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Article

Synthesis, Characterization, Absorption Spectra, and Luminescence Properties of Multinuclear Species Made of Ru(II) and Ir(III) Chromophores

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A series of new mixed-metal Ru(II)−Ir(III) trinuclear complexes have been prepared and characterized, together with their mononuclear parents and a series of closely related dinuclear and trinuclear homometallic Ru(II) and Ir(III) species, and their absorption spectra and luminescence properties (both at 77 K in rigid matrix and at room temperature in fluid solution) have been studied. The absorption spectra and luminescence properties of the Ru(II) species and subunits are dominated by metal-to-ligand charge-transfer (MLCT) transitions and excited states, whereas ligand centered (LC) transitions and excited states govern the spectroscopic and photophysical properties of most of the Ir(III) species here studied, with MLCT states playing an important role when cyclometalated Ir(III) subunits are present. Each metal-based subunit retains in the multinuclear arrays its own spectroscopic properties, but in the case of the mixed Ru−Ir species an efficient, additional decay channel is opened for the excited states involving the Ir-centered subunits, that is, photoinduced energy transfer to the lower-lying MLCT state(s) involving the Ru centers.

Introduction

The study of the photophysical properties of multinuclear metal complexes made of luminescent metal-based subunits is a quite active field of research. Such a study, which belongs to the general theme of supramolecular photochemistry from a fundamental point of view,[1] allows information to be gained on intercomponent photoinduced energy and/or electron transfer processes occurring in multichromophoric, supramolecular arrays and can give access to the preparation of artificial species designed for controlling light at the molecular level[2] as well as of artificial systems for solar energy conversion devices[3,4] and more efficient systems for illumination purposes (e.g., OLED).[5]

Whereas most of the investigations on mixed-metal multinuclear systems have dealt with species containing Ru(II), Os(II), Re(I), and Rh(III),[6] multinuclear mixed-metal species containing Ir(III)- and Ru(II)-based subunits in the same (supra)molecular array are relatively less studied,[7,8] in spite of the impressive amount of data available on the photophysics of Ru(II) polypyridine complexes, whose properties are governed by metal-to-ligand charge-transfer (MLCT) states,[1−4] and on the increasing interest in Ir(III) polyimine compounds (including cyclometalated species), whose photophysics mainly involves MLCT and ligand-centered (LC)

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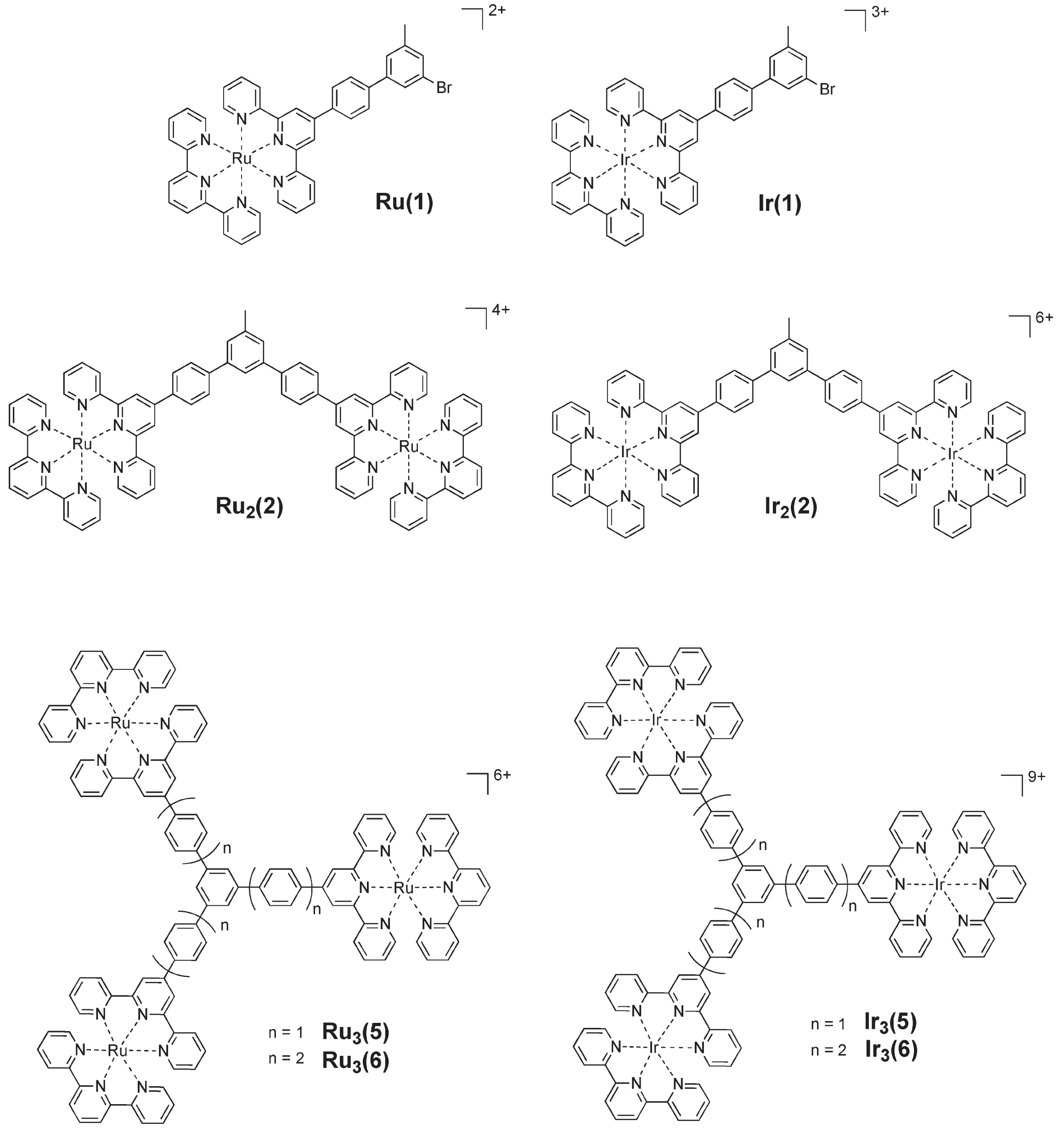

Figure 1. Structural representation of homonuclear species investigated and their abbreviations.

excited states,[5,7–10] and the efficient energy transfer processes reported to occur in most of the published papers on mixed-metal Ru–Ir compounds.[7]

Here we report the synthesis, characterization, and study of the photophysical properties of a series of multinuclear Ir–Ru compounds, together with their mononuclear parent compounds. Moreover, four trinuclear and two dinuclear homometallic Ru(II) and Ir(III) species are also studied. Figure 1 and Figure 2 show the structural formulas of all the species investigated and their abbreviations. The abbreviations are chosen to give immediate information on the type and number of metal centers coordinated to the ligands, indicated by the number in parentheses. The structural formulas are shown in Schemes 1 and 2. Some luminescence properties of **Ru$_2$(2)** and **Ir$_2$(2)** have already been communicated.[8]

Results

The Suzuki coupling between 4′-(4-neopentylglyconatoboronphenyl)-2,2′:6′,2″-terpyridine (**tpy-Bneo**)[9] and a dibromo or tribromo aromatic derivative provided an easy and quite versatile synthetic way to obtain several mono- and homo-polytopic ligands (Scheme 1). However, the molar ratios between the reacting species play an important role for the outcome of the reaction. Indeed coupling of commercially available 3,5-dibromotoluene with a substoichiometric amount of **tpy-Bneo** (0.33 mol equiv) in the presence of aqueous Na_2CO_3 as base and $[Pd(PPh_3)_4]$ as catalyst afforded monobrominated terpyridine **1** in 77% yield after purification by column chromatography. When the same reaction was carried out in the presence of 3.0 mol equiv of **tpy-Bneo** the bis-terpyridine **2** was isolated in 88% yield.

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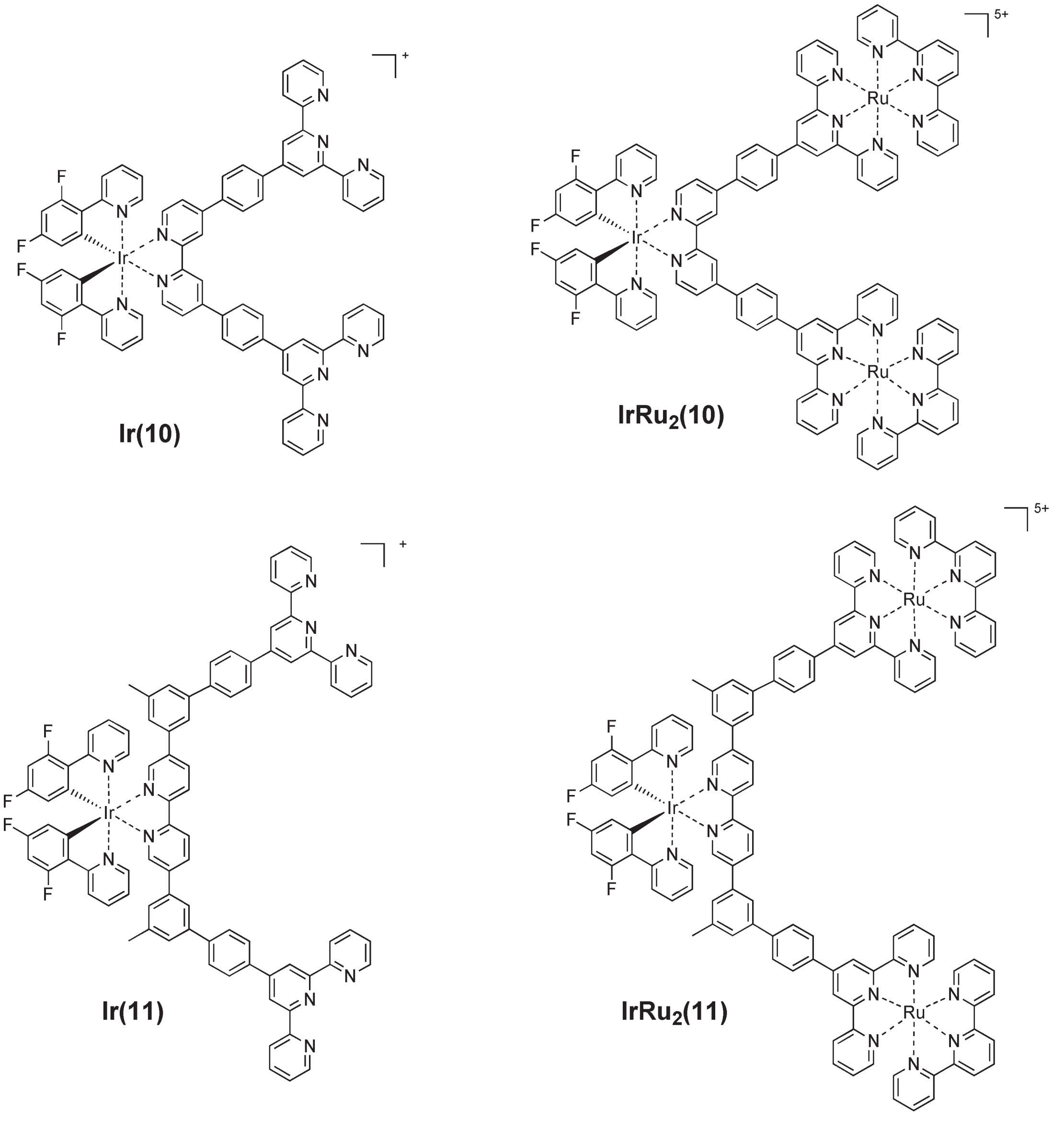

Figure 2. Structural formulas of cyclometalated homo- and heteronuclear complexes investigated and their abbreviations.

Unfortunately our first attempts to obtain the mono- and disubstituted derivatives **3** and **4** starting from commercially available 1,3,5-tribromobenzene and **tpy-Bneo** were unsuccessful. The same molar ratios adopted for the synthesis of compounds **1** and **2** were not convenient, since in both cases a remarkable amount of unreacted 1,3,5-tribromobenzene was isolated, while a precipitate was formed during the reaction. This precipitate was isolated and identified as the pure homotritopic ligand **5**. This behavior is not so surprising taking into account the poor solubility of **5** in the most common organic solvents, that could represent the effective driving force of the process. Nevertheless it was possible to synthesize compound **3** in 72% yield by a further decrease of **tpy-Bneo** with respect to 1,3,5-tribromobenzene (**tpy-Bneo**, 0.17 mol equiv). A subsequent coupling reaction between terpyridine **3** and **tpy-Bneo** (0.5 mol equiv) allowed the selective substitution of a second halide, and bis-terpyridine **4** was obtained in 77% yield after purification by column chromatography. Finally, the Pd-catalyzed Suzuki coupling involving 1,3,5-tribromobenzene or 1,3,5-tris(4-bromophenyl)benzene in the presence of an excess of boronic ester (**tpy-Bneo**, 4 mol equiv) afforded in good yield the star-shaped tris-terpyridines **5** and **6**, respectively, that directly precipitated from the reaction mixture. The homonuclear ruthenium complexes **Ru**(**1**) and **Ru$_2$**(**2**) were obtained by refluxing an ethanol solution of ligands **1** and **2** with [Ru(tpy)Cl$_3$] in the presence of *N*-ethylmorpholine, with minor adjustments to the literature procedures.[6a,10,11] In the case of complexes **Ru$_3$**(**5**) and **Ru$_3$**(**6**), better results were achieved using a mixture of DMF/THF (10:1 v/v) because of the increased solubility of ligands **5** and **6** in DMF with respect to other organic solvents. The heteroleptic iridium(III) complexes **Ir**(**1**), **Ir$_2$**(**2**), **Ir$_3$**(**5**), and **Ir$_3$**(**6**), were prepared by reaction of the corresponding ligand with 1, 2, or 3 equiv of [Ir(tpy)Cl$_3$], respectively. The reactions were carried out in refluxing ethylene glycol, followed by anion exchange with potassium hexafluorophosphate and purification by column chromatography on silica gel with CH_3CN/0.2 M aqueous KNO_3 in the appropriate ratios, as mobile phase.

