in 27% yield (2.32 g).

^{1}H NMR (200 MHz, CD_2Cl_2): δ 8.74 (m, 2H, H_6); 8.72 (s, 2H, $H_{3'}$ + $H_{5'}$); 8.69 (m, 2H, H_3); 7.91 (ddd, 2H, H_4, ^3J = 7.6 Hz, ^4J = 1.7 Hz); 7.67 (d, 2H, H_o, ^4J = 1.7 Hz); 7.58 (t, 1H, H_p, ^4J = 1.7 Hz); 7.37 (ddd, 2H, H_5, ^3J = 6 Hz, ^3J = 7.6 Hz, ^4J = 1.2 Hz); 1.43 (s, 18H, CH_3). EI$^+$-MS: m/z 421.4 (M$^+$, $C_{29}H_{31}N_3$ requires 421.58); 406.4 ([M − CH_3]$^+$); 350.3 ([M − CH_3 − t-Bu]$^+$).

Ir(tpy)Cl$_3$. 2,2′:6′,2″-Terpyridine (**tpy**, 66 mg, 0.28 mmol) and $IrCl_3$ (104 mg, 0.28 mmol) were heated at 160 °C in degassed ethylene glycol (5 mL), under argon and in the dark, for 15 min, during which a red precipitate formed. It was filtered off after cooling to room temperature and was washed with EtOH, H_2O, and Et_2O to give pure **Ir(tpy)Cl$_3$** in a 40% yield (60 mg) as an orange-red solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.23 (dd, 2H, H_6, ^3J = 5.4 Hz, ^4J = 0.7 Hz); 8.78 (d, 2H, H_3, ^3J = 8 Hz); 8.74 (d, 2H, $H_{3'}$ + $H_{5'}$, ^3J = 8 Hz); 8.34–8.20 (m, 3H, H_4 + $H_{4'}$); 7.98 (ddd, 2H, H_5, ^3J = 6 Hz, ^4J = 0.7 Hz).

Ir(tpy)$_2$(PF$_6$)$_3$ (1). Ir(tpy)Cl$_3$ (40 mg, 0.075 mmol) and **tpy** (17.5 mg, 0.075 mmol) were heated to reflux in degassed ethylene glycol (3 mL), under argon and in the dark, for 15 mn. After evaporation of the solvent and precipitation with an aqueous solution of KPF_6, crude **Ir(tpy)$_2$$^{3+}$** was purified by crystallization in acetone/MeOH/toluene and MeCN/benzene and by column chromatography (Al_2O_3, acetone/water from 100/0 to 95/5) to give **1** in a 61% yield (50 mg). Pale yellow single crystals were obtained by slow diffusion from a 1:3 (v/v) acetone/benzene mixture.

^{1}H NMR (200 MHz, acetone-d_6): δ 9.21 (d, 4H, H_6, ^3J = 8.1 Hz); 8.94 (t, 2H, $H_{4'}$, ^3J = 8.2 Hz); 8.93 (d, 4H, $H_{3'}$ + $H_{5'}$, ^3J = 8.1 Hz); 8.36 (ddd, 4H, H_4, ^3J = 7.9 Hz, ^4J = 1.5 Hz); 8.11 (dd, 4H, H_3, ^3J = 5.7 Hz, ^4J = 0.8 Hz); 7.62 (ddd, 4H, H_5, ^3J = 8 Hz, $^4J_{5-3}$ = 1.5 Hz). FAB$^+$-MS: m/z 949 ([M − PF_6]$^+$, $C_{30}H_{22}N_6IrP_2F_{12}$ requires 949).

Ir(tButpy)Cl$_3$. tButpy (120 mg, 0.28 mmol) was dissolved in refluxing absolute ethanol (100 mL). A solution of $IrCl_3 \cdot 4H_2O$ (100 mg, 0.27 mmol) in absolute ethanol (30 mL) was then added dropwise, and this mixture was heated to reflux in the dark for 3 h. The crude

mixture was evaporated to dryness, dissolved in CH_2Cl_2, and chromatographed on alumina (hexane/ether 100/0 to 0/100, then CH_2Cl_2/MeOH 99/1) to give pure **Ir(tButpy)Cl$_3$** in a 43% yield (88 mg) as an orange-red solid.

^{1}H NMR (200 MHz, CD_2Cl_2): δ 9.45 (ddd, 2H, H_6 + $H_{6''}$, ^3J = 5.7 Hz, ^4J = 1.5 Hz, ^5J = 0.7 Hz); 8.26–8.22 (m, 4H, $H_{3'}$ + $H_{5'}$ + H_3 + $H_{3''}$); 8.04 (ddd, 2H, H_4 + $H_{4''}$, ^3J = 7.9 Hz, ^4J = 1.7 Hz); 7.75 (ddd, 2H, H_5 + $H_{5''}$, ^3J = 7.3 Hz, ^4J = 1.5 Hz); 7.65 (t, 1H, H_p, ^4J = 1.7 Hz); 7.56 (d, 2H, H_o, ^4J = 1.7 Hz), 1.43 (s, 18H, CH_3). FAB$^+$-MS: m/z 719 ([M]$^+$, $C_{29}H_{31}N_3IrCl_3$ requires 720).

Ir(tButpy)$_2$(PF$_6$)$_3$ (2). Ir(tButpy)Cl$_3$ (100 mg, 0.14 mmol) and **tButpy** (60 mg, 0.14 mmol) were heated to 140 °C in degassed ethylene glycol (40 mL), under argon and in the dark, for 2 h 30. The solvent was evaporated under reduced pressure, and the crude mixture was dissolved in MeCN. After precipitation with an aqueous solution of KPF_6, the yellow solid was recrystallized twice from CH_2Cl_2/THF to give **2** in a 40% yield (82 mg).

