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# **Click-Derived Triazolylidenes as Chelating Ligands: Achievement of** a Neutral and Luminescent Iridium(III)-Triazolide Complex

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**S** Supporting Information

ABSTRACT: Versatility in the synthesis of triazole derivatives was exploited to obtain convenient mesoionic carbenes working as chelating or cyclometalating ligands for the preparation of cationic or neutral iridium(III) complexes. We present the synthesis and characterization of three new cationic cyclometalating iridium(III) complexes  $(1-3-BF_4)$  and a neutral one (4), equipped with functionalized triazolylidene ligands. All the complexes are obtained in good yields, present irreversible or quasi-reversible oxidation and reduction processes, and display good photophysical stability. The complexes emit from <sup>3</sup>MLCT or <sup>3</sup>LC states, depending on the nature of the ancillary ligand. Compounds 1-3-BF<sub>4</sub> display very low photoluminescence quantum yields (PLQY  $\approx$  1% in acetonitrile solution). Density functional theory calculations show that the luminescence of these three complexes is guenched



by the presence of low-lying <sup>3</sup>MC states, leading to a reversible detachment of the neutral ancillary ligands from the metal coordination sphere. On the contrary, this nonradiative deactivation pathway is not present in the case of the neutral complex 4, which in fact shows PLQYs above 10% and is the best emitter of the series. Moreover, complex 4 represents the first reported example of a photochemically and thermally stable neutral triazolide iridium(III) complex.

# INTRODUCTION

The outstanding success of the copper(I) catalyzed "click" azide-alkyne cycloaddition reaction (CuAAC),<sup>1,2</sup> which regioselectively yields 1,4-disubstituted 1,2,3-triazoles, can be ascribed, among others, to the possibility of synthesizing libraries of ligands to be exploited for the creation of metal complexes and related applications. Notably, by means of an alkylation-deprotonation reaction sequence, the CuAAC products can be easily converted in the corresponding triazolylidenes, which belong to the class of mesoionic carbenes (MIC),<sup>3,4</sup> that are N-heterocyclic carbenes (NHCs)<sup>5,6</sup> which structure cannot be drawn without a charge separation.

Triazolylidenes joined the parent triazoles to be used as mono- or polydentate ligands in organometallic chemistry. In fact, the synthetic strategy to form 1,2,3-triazole rings allows the easy design of final derivatives by varying the wingtip substituents. In particular, 4-phenyl- and 4-(pyrid-2'-yl)-1,2,3triazoles A (with X = C and N, respectively, Chart 1), have been extensively exploited in the formation of metal complexes acting as catalysts<sup>7,8</sup> and luminescent materials.<sup>9-18</sup> Besides such derivatives, even the corresponding triazolylidenes can offer large opportunities of application as bidentate cyclometalating or donor ligands thanks to their strong electrondonating character, which is generally higher than those of

Chart 1. Examples of Bidentate Triazole and Triazolylidene Ligands



their NHC analogues, 19-22 concurrently to their relative simple synthesis. As a consequence, their use as ligands for the synthesis of metal complexes has recently received great attention, and a wide range of applications have been reported, especially in the area of homogeneous catalysis,<sup>23-27</sup> with many examples of ruthenium(II)-23 and iridium(III)based<sup>23-27</sup> catalysts, as attested by various reviews that have appeared in the literature.<sup>7,28-30</sup>

On the contrary, luminescent complexes containing triazolylidene ligands were not extensively studied so far. Only a few examples of ruthenium(II) and  $iron(II)^{31,32}$ derivatives have been reported in literature, together with the

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only one report on an iridium (III) complex from our laboratory.  $^{\rm 33}$ 

Luminescent iridium-based complexes are one of the most widely used classes of derivatives for solid-state emitting devices such as organic light-emitting diodes (OLEDs)<sup>34–38</sup> and light-emitting electrochemical cells (LECs),<sup>39,40</sup> used for displays and lighting. In fact, such emitters exhibit unique photophysical properties (i.e., wide color tunability, high photoluminescence quantum yields, excellent stability, and good solubility), along with general easy synthesis and possibility to modify their emission output simply by a precise variation of the ligands.<sup>41</sup> By virtue of this versatility, there is still plenty of room for the design and development of new library of ligands with electronic properties suitable for the fine color tuning of luminescent complexes.

Pushing forward our investigations on nonconventional ancillary ligands for luminescent iridium(III) complexes,42-44 we focused our attention on bidentate ligands containing a 1,2,3-triazolylidene functionalized with a heteroaryl in the 4position. In fact, we recently reported the first use of 1-benzyl-3-methyl-4-(pyrid-2'-yl)-1H-1,2,3-triazolylidene **B** (R = Bz, Chart 1) as neutral ligand to obtain phosphorescent cationic cyclometalated iridium(III) complexes.<sup>33</sup> In this context, we now expanded the use of such derivatives by varying the substituents on the triazolylidene ring and by employing them as neutral ancillary or cyclometalating ligands to get new luminescent cationic and neutral iridium(III) complexes. In fact, taking into account the recent studies on the  $\sigma$ -donor and  $\pi$ -acceptor properties of bidentate ligands,<sup>45</sup> it seemed interesting to substitute the pyridine with a 1,2,3-triazole to evaluate the effects of a different heteroaryl on complex behavior, envisioning that, besides the classical coordination as N^C neutral ligand, such triazole-triazolylidene derivatives can act also as C<sup>C</sup> anionic ligand (C and D, Chart 1).

In detail, we present herein the synthesis and characterization of three new cationic iridium(III) complexes (1–3- $BF_4$ ) and a neutral one (4) carrying 2-phenylpyridine (Hppy) as cyclometalating ligand and differently functionalized triazolylidenes as ancillary ligands (Chart 2). For the sake of completeness, the properties of the obtained complexes are also compared with those of previously reported ones such as the structural analogues 5,<sup>46,47</sup> 6,<sup>48</sup> 7,<sup>48</sup> and 8<sup>10</sup> (see Chart 3).

#### RESULTS AND DISCUSSION

**Synthesis.** The 4-(heteroaryl)-1,2,3-triazoles **9a** and  $b^{49}$  and  $9c^{10}$  were synthesized through a copper-mediated azide– alkyne cycloaddition (CuAAC) by reaction of 2-ethynylpyridine and 1,4-bis(trimethylsilyl)buta-1,3-diyne, respectively, with the required organic azides, according to previously reported procedures.

To get the triazolium salts precursors of triazolylidenes, MeOTf and MeI were tested as methylating agents for 2pyridine triazoles **9a** and **b** (Scheme 1). Surprisingly, we always obtained monomethylated products, with a regioselectivity strictly connected to the nature of the methylating reagent, as determined through one-dimensional (1D) and two-dimensional (2D) NMR experiments. Indeed, with MeOTf the methylation occurs only at N-3 of the triazole ring giving **10a**-**OTf** and **10b-OTf** in 59 and 54% yield, respectively. On the contrary, the undesired methylation of the pyridine nitrogen preferentially occurred in the reaction with MeI. Pyridinium salts **11a-I** and **11b-I** were obtained as major products in over 60% yields, together with the desired triazolium salts **10a-I** and

#### Article

Chart 2. Iridium(III) Complexes Presented in This Study



Chart 3. Selected Iridium(III) Complexes as Analogues of the Investigated Series



**10b-I** both only in 13% yield. For compound **11b-I**, the structure was also confirmed by X-ray analysis (see crystal data in the Supporting Information). However, considering that the consecutive reaction conditions required for the formation of the carbene are counterion dependent, we decided to carry on the synthesis of iridium(III) complexes with both triflates and iodide precursors to evaluate potential differences.

Regarding bis-triazole 9c, the monomethylation was performed only with MeI because previous experiments carried out in our lab showed that the formation of the corresponding carbene from the triflate triazolium salt sluggishly occurred. Monomethylated triazolium  $10c-1^{50}$  was obtained in very good yields (81%) and proved to be suitable for the rapid formation of the corresponding carbene employed in the subsequent *in situ* complex formation, as discussed later in the text.



Scheme 2. Synthesis of Complexes



Once the triazolium salts were obtained, we progressed to the corresponding iridium(III) complexes. In detail, pyridine triazolium salts **10a-OTf** and **10b-OTf** reacted<sup>51</sup> with Ag<sub>2</sub>O in ACN in the presence of KCl to give the silver(I) triazolylidene complexes **12a-OTf** and **12b-OTf**, which were isolated and directly used in the next step without purification (Scheme 2). The obtained carbenes were added to a solution of  $[Ir(ppy)_2(\mu-Cl)]_2$  in DCM/EtOH = 3/1 to produce, by means of a Ag–Ir transmetalation step, the corresponding complexes **1-OTf** and **2-OTf**, which, when treated with NH<sub>4</sub>BF<sub>4</sub>, were converted to the tetrafluoroborates salts **1-BF**<sub>4</sub> and **2-BF**<sub>4</sub> in 66 and 76% overall yields, respectively.

Concerning the iodide triazolium derivatives, a one-pot procedure was set up by reacting **10a-I**, **10b-I**, and **10c-I** with  $[Ir(ppy)_2(\mu-Cl)]_2$  in DCM in the presence of Ag<sub>2</sub>O: the Agtriazolylidenes was formed *in situ*, and then a silver--iridium transmetalation took place to get the iridium complexes **1-I**, **2-I**, and **3-I** that, when treated with NH<sub>4</sub>BF<sub>4</sub>, gave the corresponding complexes **1-BF**<sub>4</sub>, **2-BF**<sub>4</sub>, and **3-BF**<sub>4</sub> by anion exchange in 49, 84, and 54% total yields, respectively (Scheme 2).

