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# Cyclometalated Iridium(III) Complexes as Photosensitizers for Long-Range Electron Transfer: Occurrence of a Coulomb Barrier

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Six cyclometalated iridium(III) complexes were investigated to assess their potential as photosensitizers for long-range electron transfer, and two of them were incorporated directly into covalent donor–bridge–acceptor molecules. The influence of ligand substitutions on the excited-state properties and the photoredox behavior of the iridium complexes was explored by optical absorption, steady-state and time-resolved luminescence spectroscopy, as well as by electrochemical methods. Bimolecular electron transfer between the photoexcited complexes and 10-methylphenothiazine and methylviologen was found to be only weakly dependent on the ligand substitutions. Intramolecular long-range electron transfer from phenothiazine to photoexcited iridium(III) in the dyads is slow due to the occurrence of a Coulomb barrier. Consequently, an electron-transfer photoproduct is only observable in the transient absorption spectrum of a donor–bridge–acceptor molecule with a fluorinated photosensitizer that exhibits a very long excited-state lifetime. A flash-quench technique is necessary for detection of an electron-transfer product in the dyad with a non-fluorinated photosensitizer. The occurrence of a Coulomb barrier associated with intramolecular (excited-state) long-range electron transfer in the dyads with cyclometalated iridium(III) photosensitizers represents an important difference to previously investigated similar donor–bridge–acceptor molecules with photosensitizers based on $d^6$ metal diimine complexes.

## Introduction

The $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) complex and its congeners play a unique role in inorganic photochemistry due to their favorable luminescence and photoredox properties.[1] In recent years, isoelectronic cyclometalated iridium(III) complexes have received increasing attention, and it has become clear that their photophysical and electrochemical properties can be controlled almost deliberately through structure and ligand variations.[2] Many applications for which ruthenium(II) α-diimine complexes have been used in the past have in the meantime been implemented also with cyclometalated iridium(III) species. Examples are iridium-based oxygen sensors,[3] luminescent DNA intercalators,[4] sensitizers for photocatalytic water splitting,[5] dye-sensitized solar cells,[6] and electroluminescent devices.[7] However, although ruthenium(II) complexes have been used extensively as photosensitizers for long-range electron transfer both in artificial and biological systems,[8] cyclometalated iridium(III) complexes are almost unexplored in this respect.[9] A cyclometalated iridium(III) complex has been used recently as a photosensitizer for long-range *energy* transfer,[10] and another one for phototriggering of a proton-coupled electron-transfer reaction.[11] Yet, the applicability of cyclometalated iridium(III) photosensitizers for kinetic investigations of long-range electron-transfer reactions remains to be explored. This is an attractive research target in view of the fact that the energy of the emissive iridium excited state can be tuned over a much greater range than is the case for ruthenium(II) polypyridyl complexes.[2,12] The associated greater tunability of excited-state redox potentials is interesting for driving-force investigations of long-range electron-transfer rates. In principle, it is conceivable that in this respect cyclometalated iridium(III) complexes will excel over the traditionally used ruthenium(II) photosensitizers. What is more, some cyclometalated iridium(III) complexes are known to have significantly longer-lived excited states than $Ru(bpy)_3^{2+}$.[5a] This is expected to be advantageous for long-range charge-transfer reactions originating from these states, simply because the inherent excited-state decay processes are less competitive. However, it is known that the lowest-lying excited state of many cyclometalated iridium(III) complexes is not a pure metal-to-ligand charge transfer (MLCT) state as the case for $Ru(bpy)_3^{2+}$-type complexes,[2,12,13] which could result in different photoredox behavior. Exploring the above-mentioned and related issues has been the motivation for the research presented in this paper.

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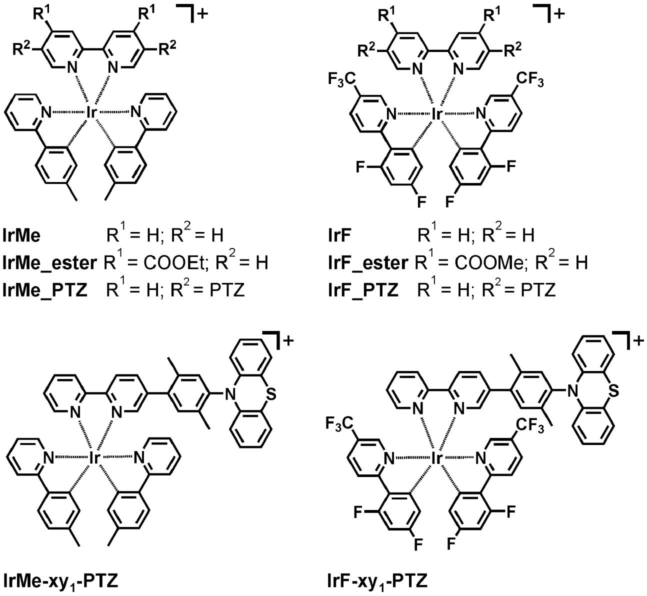
We report here on the photophysical and photoredox properties of the eight cyclometalated iridium(III) complexes shown in Scheme 1. Six of them are simple complexes with fluorinated (IrF series on the right) and non-fluorinated (IrMe series on the left) cyclometalating ligands. Their bipyridine ligands are either unsubstituted or substituted with electron-withdrawing or electron-donating groups. The two remaining complexes are donor–bridge–acceptor molecules composed of a phenothiazine (PTZ) donor, a *p*-xylene bridge, and a cyclometalated iridium(III) species acting as an acceptor upon photoexcitation. We chose this particular donor–bridge moiety for three reasons: (i) The *p*-xylene bridge is rigid, thereby keeping the donor–acceptor couple at a fixed distance, contrary to what would be expected for flexible bridging units. (ii) The methyl substituents on the bridge impede complete planarization of the phenothiazine–xylene–bipyridine moiety,[14] thereby limiting its degree of π conjugation. (iii) We have previously studied an analogous ruthenium(II)[15] dyad that will allow direct comparison of $Ru(bpy)_3^{2+}$ and cyclometalated iridium(III) photosensitizers for long-range electron transfer. Generally, an electron transfer is considered “long-range” when it occurs over a distance greater than 10 Å.[8] In the dyads from Scheme 1, the phenothiazine-to-iridium distance is 10.6 Å.



Scheme 1. Formulas of the molecules investigated in this work.

## Results and Discussion

### Structural Aspects

The synthesis of all complexes reported here passes through an intermediate that is a dichlorido-bridged metal dimer. In this species, the two cyclometalating C atoms of each iridium(III) center are in the plane formed by the two metals and the two chloride bridging ligands.[2,12a,16] Thus, only one geometrical isomer is formed upon complexation of the α-diimine ligand in the final synthetic step. Indeed, all our $^1H$ NMR spectroscopic data are consistent with the exclusive formation of one isomer.

Single crystals including the IrMe_ester cation could be grown by slow diffusion of (liquid) diisopropyl ether into a dichloromethane solution. The X-ray crystal structure analysis revealed no unusual features; all bond lengths and angles in the IrMe_ester cation shown in Figure 1 are in line with those observed previously for related species.[2b,17] Characteristic for this class of complexes are the relatively short Ir–N distances involving nitrogen atoms from the cyclometalating ligands and comparatively long Ir–N distances involving α-diimine nitrogen atoms. Here, the respective distances are 2.016(5)/2.032(5) Å and 2.129(8)/2.145(0) Å, respectively. A noteworthy observation is the fact that the pyridyl and tolyl rings in the cyclometalating ligands are significantly more coplanar than the two pyridyl rings of the bipyridine ligand. The respective dihedral angles are 0.5 and 3.8° in the two 2-(*p*-tolyl)pyridine ligands and 11.5° in the bipyridine ligand. Examination of the complete crystal structure reveals the presence of a dichloromethane molecule in immediate vicinity to the bipyridine ligand. Thus, the above comparatively large torsion angle is likely a consequence of crystal packing.