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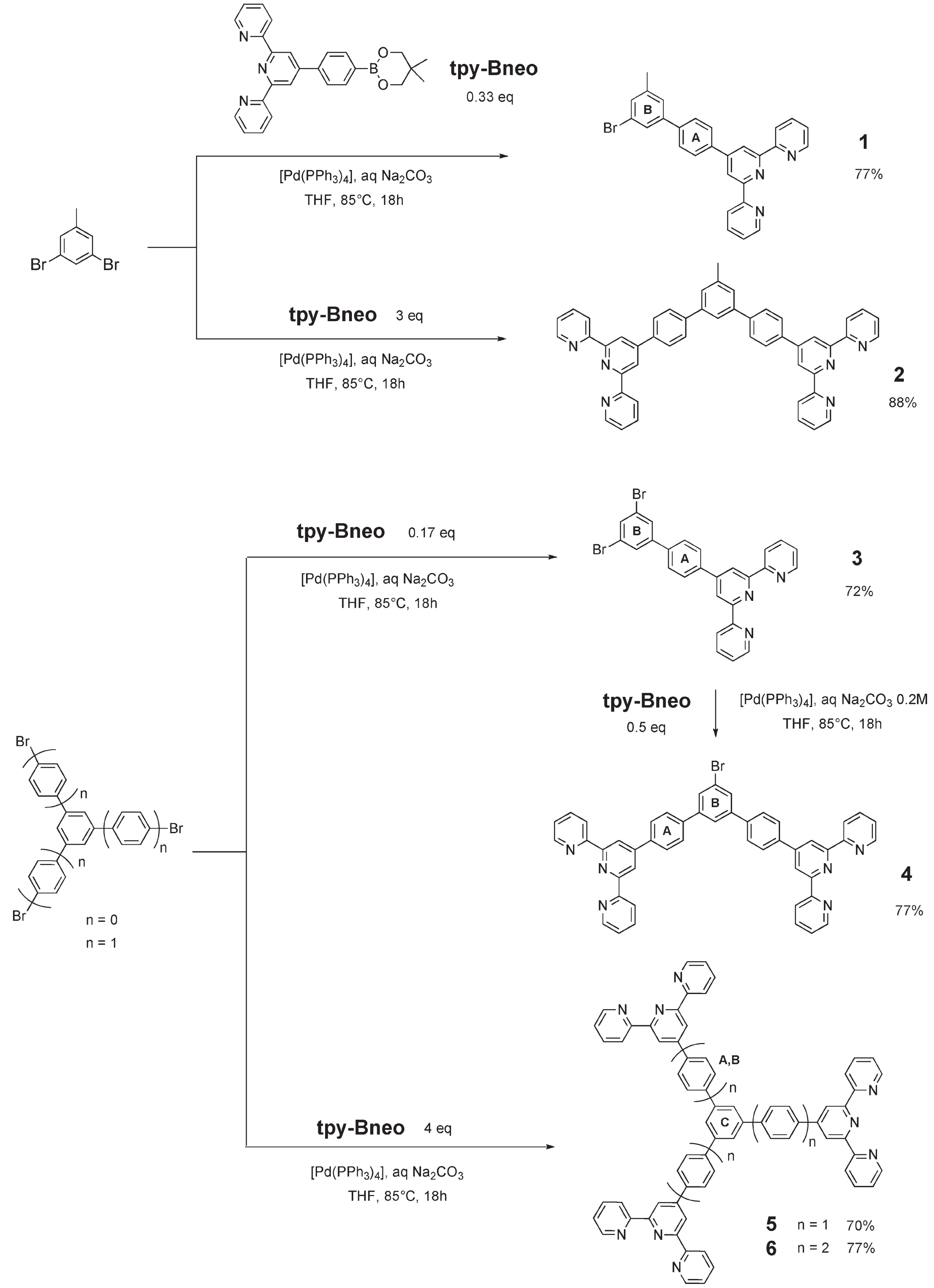
Scheme 1. Synthesis of Terpyridine-Based Ligands **1**−**6**



As previously reported in literature for the preparation of dimetallic assemblies containing mixed bipyridine−terpyridine bridging ligands,[12,13] we adopted a similar divergent approach toward the synthesis of **IrRu$_2$(10)** and **IrRu$_2$(11)** mixed complexes. The Ir(III) chloro-bridged dimer **[Ir(F$_2$ppy)$_2$Cl]$_2$** was synthesized according to the Nonoyama route by refluxing IrCl$_3$·3H $_2$O with 2.2 equiv of 2-(2,4-difluorophenyl)pyridine (F$_2$ppy) in a 3:1 mixture of 2-ethoxyethanol and water.[14]

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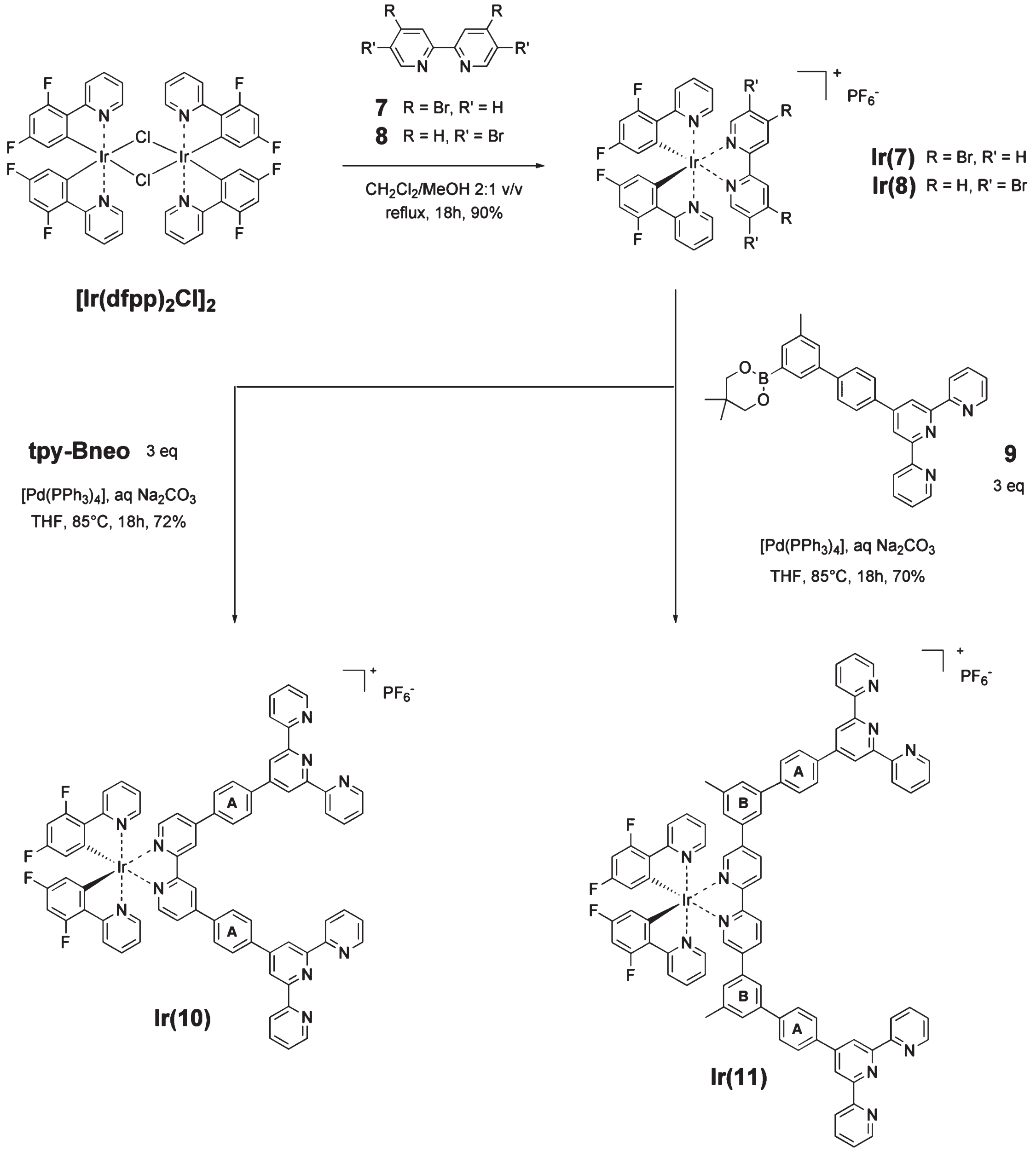
Scheme 2. Synthesis of Ir(III) Complexes **Ir(10)** and **Ir(11)**



The reaction between [**Ir**($\mathbf{F_2ppy}$)$_\mathbf{2}$**Cl**]$_\mathbf{2}$ and 4,4′-dibromo-2,2′-bipyridine **7**[15] or 5,5′-dibromo-2,2′-bipyridine **8**[16] in a refluxing mixture of CH_2Cl_2/MeOH afforded the two cyclometalated Ir(III) complexes **Ir**(**7**) and **Ir**(**8**) in high yields (Scheme 2).

Compounds **Ir**(**10**) and **Ir**(**11**) were prepared by a Suzuki cross-coupling reaction of complex **Ir**(**7**) with **tpy-Bneo** and of complex **Ir**(**8**) with terpyridinyl boronic ester **9** in THF with [Pd(PPh_3)$_4$] as the catalyst. Because of the relatively mild conditions employed, no scrambling of Ir(III) between the two distinct coordination sites was observed. Finally, a further complexation step in the presence of 2 equiv of [Ru(tpy)Cl_3] in refluxing EtOH afforded the trinuclear metal species **IrRu**$_\mathbf{2}$(**10**) and **IrRu**$_\mathbf{2}$(**11**).

The absorption spectra of all the species have been studied in acetonitrile solution at room temperature, whereas the luminescence properties have been investigated both in the same solvent at room temperature and in butyronitrile or EtOH/MeOH (4:1 v/v) matrices at 77 K. The absorption spectra of the compounds containing only Ir(III)-based subunits exhibit intense bands in the UV region which in some cases extend into the visible region. The absorption spectra of the compounds containing exclusively Ru(II)-based subunits exhibit both intense bands in the UV region and moderately intense bands in the visible region. For the mixed-metal species, the absorption spectra appear to be the sum of the absorption bands of the Ru(II)- and Ir(III)-based components. The molar absorbance is in all cases roughly linearly dependent on the number of metal-based components. Table 1 collects the relevant absorption data of all the compounds, Figure 3 shows the absorption spectra of **Ir**(**10**) and **IrRu**$_\mathbf{2}$(**10**),

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Table 1. Absorption, Photophysical, and Redox Data[a]

	absorption, 298 K	luminescence 298 K			luminescence 77 K		redox[d], 298 K	
compound	λ_{max}, nm (ε, M^{-1} cm^{-1})	λ_{max}, nm	τ, ns	Φ	λ_{max}, nm	τ, μs	E_{ox} V vs SCE	E_{red} V vs SCE
Ir(1)	281 (38800) 378 (16500)	570	1200	0.020	490	10	+1.41 irr.	*e*
Ru(1)	310 (125000) 486 (45300)				643	14	+1.23	−1.21
Ir(10)	340 (81000)	540	1300	0.29	496	6; 12[b]	+1.65	*e*
IrRu$_2$(10)	310 (285000) 485 (109000)	690	13	$< 10^{-4}$	645	15	+1.25 [2] +1.65(q.rev)	−1.13 [2]
Ir(11)	279 (144000) 340 (35000)	600	150	0.08	535	8; 10[b]	+1.64	*e*
IrRu$_2$(11)	312 (315000) 485 (105600)				640	13	+1.26 [2] +1.64	−1.21 [2]
Ir$_3$(5)	252 (110100) 281 (124800) 378 (61800)	573	3000	0.007	528	240	+1.42 irr.	*e*
Ir$_3$(6)	252 (120500) 281 (132700) 378 (62200)	593	3000	0.007	548	240	+1.44 irr.	*e*
Ru$_3$(5)	309 (341000) 487 (154800)	680	80	$< 10^{-4}$	648	13	+1.24 [3]	−1.21 [3]
Ru$_3$(6)	310 (355000) 486 (151800)	683	80	$< 10^{-4}$	645	13	+1.26 [3]	−1.22 [3]
Ru$_2$(2)	277 (173600) 309 (281000) 486 (104800)	683	83	8×10^{-5}	641 [c]	13[c]	+1.27 [2]	−1.23
Ir$_2$(2)	281 (74800) 314 (44600) 354 (32300) 378 (33200)	578	2774	0.007	524 [c]	205 [c]	+1.42 irr.	*e*

[a] In acetonitrile deaerated solution at room temperature and in EtOH/MeOH (4:1, v/v) rigid matrix at 77 K, unless otherwise stated. [b] biexponential decay. [c] in butyronitrile rigid matrix. [d] Half-wave potentials; the processes are reversible, unless otherwise noted; for multielectronic processes, the number in brackets refers to the number of electron exchanged. [e] Ill-behaved processes; reduction potentials cannot be assigned.

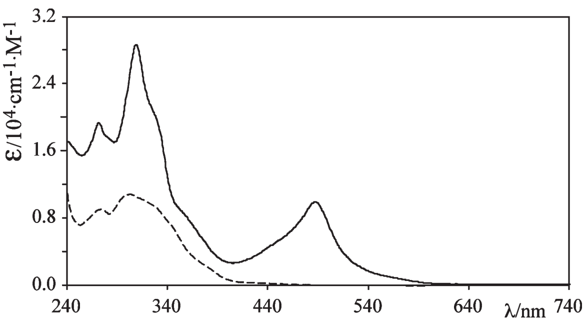

Figure 3. Absorption spectra of **Ir(10)** (dashed line) and **IrRu$_2$(10)** (solid line) in acetonitrile solution.

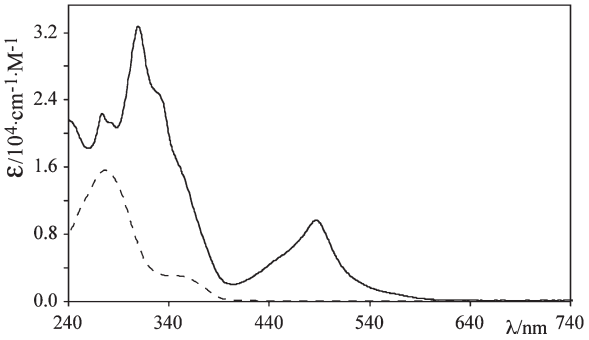

Figure 4. Absorption spectra of **Ir(11)** (dashed line) and **IrRu$_2$(11)** (solid line) in acetonitrile solution.

Figure 4 shows the absorption spectra of **Ir(11)** and **IrRu$_2$(11)**, and Figure 5 shows the absorption spectra of **Ir$_3$(6)** and **Ru$_3$(6)**.

All the compounds exhibit luminescence both at room temperature in fluid acetonitrile solution and in rigid glasses at 77 K, except **Ru(1)** and **IrRu$_2$(11)** that emit only at low temperature. The luminescence decays of most compounds are monoexponential and span a time range between 13 ns (**IrRu$_2$(10)** at room temperature) and 240 μs (**Ir$_3$(5)** and **Ir$_3$(6)** at 77 K). The mononuclear **Ir(10)** and **Ir(11)** compounds exhibit biexponential decays at 77 K, with both decays in the microsecond time range. Luminescence quantum yields, measured in fluid solution at room temperature, range from values lower than 10^{-4} for Ru(II)-containing species to 0.29 for species containing only Ir(III) chromophores. The data for all the compounds are collected in Table 1. Figure 6 shows emission spectra of **Ir(10)** and **IrRu$_2$(10)**, Figure 7 shows emission spectra of **Ir(11)** and **IrRu$_2$(11)**, and Figure 8 illustrates emission spectra of **Ir$_3$(5)**, **Ir$_3$(6)**, and **Ru$_3$(6)**.

The redox behavior of all the metal complexes has also been investigated, in acetonitrile solution, to complement the spectroscopic data. All the homometallic compounds exhibit a single oxidation process (at about +1.30 V vs SCE for the Ru species and at more positive potentials for the Ir species), involving the metal-centered orbital(s). For oligonuclear homometallic species, such oxidation processes involve multiple electrons. The mixed-metal species exhibit two oxidation processes, with the one occurring at less positive potential being bielectronic, whereas the one occurring at more positive potentials being monoelectronic in nature. On reduction, severall ill-behaved processes take place; however, extensive adsorption of the compounds on the electrode surface occurs. Redox data are collected in Table 1.

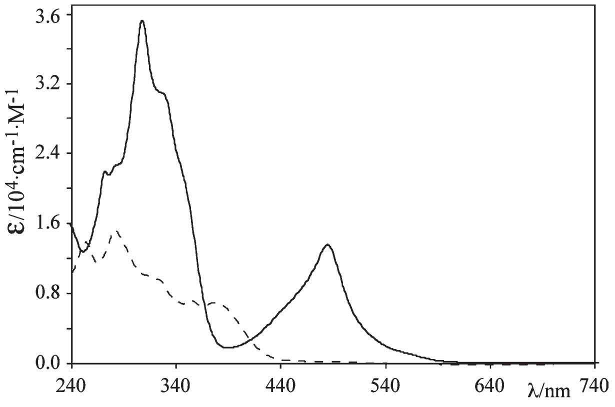

Figure 5. Absorption spectra of **Ir$_3$(6)** (dashed line) and **Ru$_3$(6)** (solid line) in acetonitrile solution.