^{1}H NMR (200 MHz, acetone-d_6): δ 9.52 (s, 2H, $H_{3'}$ + $H_{5'}$); 9.12 (d, 2H, H_6 + $H_{6''}$, ^3J = 7.4 Hz); 8.32 (ddd, 2H, H_4 + $H_{4''}$, ^3J = 7.5 Hz, ^4J = 1.2 Hz); 8.25 (dd, 2H, H_3 + $H_{3''}$, ^3J = 6.3 Hz, ^4J = 1.1 Hz); 8.10 (d, 2H, H_o, ^4J = 1.7 Hz); 7.86 (t, 1H, H_p, ^4J = 1.8 Hz); 7.65 (ddd, 2H, H_5 + $H_{5''}$, ^3J = 6.9 Hz, ^4J = 1.2 Hz); 1.50 (s, 36 H, tBu). ES$^+$-MS: m/z 1325 ([M − PF_6]$^+$, $C_{58}H_{62}N_6IrP_2F_{12}$ requires 1325).

Ir(ttpy)$_2$(PF$_6$)$_3$ (3) and Ir(ttpy)(Metpy)(PF$_6$)$_3$ (4). $IrCl_3 \cdot 4H_2O$ (120 mg, 0.34 mmol) in solution in EtOH (2.5 mL) was added to a solution of **ttpy**[17] (110 mg, 0.34 mmol) in hot EtOH (5 mL). Immediate precipitation of a red-brown solid was observed. Heating was continued for a further 5 h, and the solid was isolated by filtration and washed with EtOH, toluene, and Et_2O. This solid was assumed to be **Ir(ttpy)-Cl$_3$**, and a portion of the product (100 mg, 0.16 mmol) was taken into ethylene glycol (5 mL). **Metpy**[18] (40 mg, 0.16 mmol) was added to the resulting suspension. Upon heating to 180 °C, the solid rapidly dissolved, giving a dark green solution, which turned red after a further 1 h at this temperature. The crude mixture was then purified by column chromatography (SiO_2, from CH_3CN to 70% CH_3CN/29% H_2O/1% saturated KNO$_3$ solution). After elution of small quantities of a number of highly-colored compounds, **Ir(ttpy)$_2$(NO$_3$)$_3$ (3′)** was obtained (20 mg, 12%), followed by **Ir(ttpy)(Metpy)(NO$_3$)$_3$ (4′)** (20 mg, 13%). **3** and **4** could be separately isolated through anion exchange using NH_4PF_6.

Data for 3′. ^{1}H NMR (300 MHz, D_2O/CD$_3$CN): δ 9.11 (4H, s, $H_{3'}$); 8.72 (4H, d, H_6, J = 8.2 Hz); 8.19 (4H, dd, H_5, coupling constants too similar to allow exact values); 8.08 (4H, d, H_o, J = 8.3 Hz); 7.68 (4H, d, H_3, J = 5.3 Hz); 7.57 (4H, d, H_m, J = 8 Hz); 7.47 (4H, dd, H_4, coupling constants too similar to allow exact values); 2.49 (6H, s, CH$_3$). FAB$^+$-MS: m/z 963.5 ([M − NO$_3$]$^+$, $C_{44}H_{34}N_8O_6Ir$ requires 963).

Data for 4′. ^{1}H NMR (300 MHz, D_2O): δ 9.04 (2H, s, $H_{3'}$ (ttpy)); 8.70 (2H, s, $H_{3'}$ (Metpy)); 8.61 (2H, d, H_6 (ttpy), J = 8.2 Hz); 8.49 (2H, d, H_6 (Metpy), J = 8.3 Hz); 8.10 and 8.08 (4H, two overlapping dd, H_5 (ttpy) and H_5 (Metpy)); 7.95 (2H, d, H_o (ttpy), J = 8 Hz); 7.64 (2H, d, H_3 (ttpy), J = 10.4 Hz); 7.59 (2H, d, H_3 (Metpy), J = 8.6 Hz); 7.47 (2H, d, H_m (ttpy), J = 8.2 Hz); 7.37 and 7.35 (4H, two overlapping dd, H_4 (ttpy) and H_4 (Metpy)). FAB$^+$-MS: m/z 887 ([M − NO$_3$]$^+$, $C_{38}H_{30}N_8O_6Ir$ requires 887). ES$^+$-MS: m/z 380.4 ([M − 3NO$_3$]$^{2+}$, [$C_{38}H_{30}N_6Ir$]$^{2+}$ requires 381.5).

Equipment and Methods. ^{1}H NMR spectra were acquired on either a Bruker WP200 SY, a Bruker AC300, or a Bruker AM400 spectrometer, using the deuterated solvent as the lock and residual solvent as the internal reference. Mass spectra were obtained by using a VG ZAB-HF spectrometer (FAB), a Fisons VG Platform (ES), or a Fisons VG Trio 2000 (EI) spectrometer. Cyclic voltammetry experiments were performed using an EG&G 273A potentiostat, a Pt working electrode, a Pt counter-electrode, a saturated calomel electrode (SCE), 0.1 M Bu$_4$-NPF$_6$ as supporting electrolyte, and MeCN and DMF as solvents. Details concerning the crystal structure are given in Table 2. For all computations, the MolEN package was used.[19] Absorption spectra were recorded with a Perkin-Elmer Lambda 9 spectrophotometer in dilute ($\sim$10^{-5} M) acetonitrile solution. Luminescence experiments were performed (i) in

(16) Newman, M. S.; Lee, L. F. *J. Org. Chem.* **1972**, *26*, 4468.

(17) (a) Collin, J.-P.; Guillerez, S.; Sauvage, J.-P.; Barigelletti, F.; De Cola, L.; Flamigni, L.; Balzani, V. *Inorg. Chem.* **1991**, *30*, 4230. (b) Spahni, W.; Calzaferri, G. *Helv. Chim. Acta* **1984**, *67*, 450.

(18) Collin, J.-P.; Harriman, A.; Heitz, V.; Odobel, F.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 5679.