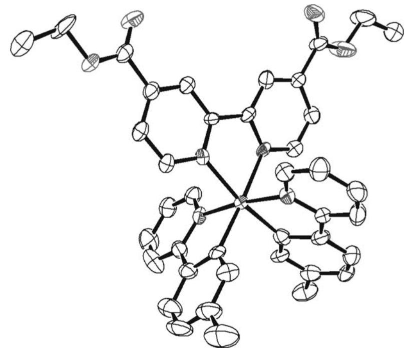


Figure 1. Crystal structure of the IrMe_ester complex. The thermal ellipsoids for the image represent the 50% probability limit. All hydrogen atoms are omitted for clarity.

### Excited-State Properties

The optical absorption properties of the complexes from Scheme 1 are very similar to those of previously investigated analogous complexes.[3b,13] As summarized in Table 1, intense bands due to spin-allowed π–π* transitions on the ligands are observed in the UV region, whereas the weaker absorptions in the blue spectral range are assigned to MLCT transitions. However, unlike in $Ru(bpy)_3^{2+}$ where the MLCT bands are spectrally well separated from intraligand absorptions, in the cyclometalated iridium(III) complexes of this work, no isolated MLCT bands can be observed. Rather, they are noticeable as long and relatively ill-defined tails to the more intense π–π* absorptions. This makes it difficult to detect a clear trend in how substituent changes affect the MLCT energy by using absorption data only. Much more promising for this is analysis of the luminescence data presented in Figure 2.

Table 1. Optical absorption ($\lambda_{abs}$) and emission ($\lambda_{em}$) wavelengths, relative luminescence intensities ($\phi_{rel}$), and luminescence lifetimes ($\tau$) in freeze–pump–thaw deoxygenated acetonitrile solution at room temperature.

| | $\lambda_{abs}$ [nm] ($\varepsilon$, 1000 dm$^3$ mol$^{-1}$ cm$^{-1}$) | $\lambda_{em}$ [nm] | $\phi_{rel}$ | $\tau$ [ns] |
|---|---|---|---|---|
| IrMe | 405 (12.3), 351 (12.0),<br>312 (16.6), 253 (40.7) | 581 | 0.18 | 230 |
| IrMe_ester | 415 (3.7), 381 (6.0),<br>303 (29.8), 269 (32.8) | 669 | 0.03 | 36 |
| IrMe_PTZ | 405 (12.1), 384 (14.6),<br>300 (48.9), 272 (58.7) | – | – | – |
| IrMe-xy$_1$-PTZ | 405 (5.1), 377 (7.4), 324 (36.7),<br>277 (56.1), 256 (90.0) | 587 | 0.16 | 180 |
| IrF | 412 (2.7), 379 (4.6), 310 (15.6),<br>275 (30.0), 259 (28.2) | 483[a] | 1.00 | 2280 |
| IrF_ester | 405 (6.8), 351 (8.9),<br>304 (16.2), 257 (31.8) | 565 | 0.05 | 602 |
| IrF_PTZ | 403 (7.4), 340 (16.2), 302 (19.9),<br>283 (24.2), 258 (55.1) | – | – | – |
| IrF-xy$_1$-PTZ | 408 (3.0), 313 (40.3),<br>272 (52.0), 256 (95.3) | 508 | 0.10 | 612 |

[a] Corresponds to the wavelength of the barycenter of the structured (double-maximum) emission band.

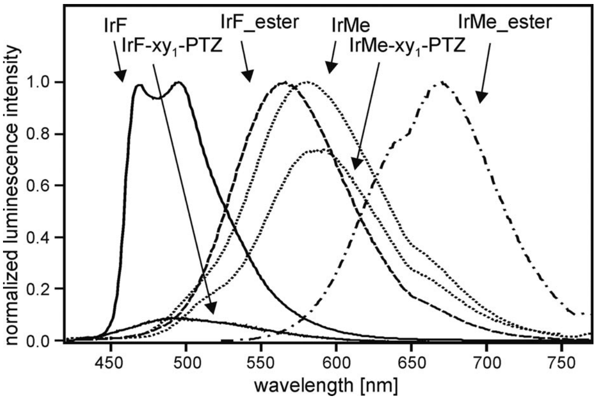


Figure 2. Luminescence spectra obtained from room-temperature acetonitrile solutions of the six emissive complexes from Scheme 1. Excitation occurred at 390 nm. Emission intensities are normalized, and only the IrF/IrF-xy$_1$-PTZ and the IrMe/IrMe-xy$_1$-PTZ intensities can be compared mutually.

Except for the IrMe_PTZ and IrF_PTZ compounds, all complexes investigated here are emissive in room-temperature acetonitrile solution. In Figure 2, the intensities of the four simple complexes are normalized for clear visualization of spectral band shifts; only the emission intensities of the two dyads are to scale with their respective reference complexes.

The emission band shifts that occur with the different ligand substitutions are in accord with prior investigations:[2,12] electron-withdrawing fluorine substituents on the cyclometalating ligand stabilize the predominantly metal-localized HOMO by removing electron density from the metal center; hence, the shorter emission wavelengths of the IrF/IrF_ester molecules with respect to the IrMe/IrMe_ester complexes.[2d,5a] Conversely, electron-withdrawing substituents on the bipyridine ligand stabilize the predominantly α-diimine-localized LUMO;[2d,5a] hence, the redshifts observed upon attachment of the ester groups. Electron-donating substituents on the α-diimine have been shown to lead to the opposite effect,[2d,5a,12,18] which was the motivation for the synthesis of the IrF_PTZ and IrMe_PTZ complexes. Prior work focused on 4,4′-dimethylamino-substituted bipyridine, as substitution in the *para* position to the coordinating nitrogen atoms is expected to lead to the strongest effect.[18] Our motivation for exploring 5,5′-substitution of bipyridine with a tertiary amine roots in the fact that such ligands are synthetically more readily accessible: thanks to an efficient palladium(0) catalyzed N–C coupling reaction,[19] the 5,5′-diphenothiazine-2,2′-bipyridine can be made in only two reaction steps. However, our iridium complexes with these ligands turn out to be nonluminescent. Nanosecond transient absorption spectroscopy fails to provide evidence for the formation of phenothiazine radical cations.[20] It is possible that a low-lying $^3\pi$–$\pi^*$ state of the new ligand causes complete quenching of the $^3$MLCT luminescence. The absorption and luminescence properties of these complexes are concentration independent between $10^{-4}$ and $10^{-6}$ M.

We note that the unsubstituted IrMe complex displays absorption and photoluminescence spectra that are virtually identical to those of the [Ir(phenylpyridine)$_2$(bpy)]$^+$ complex,[3b] that is, the electron-donating effect of the additional methyl groups in the IrMe complexes is negligible. No significant additional information can be expected from the investigation of a third series of complexes with phenylpyridine instead of tolylpyridine cyclometalating ligands. Our preference for the tolylpyridine ligand is due to practical reasons: the additional methyl group improves the solubility of the complexes and the $^1$H NMR spectra are easier to interpret.