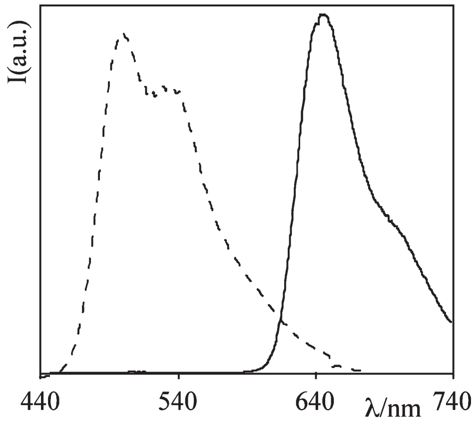

Figure 6. Emission spectra of **Ir(10)** (dashed line) and **IrRu$_2$(10)** (solid line) in EtOH/MeOH (4:1 v/v) rigid matrix at 77 K.

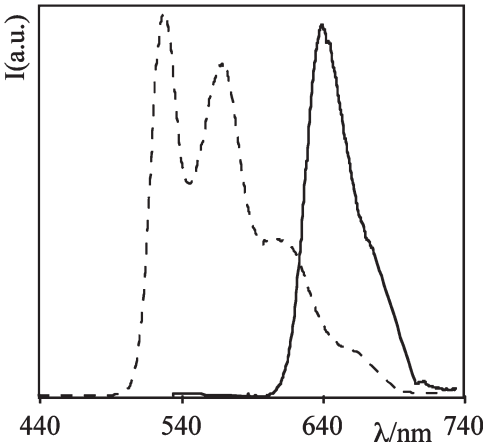

Figure 7. Emission spectra of **Ir(11)** (dashed line) and **IrRu$_2$(11)** (solid line) in EtOH/MeOH (4:1 v/v) rigid matrix at 77 K.

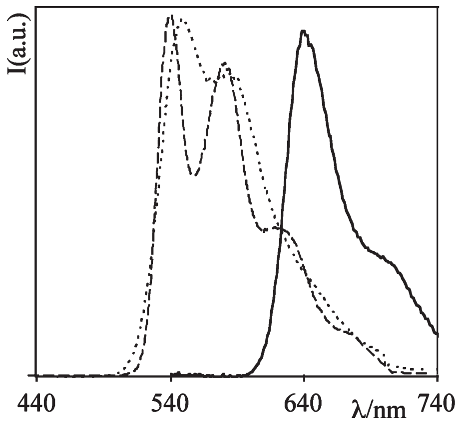

Figure 8. Emission spectra of **Ir$_3$(5)** (dashed line), **Ir$_3$(6)** (dotted line), and **Ru$_3$(6)** (solid line) in EtOH/MeOH (4:1 v/v) rigid matrix at 77 K.

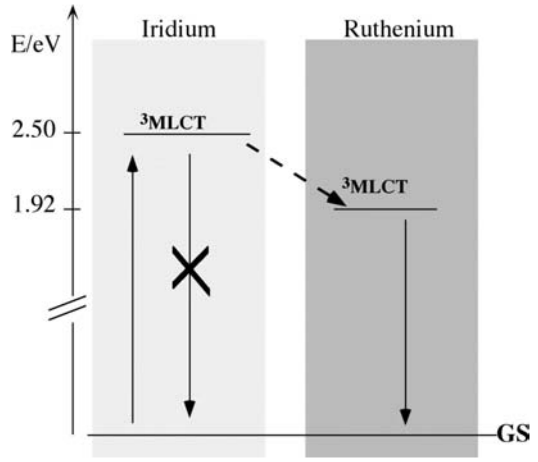

Figure 9. Schematic energy level diagram illustrating the energy transfer pathway for **IrRu2(10)**, the ^{3}MLCT energies are obtained on the basis of the 77 K emission spectra of the **Ir(10)** and **IrRu2(10)** species.

Discussion

Absorption Spectra and Luminescence Properties. Mononuclear and Dinuclear Ir(III) Compounds. The absorption spectra of **Ir(1)**, **Ir(10)**, and **Ir(11)** present strong bands in the UV region (Table 1, Figures 3 and 4), which can be assigned to metal-perturbed spin-allowed LC transitions, on the basis of the molar absorbance, energy, and comparison with literature data.[17,18] The band at lower energy most likely receives also some contribution from spin-allowed MLCT transitions involving the substituted bipyridine ligand. In some compounds, a very weak tail is seen on the red edge of the low-energy band, which can be attributed to spin-forbidden MLCT transitions.

In spite of the similarity of their structure and their cyclometalated nature, **Ir(10)** and **Ir(11)** have different emission properties, particularly at room temperature (Table 1, Figures 6 and 7). The room temperature emission of **Ir(11)** is assigned to a triplet MLCT state (namely, Ir-to-substituted bipyridine ligand) where the acceptor ligand of the MLCT transition should be largely delocalized over the phenyls connected in meta to the bipyridine ligand, so stabilizing the MLCT states. In fact, the analogous compound [Ir(F$_2$ppy)$_2$(bpy)]$^+$ (F$_2$ppy = 2-(2, 4-difluorophenyl)pyridine anion; bpy = 2,2′-bipyridine), missing the substituents on the bpy ligand, emits at higher energies, 533 nm at room temperature and 454 nm at 77 K.[7b] The relatively short (150 ns) luminescence lifetime of **Ir(11)** further supports this assignment.[17−19] In

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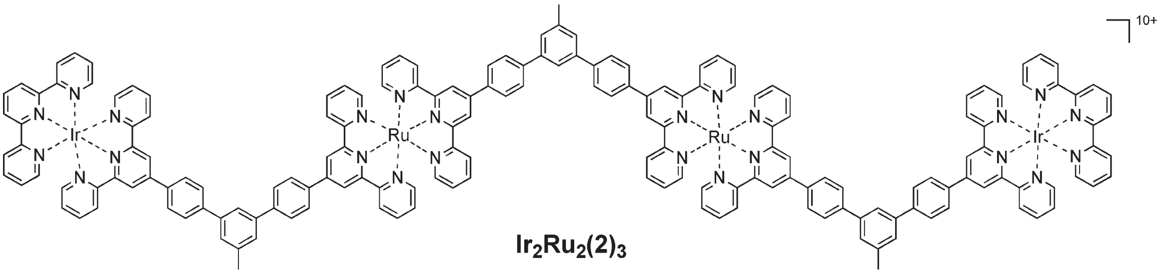

$Ir_2Ru_2(2)_3$

Figure 10. Structural formula of **$Ir_2Ru_2(2)_3$**.

comparison, **Ir(10)** emits at significantly higher energy at room temperature, and its emission energy is intermediate between that of **Ir(11)** and that of the above-mentioned $[Ir(F_2ppy)_2(bpy)]^+$ compound. Moreover, the emission lifetime of **Ir(10)** is significantly longer (1.3 μs) and its quantum yield is higher (0.29) than the respective values of **Ir(11)** (150 ns and 0.08). The room temperature emission of **Ir(10)** is still assigned to a triplet MLCT state, although a mixing with low-lying triplet LC states is quite probable, but delocalization of the acceptor ligand of the MLCT state over the *para* substituents of the bpy-type coordinated site seems to be less relevant, as suggested by the difference in emission energy between **Ir(10)** and **Ir(11)** (Table 1). The differences in emission lifetime and quantum yield between the two mononuclear cyclometalated Ir(III) complexes can be explained by the energy gap law.[20] At 77 K in rigid matrix, both the two cyclometalated compounds exhibit blue-shifted emissions compared to room temperature (see Figures 6 and 7 and Table 1), and the luminescence decay appears to be biexponential in both cases. For both compounds we attribute the emission to two closely lying, non-equilibrated excited states, most likely of ^{3}MLCT and ^{3}LC origin.

Compound **Ir(1)** differs from the other mononuclear Ir(III) compounds studied in here since it is a polypyridine complex (bis-terpyridine like) and not a cyclometalated species. As for other Ir(III) bis-terpyridine complexes,[18,19] its absorption is dominated by metal-perturbed spin-allowed LC transitions and its emission originates from a mixed ^{3}MLCT/^{3}LC state at room temperature and from a metal-perturbed ^{3}LC state at 77 K, on the basis of the energies and lifetimes of its emission properties (Table 1) and comparison with literature data.[18]

The absorption spectra and luminescence properties of **$Ir_2(2)$** have been already reported[8] and are here included (Table 1) for completeness. We note that it can be considered as derived from the mononuclear **Ir(1)** compound; in fact, its properties are quite close to those of **Ir(1)** and are interpreted in the same manner. One important information is obtained from comparison between the luminescence properties of **Ir(1)** and of its dinuclear species: each chromophore is not perturbed by the presence of the other identical one, as far as the excited state energy and decay are concerned. This indicates that the excited states are essentially localized on the mononuclear subunits, so that the mononuclear species **Ir(1)**, **Ir(10)**, and **Ir(11)** (and **Ru(1)**) can be considered as good models for the excited state properties of the corresponding components in the multinuclear compounds.

Mono- and Dinuclear Ru(II) Compounds. All the Ru(II) chromophores investigated in this work, either if they are mononuclear compounds or if they are part of polynuclear species, carry tridentate, terpyridine-like species. As such, they have relatively weak photoemissive properties compared to the tris-bipyridine species, although the absorption spectra are quite similar. Reasons for the weak emissive properties are well-known and will not be discussed here.[6a,11,20,21] The mononuclear **Ru(1)** and dinuclear **$Ru_2(2)$** are in line with the general trend of bis-terpyridine Ru(II) species (Table 1): their absorption spectra present intense LC bands in the UV and moderately intense MLCT bands in the visible, but they exhibit weak MLCT emission properties at room temperature (**$Ru_2(2)$**) or even emissions which are below the detection limit of our apparatus (**Ru(1)**). At 77 K, as usual,[11,21] both the species exhibit an intense and long-lived ^{3}MLCT emission.

Mixed-Metal Ir−Ru Multinuclear Compounds. The absorption spectra of **$IrRu_2(10)$** and **$IrRu_2(11)$** are roughly the sum of their isolated components spectra. So, the visible region is dominated by moderately intense MLCT bands involving the Ru(II) subunits and the UV region presents spin-allowed LC bands which can be attributed to both Ru(II)- and Ir(III)-based subunits (Table 1, Figures 3 and 4).

The trinuclear **$IrRu_2(10)$** and **$IrRu_2(11)$** compounds do not exhibit any emission at the wavelengths typical of their corresponding Ir(III)-based components, that is, **Ir(10)** and **Ir(11)** (Table 1, Figures 6 and 7), both at room temperature and at 77 K. This indicates that the Ir-based excited states are efficiently quenched by the presence of the Ru(II) chromophores in both complexes, in both experimental conditions. At room temperature, only **$IrRu_2(10)$** exhibits a detectable emission band, at the limit of our equipment sensitivity, which is assigned to ^{3}MLCT involving the Ru(II) component(s). The excitation spectrum for this compound overlaps with the corresponding absorption spectrum, so indicating that energy transfer from the higher-lying Ir(III)-based MLCT state to the lower-lying Ru(II)-based MLCT state is the active quenching mechanism. The energy transfer process is schematized in Figure 9. For analogy, we assume that energy transfer is the Ir-based excited state quenching mechanism also in the case of **$IrRu_2(11)$** at room temperature and for both compounds at 77 K, where

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[20] Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193.

[21] Campagna, S.; Puntoriero, F.; Nastasi, F.; Bergamini, G.; Balzani, V. *Top. Curr. Chem.* **2007**, *280*, 117.

only the typical Ru-based MLCT emission is observed (Table 1). Interestingly, whereas the Ir-based emission is quite different between **Ir(10)** and **Ir(11)**, for which the emitting MLCT state involves the central coordinating subunit of the tritopic ligands, both at room temperature and at 77 K, the Ru-based emission at 77 K of **IrRu$_2$(10)** and **IrRu$_2$(11)**, for which the emitting MLCT state involves the peripheral coordinating subunit(s) of the tritopic ligands, are quite similar. This indicates that the tritopic ligands **Ir(10)** and **Ir(11)** have "isolated" low-energy orbitals mainly localized on the chelating sites and that the electronic differences between the two ligands essentially involve the central chelating site, coordinating the Ir(III) center in the present compounds.

The photophysical properties of the trinuclear mixed-metal species discussed above, namely, the quite efficient energy transfer process from Ir-based to Ru-based chromophores, significantly differ from the previously reported[8] properties of **Ir$_2$Ru$_2$(2)$_3$**, whose structural formula is shown in Figure 10. For **Ir$_2$Ru$_2$(2)$_3$**, energy transfer from Ir to Ru chromophores only takes place at 77 K, whereas emission from both Ir(III)- and Ru(II)-components is seen at room temperature, with the emission lifetime of the Ir-based chromophore ($\lambda_{max} = 572$ nm, $\tau = 2.9\ \mu$s)[8] practically unchanged compared to the emission lifetime of **Ir$_2$(2)** (see Table 1), used as model. The weak coupling between Ir and Ru chromophores because of the meta arrangement of the polyphenyls contained in the ligand **2** was claimed as the reason for the absence of energy transfer at room temperature in **Ir$_2$Ru$_2$(2)$_3$**.[22]

The difference in the occurrence of energy transfer between the formerly studied tetranuclear species **Ir$_2$Ru$_2$(2)$_3$** and the new trinuclear compounds **IrRu$_2$(10)** and **IrRu$_2$(11)** here reported warrants some discussion. There are many differences between the tetranuclear species and the trinuclear ones (compare structural formulas in Figures 2 and 10): (i) the nature of the Ir(III) chromophores, that is, bis-terpyridine Ir(III) chromophores in **Ir$_2$Ru$_2$(2)$_3$** and cyclometalated tris-bidentate Ir(III) dyes in **IrRu$_2$(10)** and **IrRu$_2$(11)**; this difference also leads to an increased MLCT character of the Ir-based excited state in the latter, cyclometalated species, with the acceptor ligand of the MLCT transition definitely involving the Ir-chelating site of the tritopic bridging ligand(s); (ii) the Ir−Ru distance is surely smaller in **IrRu$_2$(10)** and **IrRu$_2$(11)** than in **Ir$_2$Ru$_2$(2)$_3$**; (iii) the meta arrangement is not present in IrRu$_2$(**10**), so this species is expected to have a definitely larger interchromophoric coupling than **Ir$_2$Ru$_2$(2)$_3$**; the meta arrangement is still present in **IrRu$_2$(11)**, but as discussed above the Ir-based MLCT state for this compound most likely extends over the phenyl rings directly linked to the coordinating bpy moiety, so the meta "defect" is bypassed by the electronic nature of the Ir-based MLCT state. Altogether, (i)−(iii) points justify the different behavior of the mixed-metal compounds examined here as far as the occurrence of Ir-to-Ru energy transfer is concerned.

Trinuclear Homometallic Ir(III) and Ru(II) Species. The trinuclear homometallic **Ru$_3$(5)** and **Ir$_3$(5)** can be considered as the fully developed homologues of the dinuclear homometallic species **Ru$_2$(2)** and **Ir$_2$(2)**. In fact, the bridging ligand **5** derives from the bridging ligand **2** by the addition of the third "arm", identical to the other two that are already present in **2**. The molar absorption of the various absorption bands confirm that each subunit is only weakly coupled to the others, so the spectroscopic properties of each subunit do not differ significantly on passing from dinuclear to trinuclear systems (Table 1).

The photophysical properties of **Ru$_3$(5)** and **Ir$_3$(5)**, in agreement with the above reasoning, are indeed quite similar to those of their dinuclear counterparts **Ru$_2$(2)** and **Ir$_2$(2)**, both at 77 K and at room temperature (Table 1). As a consequence, the emission of the Ru(II) species is assigned to ^{3}MLCT state involving the bridging ligand as acceptor site, and the emission of the Ir(III) compound is assigned to a predominantly ^{3}LC state with partial ^{3}MLCT contribution.