(19) Fair, C. K. In *MolEN, An interactive intelligent system for crystal structure analysis*; Nonius: Delft, The Netherlands, 1990.

air-equilibrated or deaerated acetonitrile solution at room temperature in 1-cm cuvettes, (ii) in butyronitrile rigid matrix at 77 K (liquid nitrogen temperature) by using samples contained in capillary tubes immersed in a quartz finger Dewar, and (iii) in butyronitrile solvent in the temperature interval between 293 and 90 K. For the latter case, we employed a Thor Research cryostat and temperature controller. The cryostat was home-modified by substituting the original sample holder with a cell holder for hosting sealed quartz cells. The actual temperature within the cells was obtained through calibration with the help of an external thermocouple, which enabled comparison of the temperatures indicated on the controller with true temperatures monitored by the thermocouple; the uncertainty on the measured temperature was 2 K. Deaerated samples were prepared at a vacuum line through pump−freeze−thaw repeated cycles and stored in sealed quartz cells. Luminescence spectra were obtained from a Spex Fluorolog II spectrofluorometer equipped with a Hamamatsu R928 phototube. Uncorrected luminescence band maxima are used throughout the text unless otherwise stated. Luminescence quantum yields, ϕ, were obtained as already published[20] and were computed by following the method described by Demas and Crosby.[21] The experimental uncertainty in the band maximum for absorption and luminescence spectra is 2 nm; for luminescence quantum yields it is 20%. Luminescence lifetimes were obtained with an IBH single-photon-counting apparatus (N_2 lamp, excitation at 337 nm). The uncertainty on the evaluated lifetimes is 8%.

Transient absorption spectra were acquired by a pump and probe method based on a 35-ps Nd:YAG laser (Continuum PY62-10) and an OMA detector system described elsewhere.[9c] Excitation was performed at 355 nm with 2.5 mJ/pulse; the absorbance of the samples at the excitation wavelength was 0.9. The lifetimes of absorbing states were determined by a laser flash photolysis apparatus with 20 ns resolution,[22a,b] excitation at 355 nm, and 2 mJ/pulse. The uncertainty on the evaluated lifetimes is 10%.

Results and Discussion

Syntheses. To the best of our knowledge, the synthesis of iridium(III) bisterpyridine-type complexes has only been described once in the literature, by Ayala and colleagues.[13a] This procedure is based on a previously published synthesis of $Ir(bpy)_3^{3+}$ (bpy = 2,2′-bipyridine),[14b] which entails melting the inorganic precursor at 220 °C for 30 min and then heating it at 230 °C in the presence of the ligand for 6 h. The harsh reaction conditions required and the tremendously difficult purification led us to investigate a new synthetic pathway.

Our first attempts starting from labile Ir(I) complexes ([Ir(COD)Cl]$_2$, COD = 1,5-cyclooctadiene, or [Ir$_2$(μ-Cl)$_2$(COE)$_4$],[23] COE = cyclooctene), inspired by results from Mønsted et al.[24] and from Suzuki et al.,[25] led us to the desired complexes but in poor yields (13% for **2**). The method described by Sullivan and Meyer[26] for the synthesis of $Ir(bpy)_3^{3+}$ seemed milder than that of Flynn and Demas,[14b] but in the perspective of using terpyridine ligands bearing donor or acceptor groups of the porphyrinic type, we decided to explore a simpler experimental procedure.

Table 1. Electrochemical Data of Complexes **1−4**

	$E_{red}{}^a$ (V vs SCE)		$E_{red}{}^b$ (V vs SCE)	
1	−0.77	−0.93	−0.76	−0.91
2	−0.74	−0.92	−0.77*	−0.92*
3	insoluble		−0.81	−0.91
4	−0.81	−0.97	−0.81	−0.89
				−1.04

^{a} MeCN, Bu$_4$NPF$_6$ 0.1 M. ^{b} DMF, Bu$_4$NPF$_6$ 0.1 M. All processes were irreversible, except those indicated with an asterisk.

The classical method used for ruthenium(II) and rhodium(III) terpyridine complexes starts with the preparation of M(tpy)Cl$_3$ (M = Ru(II) or Rh(III)).[27] This stepwise method also has the advantage of allowing the preparation of asymmetrical systems, provided the complexes are kinetically inert. As one would expect, the coordination of the first terpyridine is easier than the introduction of the second one, the latter requiring the dechlorination of the M(tpy)Cl$_3$ precursor. With iridium(III), the classical procedures (e.g., with AgBF$_4$ in refluxing acetone, which has been used with Ir(I)[28]) were unsuccessful, probably due to the great inertness of such complexes.

Depending on the nature of the terpyridine ligand, the reaction conditions have to be adapted. The formation of **Ir(tpy)Cl$_3$** required the reaction of IrCl$_3$ and **tpy** in ethylene glycol at 160 °C, for solubility reasons. On the other hand, **Ir(tButpy)Cl$_3$** and **Ir(ttpy)Cl$_3$** were prepared by reacting IrCl$_3$·4H$_2$O and **tButpy** or **ttpy** in refluxing ethanol, for 3 and 5 h, respectively. **Ir(tButpy)Cl$_3$** was soluble in common solvents and could, therefore, be purified by chromatography, unlike **Ir(tpy)Cl$_3$** and **Ir(ttpy)Cl$_3$**.

Complexes **1−4** were obtained by reacting Ir(L)Cl$_3$ (L = tpy derivative) with the second terpyridine ligand in degassed ethylene glycol under argon, at various temperatures (varying from 140 to 196 °C) and for relatively short periods of time (from 15 min to 2.5 h). The preparation of **1** required refluxing ethylene glycol for 15 min, whereas the preparation of **2** was achieved after 2.5 h at 140 °C. **3** and **4** were obtained by reaction of **Ir(ttpy)Cl$_3$** and **Metpy** at 180 °C for 1 h, **3** being the scrambled product. One has to keep in mind that the higher the temperature and the longer the reaction time, the higher the probability of preparing orthometalated complexes and other byproducts.[13b] For our purpose, we tried to minimize these two parameters in order to avoid orthometalation.[29] All four complexes were easily purified, either by crystallization (**1** and **2**) or by column chromatography on alumina (**1**) or on silica (**3** and **4**). **1** is pale yellow, whereas **2**, **3**, and **4** are yellow. **1** shows blue luminescence on TLC plates under 365 nm irradiation, while **2**, **3**, and **4** show bright green luminescence under similar conditions. The purity of the complexes (impurity level estimated lower than 1%) was carefully cheked by thin-layer chromatography, high-resolution ^{1}H NMR spectroscopy, and mass spectrometry.