The emission bandshapes in Figure 2 reveal an important difference between the IrF species and all other complexes investigated here: the IrF luminescence band is structured, signaling that the emissive excited state is a mixed MLCT/intraligand state, whereas all other luminescence bands are unstructured, indicating relatively pure MLCT emissions. DFT calculations can offer quantitative insight into the electronic structures of cyclometalated iridium(III) complexes,[21] but this is beyond the scope of this paper.

Inspection of the relative emission intensities and lifetimes listed in Table 1 shows that there is a correlation between luminescence wavelength on the one hand and intensity and lifetime on the other hand: the shorter the emission wavelength, the higher the luminescence intensity and the longer the excited-state lifetime, but this remains a qualitative observation. Quantitative analysis using an energy gap law model is not reasonable, as there are too important deviations from a strictly exponential correlation of lumines-

Table 2. Ground- and excited-state electrochemical potentials ($E$, V vs. SCE) and energies of the electronic origins ($E_{00}$, eV) of various iridium complexes in acetonitrile solution.

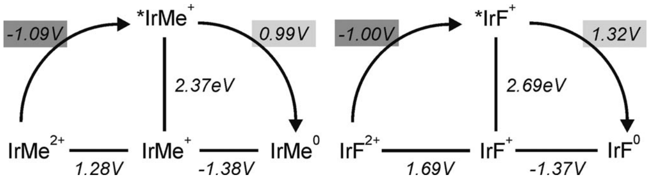
| | $E(\text{Ir}^{IV}/\text{Ir}^{III})$ | $E(\text{L}/\text{L}^-)$ | $E_{00}$[a] | $E(\text{IrL}_3^{2+}/{}^*\text{IrL}_3^+)$[b] | $E({}^*\text{IrL}_3^+/\text{IrL}_3^0)$[c] |
|---|---|---|---|---|---|
| IrMe | 1.28[d] | –1.38[d] | 2.37 | –1.09 | 0.99 |
| IrMe-xy$_1$-PTZ | 1.32 | –1.43 | 2.36 | –1.04 | 0.93 |
| IrF | 1.69[e] | –1.37[e] | 2.69 | –1.00 | 1.32 |
| IrF-xy$_1$-PTZ | 1.50 | –1.24 | 2.67 | –1.17 | 1.43 |

[a] Estimated based on room-temperature absorption and emission data. [b] Calculated using the approximation $E(\text{IrL}_3^{2+}/{}^*\text{IrL}_3^+) \approx E(\text{Ir}^{IV}/\text{Ir}^{III}) - E_{00}$. [c] Calculated using the approximation $E({}^*\text{IrL}_3^+/\text{IrL}_3^0) \approx E(\text{L}/\text{L}^-) + E_{00}$. [d] From ref.[22] [e] From ref.[5a]

cence intensity and lifetime with emission energy. There are three key observations from the luminescence intensity and lifetime data in Table 1 and Figure 2: (i) The emissive excited state of IrF lives an order of magnitude longer than that of IrMe. (ii) In the IrMe-xy$_1$-PTZ dyad the luminescence is hardly quenched with respect to the IrMe reference complexes. (iii) In the IrF-xy$_1$-PTZ dyad the excited-state is quenched substantially relative to the IrF reference. The latter two observations suggest that photoinduced phenothiazine-to-iridium electron transfer is much more efficient for the fluorinated photosensitizer than for the non-fluorinated complex. Additional support for this hypothesis will be provided by experimental data presented below.

Regarding the excited-state properties of the ester-substituted complexes, we note that their emissive excited states are strongly quenched with respect to those of the unsubstituted parent complexes. Particularly, the IrMe_ester lifetime is rather short and already close to the experimental limit imposed by nanosecond laser equipment. Therefore, we restricted all subsequent photoredox investigations to the IrF, IrMe, IrF-xy$_1$-PTZ, and IrMe-xy$_1$-PTZ compounds.

Ground- and excited-state redox potentials of these four complexes are summarized in Table 2. The non-fluorinated compounds are about 300 mV more readily oxidized than the fluorinated complexes (first column), but one-electron reduction occurs at nearly identical potentials for all four complexes (second column). The electron-withdrawing fluoro and trifluoromethyl substituents pull electron density away from the metal center, making it more difficult to oxidize.[2d,5a] Reduction, in contrast, involves mainly bipyridine-localized orbitals that are unaffected by substitution of the cyclometalating ligands. Using the energies of the electronic origins of the emissive excited states (third column) it is possible to arrive at reasonable estimates for the excited-state redox potentials.[1] The resulting values are reported in the last two columns of Table 2 and illustrated graphically in the modified Latimer diagrams of Scheme 2. The key conclusion from this is that the IrF unit should be a better excited-state electron acceptor than the IrMe unit, whereas both complexes should be similarly good excited-state donors.



Scheme 2. Latimer diagrams for the IrMe and IrF complexes based on the electrochemical and spectroscopic data from Table 2.

## Bimolecular Electron Transfer

In order to test the above predictions regarding the excited-state redox potentials, we investigated the luminescence behavior of IrF and IrMe in the presence of reductive and oxidative quenchers. 10-Methylphenothiazine [$E(\text{MePTZ}^+/\text{MePTZ})$ = 0.73 V vs. SCE][1] and methylviologen [$E(\text{MV}^{2+}/\text{MV}^+)$ = –0.46 V vs. SCE][1] were chosen for this purpose. Bimolecular quenching experiments show that reductive quenching with 10-methylphenothiazine is significantly more important for the IrF complex than for IrMe. The Stern–Volmer constants obtained from the slopes of linear regression fits to the experimental data are $K_{SV}$ = 3935 M$^{-1}$ for IrF and $K_{SV}$ = 536 M$^{-1}$ for IrMe (see Supporting Information).[23] This seems to suggest that the fluorinated complex is indeed a more potent photooxidant than IrMe, as suspected above from estimation of the excited-state redox potentials. However, calculation of the rate constants ($k_Q$) for bimolecular electron transfer from the Stern–Volmer constants and the luminescence lifetimes (Table 1) yields two essentially diffusion-limited values that differ only by 35% between IrF and IrMe (Table 3). Thus, the more efficient luminescence quenching (or higher $K_{SV}$ value) observed for IrF is a consequence of the longer excited-state lifetime of this complex, which makes bimolecular quenching reactions more competitive with inherent excited-state depopulation through other (nonradiative and radiative) processes.

Table 3. Rate constants for oxidative and reductive quenching of the excited states of the IrMe and IrF complexes and $\text{Ru(bpy)}_3^{2+}$ in acetonitrile solution at room temperature. The $\text{Ru(bpy)}_3^{2+}$ data are from ref.[1] MePTZ = 10-methylphenothiazine, $\text{MV}^{2+}$ = methylviologen.

| | $k_Q$ (MePTZ) [M$^{-1}$ s$^{-1}$] | $k_Q$ ($\text{MV}^{2+}$) [M$^{-1}$ s$^{-1}$] |
|---|---|---|
| IrMe | $2.3\times10^9$ | $1.3\times10^9$ |
| IrF | $1.7\times10^9$ | $1.7\times10^8$ |
| $\text{Ru(bpy)}_3^{2+}$ | $1.6\times10^9$ | $2.4\times10^9$ |

Oxidative quenching with methylviologen yields similar Stern–Volmer constants for the fluorinated ($K_{SV}$ = 388 M$^{-1}$) and non-fluorinated ($K_{SV}$ = 300 M$^{-1}$) complexes. Because the reactive excited state is 10 times longer-lived in the former, this yields rate constants ($k_Q$) for bimolecular quenching that differ by one order of magnitude (Table 3). Thus, IrMe turns out to be a somewhat better photoreductant than IrF, at least for the methylviologen acceptor.