The compounds **Ru$_3$(6)** and **Ir$_3$(6)** are also similar to **Ru$_3$(5)** and **Ir$_3$(5)**, as the structural difference between the two couple of trinuclear species only lies in the additional phenyl ring contained in each bridging ligand "arm" (see Figure 1). Also in this case, the metal-based subunits are essentially decoupled from one another, not surprisingly. The absorption and emission spectra of **Ru$_3$(6)** are clearly similar to those of **Ru$_3$(5)**, so further confirming that the acceptor ligand of the emitting MLCT state does not extends over the polyphenyl bridging ligand, but it only involves the phenyl directly connected to the terpyridine moiety. The photophysical properties of **Ir$_3$(6)**, on the contrary, differ from those of **Ir$_3$(5)**, as far as the emission wavelength is concerned, both at 77 K and at room temperature (Table 1, Figure 8): in both cases, a red shift of 20 nm is found for the emission spectra of **Ir$_3$(6)**. The red-shifted emission spectra are in agreement with the dominant LC nature of the emissive excited states of the Ir(III) species that, differently from MLCT states, also involve the additional phenyl ring(s) which are present in **6** compared to **5** tritopic bridging ligands.

Redox Behavior. Oxidation processes of Ru(II) and Ir(III) polypyridine compounds are usually metal centered.[17,18,21] The redox data of systems studied here (Table 1) are in agreement with such a common behavior, as the oxidation potentials of the homometallic Ru(II) species are within the potential range expected for the metal-centered oxidation for Ru(II) complexes based on bpy- and terpy-type ligands (+1.20/+1.30 V vs SCE[6a,20]) and the oxidation potentials of the homometallic Ir(III) species take place in the potential window (+1.30/+1.70 V vs SCE) expected for polypyridine and cyclometalated Ir(III) compounds.[6a] For the homometallic multinuclear complexes, all the oxidation processes involve more than one electron, in particular three electrons for **Ru$_3$(5)** and **Ru$_3$(6)**, which are attributed to three simultaneous one-electron metal-centered processes, and two electrons for the dinuclear species **Ru$_2$(2)**, which are attributed to two one-electron metal-centered oxidation processes. Similar behavior and relative attribution holds also for the homometallic multinuclear Ir(III) species. The absence of oxidation splitting in the multinuclear homometallic species confirms that each metal-centered

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[22] On passing from room temperature to 77 K the excited state lifetime of the Ir-based chromophore of **Ir$_2$Ru$_2$(2)$_3$** increases of 2 orders of magnitude, as indicated by the photophysical properties of the model **Ir$_2$(2)** species (see Table 1) and this would allow the energy transfer to successfully compete with intrinsic decay, even in the presence of a relatively low interchromophoric coupling.[8]

subunit is electronically "isolated", from the electrochemical viewpoint.

The mixed-metal compounds **IrRu$_2$(10)** and **IrRu$_2$(11)** exhibit two oxidation processes (see Table 1); in both compounds, the oxidation process occurring at less positive potential, which is bielectronic in nature, is assigned to simultaneous one-electron oxidation of the terminal Ru(II) subunits, whereas the one-electron oxidation taking place at more positive potential is assigned to the Ir(III) subunit.

Unfortunately, the reduction pattern of all the compounds is quite complicated and ill-behaved, since the reduced compounds apparently stick on the electrode. However, the first reduction potential is still safely measured in some cases, and is assigned to polypyridine ligand reduction, although more precise assignment cannot be made.

Conclusions

A series of new mixed-metal Ru(II)−Ir(III) polynuclear complexes have been prepared, together with their mononuclear parents and a series of closely related dinuclear and trinuclear homometallic Ru(II) and Ir(III) species. All the new compounds have been carefully characterized by NMR techniques, and their absorption spectra and luminescence properties (both at 77 K in rigid matrix and at room temperature in fluid solution) have been studied. The absorption spectra and luminescence properties of the Ru(II) species and subunits are dominated by MLCT transitions and excited states, whereas LC transitions and excited states govern the spectroscopic and photophysical properties of most of the Ir(III) species here studied, with MLCT states playing important role when cyclometalated Ir(III) subunits are present. The results also show that each metal-based subunit retains in the multinuclear arrays its own spectroscopic properties, but in the case of the mixed Ru−Ir species an additional decay channel is opened for the excited states involving the Ir-centered subunits, that is, photoinduced energy transfer to the lower-lying MLCT state(s) involving the Ru centers. The structure of the bridging ligand plays a key role in making such energy transfer process an effective decay route: we propose that a meta arrangement of the polyphenyl moieties which constitute the polytopic, bridging ligand framework can significantly reduce the interchromophoric electronic coupling so making the energy transfer process too slow to compete with the intrinsic decay of the Ir-based chromophore.

Work is in progress in our laboratories to design novel multinuclear heterometallic luminescent species, also including different metal centers, and to investigate the possible non-covalent interactions of the compounds containing large aromatic moieties with additional chromophores and/or donor and acceptor species.

Experimental Section

Material and Methods. All available chemicals were purchased from commercial sources and were used without any further purification. Solvents were purified by using standard methods and dried if necessary. Air- and moisture-sensitive reactions were performed under usual inert atmosphere techniques. Thin layer chromatography (TLC) was conducted on plates precoated with silica gel Si 60-F254 (Merck, Darmstadt, Germany) and aluminum oxide (Fluka, medium pore diameter 60 Å). Column chromatography was conducted by using silica gel Si 60, 230−400 mesh, 0.040−0.063 mm (Merck, Darmstadt, Germany) and neutral activated aluminum oxide 50−200 μm (Acros Organics, Geel, Belgium). Melting points have been obtained by a Büchi 535 instrument and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 (400 and 100.6 MHz, respectively); chemical shifts are indicated in parts per million downfield from SiMe$_4$, using the residual proton ($CHCl_3 = 7.26$ ppm; $CHD_2CN = 1.94$ ppm; $CF_3COOD =$ 11.6 ppm) and carbon ($CDCl_3 = 77.0$ ppm; $CD_3CN = 1.3$ ppm; $CF_3COOD = 163$ ppm) solvent resonances as internal reference. Protons and carbon assignments were achieved by ^{13}C-APT, ^{1}H−^{1}H COSY, and ^{1}H−^{13}C heteronuclear correlation experiments. ESI mass spectra were obtained with an electrospray ion-trap mass spectrometer ICR-FTMS APEX II (Bruker Daltonics). Elemental analyses were carried out by the Department Service of Microanalysis (University of Milan).

Absorption spectra were recorded with a JASCO V570 spectrophotometer. For Luminescence spectra a Jobin Yvon-Spex Fluoromax 2 spectrofluorimeter was used, equipped with a Hamamatsu R3896 photomultiplier, and the spectra were corrected for photomultiplier response using a program purchased with the fluorimeter. Luminescence lifetimes were determined by time-correlated single-photon-counting (TCSPC) with an Edinburgh OB900 spectrometer (light pulse: Hamamatsu PL2 laser diode, pulse width 59 ps at 408 nm; or nitrogen discharge, pulse width at 337 nm: 2 ns). Luminescence quantum yields have been performed by the optical dilute method.[23] As quantum yield reference, $[Ru(bpy)_3]^{2+}$ in aqueous deaerated solution was used ($\Phi = 0.028$).[24] Electrochemical measurements were carried out in argon-purged acetonitrile at room temperature with an Autolab 12 equipment interfaced to a PC. The working electrode was a glassy carbon (8 mm^2, Amel) electrode. The counter electrode was a Pt wire, and the reference electrode was an SCE separated with a fine glass frit. The concentration of the samples was about 5×10^{-4} M. Tetrabutylammonium hexafluorophosphate was used as supporting electrolyte and its concentration was 0.05 M. Cyclic voltammograms were obtained at scan rates of 20, 50, 200, and 500 mVs^{-1}. For reversible processes, half-wave potentials (versus SCE) were calculated as the average of the cathodic and anodic peaks. The criteria for reversibility were the separation of 60 mV between cathodic and anodic peaks, the close to unity ratio of the intensities of the cathodic and anodic currents, and the constancy of the peak potential on changing scan rate. The number of exchanged electrons was measured with differential pulse voltammetry (DPV) experiments performed with a scan rate of 20 mV s^{-1}, a pulse height of 75 mV, and a duration of 40 ms, and by taking advantage of the presence of ferrocene used as the internal reference.

Experimental uncertainties are as follows: absorption maxima, 2 nm; molar absorption coefficient, 10%; redox potentials, ± 20 mV; emission maxima, 5 nm; excited state lifetimes, 10%.

Synthesis. 4′-[4-(3-Bromo-5-methylphenyl)phenyl]-2,2′:6′,2″-terpyridine, 1. In a Schlenk flask placed under an atmosphere of nitrogen, 4′-(4-neopentylglyconatoboronphenyl)-2,2′:6′,2″-terpyridine **tpy-Bneo** (1.0 g, 2.37 mmol), 1,3-dibromotoluene (1.78 g, 7.12 mmol) and $[Pd(PPh_3)_4]$ (137 mg, 0.119 mmol) were dissolved in deaerated THF (50 mL). A 2 M aqueous solution of sodium carbonate (6 mL, 12 mmol) was added, and the mixture was purged with nitrogen through three freeze−pump−thaw cycles at low temperature. The reaction mixture was heated at 85 °C under vigorous stirring for 18 h. The organic solvent was removed in vacuo, and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The organic phase was dried over Na_2SO_4, and the solvent was removed. The product was purified by gravimetric column chromatography over silica gel

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(CH_2Cl_2/MeOH 95:5), to yield **1** as a pale white solid (824 mg, 77%). mp 254 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.78 (s, 2H, tpy$H^{3',5'}$), 8.75 (br d, 2H, J = 4.0 Hz, tpy$H^{6,6''}$), 8.69 (d, 2H, J = 8.0 Hz, tpy$H^{3,3''}$), 7.99 [d, 2H, J = 8.3 Hz, Ar(A)$H^{2,6}$], 7.89 (dt, 2H, J = 8.0, 2.0 Hz, tpy$H^{4,4''}$), 7.69 [d, 2H, J = 8.3 Hz, Ar(A)$H^{3,5}$], 7.61 [br s, 1H, Ar(B)H^2], 7.35−7.39 [m, 4H, tpy$H^{5,5''}$, Ar(B)H^4 and Ar(B)H^6], 2.43 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, 30 °C): δ 156.4 (q), 156.1 (q), 149.8 (q), 149.3 (tpy$C^{6,6''}$), 142.5 (q), 140.7 (q), 140.6 (q), 138.0 (q), 137.0 (tpy$C^{4,4''}$), 131.3 [Ar(B)C^4], 127.9 [Ar(A)$C^{2,6}$], 127.8 [Ar(A)$C^{3,5}$], 127.4 [Ar(B)C^2], 126.8 [Ar(B)C^6], 124.0 (tpy$C^{5,5''}$), 122.9 (q), 121.6 (tpy$C^{3,3''}$), 118.9 (tpy$C^{3',5'}$), 21.5 (CH$_3$). ESI-MS (477.1, calcd for $C_{28}H_{20}BrN_3$) m/z (%): 478.1 (100), 480.1 (97.6) $[M+H]^+$; 500.1 (100), 502.1 (97.6) $[M+Na]^+$; 979.1 (100), 980.1 (53.3) $[2M+Na]^+$. Anal. found: C 70.49, H 4.22, N 8.79%; Calcd for $C_{28}H_{20}BrN_3$: C 70.30, H 4.21, N 8.78%.

4,4″-Bis(2,2′:6′,2″-terpyridin-4′-yl)-5′-methyl-1,1′:3′1″-terphenyl, 2. Compound **2** was prepared following an analogous procedure as described for **1**, from **tpy-Bneo** (320 mg, 0.759 mmol), 1,3-dibromotoluene (64 mg, 0.256 mmol), $[Pd(PPh_3)_4]$ (20 mg, 0.017 mmol), and 0.2 M aqueous Na_2CO_3 (6.5 mL, 1.3 mmol) in THF (35 mL). The isolation of the product was performed as described above, and the residue was dissolved in CH_2Cl_2 (2 mL) and MeOH (10 mL) was added. After concentration of this solution, compound **2** was collected as a pale white solid (160 mg, 88%) by filtration. mp 214 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.81 (s, 4H, tpy$H^{3',5'}$), 8.76 (br d, 4H, J=4.4 Hz, tpy$H^{6,6''}$), 8.68 (d, 4H, J=8.0 Hz, tpy$H^{3,3''}$), 8.03 (d, 4H, J = 8.4 Hz, tph$H^{3,5}$), 7.88 (dt, 4H, J = 8.8, 2.8 Hz, tpy$H^{4,4''}$), 7.81 (d, 4H, J = 8.4 Hz, tph$H^{2,6}$), 7.75 (br s, 1H, tph$H^{2'}$), 7.50 (br s, 2H, tph$H^{4',6'}$), 7.34−7.37 (m, 4H, tpy$H^{5,5''}$), 2.54 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, 30 °C): δ 156.4 (q), 156.1 (q), 149.9 (q), 149.3 (tpy$C^{6,6''}$), 142.0 (q), 141.3 (q), 139.2 (q), 137.6 (q), 137.0 (tpy$C^{4,4''}$), 127.9 (tph$C^{2,6}$ and tph$C^{3,5}$), 127.4 (tph$C^{4',6'}$), 124.0 (tpy$C^{5,5''}$), 123.4 (tph$C^{2'}$), 121.5 (tpy$C^{3,3''}$), 118.9 (tpy$C^{3',5'}$), 21.8 (CH$_3$). ESI-MS (706.3, calcd for $C_{49}H_{34}N_6$) m/z: 707.3 (100) $[M+H]^+$; 729.3 $[M+Na]^+$. Anal. found: C 83.48, H 4.84, N 11.86%; Calcd for $C_{49}H_{34}N_6$: C 83.26, H 4.85, N 11.89%.

4′-[4-(3,5-Dibromophenyl)phenyl]-2,2′:6′,2″-terpyridine, 3. Compound **3** was prepared following an analogous procedure as described for **1**, from **tpy-Bneo** (500 mg, 1.19 mmol), 1,3,5-tribromobenzene (2.24 g, 7.14 mmol), $[Pd(PPh_3)_4]$ (68 mg, 0.059 mmol) and 1.0 M aqueous Na_2CO_3 (4 mL, 4.0 mmol) in THF (30 mL). The isolation of the product was performed as described above, and the residue was purified by gravimetric column chromatography over silica gel (CH_2Cl_2/petroleum ether, 4:1), to yield **3** as a yellow solid (470 mg, 72%). mp 294 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.78 (s, 2H, tpy$H^{3',5'}$), 8.75 (br d, 2H, J = 4.0 Hz, tpy$H^{6,6''}$), 8.69 (d, 2H, J = 8.0 Hz, tpy$H^{3,3''}$), 8.01 [d, 2H, J = 8.3 Hz, Ar(A)$H^{2,6}$], 7.90 (dt, 2H, J = 7.7, 1.7 Hz, tpy$H^{4,4''}$], 7.73 [d, 2H, J = 1.7 Hz, Ar(B)$H^{2,6}$], 7.67−7.69 [m, 3H, Ar(A)$H^{3,5}$ and Ar(B)H^4], 7.37 (dd, 2H, J=7.7, 4 Hz, tpy$H^{5,5''}$); ^{13}C NMR (101 MHz, $CDCl_3$, 30 °C): δ 156.4 (q), 156.3 (q), 149.6 (q), 149.3 (tpy$C^{6,6''}$), 144.2 (q), 139.1 (q), 138.7 (q), 137.1 (tpy$C^{4,4''}$), 133.1 [Ar(B)C^4], 129.1 [Ar(B)$C^{2,6}$], 128.2 [Ar(A)$C^{2,6}$], 127.8 [Ar(A)$C^{3,5}$], 124.1 (tpy$C^{5,5''}$), 123.6 (q), 121.6 (tpy$C^{3,3''}$), 118.9 (tpy$C^{3',5'}$). ESI-MS (541.0, calcd for $C_{27}H_{17}Br_2N_3$) m/z (%): 543.0 (100), 541.0 (51), 545.0 (49) $[M+H]^+$; 566.0 (100), 564.0 (51), 568.0 (49) $[M+Na]^+$. $]^+$. Anal. found: C 59.80, H 3.16, N 7.75%; Calcd for $C_{27}H_{17}Br_2N_3$: C 59.69, H 3.15, N, 7.73%.