The two synthetic strategies let to obtain identical complexes  $1-BF_4$  and  $2-BF_4$  in comparable yields from triazolium salts. However, considering the low selectivity in obtaining iodide derivatives 10a-I and 10b-I, the route starting from triflate salts 10a-OTf and 10b-OTf seemed preferable, despite requiring a two-step reaction sequence and longer reaction times.

Remarkably, during the synthesis of 3-I, a small amount of a luminescent byproduct, later identified as 4, was isolated. This compound proved to be much less polar than 3-I, and a comparison of their <sup>1</sup>H NMR spectra (see Figures S18 and S23) revealed the disappearance of the singlet at 9.68 ppm and

a downshift of the signal corresponding to a benzylic- $CH_2$ , suggesting that a cyclometalation occurred on the triazolyl substituent of the triazolylidene.

Given the importance of neutral tris-cyclometalated iridium-(III) complexes for applications distinct from charged ones, we investigated the possibility to increase the yield of 4. In addition, neutral complex 4 resulted a very interesting derivative considering that stable triazolide metal complexes are rather rare, being isolated only some copper-,<sup>52,53</sup> palladium-,<sup>54</sup> and platinum-<sup>55</sup> triazolides and one example of iridium(III) triazolide complex that anyway proved to rearrange to the more stable triazole derivative upon heating or light irradiation.<sup>48</sup>

Any attempt to increase the yield of 4 by changing the reaction conditions from 10c-I failed, therefore we turned our attention to the possibility to convert the cationic complex to its neutral derivative. We succeeded in this synthesis by treating complex 3-BF<sub>4</sub> with  $K_2CO_3$  in refluxing 2-ethoxyethanol to give 4 in 68% yield (Scheme 3). The relative high temperature and the presence of the base favored the switching of the binding mode of the bis-chelating ligand from

#### Scheme 3. Optimized Synthesis of the Neutral Complex 4



DOI: 10.1021/acs.inorgchem.8b01806 Inorg. Chem. XXXX, XXX, XXX–XXX CAN to CAC, furnishing the tris-cyclometalated complex 4, as an uncommon example of triazolide-containing complex. Notably, conversely to the previously reported example of iridium(III) complex 7 (see Chart 3) having a pyridine triazolide ancillary ligand,<sup>48</sup> complex 4 proved to be more stable than the starting cationic complex under heating, probably due to the higher acidity of the triazole proton produced by the electron withdrawing effect of triazolylidenes; in other words, the overall electronic properties of the triazolylidene—triazolide ligand allow the stabilization of the neutral complex 4, as further demonstrated by electrochemical studies and density functional theory (DFT) calculation, *vide infra*.

All compounds were fully characterized by NMR spectroscopy (see Figures S1–S24) and mass spectrometry. The <sup>1</sup>H NMR spectra of both triazolium salts and cationic complexes exhibit some differences depending on the counteranion; therefore, we considered important to make explicit the nature of the anion in the numbering of the salt structures. Notably, the <sup>1</sup>H NMR spectra of the final BF<sub>4</sub> complexes obtained from triflates and iodides are equivalent and display the pattern typical of *mer*-like derivatives with the N atoms of the phenyl– pyridine cyclometalating ligands in trans position.

**Electrochemistry.** We investigated the electrochemical properties of iridium(III) complexes  $1-3-BF_4$  and 4 by means of cyclic voltammetry in acetonitrile solutions at a scan rate of 100 mV/s (Figure 1).



**Figure 1.** Cyclic voltammograms of the iridium(III) complexes investigated in this work. Scan rate: 100 mV/s; CH<sub>3</sub>CN solution with 0.1 M TBAPF<sub>6</sub>.

The electrochemical cell was equipped with a Pt-disk as working electrode, a Pt wire as auxiliary electrode, and an Ag wire as quasi reference electrode. After each set of measurements, ferrocene (Fc) was added to the solution to calibrate the potential according to its value.<sup>56</sup> The voltammograms were also recorded at different scan rates (i.e., 50, 200, and 500 mV/s), and the results are reported in the Supporting Information (Figures S25–S32 and Tables S1–S4). In Table 1, the first oxidation and the first reduction potentials are reported versus the ferrocene/ferrocenium redox couple for all the investigated complexes. These redox data were also used to calculate the frontier molecular orbitals (HOMO and LUMO) of the complexes based on the value of Fc/Fc<sup>+</sup> with respect to the zero vacuum level (i.e., -4.8 eV);<sup>57</sup> these HOMO–LUMO estimates are also compared to DFT data.

All of the complexes present irreversible or quasi-reversible oxidation and reduction processes. The charged complexes (i.e.,  $1-3-BF_4$ ) have very similar oxidation potentials. In particular, the first oxidation occurs at +0.7 V, corresponding to a value of the HOMO that is almost identical for all these three complexes. On the contrary, the neutral complex 4 has the first oxidation peak at lower potential (+ 0.44 V), which is irreversible as in case of the charged complexes. This can be rationalized with the fact that the ancillary ligand of complex 4 chelates the metal through an anionic triazolide, beside the neutral mesoionic carbene unit; this results in a much stronger  $\sigma$ -donation to the positively charged iridium ion, facilitating the oxidation of the metal. The first reduction peaks of 1-BF<sub>4</sub> and  $2-BF_4$  are quasi-reversible and occur at -2.02 V; therefore, the HOMO-LUMO gap of 1-BF<sub>4</sub> and 2-BF<sub>4</sub> is very similar, as also proved by photophysical data (see below).

Interestingly, when the pyridine moiety of the ancillary ligand is replaced by a triazole unit, the reduction potentials of the corresponding complexes are lowered by approximately 300 and 600 mV for 3-BF<sub>4</sub> and 4, respectively (Table 1). Consequently, the neutral complex 4 displays a higher LUMO compared to all the cationic counterparts, as expected on purely electrostatic basis. Because the HOMO of complex 4 is destabilized by approximately 300 mV with respect to the one of 3-BF<sub>4</sub>, this results in an almost identical HOMO-LUMO gap for both complexes. This finding is corroborated by photophysical measurements (e.g., the emission energy of the two complexes is very similar). Moreover, it should be emphasized that the strong LUMO destabilization observed for complexes 3-BF<sub>4</sub> and 4 leads to an increased HOMO-LUMO gap, compared to the  $1-BF_4$  and  $2-BF_4$  analogues. This is further confirmed by theoretical calculations and by the blueshift of their emission maxima (see below).

The electrochemically calculated HOMO–LUMO gaps  $(\Delta E_{\rm HL})$  correlate very well with the ones estimated by DFT

Table 1. Electrochemical Data in Acetonitrile (0.1 M  $\mathrm{TBAPF}_6$ ) and Frontier Orbital Energy Levels of Complexes (Experimental and Calculated)

	electrochemical data <sup>a</sup>				DFT calculated energy <sup>c</sup>			
sample	$E_{\rm ox}$ (V)	$E_{\rm red}$ (V)	$E_{\rm HOMO}~({\rm eV})$	$E_{\rm LUMO}~({\rm eV})$	$\Delta E_{\rm HL}^{b}$ (eV)	$E_{\rm HOMO}~({\rm eV})$	$E_{\rm LUMO}~({\rm eV})$	$\Delta E_{\mathrm{DFT}}^{d}$ (eV)
$1-BF_4$	0.75	-2.02	-5.55	-2.78	2.78	-5.77	-2.10	3.67
$2-BF_4$	0.72	-2.02	-5.52	-2.78	2.73	-5.78	-2.12	3.66
<b>3-BF</b> <sub>4</sub>	0.72	-2.34	-5.52	-2.46	3.05	-5.77	-1.71	4.06
4	0.44	-2.63	-5.24	-2.17	3.06	-5.39	-1.28	4.11

<sup>*a*</sup>Scan rate 100 mV/s, potentials relative to ferrocene/ferrocenium couple. <sup>*b*</sup> $\Delta E_{HL} = E_{LUMO} - E_{HOMO}$ ; <sup>*c*</sup>DFT calculations were carried out at the M06/6-31G(d,p) and cc-pVTZ-ECP60MDF(Ir) level of theory in acetonitrile using PCM. <sup>*d*</sup> $\Delta E_{DFT} = E_{LUMO} - E_{HOMO}$ .



Figure 2. Energy diagram showing the energy values of the frontier Kohn–Sham molecular orbitals of  $1^+-3^+$  and 4 in acetonitrile. For some relevant orbitals, the corresponding isosurface is also displayed for the sake of clarity (isovalue = 0.04  $e^{1/2}$  bohr<sup>-3/2</sup>).

methods ( $\Delta E_{\rm DFT}$ ), as reported in Figure S33. Because the HOMO and LUMO values are indirectly related to the oxidation and reduction potentials,<sup>57–59</sup> electrochemical data are used to estimate the effect exerted by the ancillary ligands on the investigated complexes. This furnished a basis for a better understanding of the electronic features of the reported iridium(III) complexes.

