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Efficient Synthesis of Carbazolyl- and Thienyl-Substituted β-Diketonates and Properties of Their Red- and Green-Light-Emitting Ir(III) Complexes

Nan Tian,[†,||] Alexander Thiessen,[‡] Ralf Schiewek,[§] Oliver J. Schmitz,[§] Dirk Hertel,*[,‡,||] Klaus Meerholz,*[,‡,||] and Elisabeth Holder*[,†,||]

Functional Polymers Group and Institute of Polymer Technology, and Analytical Chemistry, University of Wuppertal, Gaussstrasse 20, D-42097 Wuppertal, Germany, Institute of Physical Chemistry, University of Cologne, Luxemburgerstrasse 116, D-50939 Cologne, Germany, and Dutch Polymer Institute (DPI), P.O.Box 902, 5600 AX Eindhoven, The Netherlands

dirk.hertel@uni-koeln.de; klaus.meerholz@uni-koeln.de; holder@uni-wuppertal.de

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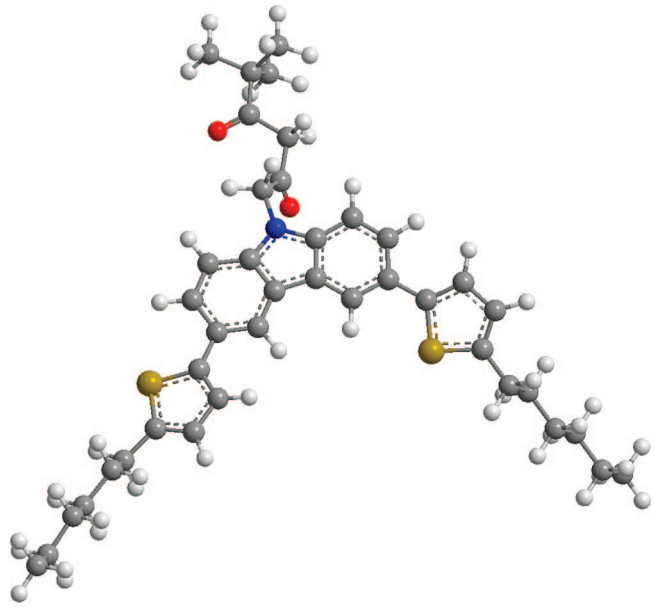

The efficient synthesis of novel β-diketonates equipped with functional carbazolyl moieties and their subsequent transformations in 5-hexyl-thienyl substituted carbazole derivatives is presented by utilizing an effective Stille cross-coupling reaction. The introduced β-diketonates served as ancillary ligands for novel heteroleptic red- and green-emitting Ir(III) complexes, when combined with 2-(naphthalen-1-yl)pyridine and 2-phenylpyridine as cyclometalating ligands. These novel Ir(III) complexes revealed color-tunability and a very good thermal stability until at least 207 °C. In polystyrene blends, the heteroleptic Ir(III) complexes revealed remarkable quantum yields up to 36% and suitably short phosphorescence lifetimes ranging from 1 to 4 μs. In the case of the orange-red Ir(III) emitter, equipped with 2-(naphthalen-1-yl)pyridine cyclometallating ligands, a luminous efficiency as high as 7.7 cd/A at 7.4 V was achieved. All fabricated diodes exhibited in addition favorable color stability.

Introduction

In recent years, the synthesis of luminescent transition-metal complexes received much attention due to their favorable optical and electrical properties making them in general perfect candidates for applications in electro-optical devices such as light-emitting devices,[1−4] solar cells,[5] or sensors.[6,7] For such electro-optical applications a wide range of transition-metal complexes have been developed; among them, prominent transition-metal cores are those of Ru(II),[8] Re(I),[8a] Os(II),[8c,d,f] Ir(III),[8e,g,9] Pt(II),[10] Au(I),[11] and Cu(I)[11] along with others. In

[†] Functional Polymers Group, University of Wuppertal.
[‡] Physical Chemistry, University of Cologne.
[§] Analytical Chemistry, University of Wuppertal.
[||] Dutch Polymer Institute (DPI).