4,4″-Bis(2,2′:6′,2″-terpyridin-4′-yl)-5′-bromo-1,1′:3′1″-terphenyl, 4. Compound **4** was prepared following an analogous procedure as described for **1**, from **tpy-Bneo** (150 mg, 0.356 mmol), terpyridine **3** (387 mg, 0.712 mmol), $[Pd(PPh_3)_4]$ (40 mg, 0.035 mmol), and 0.5 M aqueous Na_2CO_3 (4.3 mL, 2.15 mmol) in THF (35 mL). The isolation of the product was performed as described above, and the residue was purified by gravimetric column chromatography over silica gel (CH_2Cl_2/MeOH 200:1), to yield **4** as a white solid (824 mg, 77%). mp 294 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.81 (s, 4H, tpy$H^{3',5'}$), 8.75 (br d, 4H, J = 4.0, tpy$H^{6,6''}$), 8.70 (d, 4H, J = 8.0 Hz, tpy$H^{3,3''}$), 8.04 (d, 4H, J=8.3 Hz, tph$H^{3,5}$), 7.89 (dt, 4H, J=7.7, 1.8 Hz, tpy$H^{4,4''}$), 7.85 (m, 1H, tph$H^{2'}$), 7.82 (m, 2H, tph$H^{4',6'}$), 7.79 (d, 4H, J=8.3 Hz, tph$H^{2,6}$), 7.37 (br dd, 4H, J=7.7, 4.0 Hz, tpy$H^{5,5''}$). ^{13}C NMR (101 MHz, $CDCl_3$, 30 °C): δ 156.4 (q), 156.2 (q), 149.7 (q), 149.3 (tpy$C^{6,6''}$), 143.2 (q), 140.4 (q), 138.4 (q), 137.0 (tpy$C^{4,4''}$), 129.4 (tph$C^{4',6'}$), 128.1 (tph$C^{3,5}$), 127.9 (tph$C^{2,6}$), 125.0 (tph$C^{2'}$), 124.1 (tpy$C^{5,5''}$), 123.6 (q), 121.6 (tpy$C^{3,3''}$), 118.9 (tpy$C^{3',5'}$). ESI-MS (770.2, calcd for $C_{48}H_{31}BrN_6$) m/z (%): 773.2 (100), 771.2 (95.4), 772.2 (50), 774.2 (47.3) $[M+H]^+$; 795.2 (100), 793.2 (89.5), 796.2 (52.6), 794.2 (47.4) $[M+Na]^+$. Anal. found: C 74.80, H 4.06, N 11.01%; Calcd for $C_{48}H_{31}BrN_6$: C 74.71, H 4.05, N 10.87%.

1,3,5-Tris[4-(2,2′:6′,2″-terpyridin-4′-yl)phenyl]benzene, 5. Compound **5** was prepared following an analogous procedure as described for **1**, from **tpy-Bneo** (400 mg, 0.96 mmol), 1,3,5-tribromobenzene (75 mg, 0.24 mmol), $[Pd(PPh_3)_4]$ (27 mg, 0.023 mmol), and 0.2 M aqueous Na_2CO_3 (8.3 mL, 1.66 mmol) in THF (40 mL). The product precipitated from the reaction mixture and was isolated by filtration on a fritted glass. The collected solid was washed with THF (10 mL), water (20 mL), and finally Et_2O (20 mL) to afford tris-terpyridine **5** as a pale white solid (167 mg, 70%). mp 374 °C. ^{1}H NMR (400 MHz, CF_3COOD, 30 °C): δ 9.26 (br d, 6H, J = 8.0 Hz, tpy$H^{6,6''}$), 9.08 (d, 6H, J = 8.0 Hz, tpy$H^{3,3''}$), 8.94−9.01 (m, 12H, tpy$H^{3',5'}$ and tpy$H^{4,4''}$), 8.34 (m, 6H, tpy$H^{5,5''}$), 8.14−8.21 [m, 15H, Ar(A)$H^{3,5}$, Ar(A)$H^{2,6}$, and Ar(B)$H^{2,4,6}$]. ^{13}C NMR (101 MHz, CF_3COOD, 30 °C): δ 156.8 (q), 149.6 (tpy$C^{4,4''}$), 148.4 (q), 148.2 (q), 145.6 (q), 146.6 (tpy$C^{6,6''}$), 142.7 (q), 135.3 (q), 129.7 [Ar(A)$C^{2,6}$], 129.3 (tpy$C^{5,5''}$), 128.8 [Ar(A)$C^{3,5}$], 127.0 [Ar(B)$C^{2,4,6}$], 126.0 (tpy$C^{3,3''}$), 124.4 (tpy$C^{3',5'}$). ESI-MS (999.4, calcd for $C_{69}H_{45}N_9$) m/z (%): 1000.4 (100), 1001.4 (75.3), 1002.4 (23.4) $[M+H]^+$; 500.7 (100), 501.2 (74), 501.7 (24.4) $[M+2H]^{2+}$. Anal. found: C 83.04, H 4.56, N 12.63%; Calcd for $C_{69}H_{45}N_9$: C 82.86, H 4.54, N 12.60%.

1,3,5-Tris{4-[4-(2,2′:6′,2″-terpyridin-4′-yl)phenyl]phenyl}benzene, 6. Compound **6** was prepared following an analogous procedure as described for **1**, from **tpy-Bneo** (320 mg, 0.76 mmol), 1,3,5-tris-(4-bromophenyl)benzene (103 mg, 0.19 mmol), $[Pd(PPh_3)_4]$ (23 mg, 0.020 mmol) and 0.2 M aqueous Na_2CO_3 (5.7 mL, 1.14 mmol) in THF (40 mL). The product precipitated from the reaction mixture and was isolated by filtration on a fritted glass. The collected solid was washed with THF (15 mL), water (20 mL), and finally Et_2O (20 mL) to afford tris-terpyridine **6** as a white solid (180 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C): δ 8.82 (s, 6H, tpy$H^{3',5'}$), 8.75 (br d, 6H, J=5.0 Hz, tpy$H^{6,6''}$), 8.70 (d, 6H, J=8.0 Hz, tpy$H^{3,3''}$), 8.05 [d, 6H, J = 8.4 Hz, Ar(A)$H^{3,5}$], 7.94 [s, 3H, Ar(C)$H^{2,4,6}$], 7.83−7.92 [m, 24H, Ar(A)$H^{2,6}$, Ar(B)$H^{2,6}$, Ar(B)$H^{3,5}$ and tpy$H^{4,4''}$], 7.37 (dd, 6H, J = 7.7, 5.0 Hz, tpy$H^{5,5''}$). ^{13}C NMR (101 MHz, $CDCl_3$, 30 °C): δ 156.4 (q), 156.2 (q), 149.9 (q), 149.3 (tpy$C^{6,6''}$), 142.1 (q), 141.4 (q), 140.5 (q), 139.8 (q), 137.6 (q), 137.0 (tpy$C^{4,4''}$), 128.0 [Ar(A)$C^{3,5}$ and Ar(A)$C^{2,6}$], 127.8 [Ar(B)$C^{2,6}$ or Ar(B)$C^{3,5}$], 127.7 [Ar(B)$C^{2,6}$ or Ar(B)$C^{3,5}$], 125.3 [Ar(C)$C^{2,4,6}$], 124.0 (tpy$C^{5,5''}$), 121.5 (tpy$C^{3,3''}$), 118.9 (tpy$C^{3',5'}$). ESI-MS (1227.5, calcd for $C_{87}H_{57}N_9$) m/z (%): 1229.5 (100), 1228.5 (95.7), 1230.5 (42.8) $[M+H]^+$; 614.7 (100), 615.2 (96.7), 615.7 (41.8) $[M+2H]^{2+}$; 410.2 (100), 410.5 (96.2), 410.8 (40.9) $[M+3H]^{3+}$. Anal. found: C 85.28, H 4.69, N 10.24%; Calcd for $C_{87}H_{57}N_9$: C 85.06, H 4.68, N 10.26%.

[(tpy)Ru(1)][PF$_6$]$_2$, Ru(1). $[Ru(tpy)Cl_3]$ (55 mg, 0.12 mmol) was added to a solution of **1** (48 mg 0.10 mmol) in MeOH (20 mL). A few drops of *N*-ethylmorpholine were added, and the mixture was heated at reflux under nitrogen for 5 h, after which it was cooled and filtered. A saturated aqueous solution of NH_4PF_6 was added to the filtrate to give a red precipitate that was collected by filtration and purified by chromatography (SiO_2, MeCN/0.2 M aqueous KNO_3 100:1), to afford **Ru(1)**

(45 mg, 43%) after anionic exchange with hexafluorophosphate as a red microcrystalline solid. ^{1}H NMR (400 MHz, CD$_3$CN, 30 °C): δ 9.05 [s, 2H, (**1**)tpy$H^{3',5'}$], 8.77 (d, 2H, J = 8.2 Hz, tpy$H^{3',5'}$), 8.67 [br d, 2H, J = 8.0 Hz, (**1**)tpy$H^{3,3''}$], 8.50 (br d, 2H, J = 8.0 Hz, tpy$H^{3,3''}$), 8.42 (t, 1H, J = 8.2 Hz, tpy$H^{4'}$), 8.31 [d, 2H, J = 8.5 Hz, Ar(A)$H^{2,6}$], 8.01 [d, 2H, J = 8.5 Hz, Ar(A)$H^{3,5}$], 7.90−7.97 [m, 4H, (**1**)tpy$H^{4,4''}$ and tpy$H^{4,4''}$], 7.83 [br s, 1H, Ar(B)H^2], 7.66 [br s, 1H, Ar(B)H^4], 7.51 [br s, 1H, Ar(B)H^6], 7.43 [br d, 2H, J = 5.6 Hz, (**1**)tpy$H^{6,6''}$], 7.35 (br d, 2H, J = 5.6 Hz, tpy$H^{6,6''}$), 7.16−7.20 [m, 4H, (**1**)tpy$H^{5,5''}$ and tpy$H^{5,5''}$], 2.48 (s, 3H, CH_3). ^{13}C NMR (101 MHz, CD$_3$CN, 30 °C): δ 159.1 (q), 159.0 (q), 156.5 (q), 156.4 (q), 153.5 (tpy$C^{6,6''}$), 153.4 [(**1**)tpy$C^{6,6''}$], 148.6 (q), 142.7 (q), 142.5 (q), 142.4 (q), 139.1 [(**1**)tpy$C^{4,4''}$ or tpy$C^{4,4''}$], 139.0 [(**1**)tpy$C^{4,4''}$ or tpy$C^{4,4''}$], 137.2 (q), 136.8 (tpy$C^{4'}$), 132.5 [Ar(B)C^6], 129.3 [Ar(A)$C^{2,6}$], 129.17 [Ar(A)$C^{3,5}$], 128.5 [(**1**)tpy$C^{5,5''}$ and tpy$C^{5,5''}$], 128.0 [Ar(B)C^2], 127.9 [Ar(B)C^4], 125.5 [(**1**)tpy$C^{3,3''}$], 125.4 (tpy$C^{3,3''}$), 124.7 (tpy$C^{3',5'}$), 123.5 (q), 122.5 [(**1**)tpy$C^{3',5'}$], 21.3 (CH$_3$). ESI-MS: (1102.0, calcd for $C_{43}H_{31}BrF_{12}N_6P_2Ru$) m/z (%): 959.0 (100), 957.0 (95.8), 958.0 (62.3), 956.0 (58.4) [M−PF$_6$]$^+$; 407.0 (100), 406.0 (89.0), 406.5 (59.3), 405.5 (59.2) [M−2PF$_6$]$^{2+}$. Anal. found: C 46.78, H 2.87, N 7.63%; Calcd for $C_{43}H_{31}BrF_{12}N_6P_2Ru$: C 46.84, H 2.86, N 7.62%.

[(tpy)Ru(2)Ru(tpy)][PF$_6$]$_4$, Ru$_2$(2). [Ru(tpy)Cl$_3$] (62 mg, 0.14 mmol) was added to a suspension of **2** (49 mg, 0.07 mmol) in EtOH (20 mL) containing a few drops of *N*-ethylmorpholine. The mixture was heated at reflux under nitrogen for 24 h, after which it was cooled and filtered. A saturated aqueous solution of NH$_4$PF$_6$ was added to the filtrate to give a red precipitate that was collected by filtration and purified by chromatography (SiO$_2$, MeCN/0.2 M aqueous KNO$_3$ 100:1), to afford **Ru$_2$(2)** (109 mg, 80%) after anionic exchange with hexafluorophosphate as a red microcrystalline solid. ^{1}H NMR (400 MHz, CD$_3$CN, 30 °C): δ 9.10 [s, 4H, (**2**)tpy$H^{3',5'}$], 8.77 (d, 4H, J = 8.2 Hz, tpy$H^{3',5'}$), 8.70 [br d, 4H, J = 8.0 Hz, (**2**)tpy$H^{3,3''}$], 8.52 (br d, 4H, J = 8.0 Hz, tpy$H^{3,3''}$), 8.43 (t, 2H, J = 8.2 Hz, tpy$H^{4'}$), 8.39 [d, 4H, J = 8.5 Hz, (**2**)Ar(A)$H^{2,6}$], 8.20 [d, 4H, J = 8.5 Hz, (**2**)Ar(A)$H^{3,5}$], 8.09 [br s, 1H, (**2**)Ar(B)H^4], 7.92−7.99 [m, 8H, (**2**)tpy$H^{4,4''}$ and tpy$H^{4,4''}$], 7.79 [br s, 2H, (**2**)Ar(B)$H^{2,6}$], 7.47 [br d, 4H, J = 5.6 Hz, (**2**)tpy$H^{6,6''}$], 7.38 (br d, 4H, J = 5.6 Hz, tpy$H^{6,6''}$), 7.17−7.22 [m, 8H, (**2**)tpy$H^{5,5''}$ and tpy$H^{5,5''}$], 2.64 (s, 3H, CH_3). ^{13}C NMR (101 MHz, CD$_3$CN, 30 °C): δ 159.2 (q), 159.1 (q), 156.5 (q), 156.4 (q), 153.6 (tpy$C^{6,6''}$), 153.4 [(**2**)tpy$C^{6,6''}$], 148.8 (q), 143.8 (q), 141.6(q), 140.9 (q), 139.1 [(**2**)tpy$C^{4,4''}$ or tpy$C^{4,4''}$], 139.0 [(**2**)tpy$C^{4,4''}$ or tpy$C^{4,4''}$], 136.9 (q), 136.8 (tpy$C^{4'}$), 129.3 [Ar(A)$C^{2,6}$ and Ar(A)$C^{3,5}$], 128.8 [Ar(B)$C^{2,6}$], 128.5 [(**2**)tpy$C^{5,5''}$ and tpy$C^{5,5''}$], 125.6 [(**2**)tpy$C^{3,3''}$], 125.4 (tpy$C^{3,3''}$), 124.7 (tpy$C^{3',5'}$), 124.1 [Ar(B)C^4], 122.5 [(**2**)tpy$C^{3',5'}$], 21.7 (CH$_3$). ESI-MS (1956.1, calcd for $C_{79}H_{56}F_{24}N_{12}P_4Ru_2$) m/z (%): 833.1 (100), 832.6 (96.1), 833.6 (82.3), 834.1 (78.5) [M−2PF$_6$]$^{2+}$; 507.1 (100), 506.7 (93.3), 507.4 (76.3), 506.1 (75.5) [M−3PF$_6$]$^{3+}$; 344.1 (100), 343.8 (92.6), 344.3 (77.8), 343.6 (72.6) [M−4PF$_6$]$^{4+}$. Anal. found: C 48.43, H 2.90, N 8.57%; Calcd for $C_{79}H_{56}F_{24}N_{12}P_4Ru_2$: C 48.53, H 2.89, N 8.60%.