In short, the results from the bimolecular quenching experiments demonstrate that our cyclometalated iridium(III) complexes exhibit almost equally efficient photoredox chemistry with 10-methylphenothiazine donors and methylviologen acceptors – despite the fact that the fluorinated complex has a reactive excited state that is not of pure MLCT character. The bimolecular quenching behavior of the two cyclometalated iridium(III) complexes is similar to that observed for $Ru(bpy)_3^{2+}$ (Table 3, bottom line).

### Intramolecular Long-Range Electron Transfer

In a preceding paragraph we attributed the luminescence quenching observed for the IrF-$xy_1$-PTZ and IrMe-$xy_1$-PTZ dyads relative to their reference complexes (Table 1) to reductive excited-state quenching caused by the phenothiazine donors. The transient absorption data shown in Figure 3 provide direct evidence for the formation of electron-transfer products following photoexcitation of the dyads. The dashed trace in the left panel of Figure 3 is a transient absorption spectrum of a $10^{-4}$ M solution of IrF-$xy_1$-PTZ in deoxygenated acetonitrile. The data was acquired in a 10-µs time window starting 2 µs after excitation with 10-ns laser pulses at 457.9 nm.[24]

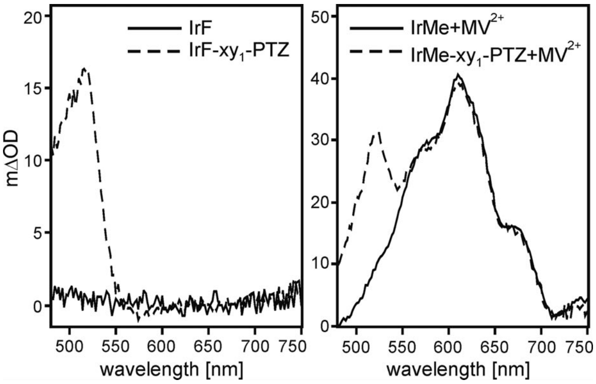
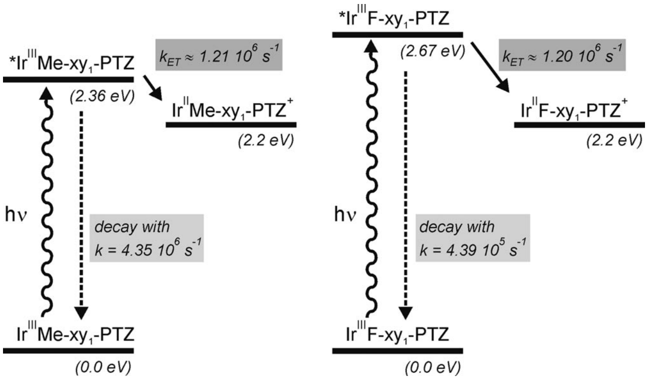


Figure 3. Left: transient absorption spectra obtained from 0.1 mM solutions of IrF and IrF-$xy_1$-PTZ following excitation at 457.9 nm with 10-ns laser pulses.[24] Detection occurred in a time window ranging from 2 to 12 µs after the laser pulse. Right: transient absorption spectra measured on deoxygenated acetonitrile solutions containing 0.1 mM iridium complex (IrMe or IrMe-$xy_1$-PTZ) and 50 mM methylviologen ($MV^{2+}$). Excitation occurred at 457.9 nm with laser pulses of ca. 10 ns duration, detection occurred in a 10-µs time window starting 500 ns after the excitation pulse.

An absorption peaking at ca. 520 nm and extending to shorter wavelengths is observed. This is the typical absorption of the phenothiazine radical cation ($PTZ^{\cdot+}$).[20,25] As expected, the spectral signature of this electron-transfer product remains unobserved for a reference solution containing only the IrF parent complex (solid line in the left panel of Figure 3). Unfortunately, the presence of luminescent impurities impedes direct measurement of the rate of $PTZ^{\cdot+}$ formation in the IrF-$xy_1$-PTZ dyad by transient absorption spectroscopy, and we are forced to estimate the rate constant ($k_{ET}$) for phenothiazine-to-iridium excited-state electron transfer based on luminescence lifetimes. A common approach is to use the approximation given in Equation (1).[26]

$$k_{ET} = \tau_{dyad}^{-1} - \tau_{ref}^{-1} \qquad (1)$$

In the present case, $\tau_{dyad}$ = 612 ns and $\tau_{ref}$ = 2280 ns (Table 1), which yields $k_{ET} \approx 1.2 \times 10^6\ s^{-1}$ (Scheme 3).

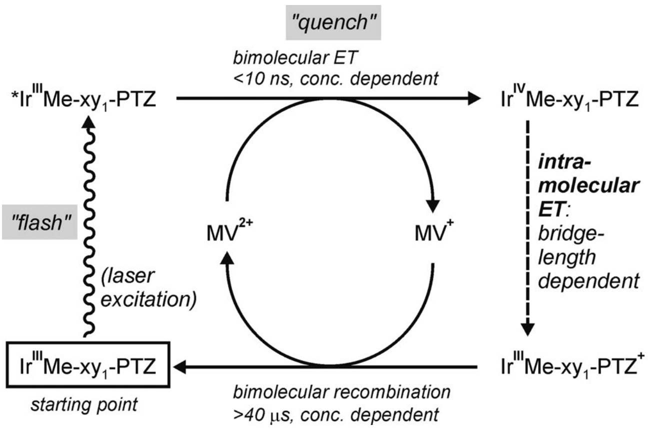


Scheme 3. Schematic diagrams illustrating the energetics and kinetics of the photoinduced processes occurring in the IrMe-$xy_1$-PTZ and IrF-$xy_1$-PTZ dyads.

Strictly analogous transient absorption experiments were performed with the non-fluorinated IrMe-$xy_1$-PTZ dyad, but in this case the phenothiazine radical cation consistently escaped detection. Yet, thermodynamic considerations led to the conclusion that in this dyad, too, excited-state PTZ-to-iridium electron transfer should occur: on the basis of the electrochemical potentials for one-electron reduction of the IrMe complex (–1.38 V vs. SCE, Table 2) and the potential for one-electron oxidation of phenothiazine (≈+0.8 V vs. SCE),[1] we estimate that the $Ir^{II}$Me-$xy_1$-$PTZ^{\cdot+}$ charge-separated state is roughly 2.2 eV above the electronic ground state (Scheme 3). The emissive MLCT excited state of IrMe is about 2.36 eV above the ground state (Table 2), and consequently excited-state electron transfer should be exergonic by about 160 meV (Scheme 3).[27,28] Interestingly, for the luminescence lifetime data of IrMe-$xy_1$-PTZ and IrMe (Table 1), Equation (1) yields $k_{ET} \approx 1.2 \times 10^6\ s^{-1}$, which is the same value as for the fluorinated dyad.