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this series, Ir(III) cores are particularly promising because of their favorable short phosphorescent lifetimes, well-suited energy levels, stability and environmental inertness.[2q,8g,9a] The decoration with heteroaromatic cyclometalating C^N ligands was also found to give rise in the variability of the emission color of Ir(III) complexes.[2a,b,8g] Generally, cyclometalating ligands that contain electron-withdrawing functions (e.g., fluorine or nitrile substituents) serve to tune the emission color of the resulting Ir(III) complexes toward higher energies and thus to the blue,[12] whereas electron-pushing functions (e.g., alkyl substituents or aromatic rings that contribute to an increased π-conjugation) will result in emission color tuning toward lower energies and thus to the red.[2a,b,8g,13] While in homoleptic Ir(III) complexes all cyclometalating ligands influences the electro-optical properties such as emission color, oxidation potentials, lifetimes, and quantum yields, to name a few, in heteroleptic Ir(III) complexes the ancillary ligands usually have almost no impact on the electro-optical properties of the Ir(III) complexes[2a,b,i,p,8g] even though some other examples are known from literature.[2i,p] Prominent ancillary ligands are acetylacetone (acac) and its derivatives.[14] Recently, the functionalization of acetylacetones gave increase to the functionality of the Ir(III) complexes without disturbing the electro-optical properties of the metal

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core.[2e,14] Using this convenient approach allows, e.g., easy copolymerization of the Ir(III) complexes or moreover the insertion of moieties with specific functions, such as units for improved charge recombination or interconnection of units to improve solubility, e.g., alkyl chains. The implementation of such precise functions allows enlarged charge recombination at the emitter as demanded in sophisticated electro-optical applications or an improved processing probability due to enhanced solubility, however, without negatively influencing the optical properties much.

In our approach, we designed and synthesized heteroleptic Ir(III) complexes equipped with C^N cyclometalating ligands such as 2-phenylpyridine (ppy) and 2-(naphthalen-1-yl)pyridine (npy). The ancillary ligand used at this point consists of a modified acetylacetone,[14a] which served to carry functions that might increase charge recombination at the emitting site, such as carbazole[14a,15] or 3,6-di(thiophen-2-yl)-9*H*-carbazole moieties flanking the acac substituent on one side. Thus, we managed to design novel heteroleptic Ir(III) complexes, based on an approach introduced by Liu et al.,[14a] that provide further functionality by introducing first bromo-functions to the carbazole unit allowing, for example, C−C coupling reactions paving the way for copolymerizations *via* metal-catalyzed polycondensation and importantly also for other C−C cross-coupling reactions of major importance, such as the Stille reaction. It has to be emphasized at this point that an efficient functionalization of carbazoles in 3,6-positions utilizing a palladium(0)-catalyzed Stille protocol has rarely been described in the literature.[16] The thienyl moieties furthermore served on one hand to introduce alkyl chains that improve the solubility and processing features of the Ir(III) complexes substantially. On the other hand, the thienyl units were especially introduced in order to improve charge recombination at the emitter site. The Ir(III) complexes introduced here are moreover air-stable and possess a favorably high thermal stability. The Ir(III) (acac) emitters reveal likewise green and red light emission of a high quantum yield and short phosphorescence lifetimes. In particular the orange-red Ir(III) (acac) emitter that is carrying 2-(naphthalen-1-yl)pyridine cyclometallating ligands possesses a very good luminous efficiency of 7.7 cd/A at 7.4 V. This very good performance is similar to that of complexes that reveal even higher quantum yields while using cyclometalating ligands that are known to predominantly influence the radiative rates positively but are not furnished with charge recombining units such as the thienyl moieties introduced in our approach. All fabricated diodes furthermore reveal encouraging color stability in the green or red spectral area.

Results and Discussion

Synthesis and Characterization. The method of synthesizing the carbazole ligands and the respective iridium(III) complexes is outlined in Scheme 1. The cyclometalating ligand **2** was obtained from the *tetrakis*(triphenylphosphine)palladium(0) catalyzed Suzuki coupling of 2-bromopyridine with 4,4,5,5-tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (**1**). After the lithiation of 1-bromonaphthalene with *n*-butyllithium (*n*-BuLi) (1.6 M in *n*-hexane), 2-*iso*propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added and yielded compound **1**[17] in 81%. Subsequently, a modified Suzuki protocol was utilized to prepare compound **2**.[18] Usually toluene is utilized as reaction solvent; however, the mixture of 1,2-dimethoxyethane and ethanol (5:2) combined with sodium carbonate (2 M in H_2O) as base was found to be preferable as the reaction solvent mixture for the described Suzuki reaction and afforded a 72% of ligand **2**. The synthesis of acac ligand **4**[14a,19] was carried out in a two-step procedure following a described method[14a] starting from 9*H*-carbazole. In the presence of sodium hydride (NaH) and ethyl-2-bromoacetate, 3,6-dibromo-9*H*-carbazole is transformed to ethyl-2-(3,6-dibromo-9*H*-carbazol-9-yl)acetate (**3**)[14a,19] when dimethylsulfoxide (DMSO) is utilized at 80 °C. The subsequent transesterification reaction of **3** with 3,3-dimethylbutan-2-one and potassium hexamethyldisilazane (KHMDS) in tetrahydrofuran (THF) at room temperature yielded 1-(3,6-dibromo-9*H*-carbazol-9-yl)-5,5-dimethylhexane-2,4-dione (**4**) in 67%. The targeted acac ligand **7** could be conveniently synthesized *via* a Stille coupling.[20] First, 2-hexylthiophene (**5**) was obtained by an alkylation of 2-thiophene with 1-bromohexane in THF at rt. Then, 2-hexylthiophene was purified by distillation, subsequently lithiated by the treatment of *n*-BuLi in THF at 0 °C and was afterward reacted with Bu_3SnCl at 0 °C yielding thiophene-stannane **6** as pale yellow oil in 95%. Compounds **4** and **6** were reacted in toluene under reflux for 24 h by using *tetrakis*(triphenylphosphine)palladium(0) as a catalyst. The product was purified by utilizing silica gel column chromatography to yield compound **7** in 56%. The heteroleptic iridium(III) complexes **9a**, **9b**, **10a**, and **10b** were synthesized following a two-step procedure.[2a,b,21] The cyclometalation of $IrCl_3 \cdot nH_2O$ with compound **2** and 2-phenylpyridine resulted in the μ-chloride-bridged Ir(III) precursor complexes **8(npy)** (76%) and **8(ppy)** (71%), respectively. Subsequently, the μ-chloride-bridged dimers **8(npy)** and **8(ppy)** can each be treated with the acac ligands **4** and **7** in 2-ethoxyethanol at 140 °C in the presence of K_2CO_3 in order to yield targeted iridium(III) complexes **9a** (41%) and **9b** (40%) from **8(npy)**, as well as **10a** (69%) and **10b** (46%) from **8(ppy)**, respectively.

