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Pd-Catalyzed Functionalization of the Thenoyltrifluoroacetone Coligands by Aromatic Dyes in Bis(cyclometallated) Ir^{III} Complexes: From Phosphorescence to Fluorescence?

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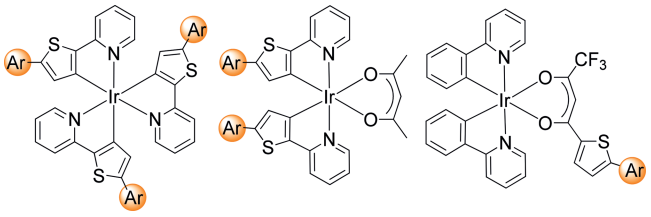
The synthesis, characterization and photophysical properties of a series of neutral Ir($C^{\wedge}N$-Meppy)$_2$($O^{\wedge}O$-tta-Ar) (MeppyH = 4-methyl-2-phenylpyridine; tta = thenoyltrifluoroacetonate) complexes containing new functionalized tta-Ar ligands in which the incorporated Ar group is an aromatic dye such as naphthalene, pyrene, naphthalimide or coumarin, are reported. The arylated proligands ttaH-Ar are readily obtained in two steps through Pd-catalyzed C–H bond activation of 2-acetylthiophene. In contrast to the parent Ir($C^{\wedge}N$)$_2$($O^{\wedge}O$) complexes, which are phosphorescent in solution at room temperature, all of the arylated complexes display fluorescence, and the phosphorescence emission is quenched. Thus, this work shows that the incorporation of such aromatic dyes in the tta ligand has a dramatic influence on the photophysical properties of the resulting Ir complexes.

Introduction

Neutral and cationic cyclometallated iridium(III) complexes have attracted much interest over the past 15 years, owing to their applications in electroluminescence,[1] photocatalysis,[2] phosphorescent molecular probes[3] and, more recently, triplet–triplet annihilation (TTA) upconversion.[4] In this field, the variation of the cyclometallated ligand, the ancillary ligands or both can profoundly affect the optical properties of the resulting Ir^{III} complexes. Thus, ligand design is crucial for the control of excited states and photophysical properties, and the preparation of new ligands containing functional groups to modulate such properties remains challenging.

Recently, we have demonstrated that palladium-catalyzed arylation through C–H activation[5,6] is a powerful tool to functionalize luminescent Ir^{III} complexes, especially those containing electron-rich thiophene rings.[7,8] For example, this direct arylation can be readily achieved with tris(cyclometallated) Ir(thpy)$_3$[7] and bis(cyclometallated) Ir($C^{\wedge}N$-thpy)$_2$($O^{\wedge}O$-acac) complexes, in which the thiophene ring is coordinated to the iridium centre, and also with Ir($C^{\wedge}N$-ppy)$_2$($O^{\wedge}O$-tta), in which the thiophene ring is located within the O^O-coordinated coligand (thpyH = 2,2′-thienylpyridine; ppyH = 2-phenylpyridine; acac = acetylacetonate; tta = thenoyltrifluoroacetonate; see Scheme 1).[8] The arylation reaction occurs regiospecifically at the 5-position of the thienyl ring and is compatible with a variety of aryl bromides. The functional-group tolerance of this method allows the easy modification of the electronic structure of the resulting complexes. Through changes to the nature of the appended aromatic group or the modification of the electron-withdrawing or -donating character of the additional aryl groups, a large panel of emitters becomes readily accessible.



Scheme 1. Chemical structures of the arylated tris- and bis(cyclometallated) Ir^{III} complexes.

As an extension of this work, we decided to investigate access to arylated Ir($C^{\wedge}N$-Meppy)$_2$($O^{\wedge}O$-tta-Ar) (MeppyH = 4-methyl-2-phenylpyridine) complexes, in which the incorporated aryl group is an aromatic chromophore such as naphthalene, pyrene, naphthalimide or coumarin, and to

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study the photophysical properties of the resulting complexes.

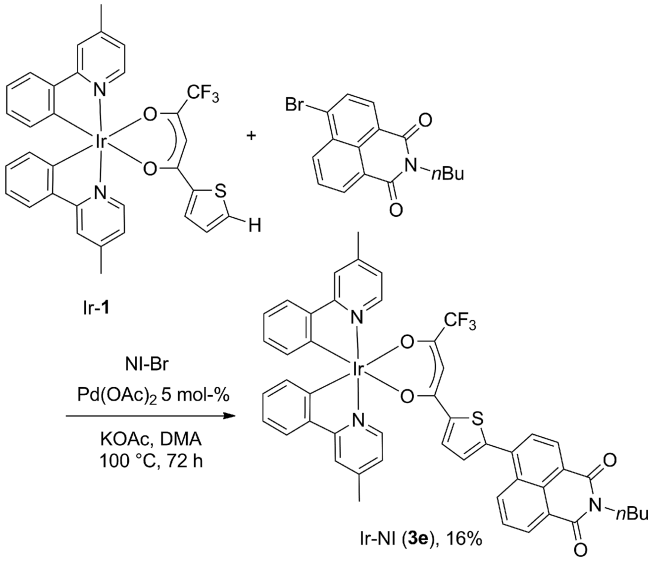
There are several reports on the combination of organic dyes with bis(cyclometallated) $[Ir(C^{\wedge}N)_2(N^{\wedge}N)]^+$ complexes.[9,10] Various designs have been reported in which the connection of a 2,2′-bipyridine (bpy) ligand through a C≡C– unit to different dyes such as Bodipy, coumarin or naphthalenediimide (NDI) leads to intriguing TTA-based upconversions.[10] The direct cyclometallation of the fluorophore has also been reported; for example, complexes incorporating cyclometallated pyrene units[11] resulted in enhanced visible absorption compared to the benchmark complexes $[Ir(C^{\wedge}N\text{-ppy})_2(N^{\wedge}N\text{-bpy})]^+$ and $Ir(C^{\wedge}N\text{-ppy})_2(O^{\wedge}O\text{-acac})$. The synthesis and photophysical properties of a series of neutral and cationic Ir^{III} complexes comprising two cyclometallating 3-(2-benzothiazolyl)-7-(diethylamino)-coumarin ligands and an acac[12] or diimine[13] ancillary ligand have also been recently described, and their use as efficient photosensitizers for visible-light-driven hydrogen generation has been demonstrated.[14] In addition, the fluorescent coumarin 343 has been connected to the $O^{\wedge}O$-ancillary ligand of a phosphorescent bis(cyclometallated) Ir complex to monitor oxygen levels in living cells and tissues, and a tetraproline linker was used to separate the phosphor from the fluorophore.[14]

In contrast, to the best of our knowledge, the molecular engineering of heteroleptic cyclometallated Ir^{III} complexes featuring functionalized "acac-type" ligands directly conjugated with aromatic dyes has not been investigated. Herein, we present an original synthesis of such ligands and their corresponding iridium(III) complexes $Ir(C^{\wedge}N\text{-Meppy})_2(O^{\wedge}O\text{-tta-Ar})$ and show that the incorporation of such dyes has a dramatic influence on the absorption and emission properties.

Results and Discussion

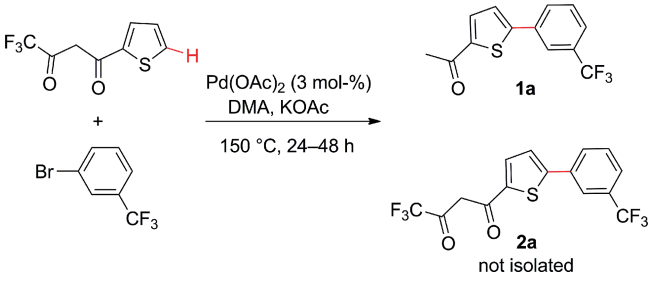
Preparation of the Arylated Proligands ttaH-Ar (2a–2f) and the Corresponding Complexes Ir-Ar (3a–3f)

We have investigated two routes to the naphthalimide-based complex $Ir(C^{\wedge}N\text{-Meppy})_2(O^{\wedge}O\text{-tta-NI})$ (Ir-NI, **3e**): (1) the Pd-catalyzed direct arylation of the coordinated tta ligand of $Ir(C^{\wedge}N\text{-Meppy})_2(O^{\wedge}O\text{-tta})$ (Ir-**1**) and (2) the synthesis of the proligand ttaH-NI (**2e**) through a Pd-catalyzed arylation step and its subsequent complexation to the $[Ir(C^{\wedge}N\text{-Meppy})_2]^+$ unit. The desired complex Ir-NI (**3e**) was formed by route (1) from Ir-**1** in the presence of 6-bromonaphthalimide under the Pd-catalyzed direct arylation conditions previously operative for aryl bromides [$Pd(OAc)_2$, KOAc in *N*,*N*-dimethylacetamide (DMA)].[8] Complex Ir-NI (**3e**), in which the naphthalimide group is incorporated at the 5-position of the thiophene ring of the coordinated tta ligand, was isolated as a red powder in 16% yield (Scheme 2). The ^1H NMR spectrum ($CDCl_3$) of **3e** exhibits signals in the aromatic region typical of the NI group at δ = 8.65, 8.56, 8.50, 7.75 and 7.69 ppm. The proton signals of the thiophene ring appear at δ = 7.73 and 7.24 ppm. It should be mentioned that the purification of **3e** was very tedious, as several purifications by column chromatography were needed to obtain the analytically pure compound. Moreover, some degradation occurred owing to the long reaction time at 100 °C. As a consequence, we decided to investigate route (2), that is, to perform the catalytic arylation on thiophene derivatives, precursors of the proligand ttaH.