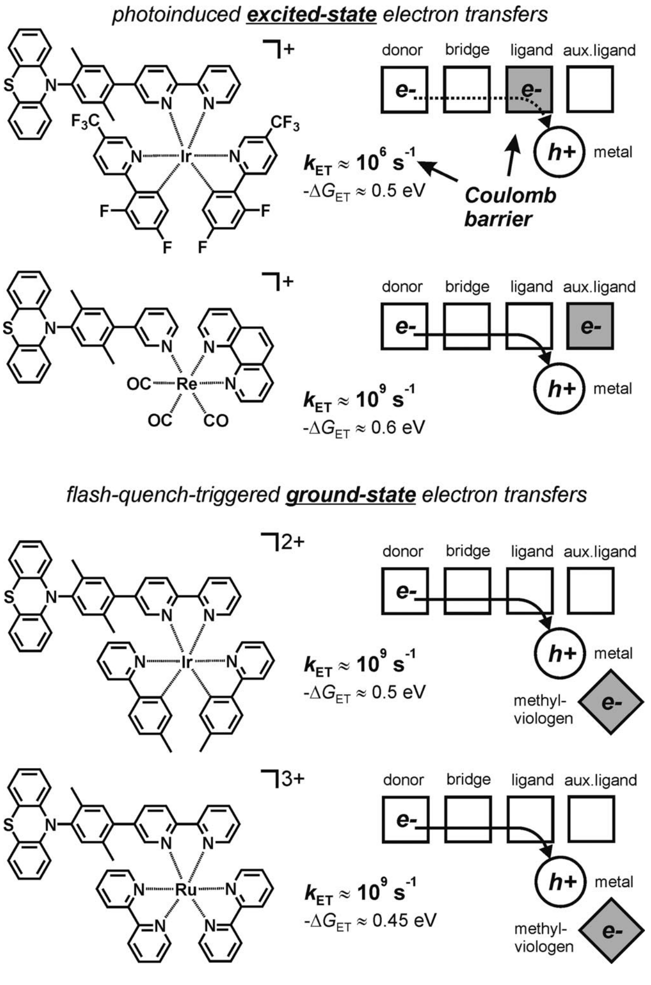
On the basis of the luminescence lifetimes of the IrF and IrMe reference complexes (Table 1) we estimate that the inherent excited-state decay of the photosensitizer fragments in IrF-$xy_1$-PTZ and IrMe-$xy_1$-PTZ occurs with $4.39 \times 10^5$ and $4.35 \times 10^6\ s^{-1}$, respectively (Scheme 3). Thus, it becomes obvious that in IrF-$xy_1$-PTZ the excited-state electron-transfer process is reasonably competitive with other deactivation pathways, whereas in the non-fluorinated dyad it must be poorly competitive. In fact, this finding reflects the results from the Stern–Volmer experiments and the larger Stern–Volmer constant ($K_{SV}$) observed for the IrF/PTZ couple with respect to the IrMe/PTZ couple. It is therefore plausible that excited-state electron transfer does occur *also* in the non-fluorinated dyad, but the kinetics are such that a significant population of the charge-separated state never builds up; hence, our difficulties in detecting the $PTZ^{\cdot+}$ species in transient absorption spectroscopy.

In certain $Ru(bpy)_3^{2+}$/phenothiazine donor–bridge–acceptor systems excited-state electron transfer is also difficult to detect because its driving force is very low.[15,29] This problem can be overcome by photochemical generation of a highly oxidizing $Ru^{III}$ species by using a quencher such as methylviologen.[15,30] We have applied such a flash-quench technique to IrMe-xy$_1$-PTZ in an attempt to find direct spectroscopic evidence for electron-transfer photoproducts in this dyad as well. The principle of this experiment is illustrated in Scheme 4. The photosensitizer (present at 0.1 mM concentration) is excited with a 10-ns laser pulse (“flash”), which induces an almost instantaneous bimolecular electron transfer (“quench”) with methylviologen ($MV^{2+}$) because this quencher is present in large excess (50 mM). The resulting $Ir^{IV}$ species is strongly oxidizing and based on the redox potentials from Table 2,[27,28] intramolecular PTZ-to-$Ir^{IV}$ electron transfer is expected to be exergonic by ca. 0.5 eV. Indeed, the transient absorption data in Figure 3 (right panel) provide spectroscopic evidence for this intramolecular charge transfer. Both data sets (solid and dashed traces) were measured in a 10-µs time window starting 500 ns after selective iridium excitation at 457.9 nm. The experiment with the IrMe reference complex (solid line) gives an absorption band with a maximum near 600 nm, which is due to one-electron reduced methylviologen ($MV^{\cdot+}$).[29a,31] Expectedly, for the IrMe-xy$_1$-PTZ dyad this $MV^{\cdot+}$ band is observed as well (dashed line), but it is overlapped by an additional absorption peaking at 520 nm that can be attributed to the phenothiazine radical cation. This signal builds up still within the 10-ns laser pulse, implying a rate constant greater than $10^8\ s^{-1}$ for the intramolecular PTZ-to-$Ir^{IV}$ electron transfer across the *p*-xylene bridge.



Scheme 4. Illustration of the flash-quench technique used to induce phenothiazine-to-$Ir^{IV}$ electron transfer in the IrMe-xy$_1$-PTZ dyad.

The rate constants extracted from the above analyses of the various bi- and intramolecular phototriggered electron-transfer processes deserve further discussion, because their relative magnitudes are striking in several respects. First, it is somewhat surprising to see that 10-methylphenothiazine reductively quenches the excited states of IrF and IrMe with rate constants ($k_Q$) near the diffusion-controlled limit (Table 3), but the intramolecular PTZ-to-$Ir^{III}$ *excited-state* electron transfers in the IrF-xy$_1$-PTZ and IrMe-xy$_1$-PTZ dyads proceed only with $k_{ET} \approx 10^6\ s^{-1}$ (Scheme 3; Scheme 5, top). Second, in a structurally very similar dyad comprised of the same phenothiazine donor, a *p*-xylene bridge, and a rhenium(I) tricarbonyl diimine acceptor (Scheme 5, second from top), intramolecular PTZ-to-$Re^I$ *excited-state* electron transfer occurs with $k_{ET} \approx 10^9\ s^{-1}$,[14a] which is three orders



Scheme 5. *Excited-state* PTZ-to-$Ir^{III}$ electron transfer is slow in the IrF-xy$_1$-PTZ and IrMe-xy$_1$-PTZ dyads (top). In an analogous rhenium(I)-based dyad (second from top), the PTZ-to-$Re^I$ *excited-state* electron transfer is three orders of magnitude faster despite identical donor–acceptor distance and similar driving force ($-\Delta G_{ET}$), but in this case the MLCT excitation does not impose a Coulomb barrier to long-range electron transfer. *Ground-state* PTZ-to-$Ir^{IV}$ and PTZ-to-$Ru^{III}$ electron transfers across the same distance and similar $-\Delta G_{ET}$ are also three orders of magnitude faster (bottom half), because in this case the MLCT excited electron is abstracted by methylviologen and there is no Coulomb barrier associated with long-range electron transfer either.

of magnitude faster than PTZ-to-Ir$^{III}$ *excited-state* electron transfer in the new dyads. Third, the flash-quench triggered *ground-state* electron transfers in IrMe-xy$_1$-PTZ (i.e., PTZ-to-Ir$^{IV}$ charge transfer) and an analogous phenothiazine–xylene–ruthenium dyad (i.e., PTZ-to-Ru$^{III}$ charge transfer) are also three orders of magnitude more rapid (Scheme 5, bottom half),[15a] although the driving forces ($-\Delta G_{ET}$) associated with these charge transfers are similar to that for *excited-state* electron transfer in IrF-xy$_1$-PTZ.