The ^{1}H NMR spectra of μ-chloride-bridged Ir(III) dimer **8(npy)** was recorded in dimethylsulfoxide-d_6, while **8(ppy)** and heteroleptic iridium(III) complexes **9a**, **9b**, **10a**, and **10b** were measured in $CDCl_3$, and the structural confirmation was

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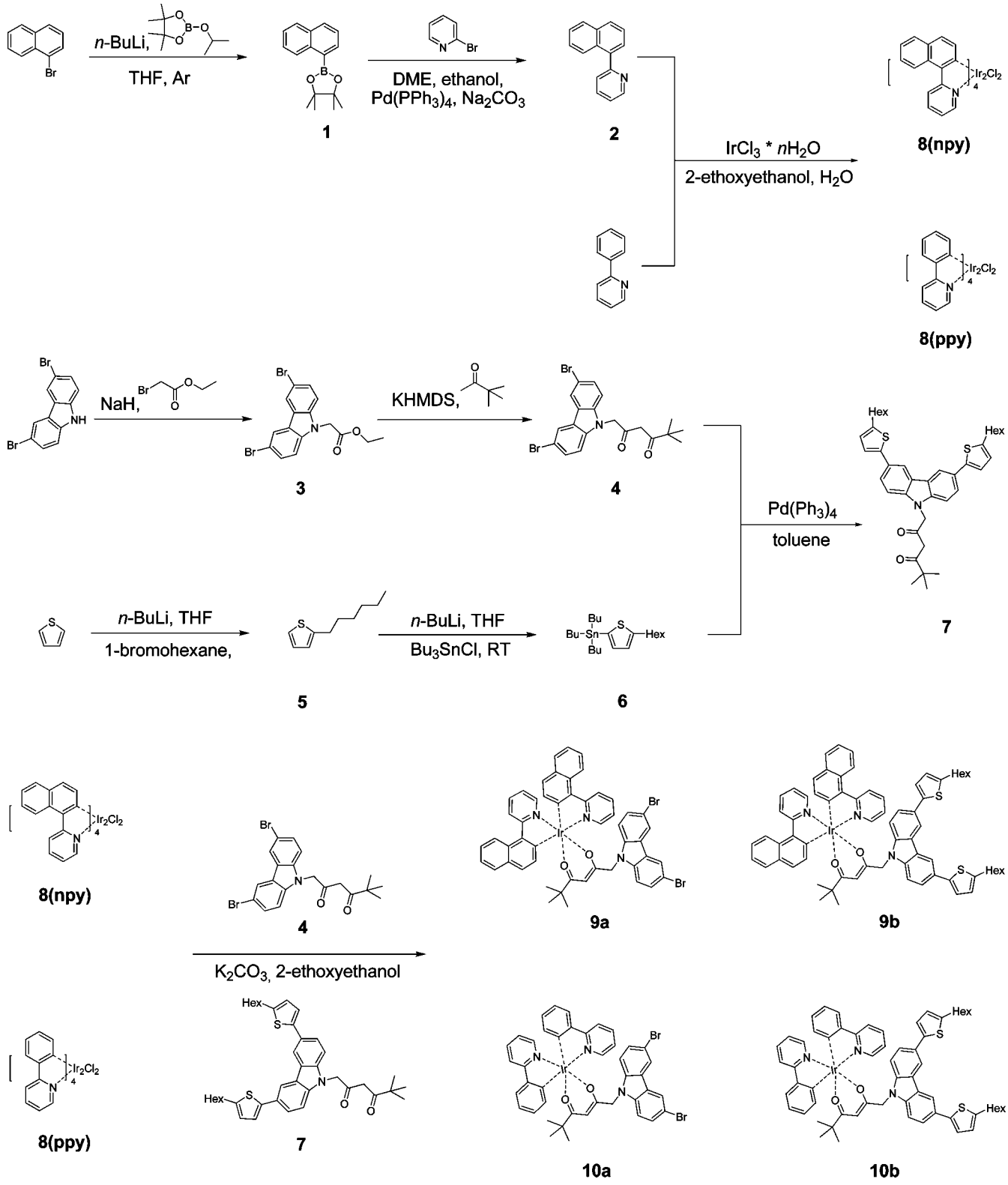
SCHEME 1. Efficient Synthetic Route to Novel Carbazolyl-Substituted β-Diketonates 4 and 7 and Their Novel Heteroleptic Iridium(III) Complexes 9a, 9b, 10a, and 10b[a]