Scheme 2. Synthesis of Ir-NI (**3e**) by the Pd-catalyzed arylation of Ir-**1**.

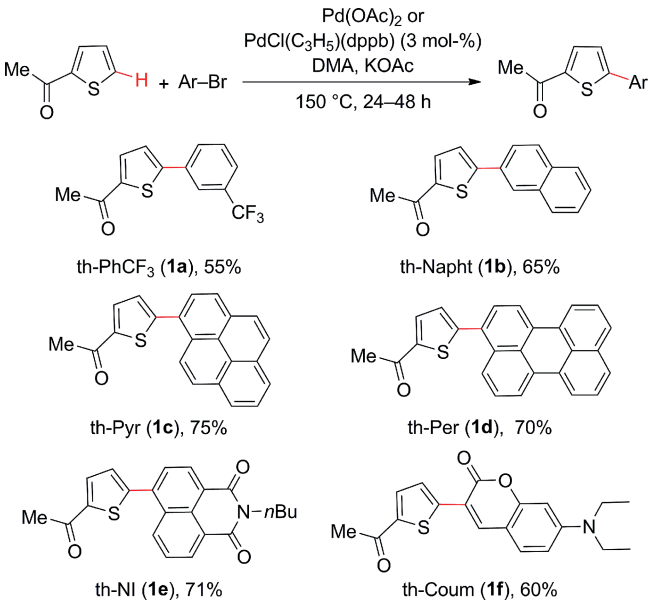
Our attempts to prepare tta-Ar (**2a**; Ar = C_6H_4-CF_3) from thenoyltrifluoroacetone and 1-bromo-3-(trifluoromethyl)benzene as the coupling partner in the presence of a palladium catalyst were not successful, as only the acetylthiophene derivative **1a** was obtained from the cleavage of a C–C bond (Scheme 3).



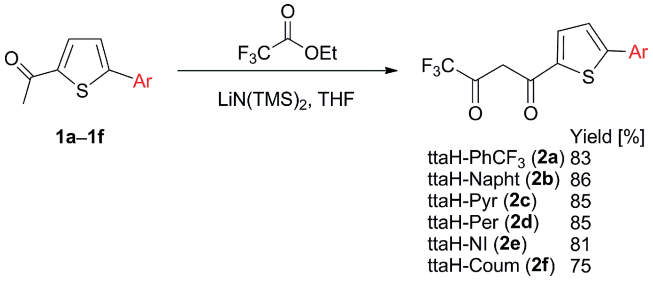
Scheme 3. Attempted Pd-catalyzed arylation of thenoyltrifluoroacetone.

Therefore, we prepared the arylated ttaH-Ar proligands **2a**–**2f** in two steps. In the first step, the Pd-catalyzed arylation of 2-acetylthiophene afforded th-Ar compounds **1a**–**1f**. Then, the condensation of the latter with ethyl trifluoroacetate in the presence of a base afforded the ttaH-Ar proligands **2a**–**2f** (Schemes 4 and 5).[15] The chromophores were used as their bromo derivatives in the catalytic reactions {conditions: $Pd(OAc)_2$ or $PdCl(C_3H_5)(dppb)$ [dppb = bis(diphenylphosphino)butane], DMA, KOAc, 150 °C, 48 h}. The new thiophene derivatives th-Ar [Ar =

m-C_6H_4-CF_3 (th-PhCF$_3$, **1a**), naphthyl (th-Napht, **1b**), pyrene (th-Pyr, **1c**), perylene (th-Per, **1d**), naphthalimide (th-NI, **1e**) and coumarin (th-Coum, **1f**)] were obtained in moderate to high yields. In all cases, the reaction was regiospecific in favour of the arylation at the 5-position of the thienyl ring.



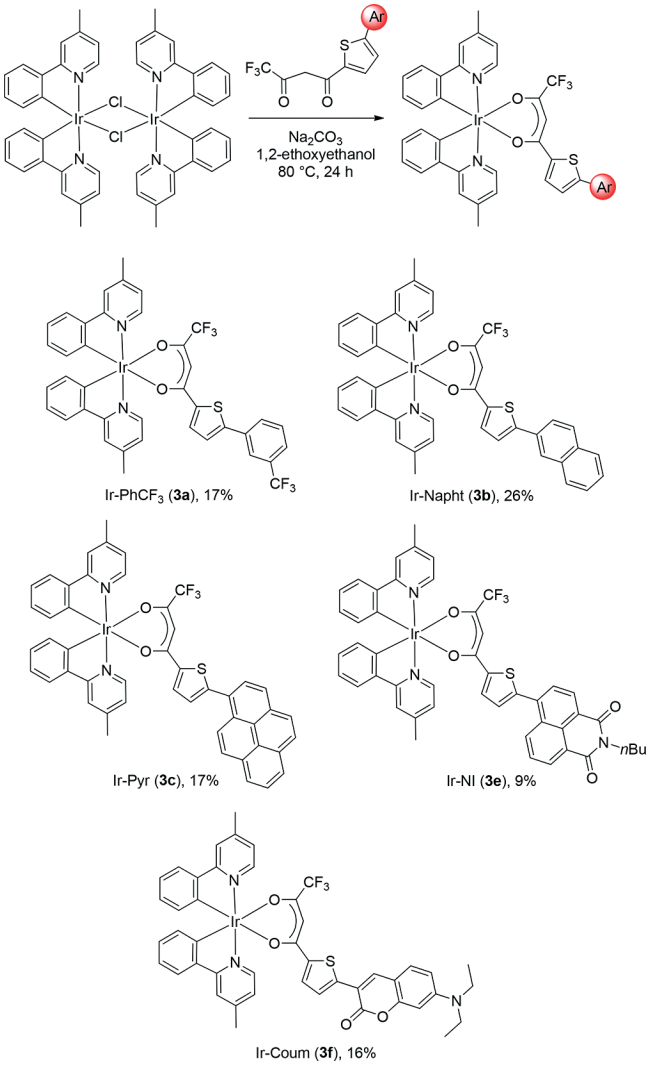
Scheme 4. Pd-catalyzed arylation of 2-acetylthiophene.



Scheme 5. Synthesis of the ttaH-Ar proligands **2a**–**2f**.

The ttaH-Ar proligands **2a**–**2f** were then obtained according to a reported procedure[15] with ethyl trifluoroacetate as the reactant and lithium bis(trimethylsilyl)amide [LiN(TMS)$_2$] as the base (Scheme 5). All of the target compounds **2a**–**2f** were isolated in high yields after column chromatography. The coumarin derivative was isolated as a deep orange solid in 75% yield. The other derivatives were yellow or brown.

The arylated complexes Ir-Ar (**3a**, **3b**, **3c**, **3e** and **3f**) were synthesized upon treatment of the chlorido-bridged dimer [Ir(*C*^*N*-Meppy)$_2$(μ-Cl)]$_2$[16] with the appropriate diketone ttaH-Ar in the presence of Na_2CO_3 (Scheme 6). All of complexes were isolated in low to moderate yields and characterized by standard techniques. The formation of the tta-Ar-based complexes was verified by the appearance of signals for the new arylthiophene protons and the formation of two sets of signals for the magnetically nonequivalent 4-methyl-2-phenylpyridine ligands in the ^{1}H NMR spectra (see Experimental Section).



Scheme 6. Synthesis of the Ir-Ar complexes **3a**–**3f**.

Photophysical Properties of the Arylated Thiophene Ketones th-Ar and Their Ir^{III} Complexes

The electronic absorption spectra of the newly prepared arylated thienyl ketones th-Ar (**1a**–**1f**) were recorded in dichloromethane solution at room temperature (Figure 1, Table 1). The thiophene derivatives th-NI (**1e**) and th-Pyr (**1c**) exhibited intense absorption bands at λ = 365 (32100) and 367 nm (33700), respectively, whereas the absorption band of th-Napht (**1b**) appears at higher energy at λ = 344 nm. The absorptions of th-Per (**1d**) and th-Coum (**1f**) were more in the visible region, and they showed maxima at $\lambda \approx 450$ nm. Note that the absorption band of th-PhCF$_3$ (**1a**, λ_{max} = 322 nm) is blueshifted compared with those of the other arylated compounds of the series, owing to the absence of an extended π-conjugated system. All of the compounds except **1a** are fluorescent in CH_2Cl_2 solution

Table 1. Photophysical data of th-PhCF$_3$, th-Napht, th-NI, th-Pyr, th-Per and th-Coum (**1a**–**1f**).