These three observations can be explained by the electronic structure of the MLCT excited state in the cyclometalated iridium(III) complexes. As discussed above, in the respective MLCT state the excited electron is located on the bipyridine ligand, not on the cyclometalating ligands. Formally, the long-range electron transfer from phenothiazine to the MLCT-excited iridium center therefore corresponds to electron transfer across a negatively charged bridge (Scheme 5, top right), which is known to decelerate electron transfer.[32] However, this effect is only important when the phenothiazine donor is attached covalently to the bipyridine ligand, that is, for bimolecular electron transfer between 10-methylphenothiazine and IrF it is unimportant; hence, the high rate for this *inter*molecular charge-transfer process. In the rhenium(I) dyad from Scheme 5, MLCT excitation also involves the α-diimine ligand, but in this case this is only an auxiliary ligand, and the donor-bridge moiety is attached to the metal through a pyridine ligand. Thus, the MLCT-excited electron does not perturb PTZ-to-Re long-range electron transfer, and the rate constant of this process is three orders of magnitude higher than in IrF-xy$_1$-PTZ. When using the flash-quench technique, the MLCT-excited electron is abstracted by methylviologen.[29a,30] Consequently, in neither of the two cases of the bottom half of Scheme 5 (IrMe dyad and ruthenium dyad) there results a negative charge on the bridge, and the PTZ-to-Ir$^{IV}$ and PTZ-to-Ru$^{III}$ electron transfers are very rapid ($k_{ET} \approx 10^9$ s$^{-1}$).

A similar Coulomb barrier phenomenon was observed in ruthenium-sensitized proton-coupled electron transfer across a guanidinium–carboxylate salt bridges,[33] and in a Ru(bpy)$_3^{2+}$-tetrathiafulvalene donor–acceptor molecule.[34]

## Conclusions

Some of the cyclometalated iridium(III) complexes investigated in this work exhibit bimolecular electron-transfer behavior with 10-methylphenothiazine and methylviologen quenchers that is very similar to that observed for Ru(bpy)$_3^{2+}$. The admixture of intraligand excited-state character to the photoactive excited state [particularly in the iridium(III) complexes with fluorinated cyclometalating ligands] represents an important difference to Ru(bpy)$_3^{2+}$ chromophores, but is found to have a negligible impact on the excited-state reactivity in the cases investigated here. As Ru(bpy)$_3^{2+}$, the cyclometalated iridium(III) complexes of this work are much better oxidants and reductants in their excited states than in their electronic ground states. For photosensitization of long-range electron transfer, the greater tunability of the excited-state properties of the cyclometalated iridium(III) complexes with respect to Ru(bpy)$_3^{2+}$-type compounds appears useful: fluorination of the cyclometalating ligand lengthens the excited-state lifetime by about an order of magnitude relative to complexes with non-fluorinated ligands, thereby making excited-state electron transfer more competitive with inherent excited-state decay.

The long excited-state lifetime (≈2.3 μs) of the fluorinated photosensitizer IrF is clearly advantageous for kinetic investigations of intramolecular long-range electron transfer, but in our case this is outweighed by the fact that intramolecular reductive quenching of this excited state in IrF-xy$_1$-PTZ is associated with a large Coulomb barrier: The MLCT-excited electron is located on the bipyridine ligand that connects the phenothiazine donor to the metal acceptor, thereby imposing an electrostatic barrier to intramolecular long-range electron transfer. The result is an electron-transfer rate constant of only ca. $10^6$ s$^{-1}$, which compares to ca. $10^9$ s$^{-1}$ in three closely related donor–bridge–acceptor molecules where there is no such electrostatic barrier.[14a,15a] This includes flash-quench triggered intramolecular electron transfer in the non-fluorinated IrMe-xy$_1$-PTZ dyad. Thus, the flash-quench method leading to phenothiazine-to-iridium(IV) (ground state) intramolecular electron transfer has several advantages over simple photoexcitation that induces phenothiazine-to-iridium(III) excited-state electron transfer: (i) electron-transfer products can be observed directly even in systems with photosensitizers that have relatively short-lived excited-states; (ii) the flash-quench triggered intramolecular electron transfer is very rapid because it is not associated with a large Coulomb barrier. An important technical advantage is that transient absorption spectroscopy is easier to perform with the flash-quench method because there is usually no interference with the luminescence from the sensitizer or strongly emissive impurities. This is particularly important for cyclometalated iridium(III) complexes because their excitation must occur at much shorter wavelengths than those used for photoexcitation of Ru(bpy)$_3^{2+}$.

If intramolecular long-range charge transfers directly from a photoexcited state of these sensitizers are to be probed, the α-diimine ligand should be connected to an oxidative quencher and/or a reductive quencher should be attached to the cyclometalating ligands.[9] This will avoid the occurrence of slow excited-state electron transfers that are associated with large electrostatic barriers.

## Experimental Section

**General Information:** $^1$H NMR spectra were measured with a Bruker Avance 400 MHz spectrometer. In the NMR spectroscopic data, all coupling constants are reported in Hz, and the following abbreviations were used to assign the signals: ph = phenyl, py = pyridine, bpy = bipyridine, PTZ = phenothiazine. Deuterated solvents were bought from Cambridge Isotope Laboratories, Inc. Low-resolution electrospray ionization mass spectrometry was performed with a Finnigan MAT SSQ 7000 instrument, and high-resolution electrospray mass spectrometry was performed with a QSTAR XL (AB/MDS Sciex) instrument. Methanol (VWR, HPLC grade) was used to solubilize the compounds. Elemental analysis was conducted by Dr. Hansjörg Eder, School of Pharmaceutical Sciences, University of Geneva, Switzerland. Optical absorption was measured with a Cary 5000 UV/Vis/NIR spectrophotometer from Varian, and steady-state luminescence spectroscopy was performed using a Horiba Fluorolog-3 instrument with the use of quartz cuvettes from Hellma (111-QS). For measurements under inert atmosphere, home-built quartz cuvettes that can be deoxygenated by freeze–pump–thaw cycles were employed. The solvent used for these measurements was acetonitrile for UV spectroscopy. The Stern–Volmer experiments were performed in acetonitrile solutions containing 0.1 M tetrabutylammonium hexafluorophosphate. Luminescence lifetimes and transient absorption was measured on the experimental setup of Professor A. Hauser, Department of Physical Chemistry, University of Geneva, Switzerland. This setup is comprised of a Quantel Brilliant Nd:YAG laser with an integrated Magic Prism OPO as an excitation source and a detection system consisting of a Spex 270M monochromator, a Hamamatsu photomultiplier, and a Tektronix TDS 540B oscilloscope. The probe beam used for transient absorption spectroscopy came from a 900-W tungsten lamp. Sample concentrations were ca. $2 \times 10^{-5}$ M for luminescence and ca. $10^{-4}$ M for transient absorption experiments. Cyclic voltammetry was performed with a Versastat3–100 Potentiostat equipped with the K0264 Micro-Cell kit and a platinum working electrode from Princeton Applied Research. A silver wire was used as a quasireference electrode. The supporting electrolyte was a 0.1 M solution of tetrabutylammonium hexafluorophosphate in dry acetonitrile. The solutions were deoxygenated prior to voltammetry sweeps by bubbling nitrogen gas.