[a] Abbreviations used: ppy (2-phenylpyridine) and npy (2-(naphthalen-1-yl)pyridine).

investigated by applying 2D $^1H-^1H$ COSY NMR experiments. For complex **8(npy)**, the resonances of the protons belonging to the C^N ligand were separated in two peaks, which possess the same integration and multiplicity. As a result of the inserted carbazolyl unit functioning as unsymmetrical ancillary ligand, complexes **9a** and **10a** as well as **9b** and **10b** are more complicated in the aromatic region of the ^1H NMR spectra as compared to the respective precursor complexes **8(npy)** and **8(ppy)**. The 2D $^1H-^1H$ COSY NMR experiment served to assign most of the proton resonances.

TABLE 1. UV−vis Absorption and Emission Maxima,[a] Solubility, Oxidation Potentials,[b] and Decomposition Temperature of Iridium(III) Complexes 9a, 9b, 9Ref, 10a, 10b, and 10Ref

compound	absorbance [nm] (log ε, L × mol^{-1} × cm^{-1})	maximum of emission [nm]	solubility [g/L][e]	E_{OX1} [V][f]	E_{OX2} [V]	T_d [°C][h]
9a	260 (4.67), 297 (4.61), 342 (4.27), 400 (3.59), 488 (3.57)	595	5	0.31		207
9b	260 (4.95), 308 (4.81), 400 (3.67), 488 (3.57)	595	10	0.30	0.49	302
9Ref[c]	304 (4.56), 346 (4.40), 483 (3.77), 549 (3.48)	630	7	0.31		
10a	270 (4.71), 342 (4.06), 408 (3.58), 459, (3.45)	522	10	0.34		330
10b	270 (4.93), 313 (4.91), 408 (3.67), 459, (3.44)	522	10	0.33	0.49	353
10Ref[d]	291 (4.39), 373 (3.82), 407 (3.64), 450 (3.22)	507	1.5	0.30[g]		

[a] As 10^{-5} M solutions in $CHCl_3$. [b] As 10^{-3} M solutions in CH_2Cl_2 containing 10^{-1} M NBu_4PF_6 as electrolyte *versus* ferrocene/ferrocenium. [c] **9Ref** denotes reference material *bis*(1-(4-*tert*-butylphenyl) isoquinoline) Ir(III) acetylacetonate. See refs 2a, 22, and 23. [d] **10Ref** denotes reference material *tris*(2-*p*-tolylpyridine) Ir(III). See refs 2a, 24, and 25. [e] In toluene. [f] All compounds featured a chemically irreversible oxidation for $E > 0.8$ V. [g] In acetonitrile. [h] 5% weight loss.

The observed IR vibration bands of μ-chloride-bridged dimers **8(npy)** and **8(ppy)** were dominated by the respective cyclometalating ligands npy and ppy. Thus, the Ir(III) complexes **8(npy)** and **8(ppy)** show almost similar vibrations in the IR spectra due to similar organic functional groups. Strong bands were observed at 3048−3044 cm^{-1} (C═C−H), 1615−1610 cm^{-1} (C═C), and 1476−1468 cm^{-1} (C═N). For the Ir(III) complexes **9b** and **10b**, the IR vibration properties were dominated by the vibrations of the acac ligand. The vibration bands at 2953 and 2852 cm^{-1} represent C-CH_3, stretching vibrations, at 1725 cm^{-1} (stretching vibration C═O) for **9b**, at 2954 and 2855 cm^{-1} (C−CH_3, stretching vibrations) and 1722 cm^{-1} (stretching vibration C═O) for **10b**.