**Theoretical Calculation: Ground-State Properties.** The molecular geometries and the electronic properties of all the synthesized complexes were investigated by means of DFT calculations. The M06 hybrid meta exchange-correlation functional<sup>60,61</sup> was used in combination with the 6-31G(d,p) basis set<sup>62</sup> for all the nonmetal atoms. On the contrary, the Stuttgart/Cologne relativistic pseudopotential and its related correlation-consistent triple- $\zeta$  basis set were adopted for the iridium center.<sup>63</sup> The ground state geometries of all complexes were fully optimized without symmetry constrains in acetonitrile and dichloromethane using the polarizable continuum model (PCM).<sup>64–66</sup>

Due to the lack of any available X-ray structure of  $1-3-BF_4$ and 4, several guesses were made to localize the global minimum on the ground-state potential energy surface of each of the investigated compounds. For all the complexes, a distorted octahedral coordination is assumed around the iridium center, with the pyridyl moieties of the two ppy ligands in trans to each other, as commonly observed in the vast majority of cyclometalated iridium(III) complexes.<sup>35,39,40</sup> Particular attention was paid to the identification of the most stable conformer in the case of complexes 1-BF<sub>4</sub>, 3-BF<sub>4</sub>, and 4 due to the presence of one or two flexible benzyl substituents on the triazolylidene ligand. In fact, if the phenyl substituent (when close to the iridium center, as in  $2-BF_4$ ) is known to make a well-defined  $\pi - \pi$  interactions with the ppy ligands generating the so-called "cage-effect", 39,67,68 the situation is more complicated for the benzyl analogue, where several conformations are experimentally observed. 46,47,69

The minimum-energy fully optimized geometries are reported in Table S5-S8 for all the investigated complexes. In the case of the ionic complexes  $1-BF_4$ ,  $2-BF_4$ , and  $3-BF_4$ , the  $BF_4^-$  counteranion was not included in the calculations,

and the corresponding model compounds are named  $1^+$ ,  $2^+$ , and  $3^+$ , respectively. It is worth noting that, despite the unsymmetrical nature of the triazolylidene-based ligand of 4, this complex adopts a pseudo- $C_2$  symmetry, indicating that the positive charge on the triazolylidene ring is relatively well delocalized over the entire ligand, as depicted in Figure S34.

In Figure 2 are reported the energy diagrams and the frontier molecular orbitals of the investigated series (Chart 2). For all the cationic complexes (i.e.,  $1^+-3^+$ ), the HOMO is mainly located on the iridium center and on both the cyclometalated moieties of each ppy ligands.<sup>13,39</sup> Moreover, also the HOMO energy is virtually identical for all these complexes (i.e.,  $\approx -5.8$  eV, Figure 2), indicating that the ancillary ligands do not strongly affect the electrostatic field around the iridium ion, as also corroborated by electrochemical data (Table 1).

A similar qualitative scenario is also observed for the LUMO, which is always centered on the  $\pi^*$  orbitals of the ancillary ligand for all the cationic complexes under investigation. Anyway, the LUMO energy is strongly affected by the type of ancillary ligand and its related substituents. In the case of complexes  $1^+$  and  $2^+$ , having a differently substituted pyridyl-triazolylidene ligand, the LUMO energy is comparable (i.e., -2.10 vs -2.12 eV, respectively), indicating that the presence of a benzyl or phenyl substituent does not strongly influence the electronic properties of the related compounds.

Notably, the replacement of the pyridyl substituent with a triazolyl one (on the triazolylidene-based ligand) is able to strongly destabilize the corresponding  $\pi^*$  orbitals and, thus, the LUMO energy (compare  $3^+$  and  $1^+$ , Figure 2); as a consequence, complex  $3^+$  displays a larger HOMO–LUMO gap. It is also worth mentioning that the LUMO of  $3^+$  becomes very close in energy to the LUMO+1 ( $\Delta E = 0.14 \text{ eV}$ , Figure 2), opening a pathway to low-lying ligand-centered excited states (see below).

On the other hand, the molecular-orbital energy diagram of complex 4 strongly differs from all the previous ones because it is shifted to more positive energies (Figure 2). This effect can be easily justified considering the charge neutrality of 4. Anyway, as for the cationic analogues, the HOMO of complex

**4** is again located on the metal center and on both the cyclometalated moieties of the ppy ligands. On the contrary, as far as the LUMO is concerned, an orbital flipping is observed; in fact, upon cyclometalation, the  $\pi^*$  orbital of the triazolyl-triazolylidene ligand of complex 4 becomes so high in energy that turns out to be the LUMO+2, while the LUMO and LUMO+1 are now centered on the  $\pi^*$  orbitals of the two ppy ligands (Figure 2). As a consequence, a predominantly LC emission (centered on the ppy ligands) would be expected for **4** (see below).

**Photophysical Properties.** All the investigated complexes  $1-3-BF_4$  and 4 are stable in acetonitrile and dichloromethane solutions for months and do not show degradation under standard laboratory conditions. The electronic absorption spectra were recorded in acetonitrile at room temperature (Figure 3).



Figure 3. UV-vis absorption spectra in CH<sub>3</sub>CN solution at 293 K.

The main absorption bands at high energy ( $\lambda \leq 340$  nm) can be assigned to  $\pi - \pi^*$  transitions, involving the ppy and the mesoionic carbene ligand.<sup>33,39,40</sup> The weaker absorption bands (350–450 nm) are assigned to spin-allowed transitions to a singlet metal-to-ligand charge-transfer state (<sup>1</sup>MLCT) and to spin-forbidden population of the triplet excited state <sup>3</sup>MLCT, although a contribution from ligand centered (LC) cannot be excluded at this stage. Interestingly, the absorption profiles of **1-BF**<sub>4</sub> and **2-BF**<sub>4</sub> are extremely similar, indicating that the different substitution in the triazole ring do not involve any substantial change in the electronic transitions of these two complexes.

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The investigated complexes show poor to moderate emission in oxygen-free acetonitrile solution (Table 2). Complexes 1-BF<sub>4</sub> and 2-BF<sub>4</sub> display a broad and structureless photoluminescence emission bands. This featureless emission is assigned to a <sup>3</sup>MLCT excited-state, as commonly observed in cationic iridium(III) complexes such as  $[Ir(ppy)_2(bpy)]^+$ (bpy = 2,2'-bipyridine).<sup>70</sup> Complexes **1-BF**<sub>4</sub> and **2-BF**<sub>4</sub> present emission features similar to the neutral iridium(III) pyridyltriazolide complexes studied by Swager and coworkers (i.e., complex 7 in Chart 3),48 such as the low quantum yield and band shape. The photoluminescence was investigated also in dichloromethane. The emission maxima have very small dependence on solvent polarity. A possible explanation is that the emissive state has a consistent contribution from <sup>3</sup>LC, but this is not confirmed by DFT calculations, so it is excluded. A more plausible explanation is that the investigated complexes possess an emitting state that is less polar than the ground state (see below).

On the contrary, the photoluminescence spectra of complexes  $3-BF_4$  and 4 present a more structured emission, both in acetonitrile and in dichloromethane.

Emission quantum yields were measured relative to known standards.<sup>71</sup> Although the photoluminescence quantum yields are not very high (Table 2), they are comparable with those reported for other iridium(III) mesoionic carbene complexes.<sup>33</sup> For the cationic complexes  $1-3-BF_4$ , PLQYs are higher in dichloromethane than in acetonitrile solutions, suggesting that in a more polar and coordinative solvent the nonradiative deactivation pathways play a more predominant role in quenching the emission. On the contrary, the neutral complex 4 does not show any remarkable difference in its PLQYs between the two solvents (i.e., about 12% for both dichloromethane and acetonitrile solutions). These experimental findings suggest that metal-centered (<sup>3</sup>MC) states could play an important role in quenching the luminescence of complexes  $1-3-BF_4$  and that such states may involve ligand decoordination, possibly assisted by the solvent (see below).

The experimental photoluminescent properties of the investigated complexes are compared with selected analogues already reported in literature, to find a relationship between their structure and their photophysical behavior. Complex 5 is the compound that has the major similarity with  $1-BF_4$ , but the ancillary ligand coordinates via a N^N chelating mode (cf. Chart 3 and 2). Notably, by going from this N^N mode to the N^C one of the triazolylidene in  $1-BF_4$ , there is a remarkable red-shift in the emission maximum (i.e., 478 vs 557 nm in acetonitrile at 298 K, respectively) and a lowering of the

sample	absorption max. $(\epsilon)^{a}$ [nm (10 <sup>3</sup> M <sup>-1</sup> cm <sup>-1</sup> )]	emission max. (nm)	$PLQY^{c}$ (%)	$\tau^d$ (ns)	$k_{\rm r}^{\ e} \ (10^4 \ {\rm s}^{-1})$	$k_{\rm nr}^{f} (10^5  {\rm s}^{-1})$
1-BF <sub>4</sub>	260(42.1); 309(13.4); 344(9.3);	557 <sup>a</sup>	1.1 <sup>a</sup>	49 <sup><i>a</i></sup>	22.5 <sup>a</sup>	202 <sup><i>a</i></sup>
	383(4.7); 415 (3.0)	560 <sup>b</sup>	4.7 <sup>b</sup>	207 <sup>b</sup>	22.8 <sup>b</sup>	46.0 <sup>b</sup>
$2-BF_4$	260(43.9); 309(14.8); 344(9.8);	574 <sup>a</sup>	0.5 <sup>a</sup>	59 <sup>a</sup>	8.5 <sup>a</sup>	169 <sup>a</sup>
	383(4.8); 415 (3.2)	573 <sup>b</sup>	7.1 <sup>b</sup>	212 <sup>b</sup>	33.5 <sup>b</sup>	43.9 <sup>b</sup>
<b>3-BF</b> <sub>4</sub>	255(43.8); 300(17.2); 343(6.5);	490(1) <sup><i>a</i></sup> , 505 (0.99) <sup><i>a</i></sup>	0.2 <sup><i>a</i></sup>	28 (52%) <sup><i>a</i></sup> , 2.1 (48%) <sup><i>a</i></sup>		
	383(4.3); 415(2.6)	$488(0.83)^{b}$ , $511(1)^{b}$	0.6 <sup>b</sup>	67 (66%) <sup>b</sup> , 2.6 (34%) <sup>b</sup>		
4	253(42.6); 265(44.6); 300(23.4);	$498(1)^{a}$ , 525 $(0.80)^{a}$	12.5 <sup><i>a</i></sup>	473 <sup>a</sup>	26.4 <sup>a</sup>	18.5 <sup>a</sup>
	320(19.1); 370(7.52); 402(4.1); 450(1.2)	$493(1)^{b}$ , 522 $(0.77)^{b}$	11.1 <sup>b</sup>	453 <sup>b</sup>	24.6 <sup>b</sup>	19.6 <sup>b</sup>