Electrochemistry. Cyclic voltammetry data are reported in Table 1. The reduction potentials we report here are analogous to those of $Ir(bpy)_3^{3+}$ published by Kahl et al.[30] Two one-electron reduction waves are observed and are ligand-centered.[31]

(20) Hammarström, L.; Barigelletti, F.; Flamigni, L.; Indelli, M. T.; Armaroli, A.; Calogero, G.; Guardigli, M.; Sour, A.; Collin, J.-P., Sauvage, J.-P. *J. Phys. Chem. A* **1997**, *101*, 9061.

(21) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.

(22) (a) Flamigni, L. *J. Phys. Chem.* **1992**, 96, 3331. (b) Flamigni, L. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2331.

(23) Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *15*, 18.

(24) Mønsted, L.; Mønsted, O.; Nord, G.; Simonsen, K. *Acta Chem. Scand.* **1993**, *47*, 439.

(25) Suzuki, T.; Rude, M.; Simonsen, K.; Morooka, M.; Tanaka, H.; Ohba, S.; Galsbøl, F.; Fujita, J. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1013.

(26) Sullivan, B. P.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1984**, 403.

(27) Sullivan, B. P.; Calvert, J. M.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 1404.

(28) Mueting, A. M.; Alexander, B. D.; Boyle, P. D.; Casalnuovo, A. L.; Ito, L. N.; Johnson, B. J.; Pignolet, L. H. *Inorg. Synth.* **1992**, *29*, 279.

(29) Nord, G.; Hazell, A. C.; Hazell, R. G.; Farver, O. *Inorg. Chem.* **1983**, *22*, 3429.

(30) Kahl, J. L.; Hanck, K. W.; DeArmond, K. *J. Phys. Chem.* **1978**, *82*, 540.

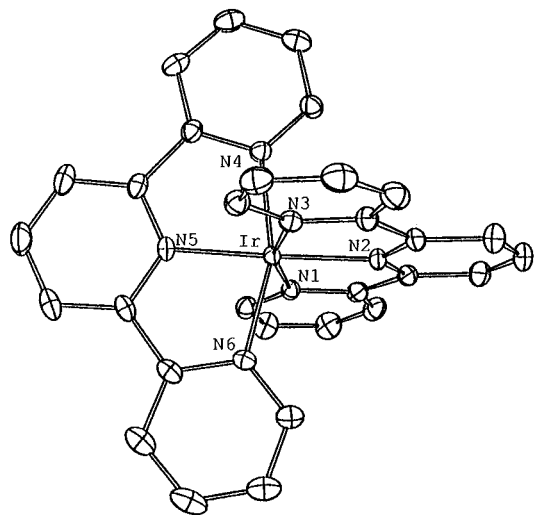(31) Coombe, V. T.; Heath, G. A.; MacKenzie, A. J.; Yellowlees, L. J. *Inorg. Chem.* **1984**, *23*, 3423.

Figure 1. ORTEP representation of the X-ray structure of **1**. The solvent molecules, PF$_6$ anions, and hydrogens have been omitted for clarity. Thermal ellipsoids are scaled to enclose 30% of the electronic density. Selected distances (Å) and angles (deg): Ir−N(1), 2.054; Ir−N(2), 1.979; Ir−N(3), 2.056; Ir−N(4), 2.058; Ir−N(5), 1.978; Ir−N(6), 2.056. N(1)−Ir−N(2), 80.3; N(1)−Ir−N(3), 160.2; N(2)−Ir−N(3), 80.0; N(1)−Ir−N(4), 92.4; N(1)−Ir−N(5), 100.4; N(1)−Ir−N(6), 91.4; N(2)−Ir−N(4), 97.9; N(2)−Ir−N(5), 177.8; N(2)−Ir−N(6), 101.7.

The oxidation of Ir(III) into Ir(IV) was not observed, probably taking place out of the potential range we used (from −1.4 to +2.4 V vs SCE, scan rate 200 mV/s). All waves were irreversible, likely due to adsorption of the reduced species, except for complex **2** in DMF.

X-ray Structure of Complex 1. Pale yellow single crystals of **1** were obtained by slow diffusion of benzene into an acetone solution of the complex (1:3 (v/v) acetone/benzene). The ORTEP representation of **1** is shown in Figure 1. By comparison with the most relevant X-ray structures of Ir(III) complexes in the literature (Ir(bipy)$_3$(ClO$_4$)·2.33H$_2$O[32] and Ir(2,3,5,6-tetrakis-(2-pyridyl)pyrazine)Cl$_3$[33]), one sees that the Ir−N distances and the N−Ir−N angles found in **1** are very close to the previously reported data. Ir−N average bond lengths are 1.980 Å for the central pyridine rings and 2.056 Å for the peripheral cycles. The angle between the two ortho substituents on the central pyridine ring is 102.5°, which reflects a relatively distorted coordination octahedron around Ir(III).

Spectroscopic and Photophysical Properties. The ground-state absorption spectra of the investigated complexes are displayed in Figure 2. Table 3 reports the absorption maxima and intensities. The energy onset and the resolved profiles characterized by peaks with extinction coefficients of the order of 10^4−10^5 M^{-1} cm^{-1} are, as expected for predominantly ligand-centered transitions (^{1}LC), consistent with previous reports of Ir(III) complexes of bpy and tpy ligands.[13−15] The absorption intensities are slightly different in the series, presumably due to the different number of aromatic rings present in the complexes (Table 3). This seems to be in agreement with the fact that the least intense spectrum in the series is that for **1**, where the coordinated ligand is unsubstituted tpy. A similar line of reasoning can likely be used for the energy onset: the onset for **1** corresponds to a higher energy level than for the other cases, which presumably may be ascribed to the smaller electronic delocalization expected for the case of tpy with respect to a 4′-aryl-2,2′:6′,2′′-terpyridine.[34]

(32) Hazell, A. C.; Hazell, R. G. *Acta Crystallogr.* **1984**, *C40*, 806.
(33) Vogler, L. M.; Scott, B.; Brewer, K. J. *Inorg. Chem.* **1993**, *32*, 898.