The existence and purity of the iridium(III) complexes **9a**, **9b**, **10a**, and **10b** were furthermore investigated and proven by MALDI-TOFMS and APLI-MS. For the μ-chloride-bridged Ir(III) precursor complexes, a molecular weight of 1271.90 g/mol for **8(npy)** and 1073.10 g/mol for **8(ppy)** could be verified by using MALDI-TOFMS. These values are in accordance with the calculated molecular weights of 1272.19 and 1072.09 g/mol, respectively. Using APLI-MS, the measured molecular weights of **9a**, **9b**, **10a**, and **10b** were almost identical with the calculated molecular weights. Therefore, the MALDI-TOFMS and APLI-MS measurements sufficiently proved the existence of the synthesized complexes **9a**, **9b**, **10a**, and **10b**. Elemental analysis also verified the existence of the carbazole-containing iridium(III) complexes **9a**, **9b**, **10a**, and **10b**.

The solubility of the light-emitting complexes was moreover investigated. When ancillary ligand **7** was interconnected to form Ir(III) complexes **9b** and **10b**, their solubility was increased by a factor of 2 compared to that of **9a** (Table 1). The solubility enhancement by a factor of 6 due to the influence of ligand **7** becomes even more remarkable when **9b** and **10b** were compared to less soluble Ir(III) complexes such as *tris*(2-*p*-tolylpyridine) Ir(III).

The thermal stability of the iridium(III) complexes was evaluated by thermogravimetric analysis (TGA) under a nitrogen atmosphere (see Table 1). The thermal decomposition temperature (T_d) was found to be >300 °C except for compound **9a**. Thus, overall the thermal stability of the complexes is sufficient to allow processing in organic light-emitting diodes (OLEDs) or polymer LEDs (PLEDs). We also investigated the glass transition temperature (T_g); however, in the differential scanning calorimetry (DSC) scan, no glass transition was observed. Crystallization or melting transitions were also not observable.

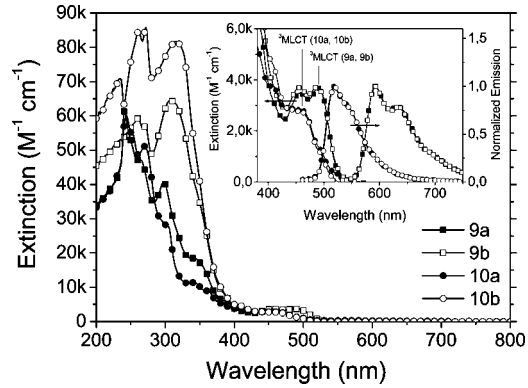


FIGURE 1. UV−vis absorption spectra of iridium(III) complexes **9a**, **9b**, **10a**, and **10b** (10^{-5} M solutions in $CHCl_3$). Inset: Indication of the ^{3}MLCT absorption bands and emission of **9a**, **9b**, **10a**, and **10b** (10^{-5} M solutions in $CHCl_3$).

Electro-optical Properties. The photophysical characteristics of the novel complexes were investigated by optical spectroscopy. In the absorption spectra spin-allowed transitions as well as spin-forbidden metal−ligand charge transfer (MLCT) transitions were found (Figure 1 and Table 1). The UV−vis spectra of the iridium(III) complexes **9a**, **9b**, **10a**, and **10b** are shown in Figure 1. For complexes **9a** and **9b**, the strong absorption bands at about 260 and 297 nm were assigned to spin-allowed $\pi \rightarrow \pi^*$ transitions of the cyclometalating ligand npy. For complexes **10a** and **10b**, the intense absorption band at about 270 and 313 nm were attributed to spin-allowed $\pi \rightarrow \pi^*$ transitions of the cyclometalating ligand ppy. For complexes **9a** and **9b**, the spin-allowed singlet ^{1}MLCT transition is located in the visible range at 400 nm, visible as a shoulder overlapping with the ligand $\pi \rightarrow \pi^*$ transitions. The absorption at 488 nm for **9a** and **9b** followed by a poorly resolved vibronic progression is due to the transition from the ground state to spin-forbidden triplet ^{3}MLCT excited state. The spin-allowed singlet ^{1}MLCT transition for **10a** and **10b** is also visible at 408 nm. For complexes **10a** and **10b**, the weak absorption for spin-forbidden ^{3}MLCT transition occurred at 459 nm with a vibronic progression. The absorptions for the Ir(III) complexes **9a**, **9b**, **10a**, and **10b** in the higher UV are most likely due to β-diketonate-based transitions that resemble the absorptions of