<sup>*a*</sup>In acetonitrile. <sup>*b*</sup>In dichloromethane. <sup>*c*</sup>Quantum yields were measured in oxygen-free solutions (i.e., argon-saturated), using [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> in air-equilibrated water solution (PLQY: 0.028) as reference for complexes **1-BF**<sub>4</sub> and **2-BF**<sub>4</sub> and norharmane in air-equilibrated 0.05 M H<sub>2</sub>SO<sub>4(aq.)</sub> (PLQY: 0.58) for complexes **3-BF**<sub>4</sub> and 4.<sup>71</sup> <sup>*d*</sup>Excited-state lifetime measured in oxygen-free solutions. <sup>*e*</sup>k<sub>r</sub> = PLQY/ $\tau$ . <sup>*f*</sup>k<sub>pr</sub> = 1/ $\tau$  - k<sub>r</sub>

photoluminescence quantum yields (i.e., 30% vs 1% in acetonitrile at 298 K).<sup>70</sup> Comparable effects are already observed for a similar couple of iridium(III) complexes (i.e., 7 and 6 in Chart 3), where the benzylic group of the triazole-based ligand was replaced by a long aliphatic chain.<sup>48</sup> In fact, also in that case, the complex having the pyridyl-triazole in the C^N cyclometalating mode (7) presents an emission at lower energy with a smaller quantum yield.<sup>48</sup>

As demonstrated by the comparison between 5 and 6 (Chart 3), the substituent in 1-position of the 1,2,3-triazole ring does not strongly affect the photophysical properties of the related complexes.<sup>48,70</sup> Accordingly, complex  $2-BF_4$ , which differs from  $1-BF_4$  only because of a phenyl substituent on the 1,2,3-triazolylidene ring instead of a benzyl one, has very similar absorption and emission properties (Chart 2, Figure 3 and 4).



Figure 4. Emission spectra in  $\rm CH_3CN$  (solid line) and in  $\rm CH_2Cl_2$  (dashed-dotted line) of Ir(III)complexes studied in this work.

On the contrary, the replacement of the pyridine moiety in 4position of the 1,2,3-triazolylidene ring with a triazole substituent has dramatic effects on the photophysical properties of the related iridium(III) complexes (e.g., compare 1-BF<sub>4</sub> and 3-BF<sub>4</sub>). In fact, the emission of complex 3-BF<sub>4</sub> becomes more structured and shifts to higher energy with respect to 1-BF<sub>4</sub>, with a remarkable decrease in the emission quantum yield (Chart 2 and Table 2). Such experimental findings can be justified considering a change in the nature of the emitting states, as better explained in the theoretical section (see below).

The triazole moiety of the mesoionic triazolylidene ligand of the cationic complex  $3-BF_4$  can be exploited for chelating the iridium center also in a C^C coordination mode, formally leading to the neutral complex 4. Surprisingly, such a substantial change does not strongly perturb the energy and the emission profile of complex 4, compared to  $3-BF_4$ , but it is able to drastically increase its emission quantum yield of more than 20 times (Table 2). This is due to the lack of low-lying <sup>3</sup>MC states that, on the contrary, are able to quench the luminescence of complex  $3-BF_4$  (see theoretical section).

Complex 4 can be compared to its analogue charged complex 8, having a bis-triazole ligand in N^N coordination mode (Chart 3).<sup>10</sup> Both complexes have the same emission profile, although 8 displays a slight hypsochromic shift compared to 4. This is in agreement with the fact that the anionic C^C ligand of 4 displays a higher field strength, compared to the neutral N^N counterpart of 8. On the

contrary, the main difference between the two complexes resides in their emission quantum yield, which is around four times lower in the case of 8 (i.e., 2.8 vs 12.5% for 8 and 4, respectively–data in acetonitrile at 298 K, see Chart 3 and Table 2). As for 3-BF<sub>4</sub>, this phenomenon can be tentatively attributed to the higher lability of the Ir–N (triazole) bond in the triplet excited states, leading to easily accessible non-emissive <sup>3</sup>MC states (see below).

**Theoretical Calculation: Excited-State Properties.** To rationalize the absorption and emission properties of all the investigated samples, a combined DFT and time-dependent DFT (TD-DFT) approach was adopted, and the excited-state properties of the complexes were investigated both in acetonitrile and dichloromethane, to allow a direct comparison with experimental data.

To model the experimental absorption spectra in Figure 3, the lowest 100 vertical excitations were calculated at the optimized geometry of the ground state  $(S_0)$  in acetonitrile, using the linear response formalism; the calculated spectra are reported in Figure S35-S38. In the case of complexes 1<sup>+</sup> and  $2^+$ , the first spin-allowed vertical excitation (i.e.,  $S_0 \rightarrow S_1$ ) is a <sup>1</sup>MLCT transition calculated at 445 nm and it is associated with a pure HOMO  $\rightarrow$  LUMO excitation with almost zero oscillator strength (i.e., f < 0.001). In fact, for these two complexes, the lowest transition which is mainly responsible for the absorption band, experimentally observed around 400 nm, is the  $S_0 \rightarrow S_2$  excitation ( $f \approx 0.05$ ), namely a mixed MCLT/LC transition involving both the iridium ion and the ppy ligands (Figures S35 and S36). On the contrary, for both  $3^+$  and 4, this latter transition corresponds to the  $S_0 \rightarrow S_1$ excitation and it is calculated to occur at approximately 405 nm with an oscillator strength around 0.03. This is the reason why all the investigated complexes appear to display a similar experimental absorption profile at longer wavelengths (Figure 3).

In Tables S9–S12 are listed the lowest-energy triplet excitations for all the complexes within the series, reported in terms of natural transition orbital (NTO) couples.<sup>72</sup> Surprisingly, for complexes 1<sup>+</sup> and 2<sup>+</sup>, the lowest-lying triplet transition (i.e.,  $S_0 \rightarrow T_1$ , estimated at approximately 2.68 eV) is not associated with a HOMO  $\rightarrow$  LUMO excitation, and it corresponds to an LC transition involving the neutral pyridyl–triazolylidene ligand, with some MLCT contribution from the iridium  $d_{\pi}$  orbitals (Table S9 and S10). The next two triplet excited states (i.e.,  $T_2$  and  $T_3$ ) lie at 2.73 and 2.77 eV above  $S_0$  and are associated with transitions mainly involving the two ppy cyclometalating ligands. Finally, only at approximately 2.79 eV above the ground state, it can be found  $T_4$ , which is the triplet state formally populated by the HOMO  $\rightarrow$  LUMO excitation.

A similar excited-state scenario is also observed for  $3^+$ , but the order of these triplet states is different (cf. Table S9–S11). In fact, while the energy of the two triplets centered on the ppy cyclometalating ligands remains virtually the same also for complex  $3^+$ , the replacement of the pyridyl moiety with the triazolyl one (on the triazolylidene ligand) lifts the energy of the corresponding triplet state to 2.99 eV above S<sub>0</sub>. As a consequence, what was T<sub>1</sub> in complexes  $1^+$  and  $2^+$  turns out to be T<sub>3</sub> in  $3^+$ .

In the case of the neutral complex 4, as for the cationic analogue  $3^+$ , the lowest triplet state at the Franck–Condon region is centered on the ppy cyclometalating ligands, with some MLCT contribution (cf. Tables S11 and S12). On the

contrary, in complex 4, the <sup>3</sup>LC transition mainly localized on the triazolylidene ligand is now lowered in energy and becomes  $T_2$  (i.e., 2.74 eV above  $S_0$  vs 2.99 in the case of  $3^+$ ).

To assess the nature of the emitting states, spin-unrestricted DFT calculations were carried out to optimize the lowest triplet state of all the investigated complexes and the corresponding geometries are reported in Tables S13–S16. In the case of both  $1^+$  and  $2^+$ , after full geometry relaxation, the lowest triplet turns out to be the forth triplet state at the Franck–Condon region (i.e.,  $T_4$ ), as reported in Figure 5. As



Figure 5. Spin-density distribution for the lowest-energy emitting triplet states of complexes  $1^+-3^+$  and 4 in their fully relaxed geometries, computed in acetonitrile (isovalues: 0.002 e bohr<sup>-3</sup>).

already mentioned above, such a state is highly MLCT in nature, resulting from a HOMO  $\rightarrow$  LUMO excitation in which one electron is promoted from the iridium d orbitals to the  $\pi^*$ on the triazolylidene ligand (cf. Figure 5 and Tables S9 and S10). This theoretical finding can justify the unstructured emission profiles experimentally observed for 1-BF<sub>4</sub> and 2-BF<sub>4</sub> (Figure 4), which is typical of MLCT transitions. The emission from that state is estimated to occur at 600 nm for both 1<sup>+</sup> and 2<sup>+</sup>, in good agreement with the experimental data; in fact, the mean-photon energy of the emission spectra recorded in roomtemperature acetonitrile solution for 1-BF<sub>4</sub> and 2-BF<sub>4</sub> is 2.15 and 2.19 eV, respectively (to be compared with the theoretical value of 2.07 eV for both 1<sup>+</sup> and 2<sup>+</sup>).