{[(tpy)Ru]$_3$(5)}[PF$_6$]$_6$, Ru$_3$(5). [Ru(tpy)Cl$_3$] (106 mg, 0.24 mmol) was added to a suspension of **5** (77 mg, 0.08 mmol) in a mixture of THF (5 mL) and DMF (50 mL) containing a few drops of *N*-ethylmorpholine. The resulting suspension was heated at reflux under nitrogen for 24 h, after which a clear red solution was obtained. This was cooled and concentrated by evaporation under reduced pressure. After addition of a saturated aqueous solution of NH$_4$PF$_6$, water (80 mL) was added to facilitate the precipitation of a deep red solid. This was collected by filtration and purified by chromatography (SiO$_2$, MeCN/0.2 M aqueous KNO$_3$ 95:5), to afford **Ru$_3$(5)** (126 mg, 55%) after anionic exchange with hexafluorophosphate as a red crystalline solid. ^{1}H NMR (400 MHz, CD$_3$CN, 30 °C): δ 9.14 [s, 6H, (**5**)tpy$H^{3',5'}$], 8.78 (d, 6H, J = 8.2 Hz, tpy$H^{3',5'}$), 8.71 [br d, 6H, J = 8.0 Hz, (**5**)tpy$H^{3,3''}$], 8.53 (br d, 6H, J = 8.0 Hz, tpy$H^{3,3''}$), 8.37−8.48 [m, 18H, (**5**)Ar(A)$H^{2,6}$, tpy$H^{4'}$, (**5**)Ar(A)$H^{3,5}$ and (**5**)Ar(B)$H^{2,4,6}$], 7.93−8.01 [m, 12H, (**5**)tpy$H^{4,4''}$ and tpy$H^{4,4''}$], 7.48 [br d, 6H, J = 5.6 Hz, (**5**)tpy$H^{6,6''}$], 7.39 (br d, 6H, J = 5.6 Hz, tpy$H^{6,6''}$), 7.19−7.23 [m, 12H, (**5**)tpy$H^{5,5''}$ and tpy$H^{5,5''}$]. ^{13}C NMR (101 MHz, CD$_3$CN, 30 °C): δ 159.2 (q), 159.1 (q), 156.6 (q), 156.4 (q), 153.6 (tpy$C^{6,6''}$), 153.4 [(**5**)tpy$C^{6,6''}$], 148.7 (q), 143.5 (q), 142.6 (q), 139.1 [(**5**)tpy$C^{4,4''}$ and tpy$C^{4,4''}$], 137.4 (q), 136.9 (tpy$C^{4'}$), 129.7 [Ar(A)$C^{2,6}$], 129.5 [Ar (A)$C^{3,5}$], 128.5 [(**5**)tpy $C^{5,5''}$ and tpy$C^{5,5''}$], 126.9 [Ar(B)$C^{2,4,6}$], 125.6 [(**5**)tpy$C^{3,3''}$], 125.5 (tpy$C^{3,3''}$), 124.8 (tpy$C^{3',5'}$), 122.6 [(**5**)tpy$C^{3',5'}$]. ESI-MS (2874.2, calcd for $C_{114}H_{78}F_{36}N_{18}P_6Ru_3$) m/z (%): 813.1 (100) [M−3PF$_6$]$^{3+}$; 573.3 (100) [M−4PF$_6$]$^{4+}$; 429.7 (100) [M−5PF$_6$]$^{5+}$; 333.9 (100) [M−6PF$_6$]$^{6+}$. Anal. found: C 47.74, H 2.75, N 8.79%; Calcd for $C_{114}H_{78}F_{36}N_{18}P_6Ru_3$: C 47.66, H 2.74, N 8.78%.

{[(tpy)Ru]$_3$(6)}[PF$_6$]$_6$, Ru$_3$(6). [Ru(tpy)Cl$_3$] (115 mg, 0.26 mmol) was added to a suspension of **6** (86 mg, 0.07 mmol) in a mixture of THF (5 mL) and DMF (50 mL) containing a few drops of *N*-ethylmorpholine. The resulting suspension was heated at reflux under nitrogen for 24 h, after which a clear red solution was obtained. This was cooled and concentrated by evaporation under reduced pressure. After addition of a saturated aqueous solution of NH$_4$PF$_6$, water (80 mL) was added to facilitate the precipitation of a deep red solid. This was collected by filtration and purified by chromatography (SiO$_2$, MeCN/0.2 M aqueous KNO$_3$ 95:5), to afford **Ru$_3$(6)** (108 mg, 50%) after anionic exchange with hexafluorophosphate as a red crystalline solid. ^{1}H NMR (400 MHz, CD$_3$CN, 30 °C): δ 9.11 [s, 6H, (**6**)tpy$H^{3',5'}$], 8.78 (d, 6H, J = 8.2 Hz, tpy$H^{3',5'}$), 8.71 [br d, 6H, J = 8.0 Hz, (**6**)tpy$H^{3,3''}$], 8.52 (br d, 6H, J = 8.0 Hz, tpy$H^{3,3''}$), 8.43 (t, 3H, J = 8.2 Hz, tpy$H^{4'}$), 8.39 [d, 6H, J = 8.5 Hz, (**6**)Ar(A)$H^{2,6}$], 8.07−8.20 [m, 21H, (**6**)Ar(A)$H^{3,5}$, (**6**)Ar(B)$H^{2,4}$, (**6**)Ar(B)$H^{3,5}$ and (**6**)Ar(C)$H^{2,4,6}$], 7.93−7.99 [m, 12H, (**6**)tpy$H^{4,4''}$ and tpy$H^{4,4''}$], 7.48 [br d, 6H, J = 5.6 Hz, (**6**)tpy$H^{6,6''}$], 7.38 (br d, 6H, J = 5.6 Hz, tpy$H^{6,6''}$), 7.18−7.22 [m, 12H, (**6**)tpy$H^{5,5''}$ and tpy$H^{5,5''}$]. ^{13}C NMR (101 MHz, CD$_3$CN, 30 °C): δ 159.2 (q), 159.1 (q), 156.5 (q), 156.4 (q), 153.6 (tpy$C^{6,6''}$), 153.4 [(**6**)tpy$C^{6,6''}$], 148.7 (q), 143.2 (q), 142.8 (q), 141.5 (q), 140.1 (q), 139.1 [(**6**)tpy$C^{4,4''}$ and tpy$C^{4,4''}$], 136.9 (q), 136.8 (tpy$C^{4'}$), 129.4 [Ar(A)$C^{2,6}$], 129.2 [Ar(A)$C^{3,5}$], 129.0 [Ar(B)$C^{2,6}$], 128.7 [Ar(B)$C^{3,5}$], 128.5 [(**6**)tpy$C^{5,5''}$ and tpy$C^{5,5''}$], 126.1 [Ar(C)$C^{2,4,6}$], 125.6 [(**6**)tpy$C^{3,3''}$], 125.5 (tpy$C^{3,3''}$), 124.8 (tpy$C^{3',5'}$), 122.5 [(**6**)tpy$C^{3',5'}$]. ESI-MS (3102.3, calcd for $C_{132}H_{90}F_{36}N_{18}P_6Ru_3$) m/z (%): 888.8 (100) [M−3PF$_6$]$^{3+}$; 630.6 (100) [M−4PF$_6$]$^{4+}$; 475.3 (100) [M−5PF$_6$]$^{5+}$; 372.9 (100) [M−6PF$_6$]$^{6+}$. Anal. found: C 51.22, H 2.92, N 8.14%; Calcd for $C_{132}H_{90}F_{36}N_{18}P_6Ru_3$: C 51.12, H 2.93, N 8.13%.

[(tpy)Ir(1)][PF$_6$]$_3$, Ir(1). A suspension of [Ir(tpy)Cl$_3$] (112 mg, 0.21 mmol) and **1** (101 mg 0.21 mmol) in ethylene glycol (20 mL) was heated under nitrogen for 2 h. After cooling at room temperature, a saturated aqueous solution of NH$_4$PF$_6$ was added. The precipitated solid was filtered, washed with water, and finally purified by column chromatography (SiO$_2$, MeCN/0.2 M aqueous KNO$_3$, 100:1 to 4:1), to yield after anionic exchange with hexafluorophosphate **Ir(1)** (70 mg, 25%) as a yellow crystalline solid. ^{1}H NMR (400 MHz, CD$_3$CN, 30 °C): δ 9.12 [s, 2H, (**1**)tpy$H^{3',5'}$], 8.86 (dd, 2H, J = 9.2, 7.6 Hz, tpy$H^{3',5'}$), 8.77 (dd, 1H, J = 9.2, 7.6 Hz, tpy$H^{4'}$), 8.74 [br d, 2H, J = 8.0 Hz, (**1**)tpy$H^{3,3''}$], 8.59 (br d, 2H, J = 8.0 Hz, tpy$H^{3,3''}$), 8.32 [d, 2H, J = 8.5 Hz, (**1**)Ar(A)$H^{2,6}$], 8.19−8.26 [m, 4H, (**1**)tpy$H^{4,4''}$ and tpy$H^{4,4''}$], 8.07 [d, 2H, J = 8.5 Hz, (**1**)Ar(A)$H^{3,5}$], 7.84 [br s, 1H, (**1**)Ar(B)H^2], 7.70 [br d, 2H, J = 5.6 Hz, (**1**)tpy$H^{6,6''}$], 7.67 [br s, 1H, (**1**)Ar(B)H^4], 7.60 (br d, 2H, J = 5.6 Hz, tpy$H^{6,6''}$), 7.47−7.52 [m, 5H, (**1**)Ar(B)H^6, (**1**)tpy$H^{5,5''}$ and tpy$H^{5,5''}$], 2.48 (s, 3H, CH_3). ^{13}C NMR (101 MHz, CD$_3$CN, 30 °C): δ 159.0 (q), 158.9 (q), 156.4 (q), 155.8 (q), 155.6 (q), 154.5 (tpy$C^{6,6''}$), 154.3 [(**1**)tpy$C^{6,6''}$], 144.7 (tpy$C^{4'}$), 143.9 [(**1**)tpy$C^{4,4''}$ or tpy$C^{4,4''}$], 143.8 [(**1**)tpy$C^{4,4''}$ or tpy$C^{4,4''}$], 142.5 (q), 142.3 (q), 135.6 (q), 132.9 [Ar(B)C^6], 130.8 [(**1**)tpy$C^{5,5''}$ and tpy$C^{5,5''}$], 130.0

[Ar(A)$C^{2,6}$], 129.4 [Ar(A)$C^{3,5}$], 128.4 [(**1**)tpy $C^{3,3''}$and tpy$C^{3,3''}$], 128.2 [Ar(B)C^{2}], 128.1 [Ar(B)C^{4}], 127.6 (tpy$C^{3',5'}$), 125.1 [(**1**)tpy$C^{3',5'}$], 123.5 (q), 21.3 (CH$_3$). ESI-MS (1338.0, calcd for $C_{43}H_{31}BrF_{18}IrN_6P_3$) *m/z*: 1193.1 (100), 1195.1 (71.5), 1194.1 (52.3), 1196.1 (33) $[M-PF_6]^{+}$; 524.1 (100), 525.1 (71.4), 524.6 (47.2), 522.6 $[M-2PF_6]^{2+}$; 301.1 (100), 301.7 (63.8), 301.4 (42), 300.4 (37.7) $[M-3PF_6]^{3+}$. Anal. found: C 38.65, H 2.35, N 6.27%; Calcd for $C_{43}H_{31}BrF_{18}IrN_6P_3$: C 38.58, H 2.33, N 6.28%.

[(tpy)Ir(2)Ir(tpy)][PF$_6$]$_6$, Ir$_2$(2). A suspension of [Ir(tpy)Cl$_3$] (64 mg, 0.12 mmol) and **2** (42 mg 0.06 mmol) in ethylene glycol (20 mL) was heated under nitrogen for 2 h. After cooling at room temperature, a saturated aqueous solution of NH$_4$PF$_6$ was added. The precipitated solid was filtered, washed with water, and finally purified by column chromatography (SiO$_2$, MeCN/0.2 M aqueous KNO$_3$, 100:1 to 4:1), to yield after anionic exchange with hexafluorophosphate **Ir$_2$(2)** (101 mg, 69%) as a yellow crystalline solid. ^{1}H NMR (400 MHz, CD$_3$CN, 30 °C): δ 9.17 [s, 4H, (**2**)tpy$H^{3',5'}$], 8.88 (dd, 4H, J = 9.2, 7.6 Hz, tpy$H^{3',5'}$), 8.76−8.81 [m, 6H, tpy$H^{4'}$ and (**2**)tpy$H^{3,3''}$], 8.61 (br d, 4H, J = 8.0 Hz, tpy$H^{3,3''}$), 8.40 [d, 4H, J = 8.5 Hz, (**2**)Ar(A)$H^{2,6}$], 8.22−8.27 [m, 12H, (**2**)tpy$H^{4,4''}$, tpy$H^{4,4''}$ and (**2**)Ar(A)$H^{3,5}$], 8.11 [br s, 1H, (**2**)Ar(B)H^{4}], 7.82 [br s, 2H, (**2**)Ar(B)$H^{2,6}$], 7.74 [br d, 4H, J = 5.6 Hz, (**2**)tpy$H^{6,6''}$], 7.61 (br d, 4H, J = 5.6 Hz, tpy$H^{6,6''}$), 7.49−7.54 [m, 8H, (**2**)tpy$H^{5,5''}$ and tpy$H^{5,5''}$], 2.64 (s, 3H, CH_3). ^{13}C NMR (101 MHz, CD$_3$CN, 30 °C): δ 159.0 (q), 158.9 (q), 156.5 (q), 155.8 (q), 155.6 (q), 154.4 (tpy$C^{6,6''}$), 154.3 [(**2**)tpy$C^{6,6''}$], 145.2 (q), 144.7 (tpy$C^{4'}$), 143.9 [(**2**)tpy$C^{4,4''}$ or tpy$C^{4,4''}$], 143.8 [(**2**)tpy$C^{4,4''}$ or tpy$C^{4,4''}$], 141.3 (q), 141.0 (q), 135.4 (q), 130.9 [(**2**)tpy$C^{5,5''}$ or tpy$C^{5,5''}$], 130.8 [(**2**)tpy$C^{5,5''}$ or tpy$C^{5,5''}$], 130.1 [Ar(A)$C^{2,6}$], 129.5 [Ar(A)$C^{3,5}$], 129.2 [Ar(B)$C^{2,6}$], 128.4 [(**2**)tpy$C^{3,3''}$ and tpy$C^{3,3''}$], 127.6 (tpy$C^{3',5'}$), 125.1 [(**2**)tpy$C^{3',5'}$], 124.4 [Ar(B)C^{4}], 21.7 (CH$_3$). ESI-MS (2428.2, calcd for $C_{79}H_{56}F_{36}Ir_2N_{12}P_6$) *m/z* (%): 1069.1 (100), 1068.1 (85.2), 1068.6 (71.8), 1069.6 (68.1) $[M-2PF_6]^{2+}$; 664.4 (100), 663.8 (85.9), 664.8 (76.8), 664.1 (75.3) $[M-3PF_6]^{3+}$. Anal. found: C 39.21, H 2.34, N 6.94%; Calcd for $C_{79}H_{56}F_{36}Ir_2N_{12}P_6$: C 39.09, H 2.33, N 6.92%.