Table 2. X-ray Experimental Data of Complex **1**

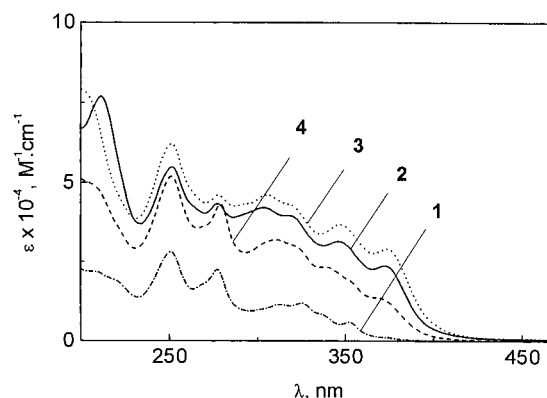| formula	C$_{30}$H$_{22}$N$_6$Ir·3PF$_6$
molecular weight	1093.64
crystal system	monoclinic
space group	$P12_1/c1$
a (Å)	19.2566(2)
b (Å)	16.3846(2)
c (Å)	11.2328(1)
β (deg)	98.349(8)
V (Å^3)	3506.5(2)
Z	4
color	yellow
crystal dimens (mm)	0.20 × 0.15 × 0.10
D_{calc} (g cm^{-3})	2.07
F_{000}	2112
μ (mm^{-1})	4.055
temp (K)	173
wavelength (Å)	0.710 73
radiation	Mo Kα graphite-monochromated
diffractometer	KappaCCD
scan mode	ϕ scans
hkl limits	0.13/0.22/ −24.24
θ limits (deg)	2.5/29.55
no. of data measd	34 171
no. of data with $I > 3\sigma(I)$	7436
weighting scheme	$4F_o{}^2/(\sigma^2(F_o{}^2) + 0.0064F_o{}^4)$
no. of variables	595
R	0.034
R_w	0.052
GOF	1.115
largest peak in final difference (e Å^{-3})	0.798

Figure 2. Room-temperature absorption spectra of acetonitrile solutions of **1**−**4**.

Table 3. Ground-State Absorption Maxima and Intensities[a]

	λ_{max}/nm (ϵ/M^{-1} cm^{-1})
1	210 (21 400); 221 (18 500); 251 (27 600); 277 (22 200); 313 (11 400); 325 (11 800); 336 (8500); 352 (5800); 374 (1300)
2	211 (77 000); 251 (55 000); 277 (43 300); 304 (42 200); 320 (39 500); 346 (31 400); 372 (23 800)
3	205 (77 400); 251 (62 300); 278 (45 900); 305 (46 200); 321 (43 000); 347 (36 800); 373 (29 000)
4	209 (48 000); 251 (52 000); 279 (43 200); 310 (31 900); 322 (29 500); 340 (23 300); 354 (18 000); 372 (13 200)

[a] Acetonitrile solvent.

Another feature of the spectral profiles of Figure 2 is the absorption tail on the low-energy side, which is apparent for all complexes but less pronounced for **1**. In principle, this tail could be due to (i) contribution from low-energy metal-to-ligand charge transfer (^{1}MLCT) transitions, (ii) formally forbidden

(34) (a) Damrauer, N. H.; Boussie, T. R.; Devenney, M.; McCusker, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 8253. (b) Damrauer, N. H.; Weldon, B. T.; McCusker, J. K. *J. Phys. Chem. A* **1998**, *102*, 3382.
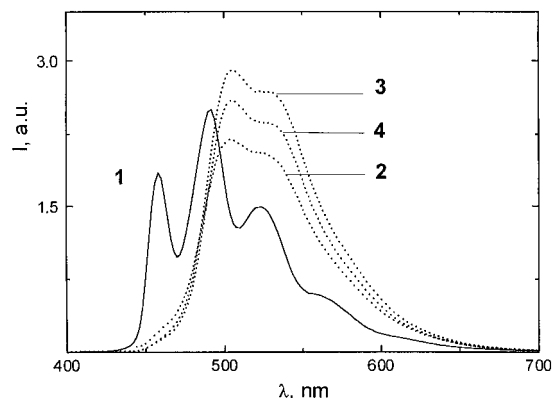
Figure 3. Room-temperature luminescence spectra of air-equilibrated isoabsorbing acetonitrile solutions of **1**−**4**; λ_{exc} was 350 nm.

transitions leading to direct population of triplet levels ($S_0 \rightarrow$ T), because of the heavy atom effect,[35] (iii) population of metal-centered (^{1}MC) levels, or (iv) conjugation effects due to the aryl group borne by the 4′-position of the tpy nucleus. Assuming an Ir^{III}/Ir^{IV} oxidation potential value of +2.4 V vs SCE or greater, and given that the tpy ligand reduction occurs at about −0.8 V vs SCE, we expect the ^{1}MLCT excited state to have an energy content of roughly 3.2 eV, which corresponds to absorption around 387 nm or below.

Figure 3 shows room-temperature luminescence spectra for air-equilibrated acetonitrile solutions of the complexes, the excitation wavelength being λ_{exc} = 350 nm in all cases. The spectra are vibrationally resolved, and their temporal decay occurs with lifetime values on the microsecond time scale (see below). On the basis of these observations, the luminescence is tentatively ascribed to ^{3}LC excited states, as had been previously reported for Ir(tpy)$_2$(CF$_3$SO$_3$)$_3$,[13a] even if some MLCT character might contribute to the emission. By comparison of the spectral profiles, one sees that the highest energy band maximum in the series is that for **1**, with λ = 458 nm, while for **2**, **3**, and **4**, λ = 506 nm. This result is in agreement with the absorption data and indicates that the luminescent level of **1** is higher in energy by ∼2000 cm^{-1} with respect to the other complexes.