It is also worth mentioning that, despite the emission of these complexes arises from <sup>3</sup>MLCT states, the energy associated with such radiative transitions is not strongly affected by the polarity of the solvent, as experimentally observed in Figure 4. For instance, in the case of complex  $1^+$ , the estimated emission in dichloromethane is calculated to occur at 609 nm, only 0.03 eV lower in energy with respect to the one computed in acetonitrile (i.e., 600 nm, see above). This absence of marked solvatochromism in the emission spectra is rather uncommon for MLCT emitting state, but it can be easily rationalized considering the dipole moments of the ground state  $(S_0)$  and of the emitting triplet  $(T_4)$ .<sup>73</sup> The mesoionic nature of the pyridyl-triazolylidene ligand, having a formally positively charged nitrogen atom on the 5-membered ring, induces a very large dipole moment on S<sub>0</sub> (e.g.,  $12.7 \pm 0.3$ D for  $1^+$ , both in acetonitrile and dichloromethane solution), with the positive charge of the dipole pointing in the direction of such ligand (Figure S39). On the contrary, the lowest triplet excited state, due to its charge-transfer nature, is much less polar than the ground state; in fact, the promotion of one electron from the HOMO to the  $\pi^*$  orbitals of the pyridyl–

triazolylidene ligand (where the LUMO is located) is able to counterbalance the ground-state dipole moment, leading to an almost apolar <sup>3</sup>MLCT excited state (i.e., the dipole moment of  $1^+$  in  $T_4$  is reduced to  $2.7 \pm 0.1$  D, see Figure S39). That is the reason why negligible solvatochromic effects are observed in the emission spectra of both 1-BF<sub>4</sub> and 2-BF<sub>4</sub>, despite the strongly predominant <sup>3</sup>MLCT nature of their emitting states.

A totally different scenario is observed for complexes 3<sup>+</sup> and 4, where the fully relaxed lowest triplet state is found to be centered on the ppy cyclometalating ligands (Figure 5), indicating an emission with a strong <sup>3</sup>LC character. This is the reason why it is experimentally found that both complexes display a very similar phosphorescence spectrum with a vibronically structured profile that is virtually unaffected by the polarity of the solvent (Figure 4). In the case of complex  $3^+$ , the emitting state is straightaway  $T_1$ , because no rootflipping phenomena are observed for such a state upon relaxation (cf. Table S11 and Figure 5). On the other hand, for complex 4, the scenario is more complicated due to the pseudo  $C_2$ -symmetry of the molecule, leading to the presence of two nearly degenerate triplet states (i.e.,  $\Delta E_{\text{SCF}} \approx 0.002 \text{ eV}$ ), each of them centered on one of the two ppy ligands. These two minima can convert into one another through an intermediate located 0.12 eV above them (Figure S40). Therefore, these two minima can be considered in fast equilibration and equally populated at room temperature. Due to their virtually identical energy and nature, from now onward, they will be treated as a unique emitting state (i.e.,  $T_1$ ).

The TD-DFT calculated emission energies are computed to be 2.26 eV (549 nm) and 2.32 eV (534 nm) for 3<sup>+</sup> and 4, respectively. These values are in good agreement with the mean-photon energy of the emission spectra recorded in roomtemperature acetonitrile solution and reported in Figure S41 (i.e., 2.46 eV for  $3-BF_4$  and 2.41 eV for 4). Despite the emission energy and the nature of the emitting state of  $3-BF_4$  is virtually identical to that of complex 4, a remarkable difference in their photoluminescence quantum yields is observed, with the emission of complex 3-BF<sub>4</sub> being almost 50 times quenched if compared to that of 4 (e.g., PLQY = 0.2 vs 12.5% for 3-BF<sub>4</sub> and 4, respectively, see data in Table 2 in room-temperature acetonitrile solutions). Such a dramatic difference can be attributed to an important nonradiative deactivation pathway that is able to effectively kill the luminescence of complex  $3^+$ , but that is not present in 4.

As already pointed out in literature,<sup>39</sup> nonemissive <sup>3</sup>MC levels are well-known to offer effective radiationless pathways to the emitting state in cyclometalated iridium(III) complexes. The population of such <sup>3</sup>MC states formally results from the excitation of an electron from the occupied pseudo- $t_{2g}$   $(d_{\pi})$ orbitals of the iridium center (where the HOMO is generally located) to the unoccupied pseudo-e<sub>g</sub>  $(d_{\sigma^*})$  orbitals of the metal itself, which are usually found at high energy and, as a consequence, not easily populated.<sup>39</sup> Anyway, it has been proved that, more often than expected, <sup>3</sup>MC states play an efficient role in quenching the phosphorescence of cyclo-metalated iridium(III) complexes, <sup>67,74–76</sup> also in combination with carbene-based ligands.<sup>77,78</sup> Generally, the optimized geometry of a <sup>3</sup>MC state in a cyclometalated iridium(III) complex involves the elongation and breaking of an Ir-N bond, resulting in the decoordination of the corresponding ancillary or cyclometalated ligand from the metal coordination sphere. As a result, five- or four-coordinated structures can be

formed, with the iridium center in a trigonal-bipyramidal or square-planar geometry, respectively.  $^{77}\,$ 

Considering the possible elongation and/or breaking of the Ir–N bond involving the triazolylidene-based ligand, we were able to localize a low-lying <sup>3</sup>MC state for complex  $3^+$ . In Figure 6 (top) is reported the fully relaxed minimum-energy geometry



**Figure 6.** Schematic energy diagram showing the adiabatic energy differences between the ground  $(S_0)$ , the emitting  $(T_{em})$ , and the metal-centered  $({}^{3}MC)$  states and the emission energy  $(E_{em})$  calculated for complex  $3^{+}$  (top) and complex  $1^{+}$  (bottom). The fully relaxed minimum-energy geometry of the  ${}^{3}MC$  state is also reported, together with the associated spin-density distribution (isovalues: 0.002 e bohr<sup>-3</sup>). All data are computed in acetonitrile using PCM.

associated with such <sup>3</sup>MC state, in which the triazole moiety of the triazolylidene ligand undergoes a full 180°-rotation around the inter-ring dihedral angle of the ligand, causing a complete decoordination from the iridium center. These excited-state distortions lead to a trigonal-bipyramidal complex that was found to be 0.42 eV more stable than the minimum-energy geometry of the emitting triplet (i.e., T<sub>1</sub>). A very effective population (if not predominant) of this <sup>3</sup>MC state is therefore expected to occur upon excitation of complex 3<sup>+</sup>, and this state would definitely play a role in the radiationless deactivation of 3<sup>+</sup> since the <sup>3</sup>MC minimum is only 0.12 eV above S<sub>0</sub> (Figure 6, top). This scenario can easily justify the extremely low PLQY experimentally observed for complex 3-BF<sub>4</sub> (Table 2).

Obviously, such a type of  ${}^{3}MC$  state cannot be present in complex 4 because the corresponding triazolylidene-based ligand chelates the metal center only through much more stable Ir–C bonds (i.e., a purely cyclometalating one and a carbene-type analogue).<sup>78</sup> The lack of such low-lying  ${}^{3}MC$  states explains the larger PLQY values reported for complex 4 (Table 2).

Following this approach, we also investigated the presence of similar <sup>3</sup>MC states for complexes 1<sup>+</sup> and 2<sup>+</sup>. In fact, both complexes display PLQYs around or below 1% in room-temperature acetonitrile solution, due to the presence of remarkably fast nonradiative processes (compare  $k_r$  and  $k_{nr}$  in Table 2) that can be ascribed to the presence of <sup>3</sup>MC states. Indeed, DFT calculations were able to locate such states very close in energy to the emitting ones. For both complexes, the

<sup>3</sup>MC minimum-energy geometry can be reached by the decoordination of the pyridyl moiety of the triazolylidene ligand, in such a way that the pyridyl nitrogen atom points outside the iridium coordination sphere (Figure 6, bottom); therefore, the partially uncoordinated ligand is no more planar and an inter-ring dihedral angle of  $55^{\circ}$  and  $64^{\circ}$  is formed for  $1^{+}$ and  $2^+$ , respectively. In the case of  $1^+$ , the <sup>3</sup>MC state is found to be only 0.01 eV above the emitting triplet (Figure 6, bottom); while, for  $2^+$ , the nonemissive state becomes even a little bit more stable than the emitting state by 0.09 eV. Despite the roughness of the adopted theoretical model (lacking the evaluation of activation energy barriers and dynamic effects), all these computational findings correlate well to the experimental trend in the emission quantum yields of 1-BF<sub>4</sub> and 2-BF<sub>4</sub>. In fact, as reported in Table 2, the PLQY of complex 1-BF<sub>4</sub> (having the  ${}^{3}MC$  state at little higher energy than the emitting one) is twice as much as the one of  $2-BF_4$  (in which the <sup>3</sup>MC level becomes slightly lower).

The minimum-energy geometries of the <sup>3</sup>MC states calculated for complexes  $1^+-3^+$  and discussed in the present section are reported in Tables S17–S19, for the sake of completeness.

# CONCLUSIONS

We have reported a series of cationic iridium(III) complexes  $1-3-BF_4$  and a neutral one 4 equipped with triazolylidenes as ancillary ligands. A simple procedure for the synthesis of the 1,2,3-triazolylidene rings with a pyridine or a triazole moiety in 4-position was efficiently set up and the corresponding iridium(III) complexes were obtained through a silver-iridium transmetalation. The complexes were synthesized in good yields and fully characterized. In particular, the switching of the binding mode of the bis-chelating ligand 10c-I from C^N to C^C furnishes the neutral tris-cyclometalated complex 4 as an uncommon example of a stable triazolide-containing complex. By comparison with the previously reported example of neutral iridium(III) complex having a pyridine-triazolide ancillary ligand (7, Chart 3), complex 4 was found to be more stable than the starting cationic complex 3-BF<sub>4</sub>, probably due to the higher acidity of the triazole proton produced by the electron withdrawing effect of triazolylidenes. In other words, the overall electronic properties of the triazolylidene-triazolide ligand allow the stabilization of the neutral complex 4. These properties are reflected on its photoluminescence quantum yield that is around four times higher than the quantum yield of its analogue charged complex 8, having a bis-triazole ligand in N^N coordination mode, 60 times higher than the quantum yield of the starting cationic complex 3-BF<sub>4</sub> and 60 times higher than the quantum yield of the neutral complex 7 having a pyridyl-triazole ligand in the C^N cyclometalating mode (Chart 2 and Chart 3). This work gives entry to a new class of charged and neutral phosphorescent iridium(III) complexes, which can be now expanded by rational design of the mesoionic carbene and/or the ancillary ligands to enhance the luminescent properties and potential applications thereof.