{[(tpy)Ir]$_3$(5)}[PF$_6$]$_9$, Ir$_3$(5). A suspension of [Ir(tpy)Cl$_3$] (191 mg, 0.36 mmol) and **5** (120 mg 0.12 mmol) in ethylene glycol (40 mL) was heated under nitrogen for 2 h. After cooling at room temperature, a saturated aqueous solution of NH$_4$PF$_6$ was added. The precipitated solid was filtered, washed with water, and finally purified by column chromatography (SiO$_2$, MeCN/0.2 M aqueous KNO$_3$, 100:1 to 9:1), to yield after anionic exchange with hexafluorophosphate **Ir$_2$(5)** (129 mg, 30%) as a yellow crystalline solid. ^{1}H NMR (400 MHz, CD$_3$CN, 30 °C): δ 9.21 [s, 6H, (**5**)tpy$H^{3',5'}$], 8.90 (dd, 6H, J = 8.8, 7.6 Hz, tpy$H^{3',5'}$), 8.77−8.82 [m, 9H, (**5**)tpy$H^{3,3''}$ and tpy$H^{4'}$], 8.62 (br d, 6H, J = 8.4 Hz, tpy$H^{3,3''}$), 8.49 [d, 6H, J = 8.8 Hz, (**5**)Ar(A)$H^{3,5}$], 8.42−8.44 [m, 9H, (**5**)Ar(A)$H^{2,6}$ and (**5**)Ar(B)$H^{2,4,6}$], 8.27 [dt, 6H, J = 1.6, 8.8 Hz, (**5**)tpy$H^{4,4''}$], 8.23 [dt, 6H, J = 1.6, 8.8 Hz, tpy$H^{4,4''}$], 7.76 [br d, 6H, J = 5.6 Hz, (**5**)tpy$H^{6,6''}$], 7.63 (br d, 6H, J = 5.6 Hz, tpy$H^{6,6''}$), 7.50−7.56 [m, 12H, (**5**)tpy$H^{5,5''}$ and tpy$H^{5,5''}$]. ^{13}C NMR (101 MHz, CD$_3$CN, 30 °C): δ 159.0 (q), 158.9 (q), 156.5 (q), 155.7 (q), 155.5 (q), 153.4 (tpy$C^{6,6''}$), 153.3 [(**5**)tpy$C^{6,6''}$], 144.8 (q), 144.7 (tpy$C^{4'}$), 143.8 [(**5**)tpy$C^{4,4''}$ and tpy$C^{4,4''}$], 142.3 (q), 135.8 (q), 130.9 [Ar(A)$C^{2,6}$], 130.7 [Ar(A)$C^{3,5}$], 130.2 129.8 [(**5**)tpy$C^{5,5''}$ and tpy$C^{5,5''}$], 128.5 [(**5**)tpy$C^{3,3''}$], 128.4 (tpy$C^{3,3''}$), 127.6 (tpy$C^{3',5'}$), 127.4[Ar(B)$C^{2,4,6}$], 125.2 [(**5**)tpy$C^{3',5'}$]. ESI-MS (3582.2, calcd for $C_{114}H_{78}F_{54}Ir_3N_{18}P_9$) *m/z*: 1048.8 (100) $[M-3PF_6]^{3+}$; 750.6 (100) $[M-4PF_6]^{4+}$; 571.1 (100) $[M-5PF_6]^{5+}$; 451.9 (100) $[M-6PF_6]^{6+}$. Anal. found: C 38.34, H 2.19, N 7.02%; Calcd for $C_{114}H_{78}F_{54}Ir_3N_{18}P_9$: C 38.23, H 2.20, N 7.04%.

{[(tpy)Ir]$_3$(6)}[PF$_6$]$_9$, Ir$_3$(6). A suspension of [Ir(tpy)Cl$_3$] (127 mg, 0.24 mmol) and **6** (98 mg 0.08 mmol) in ethylene glycol (30 mL) was heated under nitrogen for 8 h. After cooling at room temperature, a saturated aqueous solution of NH$_4$PF$_6$ was added. The precipitated solid was filtered, washed with water, and finally purified by chromatography (SiO$_2$, MeCN/0.2 M aqueous KNO$_3$, 100:1 to 4:1), to yield after anionic exchange with hexafluorophosphate **Ir$_2$(6)** (76 mg, 25%) as a yellow crystalline solid. ^{1}H NMR (400 MHz, CD$_3$CN, 30 °C): δ 9.18 [s, 6H, (**6**)tpy$H^{3',5'}$], 8.89 (br d, 6H, J = 8.0 Hz, tpy$H^{3',5'}$), 8.78−8.81 [m, 9H, (**6**)tpy$H^{3,3''}$ and tpy$H^{4'}$], 8.62 (br d, 6H, J = 8.0 Hz, tpy$H^{3,3''}$), 8.41 [d, 6H, J = 8.4 Hz, (**6**)Ar(A)$H^{2,6}$], 8.08−8.28 [m, 33H, (**6**)Ar(A)$H^{3,5}$, (**6**)Ar(B)$H^{2,6}$, (**6**)Ar(B)$H^{3,5}$, (**6**)Ar(C)$H^{2,4,6}$, (**6**)tpy$H^{4,4''}$ and tpy$H^{4,4''}$], 7.75 [br d, 6H, J = 5.6 Hz, (**6**)tpy$H^{6,6''}$], 7.64 (br d, 6H, J = 5.6 Hz, tpy$H^{6,6''}$), 7.50−7.56 [m, 12H, (**6**)tpy$H^{5,5''}$ and tpy$H^{5,5''}$]. ^{13}C NMR (101 MHz, CD$_3$CN, 30 °C): δ 159.0 (q), 158.9 (q), 156.5 (q), 155.7 (q), 155.6 (q), 154.4 (tpy$C^{6,6''}$), 154.3 [(**6**)tpy$C^{6,6''}$], 144.7 (tpy$C^{4'}$), 144.6 (q), 143.9 [(**6**)tpy$C^{4,4''}$ or tpy$C^{4,4''}$], 143.8 [(**6**)tpy$C^{4,4''}$ or tpy$C^{4,4''}$], 142.7 (q), 141.8 (q), 139.7 (q), 135.3 (q), 130.9 [(**6**)tpy$C^{5,5''}$ or tpy$C^{5,5''}$], 130.8 [(**6**)tpy$C^{5,5''}$ or tpy$C^{5,5''}$], 130.2 [Ar (A)$C^{2,6}$], 129.2 [Ar(A)$C^{3,5}$], 129.2 [Ar(B)$C^{2,6}$], 128.9 [Ar(B)$C^{3,5}$], 128.5 [(**6**)-tpy$C^{3,3''}$ and tpy$C^{3,3''}$], 127.6 [tpy$C^{3',5'}$], 126.2 [Ar(C)$C^{2,4,6}$], 125.1 [(**6**)tpy$C^{3',5'}$]. ESI-MS (3810.3, calcd for $C_{132}H_{90}F_{54}Ir_3N_{18}P_9$) *m/z* 1124.8 (100) $[M-3PF_6]^{3+}$; 807.4 (100) $[M-4PF_6]^{4+}$; 617.1 (100) $[M-5PF_6]^{5+}$; 489.9 (100) $[M-6PF_6]^{6+}$; 399.2 (100) $[M-7PF_6]^{7+}$; 331.2 (100) $[M-8PF_6]^{9+}$; 278.3 (100) $[M-9PF_6]^{9+}$. Anal. found: C 41.52, H 2.39, N 6.64%; Calcd for $C_{132}H_{90}F_{54}Ir_3N_{18}P_9$: C 41.62, H 2.38, N 6.62%.

[Ir(F$_2$ppy)$_2$(7)][PF$_6$], Ir(7). Bis-(*μ*)-chlorotetrakis-(2-(2,4-difluorophenyl) pyridinatoC^2,N)diiridium(III) **[Ir(F$_2$ppy)$_2$Cl]$_2$** (239 mg, 0.20 mmol) was added to a solution of 4,4′-dibromo-2,2′-bipyridine **7** (163 mg, 0.52 mmol) dissolved in CH$_2$Cl$_2$ (60 mL) and MeOH (30 mL). The mixture was stirred at reflux for 18 h, after which a saturated aqueous solution of NH$_4$PF$_6$ was added. The solvent was removed in vacuo, and the residue, dissolved in CH$_2$Cl$_2$ (50 mL), was washed with water (3×20 mL). The organic phase was dried over Na$_2$SO$_4$, and the solvent was evaporated. The product was purified by gravimetric column chromatography over silica gel (CH$_2$Cl$_2$/MeOH, 100:1), to afford **Ir(7)** (370 mg, 90%) as a yellow solid. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 30 °C): δ 8.59 (d, 2H, J_{H-H} = 1.8 Hz, bpyH^3), 8.31 (dd, 2H, J_{H-H} = 8.4 Hz, pyH^3), 7.86 (br t, 2H, J_{H-H} = 8.4 Hz, pyH^4), 7.80 (d, 2H, J_{H-H} = 5.8 Hz, bpyH^6), 7.70 (dd, 2H, J_{H-H} = 1.8 and 5.8 Hz, bpyH^5), 7.53 (br d, 2H, J_{H-H} = 6.0 Hz, pyH^6), 7.11 (ddd, 2H, J_{H-H} = 1.6, 6.0, and 8.4 Hz, pyH^5), 6.61 (ddd, 2H, J_{H-H} = 2.4 Hz, J_{H-F} = 9.1 and 12.1 Hz, dfphH^3), 5.71 (dd, 2H, J_{H-H} = 2.4 Hz, J_{H-F} = 8.4 Hz, dfphH^5). ^{13}C NMR (101 MHz, CD$_2$Cl$_2$, 30 °C): δ 164.3 (dd, J_{C-F} = 12.7 and 259.0 Hz, q), 164.3 (d, J_{C-F} = 7.0 Hz, q), 161.7 (dd, J_{C-F} = 12.7 and 259.0, q), 155.7 (q), 152.6 (d, J_{C-F} = 6.7 Hz, q), 151.3 (bpyC^6), 149.2 (pyC^6), 139.9 (pyC^4), 137.7 (q), 132.9 (bpyC^5), 129.3 (bpyC^3), 128.0 (q), 124.4 (pyC^5), 124.3 (pyC^3), 114.4 (d, J_{C-F} = 18.0 Hz, dfphC^5), 99.8 (t, J_{C-F} = 26.7 Hz, dfphC^3). ESI-MS (1029.9, calcd for $C_{32}H_{18}Br_2F_{10}IrN_4P$) *m/z* 886.9 (100), 884.9 (83.9), 888.9 (41.7), 887.9 (33.9) $[M-PF_6]^{+}$. Anal. found: C 37.34, H 1.77, N 5.41%; Calcd for $C_{32}H_{18}Br_2F_{10}IrN_4P$: C 37.26, H 1.76, N 5.43%.

[Ir(F$_2$ppy)$_2$(8)][PF$_6$], Ir(8). The same experimental procedure applied for **Ir(7)** has been followed to yield **Ir(8)** (349 mg, 85%) as a yellow solid. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 30 °C): δ 8.53 (d, 2H, J_{H-H} = 8.8 Hz, bpyH^3), 8.32−8.36 (m, 4H, pyH^3 and bpyH^4), 7.99 (d, 2H, J_{H-H} = 2.4 Hz, bpyH^6), 7.88 (br t, 2H, J_{H-H} = 8.0 Hz, pyH^4), 7.50 (br d, 2H, J_{H-H} = 6.8 Hz, pyH^6), 7.11 (ddd, 2H, J_{H-H} = 1.6, 6.8, and 8.0 Hz, pyH^5), 6.62 (ddd, 2H, J_{H-H} = 2.4 Hz, J_{H-F} = 9.1 and 12.1 Hz, dfphH^3), 5.68 (dd, 2H, J_{H-H} = 2.4 Hz, J_{H-F} = 8.4 Hz, dfphH^5). ^{13}C NMR (101 MHz, CD$_2$Cl$_2$, 30 °C): δ 164.3 (dd, J_{C-F} = 12.6 and 227.0 Hz, q), 164.3 (d, J_{C-F} = 6.7 Hz, q), 161.6 (dd, J_{C-F} = 12.6 and 227.0 Hz, q), 154.0 (q), 152.0 (d, J_{C-F} = 6.7 259.0 Hz, q), 151.8 (bpyC^6), 149.2 (pyC^6), 143.6 (bpyC^4), 140.0 (pyC^4), 128.0 (q), 126.9 (bpyC^3), 126.0 (q), 124.6 (pyC^3), 124.4 (pyC^5), 114.4 (d, J_{C-F} = 18.0 Hz, dfphC^5), 100.0 (t, J_{C-F} = 26.7 Hz, dfphC^3). ESI-MS (1029.9, calcd for $C_{32}H_{18}Br_2F_{10}IrN_4P$) *m/z* 886.9 (100), 884.9 (83.9), 888.9 (41.7), 887.9 (33.9) $[M-PF_6]^{+}$. Anal. found: C 37.30, H

1.78, N 5.42%; Calcd for $C_{32}H_{18}Br_2F_{10}IrN_4P$: C 37.26, H 1.76, N 5.43%.

[Ir(F_2ppy)$_2$(10)][PF$_6$], Ir(10). In a Schlenk flask placed under an atmosphere of nitrogen, 4′-(4-neopentylglyconatoboronphenyl)-2,2′:6′,2″-terpyridine **tpy-Bneo** (65 mg, 0.15 mmol), iridium complex **Ir(7)** (53 mg, 0.05 mmol), and [Pd(PPh$_3$)$_4$] (6 mg, 5.1 μmol) were dissolved in deaerated THF (10 mL). A 0.07 M aqueous solution of sodium carbonate (3.0 mL, 0.21 mmol) was added to the mixture, that was purged with nitrogen through three freeze−pump−thaw cycles at low temperature. The solution was heated at 85 °C under vigorous stirring for 18 h. After cooling, the organic solvent was removed by evaporation under reduced pressure, CH_2Cl_2 (20 mL) was added, and the organic phase was washed and separated. The organic phase was dried over Na_2SO_4, and the solvent was evaporated. The product was purified by gravimetric column chromatography over aluminum oxide (CH_2Cl_2/EtOH, 500:1) to afford **Ir(10)** (73 mg, 72%) as a yellow solid. ^{1}H NMR (400 MHz, CD_2Cl_2, 30 °C): δ 9.12 (br s, 2H, bpyH^3), 8.82 (s, 4H, tpy$H^{3'5'}$), 8.68−8.71 (m, 8H, tpy$H^{3,3''}$ and tpy$H^{6,6''}$), 8.37 (br d, 2H, J_{H-H} = 8.8 Hz, pyH^3), 8.08−8.16 [m, 10H, bpyH^6, Ar(A)$H^{3,5}$ and Ar(A)$H^{2,6}$], 7.85−7.93 (m, 6H, tpy$H^{4,4''}$ and pyH^4), 7.83 (dd, 2H, J_{H-H} = 1.6 and 5.6 Hz, bpyH^5), 7.69 (br d, 2H, J_{H-H} = 6.0 Hz, pyH^6), 7.38 (m, 4H, tpy$H^{5,5''}$), 7.12 (ddd, 2H, J_{H-H} = 1.6, 6.0, and 8.8 Hz, pyH^5), 6.65 (ddd, 2H, J_{H-H} = 2.4 Hz, J_{H-F} = 9.1 and 12.1 Hz, dfphH^3), 5.82 (dd, 2H, J_{H-H} = 2.4 Hz, J_{H-F} = 8.4 Hz, dfphH^5). ^{13}C NMR (101 MHz, CD_2Cl_2, 30 °C): δ 164.3 (dd, J_{C-F} = 12.7 and 259.0 Hz, q), 164.3 (d, J_{C-F} = 7.0 Hz, q), 161.7 (dd, J_{C-F} = 12.7 and 259.0, q), 155.7 (q), 152.6 (d, J_{C-F} = 6.7 Hz, q), 154.2 (q), 151.1 (bpyC^6), 149.6 (tpyC$^{6,6''}$), 149.2 (pyC^6), 149.1 (q), 141.7 (q), 139.7 (py^4), 137.1 (tpyC$^{4,4''}$), 136.1 (q), 128.8 (Ar(A)C^{2,6} and Ar(A)C^{3,5}), 126.5 (bpyC^5), 124.4 (tpyC$^{5,5''}$ and pyC^3), 124.2 (py^5), 123.4 (bpyC^3), 121.5 (tpyC$^{3,3''}$), 119.1 (tpyC$^{3',5'}$), 114.4 (d, J_{C-F} = 18.0 Hz, dfphC^5), 99.6 (t, J_{C-F} = 26.7 Hz, dfphC^3). ESI-MS (1488.3, calcd for $C_{74}H_{46}F_{10}IrN_{10}P$) m/z 1343.3 (100), 1344.3 (73.2), 1341.3 (52.1), 1342.3 (43.2) [M−PF$_6$]$^+$. Anal. found: C 59.72, H 3.14, N 9.39%; Calcd for $C_{74}H_{46}F_{10}IrN_{10}P$: C 59.71, H 3.12, N 9.41%.