TABLE 2. Phosphorescence Emission Maxima, Phosphorescence Lifetimes, and Phosphorescence Quantum Yields (η_{Ph}) of Iridium(III) Complexes 9a, 9b, 9Ref, 10a, 10b, and 10Ref in a Polystyrene Matrix[a]

		lifetime		
compound	maximum of emission [nm]	τ_1 [μs] (prefactor)[b]	τ_2 [μs] (prefactor)	η_{Ph} [λ_{exc} 340 nm]
9a	592	3.95		0.27
9b	592	4.01		0.36
9Ref[c]	625	1.29; 2.05 (80 K)		0.52
10a	518	1.21		0.35
10b	518	1.49 (0.65)	5.12 (0.35)	0.28
10Ref[c]	511	1.30; 3.96 (80 K)		0.81

[a] At a molar ratio of 0.1%. Lifetimes are measured at rt unless otherwise noted. [b] Prefactor is the amplitude normalized to the sum of both amplitudes of the biexponential decay. [c] References 2a, 22, and 23. [c] References 2a, 24, and 25.

the free β-diketone. In Figure 1, also the emission properties for excitation at 360 nm are featured. The compounds **9a** and **9b** both revealed a strong red emission maximum at ca. 595 nm. The complexes **10a** and **10b** displayed a deep green emission with a maximum at 522 nm. The blue-shift relative to compounds **9a** and **9b** is attributed to the smaller π-system in the ligand.

The oxidation potentials of the complexes are summarized in Table 1 together with information on other well-known green- and red-emitting reference complexes. All four complexes featured reversible oxidation around 0.3 V *versus* the ferrocene/ferrocenium redox couple. This can thus be attributed to the oxidation of the cyclometalated complex. These oxidation potentials therefore translated into highest-occupied molecular orbital (HOMO) energies of about 5.4 eV.[26] The complexes **9b** and **10b** exhibited a second reversible oxidation potential, which is related to the oxidation of the thienyl-substituted carbazolyl ligand.

The emission properties of the complexes in a polystyrene matrix were very similar to emission spectra in solution, except for a small shift in the emission wavelength. The emission wavelengths of the films are shown in Table 2, together with the phosphorescence lifetimes. Complexes **9a**, **9b**, and **10a** demonstrated a single exponential decay with a lifetime of around 4 μs for the red-emitting complexes. The lifetime of the green-emitting complex **10a** is slightly shortened to 1.21 μs. Complex **10b** possessed biexponential decay. This has been observed with the archetypical $Ir(ppy)_3$ and is due to different emission rates of the involved triplet sublevels.[27,28] The prefactors in Table 2 are the normalized amplitudes of the biexponential fit and indicate that the short lifetime of 1.49 μs dominates the intensity decay. The PL quantum efficiency of iridium(III) complexes **9a**, **9b**, **10a**, and **10b** were also determined and are summarized in Table 2. The green- (red-) emitting complexes **10a** and **10b** (**9a** and **9b**) exhibited a factor of about 3 (2) of reduced quantum yield compared to the state-of-the-art reference complexes **10Ref** and **9Ref**.

Electrophosphorescence. To test the suitability of the novel triplet emitters for electroluminescence applications, compound **9b** and **10b** were compared to the reference systems **9Ref**[2a,22,23] and **10Ref**[2a,24,25] in OLEDs. The device structure comprised the following layout: ITO//PEDOT:PSS(35 nm)//QUPD(20 nm)//OTPD(10 nm)//PVK+OXD-7+Ir(III)(80 nm)//CsF(3 nm)//Al (100 nm). Two cross-linkable hole-transporting layers, namely, *N*,*N*′-*bis*(4-[6-[(3-ethyloxetane-3-yl)methoxy]-hexyloxy)phenyl]-*N*,*N*′-*bis*(4-methoxyphenyl)biphenyl-4,4′-diamine) (QUPD)[26] and *N*,*N*′-*bis*(4-[6-[(3-ethyloxetane-3-yl)-methoxy]-hexylphenyl]-*N*,*N*′-diphenyl-4,4′-diamine) (OTPD),[26] were used in order to enhance hole injection. Poly(*N*-vinyl carbazole) (PVK) was used as a matrix polymer blended with the electron-transporting molecule 1,3-*bis*(5-(4-*tert*-butylphenyl)-1,3,4-oxadiazol-2-yl)benzene (OXD-7) (29 wt%). The blend was doped with 3.5 wt% of **9b**, **10b**, **9Ref**, and **10Ref**, respectively. This device structure was chosen according to previous results[2e,26] for a first comparison of the compounds without individual optimization. The device performances are shown in Figure 2.