# EXPERIMENTAL SECTION

**General Information.** Analytical grade solvents and commercially available reagents were used as received unless otherwise stated. Chromatographic purifications were performed using 70–230 mesh silica. <sup>1</sup>H, <sup>19</sup>F, and <sup>13</sup>C NMR spectra were recorded on a Varian Inova 300 MHz, on a Mercury 400 MHz or on an Inova 600 MHz spectrometer. Chemical shifts ( $\delta$ ) are reported in ppm relative to

residual solvent signals for <sup>1</sup>H and <sup>13</sup>C NMR (<sup>1</sup>H NMR: 7.26 ppm for CDCl<sub>3</sub>, 3.34 ppm for CD<sub>3</sub>OD, 1.94 ppm for CD<sub>3</sub>CN, 2.50 ppm for DMSO; <sup>13</sup>C NMR: 77.0 ppm for CDCl<sub>3</sub>, 48.9 ppm for CD<sub>3</sub>OD, 1.32 ppm for CD<sub>3</sub>CN, 39.5 ppm for DMSO). <sup>19</sup>F NMR spectra were recorded at 376.25 MHz or at 564.3 MHz using trichlorofluor-ometane as external standard. <sup>13</sup>C NMR spectra were acquired with <sup>1</sup>H broad band decoupled mode. Coupling constants are given in Hertz. The high-resolution mass spectra (HRMS) were obtained with a Waters Q-TOF-MS instrument using electrospray ionization (ESI).

**General Procedures.** 2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl) pyridine **9a**,<sup>49</sup> 2-(1-phenyl-1*H*-1,2,3-triazol-4-yl) pyridine **9b**,<sup>49</sup> 1,1'-dibenzyl-1*H*,1'*H*-4,4'-bi(1,2,3-triazole) **9c**,<sup>10</sup> 1-benzyl-3-methyl-4-(pyridin-2yl)-1*H*-1,2,3-triazol-3-ium trifluoromethanesulfonate **10a-OTf**,<sup>33</sup> 1,1'-dibenzyl-3-methyl-4,4'-bis(1*H*-1,2,3-triazol)-3-ium iodide **10c-** $I^{50}$  were prepared according to reported methods.

**Caution**: Although we experienced no difficulties in handling these nitrogen-rich compounds, small scale and best safety practices are strongly encouraged.

Synthesis of 1-Benzyl-3-methyl-4-(pyridin-2-yl)-1H-1,2,3-triazol-3-ium lodide 10a-I and 2-(1-Benzyl-1H-1,2,3-triazol-4-yl)-1-methylpyridin-1-ium lodide 11a-l. 2-(1-Benzyl-1H-1,2,3-triazol-4-yl) pyridine 9a (472 mg, 2.00 mmol) was dissolved in anhydrous ACN (12 mL), and MeI (0.624 mL, 10.0 mmol, 5 equiv) was added. The solution was refluxed for 24 h under N2. Then, the solvent was removed and the crude was purified by column cromatography on silica gel with DCM/MeOH as eluent, from 95/5 to 7/3 ratio, to give 10a-I (98 mg, 0.26 mmol, 13% yields). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) δ: 4.64 (s, 3H), 5.91 (s, 2H), 7.45-7.50 (m, 3H), 7.55-7.65 (m, 3H), 7.95–8.10 (m, 2H), 8.81 (bd, 1H, J<sub>HH</sub> = 5.0 Hz), 9.32 (s, 1H). <sup>13</sup>C NMR, (CD<sub>3</sub>OD, 100 MHz) δ: 151.1 (CH), 144.3 (C), 142.4 (C), 139.1 (CH), 133.2 (C), 130.7 (CH), 130.3 (CH), 130.3 (CH), 129.9 (CH), 126.8 (CH), 125.6 (CH), 58.4 (CH<sub>2</sub>), 41.6 (CH<sub>3</sub>). HRMS (ESI-QTOF) ([M]<sup>+</sup>): m/z calcd for  $[C_{15}H_{15}N_4]^+$ 251.1291; found 251.1295 and 11a-I (537 mg, 1.42 mmol, 71% yields) <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>CN) δ: 4.45 (s, 3H), 5.76 (s, 2H), 7.35–7.50 (m, 5H), 7.94 (bt, 1H,  $J_{\rm HH}$  = 7.0), 8.43 (dd, 1H,  $J_{\rm HH}$  = 8.3 Hz,  $J_{\rm HH}$  = 1.1 Hz), 8.51 (bt, 1H,  $J_{\rm HH}$  = 7.9 Hz), 8.79 (d, 1H,  $J_{\rm HH}$  = 6.3 Hz), 8.87 (s, 1H). <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN) δ: 49.4 (CH<sub>3</sub>), 55.0 (CH<sub>2</sub>), 127.4 (CH), 129.4 (CH), 129.5 (CH), 129.6 (CH), 129.7 (CH), 130.0 (CH), 135.9 (C), 139.5 (C), 146.3 (CH), 147.3 (C), 147.8 (CH). HRMS (ESI-QTOF) ([M]<sup>+</sup>): m/z calcd for  $[C_{15}H_{15}N_4]^+$  251.1291; found 251.1294.

Synthesis of 1-Phenyl-3-methyl-4-(pyridin-2-yl)-1H-1,2,3-triazol-3-ium Trifluoromethanesulfonate 10b-OTf. 2-(1-Phenyl-1H-1,2,3triazol-4-yl) pyridine 9b (460 mg, 2.07 mmol) was dissolved in anhydrous DCM (10 mL), and MeOTf (0.28 mL, 2.48 mmol, 1.2 equiv) was added dropwise. The solution was refluxed for 24 under N<sub>2</sub>; the solvent was removed, and and the crude was purified by column chromatography on silica gel (DCM/MeOH = 95/5) to give 10b-OTf (432 mg, 1.1 mmol, 54% yields. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.07 (s, 1H), 8.74 (dq,  $J_{\rm HH}$  = 0.8,  $J_{\rm HH}$  = 4.8, 1H), 8.40 (dt,  $J_{\rm HH} = 0.8, J_{\rm HH} = 8.0, 1 \text{H}$ , 8.11 - 8.07 (m, 2H),  $7.92 \text{ (dt, } J_{\rm HH} = 2.0, J_{\rm HH}$ = 8.0, 1H), 7.66–7.60 (m, 3H), 7.47 (ddd,  $J_{\rm HH}$  = 0.8,  $J_{\rm HH}$  = 4.8,  $J_{\rm HH}$  = 8.0, 1H), 4.79 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 149.6 (CH), 142.6 (C), 141.9 (C), 138.5 (CH), 134.6 (C), 132.1 (CH), 130.5 (CH), 127.6 (CH), 126.0 (CH), 125.9 (CH), 121.3 (CH), 41.8 (CH<sub>3</sub>). <sup>19</sup>F NMR (376.25 MHz, CDCl<sub>3</sub>)  $\delta$  –78.4 (s). HRMS (ESI-QTOF) ([M]<sup>+</sup>): m/z calcd for  $[C_{14}H_{13}N_4]^+$  237,1135; found: 237.1139

Synthesis of 1-Phenyl-3-methyl-4-(pyridin-2-yl)-1H-1,2,3-triazol-3-ium lodide **10b-I** and 2-(1-Phenyl-1H-1,2,3-triazol-4-yl)-1-methylpyridin-1-ium lodide **11b-I**. 2-(1-Phenyl-1H-1,2,3-triazol-4-yl) pyridine **9b** (444 mg, 2.00 mmol) was dissolved in anhydrous ACN (12 mL), and MeI (0.624 mL, 10.00 mmol, 5 equiv) was added. The solution was refluxed for 24 h under N<sub>2</sub>; the solvent was removed, and the crude was purified by column chromatography on silica gel with DCM/MeOH = 9/1 as eluent to give **10b-I** (95 mg, 0.26 mmol, 13% yields). <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>CN)  $\delta$ : 4.67 (s, 3H), 7.60–7.65 (m, 1H), 7.75–7.80 (m, 3H), 8.00–8.05 (m, 2H), 8.10–8.15 (m, 2H), 8.86 (bt, 1H, J<sub>HH</sub> = 4.9 Hz), 9.47 (s, 1H). <sup>13</sup>C NMR, (CD<sub>3</sub>CN, 100 MHz) δ: 151.3 (CH), 144.0 (C), 142.7 (C), 139.3 (CH), 136.0 (C), 133.1 (CH), 131.6 (CH), 128.4 (CH), 127.1 (CH), 125.8 (CH), 122.6 (CH), 42.1 (CH<sub>3</sub>). HRMS (ESI-QTOF) ( $[M]^+$ ): *m/z* calcd for [C<sub>14</sub>H<sub>13</sub>N<sub>4</sub>]<sup>+</sup> 237,1135; found: 237.1138 and **11b-I** (444 mg, 1.22 mmol, 61% yields) <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>CN) δ: 4.56 (s, 3H), 7.60–7.65 (m, 1H), 7.65–7.70 (m, 2H), 8.00–8.05 (m, 3H), 8.55– 8.60 (m, 2H), 8.85 (d, 1H, *J*<sub>HH</sub> = 6.3 Hz), 9.27 (s, 1H). <sup>13</sup>C NMR (100 MHz, D6-DMSO) δ: 147.4 (CH), 145.3 (CH), 145.2 (C), 139.1 (C), 135.9 (C), 130.1 (CH), 129.8 (CH), 128.1 (CH), 127.0 (CH), 126.6 (CH), 120.8 (CH), 48.6 (CH<sub>3</sub>). HRMS (ESI-QTOF) ([M]+): *m/z* calcd for [C<sub>14</sub>H<sub>13</sub>N<sub>4</sub>]<sup>+</sup> 237,1135; found: 237.1139.