Compound	λ_{abs} [nm] (ε [10^3 L mol^{-1} cm^{-1}])[a]	λ_{em} [nm] at 298 K[b]	λ_{em} [nm] at 77 K[c]
th-PhCF$_3$ (**1a**)	322 (6.1)	–	374
th-Napht (**1b**)	344 (32.1)	349	393, 414
th-Pyr (**1c**)	367 (33.7)	470	450
th-Per (**1d**)	425 (23.4), 450 (28.4)	518	490,518
th-NI (**1e**)	365 (32.1)	445	440
th-Coum (**1f**)	450 (34.0)	514	511, 532

[a] In CH_2Cl_2 solution. [b] In CH_2Cl_2 solution: th-Napht (**1b**): λ_{exc} = 320 nm; th-Pyr (**1c**): λ_{exc} = 360 nm; th-Per (**1d**): λ_{exc} = 450 nm; th-NI (**1e**): λ_{exc} = 365 nm; th-Coum (**1f**): λ_{exc} = 460 nm. [c] In diethyl ether/isopentane/ethanol (EPA, 2:2:1 v/v).

under excitation with UV or visible light. The emission spectra are broad and featureless (Figure 2). Interestingly, changes to the nature of the appended aryl group allow a fine modulation of the emission wavelength (from 360 to 514 nm). The emissions from the coumarin- and perylene-based compounds ($\lambda_{em} \approx 515$ nm) are the most redshifted, which mirrors the trends seen in the absorption spectra.

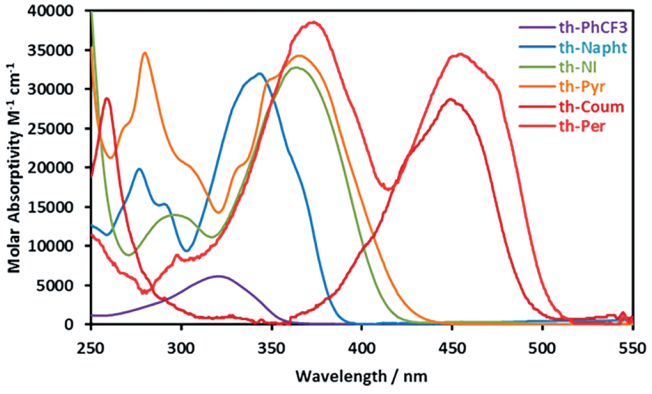


Figure 1. Absorption spectra of th-PhCF$_3$, th-Napht, th-NI, th-Pyr, th-Per and th-Coum (**1a**–**1f**) in CH_2Cl_2 solution at 298 K.

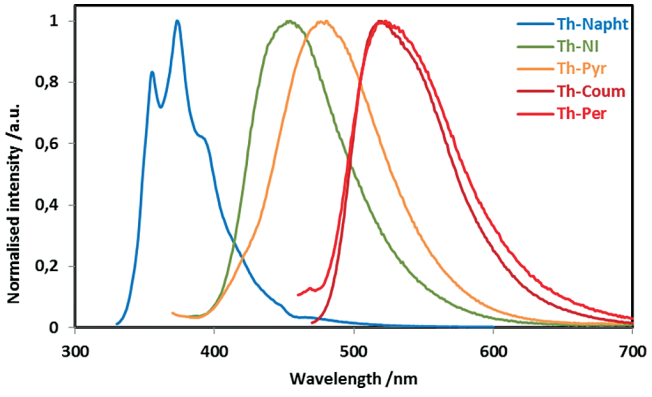


Figure 2. Emission spectra of th-Napht (**1b**, λ_{exc} = 320 nm), th-Pyr (**1c**, λ_{exc} = 360 nm), th-Per (**1d**, λ_{exc} = 450 nm), th-NI (**1e**, λ_{exc} = 365 nm) and th-Coum (**1f**, λ_{exc} = 460 nm) in CH_2Cl_2 solution at 298 K.

The electronic absorption spectra of the arylated Ir^{III} complexes in dichloromethane solution at room temperature are displayed in Figure 3, and the accompanying data are listed in Table 2. All of the complexes present similar absorption profiles (although with a significant displacement of the lowest-energy band for the coumarin complex). In the UV region, the spectra are dominated by an intense absorption band at $\lambda \approx 270$ nm, attributed to ligand-centred transitions (^{1}LC). In the lower-energy region ($\lambda > 320$ nm), the absorption spectra are characteristic of Ir^{III} complexes with a moderately intense and broad band (λ = 320 to 450 nm) tailing up to 500 nm for the non-coumarin complexes. This broad band could be assigned as a metal-to-ligand charge-transfer (^{1}MLCT) transition [dπ(Ir)→π*-(C^N)]. The spectrum of the coumarin complex is dominated by an intense band centred at λ = 482 nm, which is presumably associated predominantly with the coumarin moiety but is redshifted compared with the absorption of the corresponding proligand.

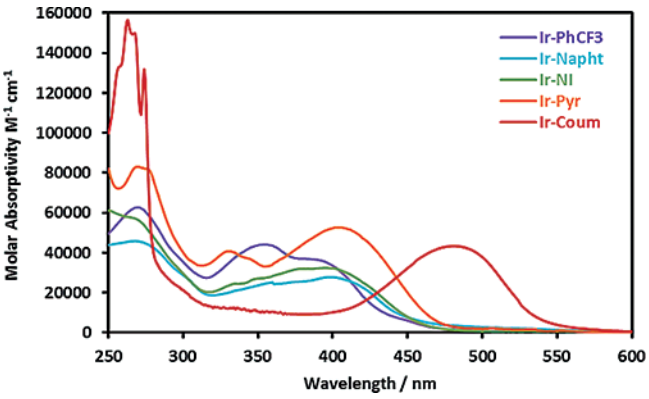


Figure 3. Absorption spectra of Ir-PhCF$_3$ (**3a**), Ir-Napht (**3b**), Ir-Pyr (**3c**), Ir-NI (**3e**) and Ir-Coum (**3f**) in CH_2Cl_2 solution at 298 K.

All of the arylated complexes **3a**–**3f** display fluorescence in solution at room temperature upon irradiation into the low-energy absorption bands. There is no detectable phosphorescence emission of the type normally found for simple Ir(*C*^*N*)$_2$(*O*^*O*) complexes (Figure 4). The emission lifetime (τ = 2.2 ns) of Ir-coum (**3f**), which is the brightest compound, supports this assignment; the excitation spectrum (λ = 600 nm) nicely matches the absorption spectrum. For the other complexes, the lifetimes could not be measured, because they are too weak, too short or both. This feature was previously observed by us for arylated tta complexes containing an electron-donating substituent on the aryl group attached to the thiophene ring (C$_6$H$_4$-*p*-OMe, C$_6$H$_4$-*p*-NH$_2$ and 3-Cl-5-NH$_2$-C$_6$H$_3$).[8] All of the emissions are insensitive to O_2, indicative of spin-allowed fluorescence from the singlet state. These results show the dramatic effect of the incorporation of an aromatic chromophore into the

Table 2. Photophysical data of Ir-tta-Ar complexes **3a**–**3f**.

Compound	λ_{abs} [nm] (ε [10^3 L mol^{-1} cm^{-1}])[a]	λ_{em} [nm] at 298 K[b]	ϕ[c]
Ir-PhCF$_3$ (**3a**)	275 (61.4), 359 (42.8), 394 (33.8)	440	≤0.01
Ir-Napht (**3b**)	275 (39.1), 364 (21.4), 400 (27.7)	473	≤0.01
Ir-Pyr (**3c**)	277 (87.1), 337 (42.0), 408 (52.2)	563	≤0.01
Ir-NI (**3e**)	270 (55.2), 400 (31.2)	440	≤0.01
Ir-Coum (**3f**)	260 (31.4), 482 (38.6)	600	0.49 (τ = 2.2 ns)

[a] In CH_2Cl_2 solution. [b] In CH_2Cl_2 solution: Ir-PhCF$_3$ (**3a**): λ_{exc} = 350 nm; Ir-Napht (**3b**): λ_{exc} = 400 nm; Ir-Pyr (**3c**): λ_{exc} = 410 nm; Ir-NI (**3e**): λ_{exc} = 350 nm; Ir-Coum (**3f**): λ_{exc} = 475 nm. [c] Reference $[Ru(bpy)_3]Cl_2$.

ancillary ligand: the extension of the π conjugation of the ancillary ligand leads to a decrease of the spin–orbit coupling influence of the metal ion. As a result, fluorescence from the π system can compete successfully with intersystem crossing (ISC) to the triplet, whereas for most of the archetypal Ir^{III} complexes, ISC is too fast to allow the observation of fluorescence.[17] Similar switches from phosphorescence to fluorescence upon extension of a remote π system have been observed for other Ir^{III}, Pt^{II}, Au^{III} and Os^{II} complexes.[18] Compared with those of the free ttaH-Ar ligands, the emission bands are redshifted (Δ = 86–124 nm), except for those of the NI-based derivatives, which are located at the same energy. The quantum yields are very low in all cases (ϕ ≤ 0.01 and detectable only with difficulty for the CF$_3$-substituted complex **3a**), except for that of Ir-Coum (**3f**), which is strongly fluorescent (ϕ = 0.49; Table 2). The weakness of the emission from **3a** is consistent with the absence of fluorescence from the corresponding proligand **2a**.