[Ir(F_2ppy)$_2$(11)][PF$_6$], Ir(11). This compound was prepared following an analogous procedure as described for **Ir(10)**, from **tpy-Bneo** (131 mg, 0.27 mmol), iridium complex **Ir(8)** (90 mg, 0.09 mmol), [Pd(PPh$_3$)$_4$] (10 mg, 8.7 μmol), and 0.2 M aqueous Na_2CO_3 (2.6 mL, 0.52 mmol) in THF (10 mL). The isolation of the product was performed as described above, and the residue was purified by gravimetric column chromatography over aluminum oxide (CH_2Cl_2/EtOH, 500:1) to afford **Ir(11)** (105 mg, 70%) as a yellow solid. ^{1}H NMR (400 MHz, CD_2Cl_2, 30 °C): δ 8.83 (s, 4H, tpy$H^{3'5'}$), 8.65−8.73 (m, 10H, tpy$H^{3,3''}$, tpy$H^{6,6''}$ and bpyH^3), 8.47 (br d, 2H, J_{H-H} = 7.6 Hz, bpyH^4), 8.38 (br d, 2H, J_{H-H} = 2.4 Hz, pyH^3), 8.32 (d, 2H, J_{H-H} = 1.6 Hz, bpyH^6), 8.01 [d, 4H, J_{H-H} = 8.4 Hz, Ar(A)$H^{2,6}$], 7.85−7.93 (m, 6H, tpy$H^{4,4''}$ and pyH^4), 7.70−7.72 [m, 6H, Ar(A)$H^{3,5}$ and pyH^6], 7.61 [br s, 2H, Ar(B)H], 7.43 [br s, 2H, Ar(B)H], 7.38 (ddd, 4H, J_{H-H} = 1.4, 4.8, and 7.6 Hz, tpy$H^{5,5''}$), 7.31 [br s, 2H, Ar(B)H], 7.13 (br t, 2H, J_{H-H} = 7.2 Hz, pyH^5), 6.73 (ddd, 2H, J_{H-H} = 2.4 Hz, J_{H-F} = 9.2 and 13.2 Hz, dfphH^3), 5.91 (dd, 2H, J_{H-H} = 2.4 Hz, J_{H-F} = 8.0 Hz, dfphH^5), 2.48 (s, 6H, CH_3). ^{13}C NMR (101 MHz, CD_2Cl_2, 30 °C): δ 164.5 (dd, J_{C-F} = 10.8 and 230.0 Hz, q), 164.5 (d, J_{C-F} = 4.0 Hz, q), 161.8 (dd, J_{C-F} = 11.8 and 259.0 Hz, q), 156.5 (d, J_{C-F} = 5.7 Hz, q), 154.4 (q), 154.1 (q), 149.8 (q), 149.6 (tpy$C^{6,6''}$), 149.3 (pyC^3), 148.7 (bpyC^5), 141. Nine (q), 141.3 (q), 140.1 (q), 140.8 (q), 139.8 (pyC^4), 138.6 (q), 137.9 (bpyC^4), 137.3 (tpy$C^{4,4''}$), 135.1 (q), 129.8 [Ar(B)C], 128.2 [Ar(A)$C^{2,6}$ or Ar(A)$C^{3,5}$], 127.9 [Ar(A)$C^{2,6}$ or Ar(A)$C^{3,5}$], 127.2 [Ar(B)C], 125.5 (bpyC^3), 124.3 (pyC^3, pyC^5 and tpy$C^{5,5''}$), 123.0 [Ar(B)C], 121.5 (tpy$C^{3,3''}$), 118.9 (tpy$C^{3',5'}$), 114.8 (d, J_{C-F} = 17.0 Hz, dfphC^5), 99.5 (t, J_{C-F} = 28.0 Hz, dfphC^3), 21.6 (CH_3). ESI-MS (1668.4, calcd for $C_{88}H_{58}F_{10}IrN_{10}P$) m/z 1523.4 (100), 1524.4 (86.8), 1522.4 (41.8), 1521.4 (40.9) [M−PF$_6$]$^+$. Anal. found: C 63.49, H 3.52, N 8.40%; Calcd for $C_{88}H_{58}F_{10}IrN_{10}P$: C 63.34, H 3.50, N 8.39%.

{[(tpy)Ru]$_2$Ir(10)}[PF$_6$]$_5$, IrRu$_2$(10). [Ru(tpy)Cl$_3$] (26 mg, 0.06 mmol) was added to a suspension of **Ir(10)** (45 mg, 0.03 mmol) in EtOH (20 mL) containing a few drops of *N*-ethylmorpholine. The mixture was heated at reflux under nitrogen for 24 h, after which it was cooled and filtered. A saturated aqueous solution of NH_4PF_6 was added to the filtrate to give a red precipitate that was collected by filtration and purified by chromatography (SiO_2, MeCN/0.2 M aqueous KNO_3 9:1), to afford **IrRu$_2$(10)** (41 mg, 80%) after anionic exchange with hexafluorophosphate as a red microcrystalline solid. ^{1}H NMR (400 MHz, CD_3CN, 30 °C): δ 9.20 (br d, 2H, J_{H-H} = 1.6 Hz, bpyH^3), 9.09 [s, 4H, (**10**)tpy$H^{3',5'}$], 8.76 (d, 4H, J_{H-H} = 8.0 Hz, tpy$H^{3',5'}$), 8.69 [br d, 4H, J_{H-H} = 8.0 Hz, (**10**)tpy$H^{3,3''}$], 8.41−8.52 [m, 12H, tpy$H^{3,3''}$, Ar(A)$H^{2,6}$, tpy$H^{4'}$ and pyH^3], 8.38 [d, 4H, J_{H-H} = 8.4 Hz, Ar(A)$H^{3,5}$], 8.19 (d, 2H, J_{H-H} = 5.6 Hz, bpyH^6], 7.91−8.03 [m, 12H, bpyH^5, tpy$H^{4,4''}$, (**10**)tpy$H^{4,4''}$ and pyH^4], 7.87 (br d, 2H, J_{H-H} = 6.0 Hz, pyH^6), 7.45 [br d, 4H, J_{H-H} = 5.6 Hz, (**10**)tpy$H^{6,6''}$], 7.37 [br d, 4H, J_{H-H} = 5.6 Hz, tpy$H^{6,6''}$], 7.16−7.24 [m, 10H, tpy$H^{5,5''}$, (**10**)tpy$H^{5,5''}$ and pyH^5], 6.79 (ddd, 2H, J_{H-H} = 2.4 Hz, J_{H-F} = 9.6, 12.8 Hz, dfphH^3), 5.87 (dd, 2H, J_{H-H} = 2.0 Hz, J_{H-F} = 8.4 Hz, dfphH^5). ^{13}C NMR (101 MHz, CD_3CN, 30 °C): δ 165.9 (dd, J_{C-F} = 12.5 and 222.0 Hz, q), 165.9 (d, J_{C-F} = 7.0 Hz, q), 162.3 (dd, J_{C-F} = 12.3 and 218.0 Hz, q), 159.1 (q), 157.3 (q), 156.6 (q), 156.3 (q), 155.7 (d, J_{C-F} = 6.6 Hz, q), 153.6 (tpy$C^{6,6''}$), 153.4 [(**10**)tpy$C^{6,6''}$], 151.5 (q), 150.7 (bpyC^6), 147.9 (q), 140.7 (pyC^4), 140.0 (q), 139.2 [tpy$C^{4,4''}$ or (**10**)tpy$C^{4,4''}$], 139.1 [tpy$C^{4,4''}$ or (**10**)tpy$C^{4,4''}$], 138.4 (q), 136.9 (tpy$C^{4'}$), 129.9 [Ar(A)$C^{2,6}$], 129.8 [Ar(A)$C^{3,5}$], 129.1 (q), 128.6 [tpy$C^{5,5''}$ or (**10**)tpy$C^{5,5''}$], 128.5 [tpy$C^{5,5''}$ or (**10**)tpy$C^{5,5''}$], 127.4 (bpyC^5), 125.6 [(**10**)tpy$C^{3,3''}$], 125.5 (tpy$C^{3,3''}$), 125.1 (pyC^3 and pyC^5), 124.8 (tpy$C^{3',5'}$), 124.1 (bpyC^3), 122.7 [(**10**)tpy$C^{3',5'}$], 114.8 (d, J_{C-F} = 18.5 Hz, dfphC^5), 99.9 (t, J_{C-F} = 27.2 Hz, dfphC^3). ESI-MS (2738.2, calcd for $C_{104}H_{68}F_{34}IrN_{16}P_5Ru_2$) m/z 1224.1 (100) [M−2PF$_6$]$^{2+}$; 767.8 (100) [M−3PF$_6$]$^{3+}$; 539.6 (100) [M−4PF$_6$]$^{4+}$. Anal. found: C 45.74, H 2.51, N 8.20%; Calcd for $C_{104}H_{68}F_{34}IrN_{16}P_5Ru_2$: C 45.64, H 2.50, N 8.19%.

{[(tpy)Ru]$_2$Ir(11)}[PF$_6$]$_5$, IrRu$_2$(11). [Ru(tpy)Cl$_3$] (44 mg, 0.1 mmol) was added to a suspension of **Ir(11)** (83 mg, 0.05 mmol) in EtOH (35 mL) containing a few drops of *N*-ethylmorpholine. The mixture was heated at reflux under nitrogen for 24 h, after which it was cooled and filtered. A saturated aqueous solution of NH_4PF_6 was added to the filtrate to give a red precipitate that was collected by filtration and purified by chromatography (SiO_2, MeCN/0.2 M aqueous KNO_3 9:1), to afford **IrRu$_2$(11)** (106 mg, 73%) after anionic exchange with hexafluorophosphate as a red crystalline solid. ^{1}H NMR (400 MHz, CD_3CN, 30 °C): δ 9.07 [s, 4H, (**11**)tpy$H^{3',5'}$], 8.77 (d, 4H, J_{H-H} = 8.0 Hz, tpy$H^{3',5'}$), 8.68−8.73 [m, 6H, bpyH^3 and (**11**)tpy$H^{3,3''}$], 8.61 (dd, 2H, J_{H-H} = 2.0, 8.4 Hz, bpyH^4), 8.51 (d, 4H, J_{H-H} = 8.0 Hz, tpy$H^{3,3''}$), 8.34−8.45 [m, 8H, tpy$H^{4'}$, pyH^3 and Ar(A)$H^{2,6}$], 7.89−8.02 [m, 16H, tpy$H^{4,4''}$, (**11**)tpy$H^{4,4''}$, pyH^4, bpyH^6 and Ar(A)$H^{3,5}$], 7.80 [br s, 2H, Ar(B)$H^{2 \text{ or } 4 \text{ or } 6}$], 7.64 [br s, 2H, Ar(B)$H^{2 \text{ or } 4 \text{ or } 6}$], 7.48−7.50 [m, 4H, py$H^6$ and Ar(B)$H^{2 \text{ or } 4 \text{ or } 6}$], 7.45 [br d, 4H, J_{H-H} = 5.6 Hz, (**11**)tpy$H^{6,6''}$], 7.38 (br d, 4H, J_{H-H} = 5.6 Hz, tpy$H^{6,6''}$), 7.17−7.25 [m, 10H, pyH^5, tpy$H^{5,5''}$ and (**11**)tpy$H^{5,5''}$], 6.90 (m, 2H, dfphH^3), 5.98 (m, 2H, dfphH^5), 2.54 (s, 6H, CH_3). ^{13}C NMR (101 MHz, CD_3CN, 30 °C): δ 164.9 (dd, J_{C-F} = 12.2 and 225.0 Hz, q), 164.7 (d, J_{C-F} = 7.0 Hz, q), 162.4 (dd, J_{C-F} = 12.3 and 218.0 Hz, q), 161.2 (q), 159.1 (q), 156.4 (d, J_{C-F} = 15.0 Hz, q), 155.6 (q), 155.0 (q), 153.6 (tpy$C^{6,6''}$), 153.3 [(**11**)tpy$C^{6,6''}$], 151.1 (bpyC^5), 149.8 (pyC^3), 148.6 (q), 142.9 (q), 141.7 (q), 141.5 (q), 141.4 (q), 140.6 (pyC^4), 139.1 [(**11**)tpy$C^{4,4''}$ and tpy$C^{4,4''}$], 138.4 (bpyC^4), 137.3 (q), 136.8 (tpy$C^{4'}$), 136.4 (q), 130.3 [Ar(B)$C^{2 \text{ or } 4 \text{ or } 6}$], 129.4 [Ar(A)$C^{2,6}$], 129.1 [Ar(A)$C^{3,5}$], 128.5 [Ar(B)$C^{2 \text{ or } 4 \text{ or } 6}$, (**11**)tpy$C^{5,5''}$, tpy$C^{5,5''}$ and pyC^6], 126.0 (bpyC^3), 125.6 [tpy$C^{3,3''}$ or (**11**)tpy$C^{3,3''}$], 125.5 [tpy$C^{3,3''}$ or (**11**)tpy$C^{3,3''}$], 125.1 (pyC^5), 124.7 (tpy$C^{3',5'}$), 123.8 [Ar(B)$C^{2\text{ or }4\text{ or }6}$], 122.6 [(**11**)tpy$C^{3',5'}$], 115.2 (d, J_{C-F} = 18.3 Hz, dfphC^5), 99.8 (t, J_{C-F} = 26.2 Hz, dfphC^3), 21.6 (CH_3). ESI-MS (2918.3, calcd for $C_{118}H_{80}F_{34}IrN_{16}P_5Ru_2$) *m/z* 827.8 (100) $[M-3PF_6]^{3+}$; 584.6 (100) $[M-4PF_6]^{4+}$; 438.7 (100) $[M-5PF_6]^{5+}$. Anal. found: C 48.47, H 2.77, N 7.70%; Calcd for $C_{118}H_{80}F_{34}IrN_{16}P_5Ru_2$: C 48.58, H 2.76, N 7.68%.

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Supporting Information Available: Relevant absorption, emission and excitation spectra of the metal complexes, cyclic voltammograms of selected compounds, and proton NMR spectra of all the free ligands and metal complexes (44 pages). This material is available free of charge via the Internet at http://pubs.acs.org.