It can be noted that the room-temperature luminescence profiles of **2**−**4** closely overlap each other and that they are less vibrationally resolved than the spectrum of **1**. The difference in energy and shape between the luminescence spectra for **1** and the other complexes can likely be ascribed to the predominant LC nature of the excited states. Actually, (i) for **1** the LC excited state is to be restricted on the tpy frame, while, on the contrary, for **2**−**4** a larger ligand framework is available and (ii) for the latter complexes, the dihedral angle between the proximate rings of the tolyl and terpy fragments is ∼30° in the solid state.[36] In solution, however, thermal distribution of conformers might result in less resolved luminescence spectra (Figure 3). Other explanations for the difference in energy and spectral shape between complex **1** on one hand and complexes **2**−**4** on the other hand could be based on the presence of energetically accessible excited states of MLCT nature, which are known to exhibit unresolved luminescence bands (the MC excited states can reasonably be located above 3.5 eV and, therefore, can be excluded as a deactivation pathway).[37a,b]

(35) (a) Pankuch, B. J.; Lacky, D. E.; Crosby, G. A. *J. Phys. Chem.* **1980**, *84*, 2061. (b) Kober, E. M.; Marshall, J. L.; Dressick, W. J.; Sullivan, B. P.; Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 2755.
(36) (a) Kim, Y.; Lieber, C. M. *Inorg. Chem.* **1989**, *28*, 3990. (b) Helms, H.; Heiler, D.; McLendon, G. *J. Am. Chem. Soc.* **1991**, *113*, 4325.
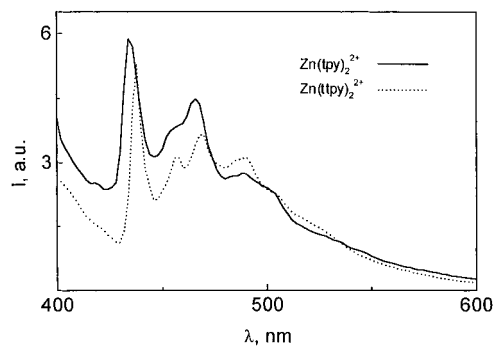

Figure 4. Luminescence spectra of Zn(tpy)$_2$$^{2+}$ and Zn(ttpy)$_2$$^{2+}$ in butyronitrile solutions at 77 K.

Table 4. Luminescence Properties and Photophysical Parameters

	293 K^a					77 K^b	
	λ^c (nm)	τ^d (μs)	$10^2 \times \phi^e$	$10^{-4} \times k_r$ (s^{-1})	$10^{-5} \times k_{nr}$ (s^{-1})	λ^c (nm)	τ^d (μs)
1	458	1.0 (1.2)	2.5	2.5	9.8	458	26
2	506	1.6 (6.8)	2.2	1.4	6.1	486	39
3	506	2.4 (9.5)	2.9	1.2	4.0	494	39
4	506	2.3 (5.8)	2.6	1.1	4.2	490	37

^{a} Acetonitrile solvent. ^{b} Butyronitrile solvent. ^{c} Band maximum for the highest-energy peak, uncorrected spectra. ^{d} Air-equilibrated samples, values in parentheses for deaerated solvent. ^{e} Quantum yields obtained from corrected spectra.

To better understand the nature of the luminescent levels of the studied complexes, we have obtained the 77 K luminescence spectra for butyronitrile solutions of Zn(tpy)$_2$$^{2+}$ and Zn(ttpy)$_2$$^{2+}$ (Figure 4).

The luminescence profiles in both cases, expected to conform to pure LC emissions from tpy and ttpy ligands,[13a] were closely similar to that exhibited by **1** but somewhat different from the spectra exhibited by **2**−**4**. This seems to indicate that the luminescence of the complexes containing an aryl tpy ligand is not of pure LC nature and might involve excited states of MLCT nature.

Room-temperature luminescence data, together with derived photophysical parameters and some luminescence results obtained at 77 K, are gathered in Table 4. From these it can be seen that (i) the energy stored within the excited state is 2.7 eV for **1** and 2.5 eV for **2**−**4**, (ii) for all complexes, the room-temperature luminescence quantum yields and lifetimes obtained in air-equilibrated solvent are $\phi \approx 10^{-2}$ and 1−2 μs, respectively,[38] and (iii) at 77 K and with respect to room temperature, (a) the luminescence lifetime increases by ca. 1 order of magnitude in each case and (b) the highest energy band maximum is unchanged for **1** while, by contrast, it undergoes a slight hypsochromic shift for **2**−**4**.

To further characterize the excited states of the complexes, the transient absorption spectra were measured. The spectra, as detected at the end of a 35-ps laser pulse for the different complexes in acetonitrile solutions in comparable experimental conditions, are shown in Figure 5. Compounds **2**−**4** display the same spectral profile with a broad band around 650−700 nm, while complex **1** has a much weaker transition toward the UV side of the spectrum.

The decay of the transients in deaerated acetonitrile solutions was a single exponential with lifetimes of 1.1 μs for **1**, 6 μs for

(37) (a) Roundhill, D. M. *Photochemistry and Photophysics of Metal Complexes*; Plenum: New York, 1994. (b) Horváth, O.; Stevenson, K. L. *Charge Transfer Photochemistry of Coordination Compounds*; VCH: Weinheim, 1993. (c) Demas, J. N.; Harris, E. W.; McBride, R. P. *J. Am. Chem. Soc.* **1977**, *99*, 3547.
(38) Ir(tpy)$_2$(CF$_3$SO$_3$)$_3$ was reported to exhibit τ_{em} = 70 ns; see ref 13a.

2, 9.5 μs for **3**, and 6.6 μs for **4**, in good agreement with the luminescence lifetimes of the excited state (Table 4). The effect of air on the lifetimes of the transients is in full agreement with the luminescence data. Therefore, the observed bands are assigned to a triplet excited state of the complexes, also responsible for their luminescence.

The excited states of the complexes are quenched by oxygen with a rate which can be derived from the data of Table 4. This is of the order of 10^8 M^{-1} s^{-1}, in agreement with previously reported values,[13a] and somehow smaller than the quenching constants of other polypyridine transition metal complexes.[37a,c] The poor spectral overlap between the donor's emission and acceptor's absorption, and the unfavorable driving force for electron transfer to dioxygen, could be the reason for such inefficient quenching.

The effect of counterion on the photophysical properties of the complexes has been considered for compound **3**, with NO$_3^-$ as the anion. All the photophysical properties detailed above for compound **3** with PF$_6^-$ anion were maintained, within experimental uncertainty, by the corresponding NO$_3^-$ salt.