General Procedure for the Synthesis of Complexes 1-BF<sub>4</sub> and 2-BF₄ from 1H-1,2,3-Triazól-3-ium Triflates. The desired 1H-1,2,3-triazol-3-ium triflate (0.08 mmol) was dissolved in ACN (6 mL), and then KCl (0.80 mmol, 10 equiv) and  $Ag_2O$  (0.28 mmol, 3.5 equiv) were added. The resulting mixture was stirred under N2 at room temperature in the absence of light. After 24 h, the formed solid was filtered off and washed with ACN (10 mL). The resulting solution was then concentrated under reduced pressure to give a white solid that was dissolved in DCM/EtOH = 3/1 (8 mL), and  $[Ir(ppy)_2Cl]_2$  (0.04 mmol, 0.5 equiv) was added. After the solution was stirred for 24 h at room temperature, the solvent was evaporated, and the crude reaction mixture was purified by column chromatography to give the expected Ir-complex as triflate salt that was dissolved in DCM/EtOH = 5/1 (12 mL). Then, NH<sub>4</sub>BF<sub>4</sub> (40 equiv) was added. The resulting mixture was stirred at rt for 2 h; water (10 mL) was added, and the product was extracted with DCM ( $2 \times 10$  mL). The organic layer was dried over  $Na_2SO_4$  and the solvent evaporated. The obtained solid was dissolved in a minimum amount of DCM, precipitated by Et<sub>2</sub>O addition, and filtered to give Ir-complex as tetrafluoroborate salt.

General Procedure for the Synthesis of the Complexes from 1H-1,2,3-Triazol-3-ium lodides. The desired 1H-1,2,3triazol-3-ium iodide (0.06 mmol) was dissolved in DCM (15 mL), and Ag<sub>2</sub>O (0.15 mmol, 2.6 equiv) was added. The resulting mixture was stirred under N2 at room temperature in the absence of light. After 2 h, [Ir(ppy)<sub>2</sub>Cl]<sub>2</sub> (0.03 mmol, 0.5 equiv) was added, and the mixture was stirred for additional 24 h at room temperature under N<sub>2</sub> in the absence of light. Then, the solid was filtered off, washed with DCM (25 mL), and the combined solutions were concentrated under reduced pressure. The crude product was purified by column chromatography to give the expected Ir-complex as iodide salt that was dissolved in DCM/EtOH = 5/1 (20 mL), and NH<sub>4</sub>BF<sub>4</sub> (40 equiv) was added. The resulting mixture was stirred at rt for 48 h; water (15 mL) was added, and the product was extracted with DCM  $(2 \times 20 \text{ mL})$ . The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent evaporated. The obtained solid was dissolved in a minimum amount of DCM, precipitated by Et<sub>2</sub>O addition and filtered to give Ircomplex as tetrafluoroborate salt.

 $[Ir(ppy)_2(ptb)]^+BF_4^-$  (1-BF<sub>4</sub>). From triazolium triflate 10a-OTf 44 mg, 0.053 mmol yields = 66%. From triazolium iodide 10a-I 25 mg, 0.029 mmol yields = 49%. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$ : 4.67 (s, 3H), 4.90–4.97 (AB system, 2H), 6.25 (d, 1H,  $J_{\rm HH}$  = 7.4 Hz), 6.33 (d, 1H,  $J_{HH}$  = 7.7 Hz), 6.55 (d, 2H,  $J_{HH}$  = 7.6 Hz), 6.82 (bd, 1H,  $J_{HH}$ = 7.5 Hz), 6.85–7.00 (m, 4H), 7.01 (bt, 1H,  $J_{\rm HH}$  = 7.5 Hz), 7.05– 7.15 (m, 3H), 7.18 (bt, 1H,  $J_{\rm HH}$  = 7.5 Hz), 7.44 (d, 1H,  $J_{\rm HH}$  = 7.7 Hz), 7.49 (d, 1H, J<sub>HH</sub> = 5.7 Hz), 7.60–7.70 (m, 4H), 7.82 (d, 2H, J<sub>HH</sub> = 7.0 Hz), 7.95 (d, 1H,  $J_{\rm HH}$  = 5.7 Hz), 8.04 (dt, 1H,  $J_{\rm HH}$  = 7.9 Hz,  $J_{\rm HH}$ = 1.4 Hz), 8.32 (d, 1H,  $J_{HH}$  = 8.2 Hz). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 39.4 (CH<sub>3</sub>), 56.1 (CH<sub>2</sub>), 118.9 (CH), 119.3 (CH), 121.0 (CH), 122.3 (CH), 122.6 (CH), 122.7 (CH), 123.6 (CH), 124.5 (CH), 124.5 (CH), 125.7 (CH), 126.8 (CH), 128.0 (CH), 128.4 (CH), 130.1 (CH), 130.6 (CH), 131.1 (CH), 131.3 (CH), 134.3 (C), 136.3 (CH), 137.4 (CH), 139.8 (CH), 142.6 (C), 144.4 (C), 148.0 (CH), 148.8 (C), 149.7 (C), 150.3 (C), 152.1 (CH), 153.9 (CH), 164.9 (C), 167.2 (C), 168.7 (C), 171.4 (C). <sup>19</sup>F NMR (564.3 MHz, CDCl<sub>3</sub>)  $\delta$ : -153.22 (s). HRMS (ESI-QTOF) ([M]<sup>+</sup>): m/z calcd for C<sub>37</sub>H<sub>30</sub>IrN<sub>6</sub>: 749,2132; found: 749,2115.

 $[Ir(ppy)_2(ptp)]^+BF_4^-$  (2-BF<sub>4</sub>). From triazolium triflate 10b-OTf 50 mg, 0.06 mmol, yields = 76%. From triazolium iodide 10b-I 42 mg,

0.05 mmol, yields = 84%. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$ : 4.75 (s, 3H), 5.93 (d, 1H,  $J_{\rm HH}$  = 7.6 Hz), 6.20 (d, 1H,  $J_{\rm HH}$  = 7.4 Hz), 6.47 (bt, 1H,  $J_{\rm HH}$  = 7.2 Hz), 6.70 (bt, 1H,  $J_{\rm HH}$  = 7.6 Hz), 6.90–7.05 (m, 7H), 7.07 (bt, 1H,  $J_{\rm HH}$  = 6.5 Hz), 7.15–7.20 (m, 2H), 7.37 (d, 1H,  $J_{\rm HH}$  = 7.8 Hz), 7.56 (d, 1H,  $J_{\rm HH}$  = 5.8 Hz), 7.60–7.70 (m, 3H), 7.75–7.85 (m, 2H), 7.85 (bt, 1H,  $J_{\rm HH}$  = 5.6 Hz), 8.06 (bt, 1H,  $J_{\rm HH}$  = 7.9 Hz), 8.19 (bt, 1H,  $J_{\rm HH}$  = 5.9 Hz), 8.36 (d, 1H,  $J_{\rm HH}$  = 8.1 Hz). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$ : 39.6 (CH<sub>3</sub>), 118.8 (CH), 119.3 (CH), 120.7 (CH), 122.3 (CH), 122.5 (CH), 122.6 (CH), 123.9 (CH), 123.9 (CH), 124.2 (CH), 130.6 (CH), 130.9 (CH), 131.2 (CH), 136.5 (CH), 137.2 (C), 137.4 (CH), 139.6 (CH), 142.1 (C), 144.3 (C), 149.0 (CH), 149.6 (C), 149.7 (C), 150.4 (C), 152.0 (CH), 15308 (CH), 164.0 (C), 167.5 (C), 168.6 (C), 171.1 (C). <sup>19</sup>F NMR (564.3 MHz, CDCl<sub>3</sub>)  $\delta$ : –153.11 (s). HRMS (ESI-QTOF) ([M]<sup>+</sup>): *m*/z calcd for C<sub>36</sub>H<sub>28</sub>IrN<sub>6</sub>: 735,1976; found: 735,1965.