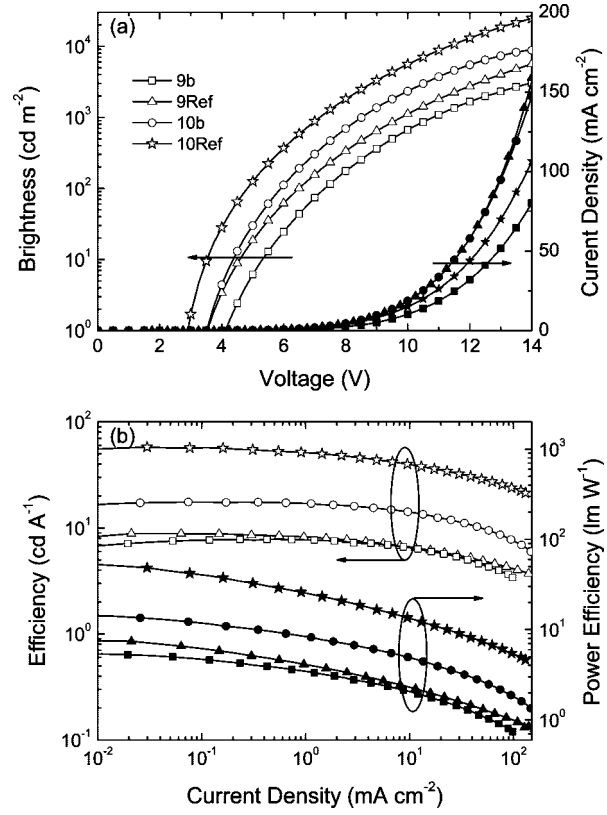


FIGURE 2. Performance of the investigated OLEDs. (a) Brightness (open symbols) and current density (filled symbols) of the devices with the compounds **9b**, **9Ref**, **10b**, and **10Ref** plotted as a function of voltage. (b) Luminance efficiency (open symbols) and power efficiency (filled symbols) depicted as a function of current density.

The efficiency of the red-emitting OLEDs is proven to be within the best for solution processed devices.[29] Whereas the luminous efficiency of the red-emitting devices with **9b** and **9Ref** were similar (7.7 and 8.1 cd/A at 100 cd/m^2, Table 3), a significant difference between the green-emitting OLEDs with **10b** and **10Ref** (17.3 cd/A and 56.7 cd/A at 100 cd/m^2) was found. One has to note that the efficiency of **10Ref** is 20% lower compared to literature data.[29] Here we used a lower concentration of the Ir(III) complex and slightly different device thickness resulting in lower light outcoupling and abandoned any annealing steps. The remarkable higher performance of **10Ref**

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TABLE 3. Performance Data of Investigated OLED Devices with iridium(III) Complexes 9b, 9Ref, 10b, and 10Ref

compound	max luminous efficiency [cd/A]	max power efficiency [lm/W]	performance at 100 cd/m^2 [cd/A] at [V]	performance at 1000 cd/m^2 [cd/A] at [V]	CIE (X, Y)
9b	7.8	5.4	7.7 at 7.4	6 at 10.8	0.60, 0.38
9Ref[a]	8.7	7.5	8.1 at 6.5	6.2 at 9.8	0.68, 0.31
10b	17.6	14.2	17.3 at 6.9	14.9 at 8.5	0.33, 0.60
10Ref[b]	57.9	53.3	56.7 at 4.8	48.2 at 7.2	0.32, 0.61

[a] References 2a, 22, and 23. [b] References 2a, 24, and 25.

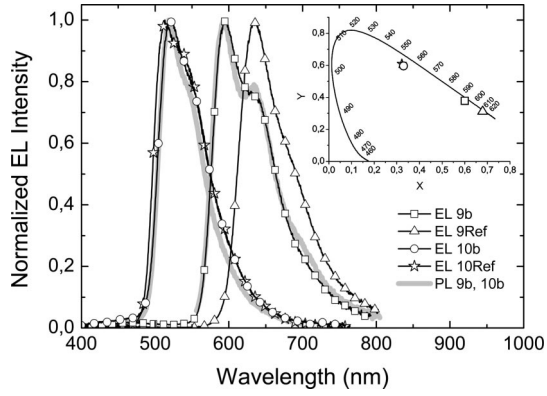

FIGURE 3. Electroluminescence spectra (thin black lines with open symbols) of the investigated OLED devices containing compounds **9b**, **9Ref**, **10b**, and **10Ref** and photoluminescence spectra (thick gray lines) reprinted from Figure 1 for comparison. Inset shows CIE coordinates calculated from EL spectra shown in (a).

compared to **10b** may be due to the fact that **10Ref** is a homoleptic Ir(III) complex, while complexes **9b**, **9Ref**, and **10b**are comprised of a heteroleptic structure. This structural property becomes perceivable also in a significantly higher PL quantum efficiency compared to the other compounds studied here (Table 2). The electroluminescence spectra (Figure 3) of the synthesized compounds **9b** and **10b** are in a good agreement with the photoluminescence spectra from Figure 1 (reprinted in Figure 3).