Temperature Dependence of Luminescence. Following an approach employed in previous studies of luminescent Ru- and Os-tpy-type complexes,[17a,20,39,40] we further investigated the possible role of the interplay of excited states involved in the luminescence of complexes **1**−**4**.

In general terms, the room-temperature photophysical behavior of a luminophore is governed by the electronic properties of its lowest-lying excited state; however, it may be affected by higher-lying energy levels. For instance, for the largely studied Ru(II)-polypyridine complexes, the luminescence level is of ^{3}MLCT nature, but thermally accessible ^{3}MC levels play an important role.[20,40] This is because the potential energy curve for MC states is strongly displaced with respect to that of the ground state, which results in their effective coupling and, in turn, in fast deactivation pathways for the MLCT state.

Temperature-dependent studies of the luminescence may provide the energy gap, ΔE, between the luminescent and thermally accessible higher-lying levels, together with the related kinetic parameter, A, in terms of Arrhenius-like equations (eq 2), where k_o is a low-temperature limiting value.[40,41]

$$1/\tau = A \exp\left(\frac{-\Delta E}{RT}\right) + k_o \qquad (2)$$

In the present cases, the luminescent level is probably of predominant ^{3}LC nature, as discussed above, and the luminescence lifetime is $\tau \geq 1$ μs. It may be noted that the lifetime of complex **1** is significantly shorter than that of **2**, **3**, and **4** (ca. 1 vs. 2 μs in air-equilibrated solvent), the difference being
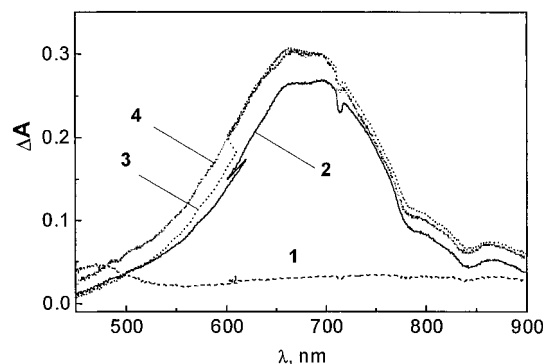
(39) Collin, J.-P.; Guillerez, S.; Sauvage, J.-P.; Barigelletti, F.; De Cola, L.; Flamigni, L.; Balzani, V. *Inorg. Chem.* **1992**, *31*, 4112.

(40) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.

(41) (a) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193. (b) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163. (c) Macatangay, A.; Zheng, G. Y.; Rillema, D. P.; Jackman, D. C.; Merkert, J. W. *Inorg. Chem.* **1996**, *35*, 6823. (d) Islam, A.; Ikeda, N.; Nozaki, K.; Ohno, T. *Chem. Phys. Lett.* **1996**, *263*, 209. (e) Wallace, L.; Jackman, D. C.; Rillema, D. P.; Merkert, J. W. *Inorg. Chem.* **1995**, *34*, 5210. (f) Hughes, H. P.; Vos, J. G. *Inorg. Chem.* **1995**, *34*, 4001. (g) Maruszewski, K.; Kincaid, J. R. *Inorg. Chem.* **1995**, *34*, 2002. (h) Maruszewski, K.; Bajdor, K.; Strommen, D. P.; Kincaid, J. R. *J. Phys. Chem.* **1995**, *99*, 6286. (i) Sykora, M.; Kincaid, J. R. *Inorg. Chem.* **1995**, *34*, 5852. (j) Wang, R.; Vos, J. G.; Schmehl, R. H.; Hage, R. *J. Am. Chem. Soc.* **1992**, *114*, 1964. (k) Barigelletti, F.; De Cola, L.; Juris, A. *Gazz. Chim. Ital.* **1990**, *120*, 545. (l) Lumpkin, R. S.; Kober, E. M.; Worl, L. A.; Murtaza, Z.; Meyer, T. J. *J. Phys. Chem.* **1990**, *94*, 239. (m) Ryu, C. K.; Schmehl, R. H *J. Phys. Chem.* **1989**, *93*, 7966. (n) Kawanishi, Y.; Kitamura, N.; Tazuke, S. *Inorg. Chem.* **1989**, *28*, 2968.

Figure 5. Absorption changes at the end of a 35 ps laser pulse (355 nm, 2.5 mJ) detected in acetonitrile solutions of **1**−**4**. Absorbance of the solutions at the excitation wavelength was 0.9.
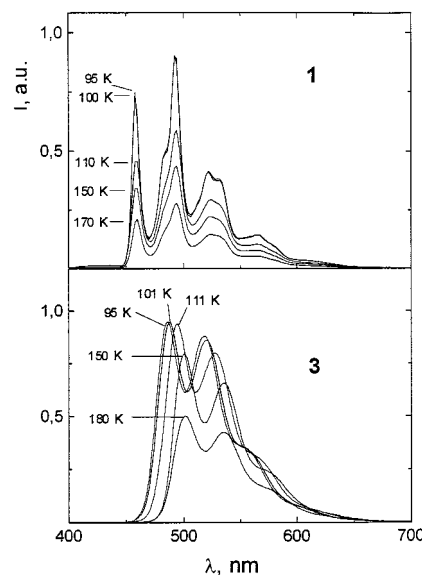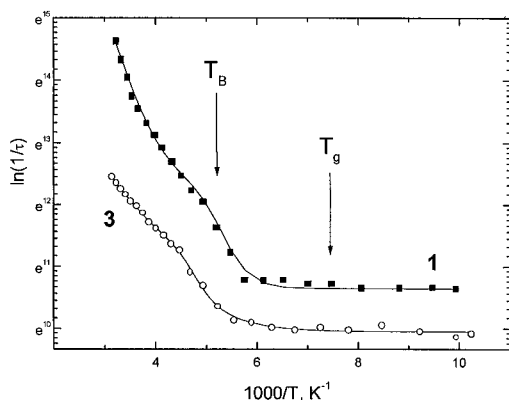

Figure 6. Luminescence spectra of butyronitrile solutions of **1** (top panel) and **3** (bottom panel) in the 95−180 K range.

sharper in degassed solvent (Table 4). Given that the energy level of the emissive state of **1** is some 2000 cm^{-1} higher in energy than the corresponding levels of the other complexes, it may well be that the energy layout of higher-lying states plays a different role in the two cases.