**Synthetic Procedures and Product Characterization Data:** Two of the ligands used in this work are commercially available: 2,2′-bipyridine (Fluka, product no. 14453) and 2-(*p*-tolyl)pyridine (Sigma–Aldrich, product no. 198870). The other ligands were synthesized according to the following experimental protocols: The cyclometalating 5-(trifluoromethyl)-2-(2,4-difluorophenyl)pyridine ligand was obtained in a Suzuki coupling reaction between 2,4-difluorophenylboronic acid and 2-bromo-5-(trifluoromethyl)pyridine.[35] The methyl and ethyl 2,2′-bipyridine-4,4′dicarboxylates were obtained from 2,2′-bipyridine-4,4′-dicarboxylic acid.[36]

The 5,5′-diphenothiazine-2,2′-bipyridine ligand is accessible in two consecutive reactions: In the first step, 5,5′-dibromo-2,2′-bipyridine is synthesized through homocoupling of two 2,5-dibromopyridine molecules in presence of hexabutyldistannane and tetrakis(triphenylphosphane)palladium(0) catalyst.[37] In the second step, the phenothiazine moieties can be coupled to 5,5′-dibromo-2,2′-bipyridine in a palladium-catalyzed reaction. For this purpose, a solution of 5,5′-dibromo-2,2′-bipyridine (0.65 g, 2 mmol), phenothiazine (0.83 g, 4 mmol), tris(dibenzylideneacetone)dipalladium(0) (30 mg, 0.05 mmol), tri-*tert*-butylphosphane (20 mg, 0.08 mmol), and potassium *tert*-butoxide (0.70 g, 5 mmol) in toluene was heated at reflux for 12 h under a nitrogen atmosphere. Before cooling to room temperature, the insoluble solids were filtered off the hot solution, and then the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on a silica gel stationary phase (Fluka, product no. 60745) using pentane/dichloromethane (1:1), thereby yielding a slightly yellow solid (0.80 g, 70%). $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta$ = 6.56 (dd, *J* = 8.0, 1.0 Hz, 4 H, PTZ-H), 6.98 (m, 4 H, PTZ-H), 7.01 (m, 4 H, PTZ-H), 7.17 (dd, *J* = 8.0, 1.0 Hz, 4 H, PTZ-H), 7.80 [dd, *J* = 8.5, 2.4 Hz, 2 H, bpy C(4)H], 8.56 [d, *J* = 8.5 Hz, 2 H, bpy C(3) H], 8.67 [d, *J* = 2.4 Hz, 2 H, bpy C(6)H] ppm.

Synthetic procedures and characterization data for the monosubstituted bipyridine ligands used for the IrMe-xy$_1$-PTZ and IrF-xy$_1$-PTZ dyads have been reported in one of our prior publications.[15a]

The first step in the synthesis of the iridium complexes from Scheme 1 is the cyclometalation of IrCl$_3$ to afford dichlorido-bridged iridium dimer species of the type [Ir(C^N)$_2$Cl]$_2$. In a typical procedure, the cyclometalating ligand (2.2 equiv.) was treated with IrCl$_3$·3H$_2$O (1 equiv.) in a 3:1 mixture of 2-ethoxyethanol and deionized water at reflux for 24 h. The resulting yellow precipitate was collected by suction filtration, washed with water and diethyl ether. Yields varied from 40 to 80%. The two [Ir(C^N)$_2$Cl]$_2$ dimers used in this work have been synthesized and characterized previously.[38]

The second step is the reaction of [Ir(C^N)$_2$Cl]$_2$ dimers with α-diimine ligands to afford the final [Ir(C^N)$_2$(N^N)]$^+$ complexes. This was accomplished by treating the dimer (1 equiv.) with the α-diimine ligand (2.1 equiv.) in refluxing ethanol overnight. (For the IrMe-xy$_1$-PTZ and IrF-xy$_1$-PTZ dyads the solvent was an 8:2 mixture of ethanol and chloroform). After cooling to room temperature and subsequent suction filtration, the target complex was precipitated as its hexafluorophosphate salt through addition of saturated aqueous NH$_4$PF$_6$ solution. The yellow precipitate was filtered, washed with water, cold ethanol, and diethyl ether. Additional purification occurred by column chromatography on silica gel using an eluent mixture composed of acetonitrile/H$_2$O/saturated aqueous KNO$_3$ (100:10:1). Then the complex was reprecipitated as its hexafluorophosphate salt after acetonitrile evaporation under reduced pressure and subsequent addition of saturated aqueous KPF$_6$ solution. For the IrMe-xy$_1$-PTZ and IrF-xy$_1$-PTZ dyads, an additional silica gel column chromatography using an eluent mixture composed of dichloromethane and methanol (98:2) was necessary. The yield for this second step varied from 65 to 90%. Characterization data for the eight complexes from Scheme 1 are as follows:

**IrMe:** $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta$ = 2.14 (s, 3 H, Me), 6.09 (m, 2 H), 6.86 (dm, *J* = 8.4 Hz, 2 H), 6.97 (ddd, *J* = 8.8, 3.0, 1.2 Hz, 2 H), 7.40 (ddd, *J* = 7.6, 5.2, 1.2 Hz, 2 H), 7.46 (dm, *J* = 5.6 Hz, 2 H), 7.58 (d, *J* = 8.0 Hz, 2 H), 7.72 (ddd, *J* = 7.6, 7.6, 1.6 Hz, 2 H), 7.85 (dm, *J* = 7.2 Hz, 2 H), 7.92 (dm, *J* = 5.2 Hz, 2 H), 8.14 (ddd, *J* = 8.0, 8.0, 1.6 Hz, 2 H), 8.65 (dm, *J* = 8.0 Hz, 2 H) ppm. HRMS (ESI): calcd. for $C_{34}H_{28}N_4Ir^+$ 685.1937; found 685.1915. $C_{34}H_{28}F_6IrN_4P \cdot 0.4CHCl_3$ (877.55): calcd. C 47.15, H 3.27, N 6.40; found C 47.18, H 3.28, N 6.20.

**IrMe_ester:** $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta$ = 1.44 (t, *J* = 7.2 Hz, 6 H, CH$_2$C*H*$_3$), 1.99 (s, 6 H, Me), 4.50 (q, *J* = 7.2 Hz, 4 H C*H*$_2$CH$_3$), 6.06 [s, 2 H, ph C(6)H], 6.86 [dd, *J* = 8.1, 2.0 Hz, 2 H, ph C(4)H], 7.02 [td, *J* = 5.6, 1.3 Hz, 2 H, py C(5)H], 7.54 [d, *J* = 5.6 Hz, 2 H, py C(6)H], 7.57 [d, *J* = 8.1 Hz, 2 H, ph C(3)H], 7.73 [td, *J* = 8.1, 1.3 Hz, 2 H, py C(4)H], 7.84 [d, *J* = 8.1 Hz, 2 H, py C(3)H], 7.99 [d, *J* = 5.6 Hz, 2 H, bpy C(5)H], 8.10 [d, *J* = 5.6 Hz, 2 H, bpy C(6)H], 9.24 [s, 2 H, bpy C(3)H] ppm. HRMS (ESI): calcd. for $C_{40}H_{36}N_4O_4Ir^+$ 829.2365; found 829.2351.