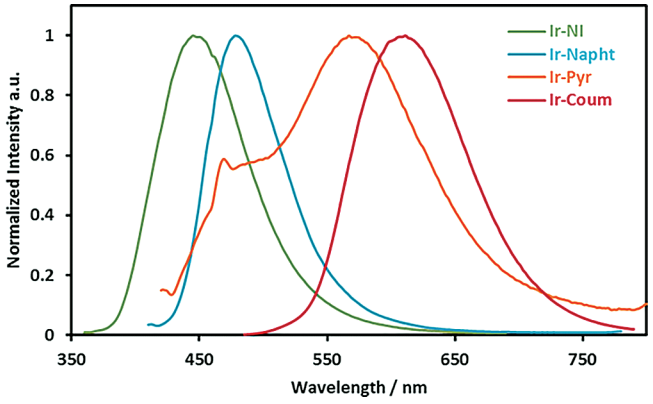


Figure 4. Normalized fluorescence spectra in CH_2Cl_2 at 298 K: Ir-Napht (**3b**): λ_{exc} = 400 nm (blue); Ir-Pyr (**3c**): λ_{exc} = 410 nm (orange); Ir-NI (**3e**): λ_{exc} = 350 nm (green); Ir-Coum (**3f**): λ_{exc} = 475 nm (red).

Conclusions

We have prepared a series of neutral bis(cyclometallated) iridium complexes with aromatic chromophores incorporated in the ancillary, O^O-coordinated ligand. The combination of these two organic and organometallic chromophores leads to ligand-based fluorescence at room temperature rather than the ^{3}MLCT phosphorescence typically observed in the simpler, parent cyclometallated iridium(III) complexes. Apparently, as the π system remote to the metal ion is extended, the spin–orbit coupling effect of the metal atom is attenuated to such an extent that fluorescence can compete with intersystem crossing to the triplet. On the other hand, the fluorescence of all of the complexes (with the exception of the coumarin derivative) is weak, which suggests that nonradiative decay pathways dominate.

Experimental Section

General: All of the catalytic reactions were performed in Schlenk tubes under argon with analytical-grade DMA and potassium acetate (>99%). Commercial bromoaryl reagents and 2-acetylthiophene were used without purification. The cyclometallated Ir^{III} μ-chlorido-bridged dimer complex $[Ir(C^{\wedge}N\text{-Meppy})_2(\mu\text{-Cl})]_2$ was prepared according to a reported procedure.[16] Flash chromatography was performed with silica gel (230–400 mesh). ^{1}H (500, 400 or 300 MHz) and ^{13}C (125, 100 or 75 MHz) NMR spectra were recorded with samples in $CDCl_3$ solution at 298 K. Chemical shifts are reported in ppm and were referenced to $CDCl_3$ (^{1}H: δ = 7.29 ppm; ^{13}C: δ = 77.0 ppm).

UV/Vis and Emission Spectroscopy: The UV/Vis absorption spectra were recorded with an Analytik Jena SPECORD 205 spectrophotometer by using quartz cuvettes of 1 cm pathlength. The steady-state luminescence spectra were measured with a Jobin Yvon FluoroMax-2 spectrometer fitted with a red-sensitive Hamamatsu R928 photomultiplier tube or an Edinburgh Instruments FLSP920 steady-state spectrometer. The spectra were corrected for the wavelength dependence of the detector, and the quoted emission maxima refer to the values after correction.

HRMS: The mass spectra were recorded at the Centre de mesures physiques de l'Ouest (CRMPO) of the University of Rennes 1 by Philippe Jéhan with a Thermo Fisher Scientific Q-Exactive instrument with an ESI+ source.

General Procedures for the Synthesis of 5-Arylated 2-Acetylthiophenes 1a–1f. Method A: In a typical experiment, the reaction of the aryl bromide (1 equiv.), 2-acetylthiophene (3 equiv.), $Pd(OAc)_2$ (3 mol-%) and KOAc (5 equiv.) in DMA (5–15mL) under argon in a Schlenk tube at 150 °C for 48 h afforded the 5-arylated 2-acetylthiophene. The products were purified by silica gel column chromatography. **Method B:** In a typical experiment, the reaction of the aryl bromide (1 equiv.), 2-acetylthiophene (3 equiv.), $PdCl(C_3H_5)$dppb (3 mol-%)[19] and KOAc (5 equiv.) in DMA (5–15mL) under argon in a Schlenk tube at 150 °C for 24 h afforded the 5-arylated 2-acetylthiophene. The products were purified by silica gel column chromatography.

1-{5-[3-(Trifluoromethyl)phenyl]thiophen-2-yl}ethanone (th-PhCF$_3$, 1a):[20] Method B. From 1-bromo-3-(trifluoromethyl)benzene (1.35 g, 6 mmol) and 2-acetylthiophene (2.27 g, 18 mmol), the

product was obtained in 55% yield (0.891 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (s, 1 H), 7.76 (d, J = 7.6 Hz, 1 H), 7.63 (d, J = 3.9 Hz, 1 H), 7.57 (d, J = 7.6 Hz, 1 H), 7.50 (t, J = 7.6 Hz, 1 H), 7.33 (d, J = 3.9 Hz, 1 H), 2.54 (s, 3 H) ppm.

1-[5-(Naphthalen-2-yl)thiophen-2-yl]ethanone (th-Napht, 1b): Method B. From 2-bromonaphthalene (1.04 g, 5 mmol) and 2-acetylthiophene (1.89 g, 15 mmol), the product was obtained in 65% yield as a yellow solid (0.819 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (s, 1 H), 7.88–7.80 (m, 3 H), 7.73 (dd, J = 8.5, 1.9 Hz, 1 H), 7.68 (d, J = 3.9 Hz, 1 H), 7.52–7.47 (m, 2 H), 7.42 (d, J = 3.9 Hz, 1 H), 2.56 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.5, 152.7, 143.2, 133.5, 133.4, 130.6, 128.9, 128.3, 127.7, 126.8, 126.7, 125.3, 124.2, 124.0, 26.6 ppm. $C_{16}H_{12}OS$ (252.33): calcd. C 76.16, H 4.79; found C 76.25, H 4.99. MS: m/z = 252 $[M]^+$.

1-[5-(Pyren-1-yl)thiophen-2-yl]ethanone (th-Pyr, 1c): Method A. From 4-bromopyrene (0.562 g, 2 mmol) and 2-acetylthiophene (0.756 g, 6 mmol), the product was obtained in 75% yield as a brown solid (0.489 g) after additional recrystallization from toluene. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, J = 9.3 Hz, 1 H), 8.22–7.98 (m, 8 H), 7.79 (d, J = 3.9 Hz, 1 H), 7.36 (d, J = 3.9 Hz, 1 H), 2.64 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.8, 151.6, 144.7, 132.9, 131.8, 131.5, 130.9, 129.1, 129.0, 128.7, 128.6, 128.5, 128.2, 127.4, 126.5, 125.9, 125.5, 125.1, 124.8, 124.7, 124.4, 26.9 ppm. $C_{22}H_{14}OS$ (326.41): calcd. C 80.95, H 4.32; found C 80.71, H 4.20. MS: m/z = 326 $[M]^+$.

1-[5-(Perylen-3-yl)thiophen-2-yl]ethanone (th-Per, 1d): Method A. From 3-bromoperylene (0.662 g, 2 mmol) and 2-acetylthiophene (0.756 g, 6 mmol), the product was obtained in 70% yield as a brown solid (0.526 g) after additional recrystallization from toluene. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23–8.12 (m, 4 H), 8.02 (d, J = 8.3 Hz, 1 H), 7.74 (d, J = 3.8 Hz, 1 H), 7.70 (d, J = 7.8 Hz, 1 H), 7.68 (d, J = 7.8 Hz, 1 H), 7.54 (d, J = 3.8 Hz, 1 H), 7.51–7.44 (m, 3 H), 7.28 (d, J = 3.8 Hz, 1 H), 2.61 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.7, 151.1, 144.3, 134.8, 133.0, 132.9, 132.6, 131.9, 131.3, 131.1, 130.9, 129.4, 129.2, 128.8, 128.7, 128.6, 128.3, 127.5, 127.0, 126.9, 125.4, 121.1, 121.0, 120.9, 119.8, 27.0 ppm. $C_{26}H_{16}OS$ (376.47): calcd. C 82.95, H 4.28; found C 83.13, H 4.22.