 $[lr(ppy)_2(btb)]^+BF_4^-$  (3-BF<sub>4</sub>). 29.7 mg, 0.032 mmol Yields= 54% from triazolium iodide 10c-I. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$ : 4.42 (s, 3H), 4.80 (d, 1H,  $J_{\rm HH}$  = 14.5 Hz), 4.86 (d, 1H,  $J_{\rm HH}$  = 14.5 Hz), 5.50 (d, 1H,  $J_{\rm HH}$  = 14.4 Hz), 5.54 (d, 1H,  $J_{\rm HH}$  = 14.4 Hz), 6.29 (dd, 1H,  $J_{\rm HH}$  = 7.5 Hz,  $J_{\rm HH}$  = 0.7 Hz), 6.38 (dd, 1H,  $J_{\rm HH}$  = 7.7 Hz,  $J_{\rm HH}$  = 0.7 Hz), 6.57 (d, 2H,  $J_{\rm HH}$  = 7.7 Hz), 6.75–6.80 (m, 1H), 6.82 (dt, 1H,  $J_{\rm HH} = 7.5 \text{ Hz}, J_{\rm HH} = 1.2 \text{ Hz}), 6.85-6.95 \text{ (m, 3H)}, 6.98 \text{ (bt, 1H, } J_{\rm HH} = 1.2 \text{ Hz})$ 7.8 Hz), 7.11 (bt, 2H,  $J_{\rm HH}$  = 7.7 Hz), 7.20 (bt, 1H,  $J_{\rm HH}$  = 7.4 Hz), 7.25–7.35 (m, 5H), 7.45 (d, 1H,  $J_{\rm HH}$  = 7.8 Hz), 7.55 (d, 1H,  $J_{\rm HH}$  = 5.7 Hz), 7.60–7.70 (m, 4H), 7.80–7.85 (m, 2H), 8.85 (s, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 38.3 (CH<sub>3</sub>), 55.5 (CH<sub>2</sub>), 56.1 (CH<sub>2</sub>), 118.8 (CH), 119.2 (CH), 121.0 (CH), 122.2 (CH), 122.6 (CH), 122.7 (CH), 122.8 (CH), 124.0 (CH), 124.4 (CH), 126.9 (CH), 128.2 (CH), 128.4 (CH), 128.8 (CH), 128.9 (CH), 129.0 (CH), 129.9 (CH), 130.0 (CH), 131.1 (CH), 131.6 (CH), 133.6 (C), 134.3 (C), 136.3 (CH), 137.1 (CH), 139.9 (C), 142.8 (C), 143.4 (C), 144.5 (C), 147.7 (C), 149.2 (CH), 153.0 (CH), 160.7 (C), 167.0 (C), 168.9 (C), 169.6 (C).  $^{19}$ F NMR (564.3 MHz, CDCl<sub>3</sub>)  $\delta$ : -156.87 (s). HRMS (ESI-QTOF) ([M]<sup>+</sup>): m/z calcd for C<sub>41</sub>H<sub>34</sub>IrN<sub>8</sub>: 829,2507; found: 829,2512.

Synthesis of Complex [lr(ppy)<sub>2</sub>(btb)] 4. Complex 3-BF<sub>4</sub> (25 mg, 0.027 mmol, 1 equiv) was dissolved in 2-ethoxyethanol (5.0 mL), and K<sub>2</sub>CO<sub>3</sub> (37 mg, 0.27 mmol, 10.0 equiv) was added. The resulting mixture was refluxed under N2 for 24 h. After cooling, the reaction was quenched with water (15 mL), and the product was extracted with DCM (2  $\times$  10 mL). The combined organic layers were dried over Na2SO4, filtered, and the solvent evaporated under vacuum. The crude was purified by flash chromatography on silica gel (petroleum ether/EtOAc= 1/1) to give complex 4 (15 mg, 0.018 mmol) in 67 yields %. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 4.45 (s, 3H), 4.67 (d, 1H,  $J_{\rm HH} = 14.5~{\rm Hz}$ ), 4.75 (d, 1H,  $J_{\rm HH} = 14.5~{\rm Hz}$ ), 4.81 (d, 1H,  $J_{\rm HH} = 15.2$ Hz), 4.86 (d, 1H,  $J_{HH}$  = 15.2 Hz), 6.30 (dd, 1H,  $J_{HH}$  = 7.1 Hz,  $J_{HH}$  = 1.3 Hz), 6.40–6.45 (m, 3H), 6.55–6.65 (m, 2H), 6.65 (d, 2H, J<sub>HH</sub> = 7.6 Hz), 6.75–6.80 (m, 4H), 6.90–6.95 (m, 2H), 7.01 (bt, 1H, J<sub>HH</sub> = 7.3 Hz), 7.05–7.10 (m, 2H), 7.16 (bt, 1H,  $J_{HH}$  = 7.4 Hz), 7.30–7.35 (m, 1H), 7.40–7.45 (m, 2H), 7.45–7.50 (m, 2H), 7.60 (d, 1H, J<sub>HH</sub> = 8.2 Hz), 7.89 (bt, 2H,  $J_{\rm HH}$  = 6.1 Hz). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 37.0 (CH<sub>3</sub>), 53.0 (CH<sub>2</sub>), 55.1 (CH<sub>2</sub>), 118.3 (CH), 118.4 (CH), 120.0 (CH), 120.2 (CH), 121.4 (CH), 121.7 (CH), 124.1 (CH), 124.2 (CH), 126.2 (CH), 126.4 (CH), 127.2 (CH), 127.4 (CH), 127.6 (CH), 128.1 (CH), 129.3 (CH), 129.4 (CH), 131.3 (CH), 132.0 (CH), 134.5 (CH), 134.8 (CH), 135.8 (C), 138.7 (C), 143.8 (C), 144.2 (C), 149.1 (C), 150.5 (C), 152.7 (CH), 153.3 (CH), 160.0 (C), 163.1 (C), 164.4 (C), 165.3 (C), 168.9 (C), 169.1 (C). HRMS (ESI-QTOF): m/z calcd for  $C_{41}H_{33}IrN_8$ : 829,2507; found: 829,2500 [M + H]<sup>+</sup>.

**Electrochemical Characterization.** Cyclic voltammetry experiments were performed with a Metrohm Autolab PGSTAT101 at room temperature inside a glovebox. The electrochemical cell was equipped with a Pt-disc as working electrode, an Ag-wire quasi-reference electrode, and a Pt wire as counter electrode. Ferrocene was used as internal standard (0.38 V vs SCE).<sup>79</sup> The electrochemical characterization, cyclic voltammetry (CV), was performed in dry acetonitrile/0.1 M tetrabutylammonium hexafluorophosphate

(TBAPF<sub>6</sub>). The concentration of the samples was in the millimolar range (3 mM for complexes **1-BF**<sub>4</sub>, **2-BF**<sub>4</sub>, and **3-BF**<sub>4</sub>, and **1.5** mM for complex 4). TBAPF<sub>6</sub> (electrochemical grade, 99%, Fluka) was used as the supporting electrolyte, subject to recrystallization from an ethanol solution and dried at 60 °C under vacuum.

**Photophysics.** UV–vis absorption spectra were recorded with a PerkinElmer Lambda 750 double-beam UV/vis-NIR spectrometer equipped with a  $6 \times 6$  cell changer unit at 20 °C. Luminescence at room temperature was measured using a Jobin–Yvon Fluoromax 4 fluorimeter with a step width of 1 nm and an integration time of 0.8 s. All measurements were performed in pressure resistant quartz cuvettes with septum from Hellma. CH<sub>2</sub>Cl<sub>2</sub> solvent for spectroscopic measurements was supplied by Merck (Uvasol). Photoluminescence quantum yields were determined utilizing as reference Ru(bpy)<sub>3</sub>Cl<sub>2</sub> ( $6 H_2O$ ) in water or normharmane in 0.1 N aqueous solution of H<sub>2</sub>SO<sub>4</sub>. Lifetime measurements were performed by time-correlated single-photon counting method (TCSPC) with a DeltaTime kit for DeltaDiode source on FluoroMax systems, including DeltaHub and DeltaDiode controller. The light-source was a NanoLED 366 nm.

**Computational Details.** DFT calculations were carried out using the D.01 revision of the Gaussian 09 program package<sup>80</sup> in combination with the M06 global-hybrid meta-GGA exchangecorrelation functional.<sup>60,61</sup> The fully relativistic Stuttgart/Cologne energy-consistent pseudopotential with multielectron fit was used to replace the first 60 inner-core electrons of the iridium metal center (i.e., ECP60MDF)<sup>63</sup> and was combined with the associated triple- $\zeta$ basis set (i.e., cc-pVTZ-PP basis);<sup>63</sup> for all other atoms, the Pople 6-31G(d,p) basis set was adopted.<sup>62</sup>

All the reported complexes were fully optimized without symmetry constraints, using a time-independent DFT approach, in their ground state (S<sub>0</sub>), triplet emitting state and metal-center one ( ${}^{3}MC$ ); all the optimization procedures were performed using the PCM to simulate acetonitrile or dichloromethane solvation effects.<sup>64-66</sup> Frequency calculations were always used to confirm that every stationary point found by geometry optimizations was actually a minimum on their corresponding potential-energy surfaces (no imaginary frequencies). For all the complexes, the S<sub>0</sub> minimum-energy geometry was optimized starting from several possible conformers, suggested by both chemical intuition or available X-ray structures for analogue structures. To investigate the nature of the emitting state, geometry optimizations and frequency calculations were performed at the spinunrestricted UM06 level of theory (imposing a spin multiplicity of 3), using the S<sub>0</sub> minimum-energy geometry as starting point. The emission energy from the lowest triplet excited state was estimated by subtracting the SCF energy of the emitting state  $(T_n)$  in its minimum conformation from that of the singlet ground state having the same geometry of T<sub>n</sub>. The <sup>3</sup>MC states were optimized using the same spinunrestricted DFT approach, but several educated guesses were used as starting geometries.

TD-DFT calculations,<sup>81–83</sup> carried out at the same level of theory used for geometry optimizations, were used to simulate the electronic absorption spectra of the investigated molecules in their optimized S<sub>0</sub> geometry, by computing the lowest-energy 100 vertical excitations of singlet spin multiplicity. Using the same approach, also the first 25 triplet excitations were calculated and their nature was assessed by the help of NTO analysis.<sup>72</sup>

All the pictures showing molecular geometries, orbitals, and spindensity surfaces were created using GaussView 5.<sup>84</sup>

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b01806.

Crystal structures and crystallographic data of compound 11b-I; NMR spectra of the ligands and of complexes  $1-3-BF_4$  and 4; electrochemical data of complexes  $1-3-BF_4$  and 4 in acetonitrile solutions at different scan rates; DFT and TD-DFT data with the optimized geometries of the ground state, of the lowest triplet state, and of the metal-centered state of complexes  $1^+-3^+$  and 4 calculated in acetonitrile; emission and excitation spectra of all the complexes in room-temperature acetonitrile solution (PDF)

# Accession Codes

CCDC 1844614 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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# Notes

The authors declare no competing financial interest.

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