To get a picture of the possible interplay of excited states in the two cases, we have performed temperature-dependent studies on the luminescence properties of complexes **1** and **3**. In Figures 6 and 7 are collected luminescence spectra and luminescence lifetimes of ~10^{-5} M deaerated butyronitrile solutions of the two complexes, as registered against the temperature.

From Figure 6, it can be seen that the energy position of **3** is affected by the temperature, showing a bathochromic shift (by ~600 cm^{-1}) on going from glassy to fluid solvent, i.e., in the 110−150 K interval, which includes the glass-to-fluid transition temperature of the solvent ($T_g \approx 125$ K).[12,40] This behavior usually indicates that the luminescent excited state is coupled with nuclear rearrangements which are affected by the state of the solvent. By contrast, no energy variation is registered for the spectrum of **1**. One may further notice that, for both cases, the spectral shape is not affected by the temperature nor by the rigidity of the solvent. An explanation for these observations could be based on the role of torsional rearrangements, expected for **3** but not for **1**, between the plane of the tolyl ring and that of the terpyridine fragment. Actually, it is known that, for the ground state of a biphenyl-like fragment, this dihedral angle is

Figure 7. Luminescence lifetimes of butyronitrile solutions of **1** and **3** in the 95−298 K interval. The full lines are the result of a fitting procedure according to eq 3 of text.

Table 5. Kinetic Parameters for Excited-State Decay[a]

	A (s^{-1})	ΔE (cm^{-1})	k_0 (s^{-1})	B (s^{-1})	T_B (K)
1	7.6×10^9	1790	4.2×10^4	1.7×10^5	197
3	2.2×10^7	1040	2.1×10^4	3.9×10^4	215

[a] Butyronitrile solvent, degassed samples unless otherwise specified. Parameters obtained from least-squares nonlinear fitting of eq 3 of the text to the experimental points of Figure 7.

around 30°, while for the corresponding lowest-lying excited state, the two fragments are close to planarity.[36]

In Figure 7 are reported the $1/\tau$ vs $1/T$ experimental points, together with the results of a fitting procedure based on the following equation,[12,40]

$$\frac{1}{\tau} = A \exp\left(\frac{-\Delta E}{RT}\right) + \frac{B}{1 + \exp[C(1/T - 1/T_B)]} + k_0 \quad (3)$$

where A and ΔE are the preexponential factor and the energy barrier, respectively, for an Arrhenius-type process, B is the increase in radiationless rate occurring at a certain temperature, T_B, C is an empirical parameter, and k_0 is a low-temperature limiting rate. Results of the numerical analyses based on eq 3 are collected in Table 5.

Some interesting points are the following.

(i) In both cases, the lifetime values are not affected by the glass-to-fluid transition of the solvent (occurring at $T_g \approx 125$ K), whereas they are affected by a process taking place at higher temperature ($T_B \geq 200$ K) and resulting in an increase in the nonradiative rate, B. This process appears to be allowed by a certain degree of fluidity of the solvent and is, therefore, likely to be due to some type of physical interaction. Self-association processes should be excluded, on the basis both of the low concentration employed ($\sim 10^{-5}$ M) and of the 3+ charge of the species. In conclusion, some interaction with the solvent is likely taking place, the nature of which we are unable to identify better at the moment.

(ii) For the case of the well-documented ^{3}MLCT−^{3}MC coupling occurring in Ru(II)-polypyridine emitters, the pre-

exponential factor A is of the order of 10^{12} s^{-1}.[40,41] By contrast, for both **1** and **3**, $A \ll 10^{12}$ s^{-1} (Table 5). This result suggests that the thermally accessible energy level is not responsible for fast deactivation paths. As discussed above, for **1** and probably also for **3**, the luminescent level is of predominant ^{3}LC nature, and the fact that thermal population of an upper-lying level, which might be of MLCT nature, does not cause a substantial enhancement of the decay rate suggests that this latter level is not an efficient doorway for radiationless deactivation.

Conclusion

Many examples of multicomponent systems containing poly-pyridine complexes of the Ru(II), Os(II), Rh(III), and Ir(III) families are known.[3,11] As mentioned above, from the viewpoint of the control of the geometric properties, the use of M(tpy)$_2$$^{n+}$ templating units offers remarkable advantages because the introduction of substituents at the 4′-terpyridine position allows the development of linearly arranged arrays.[3,6,7,10,12,42] In view of photoinduced electron transfer, drawbacks are predicted upon the use of templating units of the Ru(tpy)$_2$$^{2+}$ and Os(tpy)$_2$$^{2+}$ types: the former chromophore exhibits a short-lived MLCT excited state (<1 ns), and the latter can store excitation energy at a low energy level (~ 1.6 eV).[12] In this respect, both units are unsuited to play a templating role for the assembly of linearly arranged arrays because they represent an energy trap interposed between the other two active units. By contrast, for both types of systems shown in Chart 2, the series of the presently investigated Ir(III) complexes offers a good combination of advantages, given that (i) a synthetic procedure is now available which makes such complexes relatively accessible, in particular asymmetrical systems due to the two-step synthesis described here, (ii) their excited states levels are located above 2.5 eV, and (iii) their decay occurs on the microsecond time scale even in air-equilibrated solutions. For the multicomponent arrays we plan to develop, these points represent remarkable properties in order for intercomponent processes to be competitive with respect to the intrinsic deactivation at the templating center.

Supporting Information Available: X-ray data of **1** (PDF). These data are also available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

(42) (a) Constable, E. C.; Cargill Thompson, A. M. W. *J. Chem. Soc., Dalton Trans.* **1992**, 3467. (b) Constable, E. C.; Cargill Thompson, A. M. W.; Harveson, P.; Macko, L.; Zehnder, M. *Chem. Eur. J.* **1995**, *1*, 360. (c) Grosshenny, V.; Harriman, A.; Hissler, M.; Ziessel, R. *Platinum Metals Rev.* **1996**, *40*, 72.