6-(5-Acetylthiophen-2-yl)-2-*n*-butylbenzo[*de*]isoquinoline-1,3(2*H*)-dione (th-NI, 1e): Method A. From 6-bromo-2-*n*-butylbenzo[*de*]isoquinoline-1,3(2*H*)-dione (0.996 g, 3 mmol) and 2-acetylthiophene (1.14 g, 9 mmol), the product was obtained in 71% yield as a yellow solid (0.803 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (d, J = 7.3 Hz, 1 H), 8.47 (d, J = 7.5 Hz, 1 H), 8.43 (d, J = 8.5 Hz, 1 H), 7.74 (d, J = 3.8 Hz, 1 H), 7.72 (d, J = 7.5 Hz, 1 H), 7.67 (t, J = 7.8 Hz, 1 H), 7.29 (d, J = 3.8 Hz, 1 H), 4.09 (t, J = 7.6 Hz, 2 H), 1.62 (quint, J = 7.6 Hz, 2 H), 1.38 (sext, J = 7.6 Hz, 2 H), 2.58 (s, 3 H), 0.91 (t, J = 7.6 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.4, 163.9, 163.6, 147.8, 145.8, 137.6, 132.5, 131.5, 131.4, 130.4, 129.6, 129.5, 128.7, 128.6, 127.6, 123.1, 123.0, 40.3, 30.2, 26.8, 20.3, 13.8 ppm. $C_{22}H_{19}NO_3S$ (377.46): calcd. C 70.00, H 5.07; found C 70.10, H 5.23.

3-(5-Acetylthiophen-2-yl)-7-(diethylamino)chromen-2-one (th-Coum, 1f): Method B. From 3-bromo-7-(diethylamino)chromen-2-one (0.740 g, 2.5 mmol) and 2-acetylthiophene (0.945 g, 7.5 mmol), the product was obtained in 60% yield as an orange solid (0.512 g) after additional recrystallization from acetonitrile. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (s, 1 H), 7.67 (d, J = 4.1 Hz, 1 H), 7.64 (d, J = 4.1 Hz, 1 H), 7.32 (d, J = 8.9 Hz, 1 H), 6.61 (dd, J = 8.9, 2.4 Hz, 1 H), 6.50 (d, J = 2.4 Hz, 1 H), 3.42 (q, J = 7.6 Hz, 4 H), 2.55 (s, 3 H), 1.22 (t, J = 7.6 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.6, 160.0, 156.1, 151.3, 145.9, 142.5, 138.8, 132.7, 129.5, 125.4, 113.3, 109.6, 108.5, 97.0, 45.0, 26.8, 12.5 ppm. $C_{19}H_{19}NO_3S$ (341.42): calcd. C 66.84, H 5.61; found C 66.98, H 5.40. MS: m/z = 341 $[M]^+$.

Procedures for Synthesis of Butane-1,3-diones 2a–2f. Method A: In a Schlenk tube, to a solution of dry tetrahydrofuran (THF, 15 mL) was added the 2-acetyl-5-arylthiophene (1 equiv.) and lithium bis(trimethylsilyl)amide (1.5 equiv.), and then the mixture was stirred vigorously at room temperature under argon for 1 h. Ethyl trifluoroacetate (1.2 equiv.) was added, and the mixture was stirred at room temperature overnight. EtOH (2 mL) was then added to quench the reaction. The crude product was obtained after evaporation of the organic solvent. The product was purified by column chromatography with acetone and pentane. **Method B:** Same as Method A, but the final product was purified by centrifugation to afford a solid product, which was washed three times with an acetone/pentane mixture (1:2.5) and three times with dichloromethane.

4,4,4-Trifluoro-1-{5-[3-(trifluoromethyl)phenyl]thiophen-2-yl}butane-1,3-dione (ttaH-PhCF$_3$, 2a): Method A. From 1-{5-[3-(trifluoromethyl)phenyl]thiophen-2-yl}ethanone (0.675 g, 2.5 mmol), $LiN(TMS)_2$ (4.2 mL, 0.9 M, 3.75 mmol) and ethyl trifluoroacetate (0.426 g, 3 mmol), the product was obtained in 83% yield as a yellow solid (0.759 g). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 7.90 (s, 1 H), 7.88 (d, J = 8.0 Hz, 1 H), 7.76 (d, J = 3.8 Hz, 1 H), 7.60–7.55 (m, 2 H), 7.54 (d, J = 3.8 Hz, 1 H), 6.18 (s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 181.5, 172.4 (q, J = 30.4 Hz), 149.1, 147.2, 136.0, 131.9 (q, J = 31.9 Hz), 131.1, 130.4, 130.1, 126.4, 125.6, 125.2 (q, J = 271.9 Hz), 123.0, 120.1 (q, J = 286.7 Hz), 89.3 ppm. MS: m/z = 366 $[M]^+$.

4,4,4-Trifluoro-1-[5-(naphthalen-2-yl)thiophen-2-yl]butane-1,3-dione (ttaH-Napht, 2b): Method A. From 1-[5-(naphthalen-2-yl)thiophen-2-yl]ethanone (0.504 g, 2 mmol), $LiN(TMS)_2$ (3.33 mL, 0.9 M, 3 mmol) and ethyl trifluoroacetate (0.341 g, 2.4 mmol), the product was obtained in 86% yield as a yellow solid (0.599 g). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 8.28 (s, 1 H), 7.99–7.85 (m, 5 H), 7.65 (d, J = 3.9 Hz, 1 H), 7.56–7.48 (m, 2 H), 6.33 (s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 183.0, 172.3 (q, J = 31.1 Hz), 151.0, 145.9, 134.5, 134.2, 132.0, 131.7, 129.5, 128.8, 128.3, 127.4, 127.2, 125.4, 125.2, 124.4, 120.0 (q, J = 286.3 Hz), 90.4 ppm.

4,4,4-Trifluoro-1-[5-(pyren-1-yl)thiophen-2-yl]butane-1,3-dione (ttaH-Pyr, 2c): Method B. From 1-[5-(pyren-1-yl)thiophen-2-yl]ethanone (0.528 g, 1.62 mmol), $LiN(TMS)_2$ (2.71 mL, 0.9 M, 2.44 mmol) and ethyl trifluoroacetate (0.267 g, 1.88 mmol), the product was obtained in 85% yield as a brown solid (0.581 g). After the addition of ethyl trifluoroacetate, the reaction mixture was heated at 60 °C overnight. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 8.47 (d, J = 9.3 Hz, 1 H), 8.35–7.98 (m, 9 H), 7.47 (d, J = 3.9 Hz, 1 H), 6.41 (s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 183.3, 172.3 (q, J = 31.1 Hz), 149.5, 147.6, 132.6, 132.5, 131.9, 131.2, 130.2, 130.0, 129.7, 129.4, 129.2, 129.1, 128.3, 127.5, 126.8, 126.4, 125.8, 125.7, 125.4, 125.3, 120.3 (q, J = 287.3 Hz), 90.8 ppm.

4,4,4-Trifluoro-1-[5-(perylen-3-yl)thiophen-2-yl]butane-1,3-dione (ttaH-Per, 2d): Method B. From 1-[5-(perylen-3-yl)thiophen-2-yl]-ethanone (0.398 g, 1.06 mmol), $LiN(TMS)_2$ (1.76 mL, 0.9 M, 1.5 mmol) and ethyl trifluoroacetate (0.180 g, 1.27 mmol), the product was obtained in 85% yield as a brown solid (0.425 g). After the addition of ethyl trifluoroacetate, the reaction mixture was heated at 60 °C overnight. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 8.45–8.35 (m, 4 H), 8.13 (d, J = 8.6 Hz, 1 H), 7.83 (d, J = 3.8 Hz, 1 H), 7.82–7.77 (m, 2 H), 7.64 (d, J = 7.9 Hz, 1 H), 7.62–7.52 (m, 3 H), 7.35 (d, J = 3.8 Hz, 1 H), 6.19 (s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 181.9, 172.1 (q, J = 30.0 Hz), 148.8, 147.4, 135.8, 133.7, 132.7, 132.5, 131.9, 131.6, 130.0, 129.9, 129.5,

129.4, 129.3, 129.1, 128.4, 127.9, 127.8, 126.3, 122.0, 121.9, 121.0, 117.6 (q, J = 296.8 Hz), 89.3 ppm.