**IrMe_PTZ:** $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta$ = 2.02 (s, 6 H, Me), 5.86 [s, 2 H, ph C(6)H], 6.77 [d, *J* = 5.8, 1.5 Hz, 2 H, ph C(4) H], 7.06 [ddd, *J* = 7.4, 5.8, 1.5 Hz, 2 H, py C(4)H], 7.19 (m, 16 H, PTZ), 7.42 [d, *J* = 8.6 Hz, 2 H, py C(6)H], 7.50 [d, *J* = 5.8 Hz, 2 H, py C(3)H], 7.57 [dd, *J* = 8.6, 7.4 Hz, 2 H, py C(5)H], 7.60 [s, 2 H, bpy C(6)H], 7.75 (dd, *J* = 8.6, 7.4 Hz, 2 H), 7.81 [d, *J* = 7.4 Hz, 2 H, ph C(3)H], 8.65 (d, *J* = 8.6 Hz, 2 H) ppm. HRMS (ESI): calcd. for $C_{58}H_{42}N_6S_2Ir^+$ 1079.2573; found 1079.2536.

**IrMe-xy$_1$-PTZ:** $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.91 (s, 3 H, Me), 2.07 (s, 3 H, Me), 2.11 (s, 3 H, Me), 2.13 (s, 3 H, Me), 6.11 (s, 1 H), 6.16 (s, 1 H), 6.83 (m, 3 H), 6.94 (m, 2 H), 7.01 (m, 2 H), 7.41 (m, 2 H), 7.53 (dm, $J$ = 3.2 Hz, 1 H), 7.60 (m, 4 H), 7.75 (m, 2 H), 7.88 (dd, $J$ = 8.0, 4.4 Hz, 2 H), 7.97 (dm, $J$ = 7.2 Hz, 1 H), 8.07 (m, 2 H), 8.60 (dm, $J$ = 5.6 Hz, 1 H) ppm. HRMS (ESI): calcd. for $C_{54}H_{43}N_5SIr^+$ 986.2863; found 986.2876. $C_{54}H_{43}F_6IrN_5PS\cdot H_2O$ (1131.21): calcd. C 56.44, H 3.95, N 6.09; found C 56.21, H 3.77, N 5.96.

**IrF:** $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 5.64 (dd, $J$ = 8.0, 2.0 Hz, 2 H), 6.64 (ddd, $J$ = 8.8, 8.8, 8.0 Hz, 2 H), 7.58 (m, 4 H), 7.90 (dd, $J$ = 5.2, 1.2 Hz, 2 H), 8.03 (dd, $J$ = 8.8, 2.0 Hz, 2 H), 8.35 (ddd, $J$ = 8.0, 8.0, 1.6 Hz, 2 H), 8.47 (dd, $J$ = 8.8, 3.2 Hz, 2 H), 8.09 (d, $J$ = 8.0 Hz, 2 H) ppm. HRMS (ESI): calcd. for $C_{34}H_{18}N_4F_{10}Ir^+$ 865.0995; found 865.1011. $C_{34}H_{18}F_{16}IrN_4P$ (1009.70): calcd. C 40.44, H 1.80, N 5.55; found C 40.77, H 1.98, N 5.41.

**IrF_ester:** $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 2.11 (s, 6 H, Me), 5.57 [d, $J$ = 7.8 Hz, 2 H, ph C(6)H], 6.63 [d, $J$ = 7.8 Hz, 2 H, ph C(4)H], 7.48 [s, 2 H, bpy C(3)H], 8.04 [d, $J$ = 8.8 Hz, 2 H, py C(4)H], 8.14 (m, 4 H, bpy), 8.46 [d, $J$ = 8.8 Hz, 2 H, py C(3)H], 9.12 [s, 2 H, py C(6)H] ppm. HRMS (ESI): calcd. for $C_{38}H_{22}N_4O_4F_{10}Ir^+$ 981.1072; found 981.1105.

**IrF_PTZ:** $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 5.31 [dd, $J$ = 8.1, 2.0 Hz, 2 H, ph C(6)H], 6.50 [dd, $J$ = 8.1, 2.0 Hz, 2 H, ph C(4) H], 7.24 (m, 16 H, PTZ), 7.50 [d, $J$ = 6.0 Hz, 2 H, bpy C(3)H], 7.58 [s, 2 H, bpy C(6)H], 7.70 [dd, $J$ = 6.0, 3.0 Hz, 2 H, bpy C(4) H], 8.06 [d, $J$ = 8.8 Hz, 2 H, py C(4)H], 8.41 [d, $J$ = 8.8 Hz, 2 H, py C(3)H], 8.72 [d, $J$ = 9.4 Hz, 2 H, py C(6)H] ppm. HRMS (ESI): calcd. for $C_{58}H_{32}N_6F_{10}S_2Ir^+$ 1259.2; found 1259.6.

**IrF-xy$_1$-PTZ:** $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 2.06 (s, 3 H, Me), 2.19 (s, 3 H, Me), 5.67 (ddd, $J$ = 8.0, 8.0, 2.4 Hz, 2 H), 6.67 (ddd, $J$ = 8.8, 7.6, 2.4 Hz, 2 H), 7.60 (m, 1 H), 7.67 (m, 2 H), 8.00 (dd, $J$ = 5.6, 0.8 Hz, 2 H), 8.01 (d, $J$ = 2.4 Hz, 1 H), 8.09 (m, 1 H), 8.11 (m, 1 H), 8.33 (ddd, $J$ = 7.6, 7.6, 1.6 Hz, 1 H), 8.38 (dd, $J$ = 8.4, 2.0 Hz, 2 H), 8.52 (ddd, $J$ = 8.8, 8.8, 3.2 Hz, 2 H), 8.84 (dm, $J$ = 8.4 Hz, 1 H), 8.96 (d, $J$ = 8.4 Hz, 1 H) ppm. HRMS (ESI): calcd. for $C_{53}H_{33}N_5F_{10}SIr^+$ 1166.1920; found 1166.1925. $C_{53}H_{33}F_{16}IrN_5PS\cdot 3CH_3COCH_3$ (1299.10): calcd. C 50.98, H 3.75, N 4.57; found C 50.88, H 3.45, N 4.39.

**Crystal Data for IrMe_ester:** $[C_{40}H_{36}N_4O_4Ir]^+PF_6^-\cdot CH_2Cl_2$, $M$ = 1058.90, monoclinic, space group $Pc$, $a$ = 8.6551(7) Å, $b$ = 15.0012(8) Å, $c$ = 15.8243(11) Å, $\beta$ = 93.416(9)°, $U$ = 2050.9(2) Å$^3$, $Z$ = 2, Mo-$K_\alpha$ radiation ($\lambda$ = 0.7103 Å), $\mu$ = 3.50 mm$^{-1}$, $T$ = 150 K, Stoe IPDS-II diffractometer, 25450 reflections measured, 9784 unique ($R_{int}$ = 0.039) of which 7190 with $|F_o| > 4\sigma(F_o)$. Final values $R$ = 0.030, $\omega R$ = 0.031, and $S$ = 1.85(2). CCDC-737590 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Supporting Information** (see footnote on the first page of this article)**:** Cyclic voltammograms of the IrF-xy$_1$-PTZ and IrMe-xy$_1$-PTZ dyads; Stern–Volmer plots used to determine the quenching constants $k_Q$; luminescence decays used to determine the excited-state lifetimes.

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