2-*n*-Butyl-6-[5-(4,4,4-trifluoro-3-oxobutanoyl)thiophen-2-yl]benzo-[*de*]isoquinoline-1,3(2*H*)-dione (ttaH-NI, 2e): Method B. From 6-(5-acetylthiophen-2-yl)-2-*n*-butylbenzo[*de*]isoquinoline-1,3(2*H*)-dione (0.464 g, 1.23 mmol), $LiN(TMS)_2$ (2.1 mL, 0.9 M, 1.85 mmol) and ethyl trifluoroacetate (0.210 g, 1.48 mmol), the product was obtained in 81% yield as a brown solid (0.471 g). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.50–8.30 (m, 3 H), 8.02 (d, J = 3.4 Hz, 1 H), 7.88–7.70 (m, 2 H), 7.46 (d, J = 3.4 Hz, 1 H), 6.33 (s, 1 H), 3.96 (t, J = 7.6 Hz, 2 H), 1.62 (quint, J = 7.6 Hz, 2 H), 1.35 (sext, J = 7.6 Hz, 2 H), 0.91 (t, J = 7.6 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 181.0, 170.5 (q, J = 30.7 Hz), 163.0, 162.7, 147.4, 144.7, 137.2, 131.4, 130.8, 130.5, 129.9, 128.6, 128.5, 127.8, 127.7, 122.3, 121.8, 119.0 (q, J = 286.8 Hz), 89.4, 29.5, 19.8, 13.7 ppm.

1-{5-[7-(Diethylamino)-2-oxochromen-3-yl]thiophen-2-yl}-4,4,4-trifluorobutane-1,3-dione (ttaH-Coum, 2f): Method B. From 3-(5-acetylthiophen-2-yl)-7-(diethylamino)chromen-2-one (0.716 g, 2.1 mmol), $LiN(TMS)_2$ (3.5 mL, 0.9 M, 3.1 mmol) and ethyl trifluoroacetate (0.358 g, 2.52 mmol), the product was obtained in 75% yield as an orange solid (0.688 g). After the addition of ethyl trifluoroacetate, the reaction mixture was heated at 60 °C overnight. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 8.26 (s, 1 H), 7.61 (s, 2 H), 7.46 (d, J = 9.0 Hz, 1 H), 6.71 (dd, J = 9.0, 2.2 Hz, 1 H), 6.49 (d, J = 2.2 Hz, 1 H), 6.10 (s, 1 H), 3.48 (q, J = 7.6 Hz, 4 H), 1.17 (t, J = 7.6 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 182.3, 171.6 (q, J = 30.1 Hz), 160.5, 157.0, 152.3, 147.6, 143.3, 138.9, 130.7, 129.1, 125.6, 120.6 (q, J = 288.5 Hz), 114.5, 110.6, 109.5, 97.5, 89.5, 45.5, 12.9 ppm.

Synthesis of the Iridium Complexes 3a–3f: The dimer [Ir($C^\wedge N$-Meppy)$_2$(μ-Cl)]$_2$ was converted into the corresponding tta-Ar complexes of general formula Ir($C^\wedge N$-Meppy)$_2$($O^\wedge O$-tta-Ar) according to a reported procedure.[16] The dimer [Ir($C^\wedge N$-Meppy)$_2$(μ-Cl)]$_2$ (1 equiv.), the corresponding thenoyltrifluoroacetone (2.5 equiv.) and Na_2CO_3 (10 equiv.) were suspended in 2-ethoxyethanol and heated at 80 °C for 24 h. Then, water was added, and the precipitate was collected by centrifugation. The residue was purified by chromatography (silica), and the product was recrystallized from a mixture of dichloromethane/pentane.

Complex Ir-PhCF$_3$ (3a): From [Ir($C^\wedge N$-Meppy)$_2$(μ-Cl)]$_2$ (0.193 g, 0.172 mmol), 4,4,4-trifluoro-1-{5-[3-(trifluoromethyl)phenyl]-thiophen-2-yl}butane-1,3-dione (0.157 g, 0.430 mmol) and Na_2CO_3 (0.182 g, 1.72 mmol) in 2-ethoxyethanol (15 mL), the product was isolated in 17% yield as a red powder (0.053 g). Eluent: diethyl ether/pentane (1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (d, J = 6.0 Hz, 1 H), 8.33 (d, J = 6.0 Hz, 1 H), 7.85–7.45 (m, 9 H), 7.23 (d, J = 3.9 Hz, 1 H), 6.98 (d, J = 6.0 Hz, 1 H), 6.94 (d, J = 6.0 Hz, 1 H), 6.86 (t, J = 7.5 Hz, 1 H), 6.82 (t, J = 7.5 Hz, 1 H), 6.73 (t, J = 7.5 Hz, 1 H), 6.69 (t, J = 7.5 Hz, 1 H), 6.31 (d, J = 7.7 Hz, 1 H), 6.25 (d, J = 7.7 Hz, 1 H), 6.16 (s, 1 H), 2.57 (s, 3 H), 2.56 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.0, 167.7, 149.0, 148.9, 147.7, 147.2, 147.1, 146.1, 145.0, 144.9, 144.8, 144.3, 134.6, 133.3, 133.2, 131.7, 131.4, 129.6, 129.3, 129.1, 128.9, 128.8, 128.7, 125.1, 124.8, 123.5, 123.4, 122.9, 122.8, 122.4 (m), 121.0, 120.9, 119.4, 119.2, 21.4, 21.3 ppm. $C_{39}H_{27}F_6IrN_2O_2S{\cdot}1/3C_5H_{12}$ (917.96): calcd. C 53.21, H 3.40, N 3.05, S 3.49; found C 53.03, H 3.21, N 2.71, S 3.80. HRMS: calcd. for $C_{39}H_{27}F_6IrN_2O_2S$ [M]$^+$ 894.13214; found 894.1321.

Complex Ir-Napht (3b): From [Ir($C^\wedge N$-Meppy)$_2$(μ-Cl)]$_2$, 4,4,4-trifluoro-1-[5-(naphthalen-2-yl)thiophen-2-yl]butane-1,3-dione (0.150 g, 0.430 mmol) and Na_2CO_3 (0.182 g, 1.72 mmol) in 2-ethoxyethanol (15 mL), the product was isolated in 26% yield as a red powder (0.078 g). Eluent: diethyl ether/pentane (1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (d, J = 6.0 Hz, 1 H), 8.33 (d, J = 6.0 Hz, 1 H), 8.04 (s, 1 H), 7.83–7.75 (m, 3 H), 7.70–7.65 (m, 3 H), 7.64 (d, J = 4.0 Hz, 1 H), 7.57 (d, J = 7.1 Hz, 1 H), 7.54 (d, J = 7.1 Hz, 1 H), 7.50–7.45 (m, 2 H), 7.33 (d, J = 4.0 Hz, 1 H), 7.00 (d, J = 6.0 Hz, 1 H), 6.95 (d, J = 6.0 Hz, 1 H), 6.87 (t, J = 7.5 Hz, 1 H), 6.82 (t, J = 7.5 Hz, 1 H), 6.75 (t, J = 7.5 Hz, 1 H), 6.69 (t, J = 7.5 Hz, 1 H), 6.32 (d, J = 7.7 Hz, 1 H), 6.25 (d, J = 7.7 Hz, 1 H), 6.17 (s, 1 H), 2.57 (s, 3 H), 2.58 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.2, 167.7, 167.6, 150.0, 148.9, 148.8, 147.3, 147.2, 145.3, 145.0, 144.9, 144.8, 144.6, 133.5, 133.3, 133.2, 133.1, 131.1, 129.6, 128.7, 128.6, 128.3, 128.1, 127.7, 126.8, 126.4, 124.6, 124.4, 123.8, 123.5, 123.4, 122.9, 122.8, 92.2, 21.4, 21.3 ppm. $C_{42}H_{30}F_3IrN_2O_2S$ (876.00): calcd. C 57.59, H 3.45, N 3.20, S 3.66; found C 57.44, H 3.30, N 3.00, S 3.23. HRMS: calcd. for $C_{42}H_{30}F_3IrN_2O_2S$ [M]$^+$ 876.1604; found 876.1603.

Complex Ir-Pyr (3c): From [Ir($C^\wedge N$-Meppy)$_2$(μ-Cl)]$_2$ (0.193 g, 0.172 mmol), 4,4,4-trifluoro-1-[5-(pyren-1-yl)thiophen-2-yl]butane-1,3-dione (0.182 g, 0.430 mmol) and Na_2CO_3 (0.182 g, 1.72 mmol) in 2-ethoxyethanol (15 mL), the product was isolated in 17% yield as a red powder (0.057 g). Eluent: diethyl ether/pentane (1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42–8.35 (m, 3 H), 8.20 (d, J = 7.6 Hz, 1 H), 8.18 (d, J = 7.6 Hz, 1 H), 8.14–7.96 (m, 6 H), 7.76 (d, J = 3.9 Hz, 1 H), 7.69 (s, 1 H), 7.66 (s, 1 H), 7.57–7.50 (m, 2 H), 7.27 (d, J = 3.9 Hz, 1 H), 7.01 (d, J = 6.0 Hz, 1 H), 6.99 (d, J = 6.0 Hz, 1 H), 6.82 (t, J = 7.5 Hz, 2 H), 6.70 (t, J = 7.5 Hz, 2 H), 6.32 (d, J = 7.7 Hz, 1 H), 6.27 (d, J = 7.7 Hz, 1 H), 6.24 (s, 1 H), 2.59 (s, 3 H), 2.57 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.4, 167.8, 167.7, 166.4, 166.1, 148.9, 148.8, 148.5, 147.3, 147.2, 146.3, 145.2, 144.9, 144.8, 144.6, 133.3, 133.2, 131.4, 130.8, 129.2, 129.1, 129.0, 128.7, 128.6, 128.3, 128.1, 128.0, 127.3, 126.3, 125.6, 125.2, 125.0, 124.7, 124.6, 124.5, 123.5, 123.4, 122.9, 122.8, 121.0, 120.9, 120.2, 119.3, 119.2, 92.4, 21.5, 21.4 ppm. $C_{48}H_{32}F_3IrN_2O_2S$ (950.07): calcd. C 60.68, H 3.40, N 2.95, S 3.37; found C 60.54, H 3.98, N 2.67, S 3.09. HRMS: calcd. for $C_{48}H_{32}F_3IrN_2O_2S$ [M]$^+$ 950.17605; found 950.1764.

Complex Ir-NI (3e). Route (2): From [Ir($C^\wedge N$-Meppy)$_2$(μ-Cl)]$_2$ (0.193 g, 0.172 mmol), 2-*n*-butyl-6-[5-(4,4,4-trifluoro-3-oxobutanoyl)thiophen-2-yl]benzo[*de*]isoquinoline-1,3(2*H*)-dione (0.204 g, 0.430 mmol) and Na_2CO_3 (0.182 g, 1.72 mmol) in 2-ethoxyethanol (15 mL), the product was isolated in 9% yield as a red powder (0.030 g). Eluent: diethyl ether/pentane (1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (d, J = 7.6 Hz, 1 H), 8.54 (d, J = 7.6 Hz, 1 H), 8.47 (d, J = 8.5 Hz, 1 H), 8.35 (d, J = 6.0 Hz, 1 H), 8.33 (d, J = 6.0 Hz, 1 H), 7.76–7.74 (m, 2 H), 7.73 (d, J = 3.9 Hz, 1 H), 7.69 (s, 1 H), 7.66 (s, 1 H), 7.56–7.50 (m, 2 H), 7.20 (d, J = 3.9 Hz, 1 H), 7.01 (d, J = 6.0 Hz, 1 H), 6.97 (d, J = 6.0 Hz, 1 H), 6.82 (t, J = 7.5 Hz, 2 H), 6.70 (t, J = 7.5 Hz, 2 H), 6.30 (d, J = 7.7 Hz, 1 H), 6.24 (d, J = 7.7 Hz, 1 H), 6.20 (s, 1 H), 4.19 (t, J = 7.6 Hz, 2 H), 2.59 (s, 3 H), 2.57 (s, 3 H), 1.72 (quint, J = 7.6 Hz, 2 H), 1.46 (sext, J = 7.6 Hz, 2 H), 0.98 (t, J = 7.6 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.7, 167.7, 164.0, 163.8, 149.0, 147.9, 147.3, 147.1, 145.0, 144.9, 144.8, 144.7, 144.2, 138.3, 133.3, 133.2, 131.4, 130.4, 129.8, 129.5, 128.8, 128.7 (m), 128.6, 128.5, 128.4, 127.4, 123.5, 123.4, 123.0, 122.9, 122.8, 122.6, 121.1, 121.0, 119.4, 119.3, 92.3, 40.3, 30.2, 29.5, 21.4, 20.4, 13.8 ppm. $C_{48}H_{37}F_3IrN_3O_4S{\cdot}C_5H_{12}$ (1073.30): calcd. C 59.31, H 4.60, N 3.92, S 2.99; found C 59.36, H 4.67, N 3.66, S 2.96. HRMS: calcd. for $C_{48}H_{37}F_3IrN_3O_4S$ [M]$^+$ 1001.20808; found 1001.2079. **Route (1):** DMA (4 mL) was added to a Schlenk tube charged with 4-bromo-*N*-butylnaphthalimide (0.026 g, 0.080 mmol), Ir($C^\wedge N$-Meppy)$_2$-

(*O*^*O*-tta-Ar) (Ir-**1**; 0.050 g, 0.067 mmol), KOAc (0.010 g, 0.1 mmol) and $Pd(OAc)_2$ (0.2 mg, 0.0066 mmol). Then, the mixture was heated under argon at 100 °C for 72 h. After the mixture had cooled to room temperature, water (10 mL) was added, and the resulting precipitate was washed several times with ethanol and diethyl ether. The resulting mixture was purified by silica gel column chromatography (eluent: hexane/diethyl ether, 9:1 and then 7:3). The solvent was removed under reduced pressure to afford red solid **3e** (0.011 g, 16.5%). The NMR spectroscopic data are similar to those of the compound obtained by Route (2).

Complex Ir-coum (3f): From $[Ir(C^N\text{-Meppy})_2(\mu\text{-Cl})]_2$ (0.193 g, 0.172 mmol), 1-{5-[7-(diethylamino)-2-oxochromen-3-yl]thiophen-2-yl}-4,4,4-trifluorobutane-1,3-dione (0.193 g, 0.443 mmol) and Na_2CO_3 (0.187 g, 1.77 mmol) in 2-ethoxyethanol (15 mL), the product was isolated in 16% yield as a red powder (0.053 g). Eluent: diethyl ether. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.35 (d, J = 6.0 Hz, 1 H), 8.32 (d, J = 6.0 Hz, 1 H), 7.86 (s, 1 H), 7.65 (s, 1 H), 7.64 (s, 1 H), 7.57 (d, J = 4.1 Hz, 1 H), 7.55–7.50 (m, 3 H), 7.26 (d, J = 8.2 Hz, 1 H), 6.98 (d, J = 6.0 Hz, 1 H), 6.93 (d, J = 6.0 Hz, 1 H), 6.84 (t, J = 7.5 Hz, 1 H), 6.80 (t, J = 7.5 Hz, 1 H), 6.72 (t, J = 7.5 Hz, 1 H), 6.69 (t, J = 7.5 Hz, 1 H), 6.57 (dd, J = 9.0, 2.3 Hz, 1 H), 6.48 (d, J = 2.3 Hz, 1 H), 6.30 (d, J = 7.7 Hz, 1 H), 6.24 (d, J = 7.7 Hz, 1 H), 6.17 (s, 1 H), 3.40 (q, J = 7.6 Hz, 4 H), 2.56 (s, 3 H), 2.54 (s, 3 H), 1.20 (t, J = 7.6 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.4, 167.7, 167.6, 159.9, 155.8, 151.0, 148.8, 148.7, 147.2 (m), 145.4, 144.9, 144.8, 144.7, 144.5, 143.3, 137.9, 133.3, 133.2, 129.3, 129.2, 128.7, 128.6, 125.9, 123.4, 123.3, 122.9, 122.8, 120.9, 120.7, 119.9, 119.3, 119.2, 117.6, 113.8, 109.5, 108.6, 97.0, 92.6, 44.9, 21.4, 31.3, 12.4 ppm. $C_{45}H_{37}F_3IrN_3O_4S\cdot 1/4CH_2Cl_2$ (1305.02): calcd. C 55.10, H 3.83, N 4.26, S 3.25; found C 55.10, H 3.83, N 4.08, S 3.19. HRMS: calcd. for $C_{45}H_{37}F_3IrN_3O_4S$ $[M]^+$ 965.20808; found 965.2079.

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[1] a) C. Fan, C. Yang, *Chem. Soc. Rev.* **2014**, *43*, 6439–6469; Y. Chi, P.-T. Chou, *Chem. Soc. Rev.* **2010**, *39*, 638–655; b) P.-T. Chou, Y. Chi, M.-W. Chung, C.-C. Lin, *Coord. Chem. Rev.* **2011**, *255*, 2653–2665; c) Z. Liu, Z. Bian, C. Huang in *Top. Organomet. Chem.* **2010**, *28*, 113–142; Y. You, W. Nam, *Chem. Soc. Rev.* **2012**, *41*, 7061–7084.

[2] a) J. I. Goldsmith, W. R. Hudson, M. S. Lowry, T. H. Anderson, S. Bernhard, *J. Am. Chem. Soc.* **2005**, *127*, 7502–7510; b) B. F. DiSalle, S. Bernhard, *J. Am. Chem. Soc.* **2011**, *133*, 11819–11821; c) Y.-J. Yuan, J.-Y. Zhang, Z.-T. Yu, J.-Y. Feng, W.-J. Luo, J.-H. Ye, Z.-G. Zou, *Inorg. Chem.* **2012**, *51*, 4123–4133; d) M. S. Lowry, S. Bernhard, *Chem. Eur. J.* **2006**, *12*, 7970–7977; e) S. Takizawa, R. Aboshi, S. Murata, *Photochem. Photobiol. Sci.* **2011**, *10*, 895–903.

[3] a) K. K.-W. Lo, K. H.-K. Tsang, K.-S. Sze, C.-K. Chung, T. K.-M. Lee, K. Y. Zhang, W.-K. Hui, C.-K. Li, J. S.-Y. Lau, D. C.-M. Ng, N. Zhu, *Coord. Chem. Rev.* **2007**, *251*, 2292–2310; b) V. Fernandez-Moreira, F. L. Thorp-Greenwood, M. P. Coogan, *Chem. Commun.* **2010**, *46*, 186–202; c) V. Guerchais, J.-L. Fillaut, *Coord. Chem. Rev.* **2011**, *255*, 2448–2457; K. K.-W. Lo, M.-W. Louie, K. Y. Zhang, *Coord. Chem. Rev.* **2010**, *254*, 2603–2622; d) K. K.-W. Lo, S. P.-Y. Li, K. Y. Zhang, *New J. Chem.* **2011**, *35*, 265–287.

[4] a) T. N. Singh-Rachford, F. N. Castellano, *Coord. Chem. Rev.* **2010**, *254*, 2560–2573; b) J. Zhao, W. Wu, J. Sun, S. Guo, *Chem. Soc. Rev.* **2013**, *42*, 5323–5351; c) J. Zhao, S. Ji, H. Guo, *RSC Adv.* **2011**, *1*, 937–950; d) J. Zhao, S. Ji, W. Wu, W. Wu, H. Guo, J. Sun, H. Sun, Y. Liu, Q. Li, L. Huang, *RSC Adv.* **2012**, *2*, 1712–1728; e) F. N. Castellano, *Dalton Trans.* **2012**, *41*, 8493–8501.

[5] For reviews on Pd-catalyzed C–H bond functionalization, see: a) D. Alberico, M. E. Scott, M. Lautens, *Chem. Rev.* **2007**, *107*, 174–238; b) F. Bellina, R. Rossi, *Tetrahedron* **2009**, *65*, 10269–10310; c) L. Ackermann, R. Vicente, A. Kapdi, *Angew. Chem. Int. Ed.* **2009**, *48*, 9792–9826; *Angew. Chem.* **2009**, *121*, 9976; d) X. Chen, K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem. Int. Ed.* **2009**, *48*, 5094–5115; *Angew. Chem.* **2009**, *121*, 5196; e) G. P. McGlacken, L. M. Bateman, *Chem. Soc. Rev.* **2009**, *38*, 2447–2464; f) C.-L. Sun, B.-J. Li, Z.-J. Shi, *Chem. Commun.* **2010**, *46*, 677–685; g) H. Li, B.-J. Li, Z.-J. Shi, *Catal. Sci. Technol.* **2011**, *1*, 191–206; h) N. Kuhl, M. N. Hopkinson, J. Wencel-Delord, F. Glorius, *Angew. Chem. Int. Ed.* **2012**, *51*, 10236–10254; i) J. Wencel-Delord, F. Glorius, *Nature Chem.* **2013**, *5*, 369–375; j) K. Yuan, H. Doucet, *ChemCatChem* **2013**, *5*, 3495–3496; k) R. Rossi, F. Bellina, M. Lessi, C. Manzini, *Adv. Synth. Catal.* **2014**, *356*, 17–117; l) M. He, J. F. Soulé, H. Doucet, *ChemCatChem* **2014**, *6*, 1824–1859; m) K. Yuan, J.-F. Soulé, H. Doucet, *ACS Catal.* **2015**, *5*, 978–991.

[6] For selected recent examples of direct C5 arylations of thiophenes, see: a) K. Kobayashi, A. Sugie, M. Takahashi, K. Masui, A. Mori, *Org. Lett.* **2005**, *7*, 5083–5085; b) M. Nakano, H. Tsurugi, T. Satoh, M. Miura, *Org. Lett.* **2008**, *10*, 1851–1854; c) B. Liégaut, D. Lapointe, L. Caron, A. Vlassova, K. Fagnou, *J. Org. Chem.* **2009**, *74*, 1826–1834; d) J. J. Dong, J. Roger, H. Doucet, *Tetrahedron Lett.* **2009**, *50*, 2778–2781; e) D. J. Schipper, K. Fagnou, *Chem. Mater.* **2011**, *23*, 1594–1600.

[7] K. Beydoun, M. Zaarour, J. A. G. Williams, H. Doucet, V. Guerchais, *Chem. Commun.* **2012**, *48*, 1260–1262.

[8] K. Beydoun, M. Zaarour, J. A. G. Williams, T. Roisnel, V. Dorcet, A. Planchat, A. Boucekkine, D. Jacquemin, H. Doucet, V. Guerchais, *Inorg. Chem.* **2013**, *52*, 12416–12428.

[9] J. Howarth, D. L. Davies, F. Lelj, M. O. Wolf, B. O. Patrick, *Inorg. Chem.* **2014**, *53*, 11882–11889.

[10] a) A. A. Rachford, R. Ziessel, T. Bura, P. Retailleau, F. N. Castellano, *Inorg. Chem.* **2010**, *49*, 3730–3736; b) J. Sun, F. Zhong, X. Yi, J. Zhao, *Inorg. Chem.* **2013**, *52*, 6299–6310; c) X. Yi, C. Zang, S. Guo, J. Ma, J. Zhao, *Dalton Trans.* **2014**, *43*, 1672–1683; d) L. Ma, S. Guo, J. Sun, C. Zhang, J. Zhao, H. Guo, *Dalton Trans.* **2013**, *42*, 6478–6488.

[11] J. Hallett, N. White, W. Wu, X. Cui, P. N. Horton, J. S. Coles, J. Zhao, S. J. A. Pope, *Chem. Commun.* **2012**, *48*, 10838–10840.

[12] S. M. Borisov, I. Klimant, *Anal. Chem.* **2007**, *79*, 7501–7509.

[13] S.-Y. Takizawa, C. Pérez-Bolívar, P. Anzenbacher Jr., S. Murata, *Eur. J. Inorg. Chem.* **2012**, 3975–3979.

[14] a) M. C. DeRosa, D. J. Hodgson, G. D. Enright, B. Dawson, C. E. B. Evans, R. J. Crutchley, *J. Am. Chem. Soc.* **2004**, *126*, 7619–7626; b) T. Yoshihara, Y. Yamaguchi, M. Hosaka, T. Takeuchi, S. Tobita, *Angew. Chem. Int. Ed.* **2012**, *51*, 4148–4151.

[15] K. Ono, A. Nakashima, Y. Tsuji, T. Kinoshita, M. Tomura, J.-i. Nishida, Y. Yamashita, *Chem. Eur. J.* **2010**, *16*, 13539–13546.

[16] M. Lepeltier, T. K.-M. Lee, K. K.-W. Lo, L. Toupet, H. Le Bozec, V. Guerchais, *Eur. J. Inorg. Chem.* **2005**, 110–117.

[17] ISC rate constants of more than 10^{12} s^{-1} have been measured experimentally for some of the archetypal Ir^{III} complexes; see, for example: G. J. Hedley, A. Ruseckas, I. D. W. Samuel, *J. Phys. Chem. A* **2009**, *113*, 2–4; G. J. Hedley, A. Ruseckas, I. D. W. Samuel, *J. Phys. Chem. A* **2010**, *114*, 8961–8968.

[18] a) D. N. Kozhevnikov, V. N. Kozhevnikov, M. Z. Shafikov, A. M. Prokhorov, D. W. Bruce, J. A. G. Williams, *Inorg. Chem.* **2011**, *50*, 3804–3815; b) Y. L. Chen, S. W. Li, Y. Chi, Y. M. Cheng, S. C. Pu, Y. S. Yeh, P. T. Chou, *ChemPhysChem* **2005**, *6*, 2012–2017; c) P. T. Chou, Y. Chi, M. W. Chung, C. C. Lin,

Coord. Chem. Rev. **2011**, *255*, 2653–2665; d) Z. He, W. Y. Wong, X. Yu, H. S. Kwok, Z. Lin, *Inorg. Chem.* **2006**, *45*, 10922–10937.
[19] T. Cantat, E. Génin, C. Giroud, G. Meyer, A. Jutand, *J. Organomet. Chem.* **2003**, *687*, 365–376.
[20] Y.-H. Chen, P. Knochel, *Angew. Chem. Int. Ed.* **2008**, *47*, 7648–7651; *Angew. Chem.* **2008**, *120*, 7760.

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