However, the comparison of the efficiencies of the devices comprising **9b** and **9Ref** should be regarded with care, because of a slight red shift in emission spectra of **9Ref** compared to **9b** (Figure 3). However, all devices revealed good color stability, and the CIE coordinates (inset of Figure 3) remained unchanged within the resolution of the spectrometer.

Note that the very good electrophosphorescence performance of **9b** is similar to that of complexes that reveal even two times higher quantum yield, however, while equipped with cyclometalating ligands that are known to positively influence the radiative rate. Consequently, following our here introduced dual donor species design concept, which is based on the interconnection of carbazolyl and thienyl moieties, is supposed to potentially improve charge recombination at the emitter. The introduced design concept will not only allow for easily tuning the emission colors, when combined with the respective cyclometallating coligands, but might thus be useful to enhance the diode performance as well. This hypothesis will be investigated in the future in a more detailed physical study exploring the charge transport behavior, while the emitter design will follow the here introduced synthetic design concept.

In summary, we synthesized and characterized a series of novel Ir(III) complexes with functional β-diketonate ancillary ligands that are furnished with a carbazolyl moiety. At this point, we furthermore described the interconnection to *n*-hexyl-modified thienyl substituents in the 3,6-positions of the carbazole *via* an uncommonly described Stille protocol in good yields. All introduced Ir(III) complexes showed a high thermal stability of at least 207 °C and no phase transitions or crystallization tendency. The Ir(III) complexes demonstrated favorable short phosphorescence lifetimes (1−4 μs), high photoluminescence quantum yields of up to 36% (in polystyrene blends), and favorable oxidation potentials, while allowing convenient color tuning at the Ir(III) core, when the different Ir(III) complex precursors were treated with one type of functional β-diketonate as ancillary ligand. All fabricated OLEDs revealed favorable color stability. In the case of the novel orange-red Ir(III) (acac) emitter, a luminous efficiency as high as 7.7 cd/A at 7.4 V was achieved. This very good performance is similar to that of complexes that revealed even two times higher quantum yields while using cyclometalating ligands that are known to positively influence the radiative rates. Further detailed physical studies on the charge transport behavior of the compounds are currently in progress in our laboratories.

Experimental Section

Synthetic Procedures. 1-(3,6-Dibromo-9*H*-carbazol-9-yl)-5,5-dimethylhexane-2,4-dione (4). To a solution of the starting 3,3-dimethylbutan-2-one (1.83 g, 18.24 mmol) in THF (20 mL) was added KHMDS (38.9 mL of a 0.5 M solution in toluene, 19.46 mmol) dropwise at 0 °C. Subsequently, the solution was stirred at room temperature for 1 h. After this time, compound **2** (5 g, 12.16 mmol) in THF (20 mL) was added dropwise, and the resulting reaction mixture was stirred at room temperature for 12 h. Afterwards, the mixture was poured into water and acidified with diluted hydrochloric acid. The organic layer was extracted with $CHCl_3$ (3 × 50 mL), washed with water, and then dried with anhydrous sodium sulfate. The solvent was removed by reduced pressure. The crude product was purified by silica column chromatography (*n*-hexane/ethyl acetate, 10:3, v/v) to give a white powder. Yield: (3.86 g, 67%). Anal. Calcd for $C_{20}H_{19}Br_2NO_2$: C 51.64, H 4.12, N 3.01. Found: C 51.80, H 4.14, N 2.89. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.20−1.24[f] (m, 9H), 4.93[e] (s, 2H), 5.31[d] (s, 2H), 7.19−7.21[c] (d, ^3J = 8.1 Hz, 2H), 7.55−7.58(ppy) (dd, ^3J = 8.6 and 2.1 Hz, 2H), 8.15−8.16[a] (d, ^3J = 2.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 27.1[1], 38.8[2], 48.7[4], 92.5[6], 110.3[8], 113.0[10], 123.5[12], 123.8[11], 129.5[9], 139.5[7], 190.1[5], 200.2[3]. IR (cm^{-1}): 3078 (C═C−H), 2964, 2932, 2867 (C−H), 1706, 1596 (C═C), 1392, 1289, 1096, 887, 873, 834, 756, 691. HRMS (ESI) *m/z* calcd for $C_{20}H_{19}Br_2NO_2$ $(M+H)^+$ 465.18, found 465.10.

Tributyl(5-hexylthiophen-2-yl)stannane (6) and 1-(3,6-*Bis*(4-hexylcyclopenta-1,3-dienyl)-9*H*-carbazol-9-yl)-5,5-dimethylhexane-2,4-dione (7). A solution of *n*-BuLi (20.4 mL, 1.6M, 32.7 mmol) in *n*-hexane was added dropwise to a solution of 2-hexylthiophene (5 g, 29.7 mmol) in anhydrous THF (20 mL) at −25 °C. After 1 h of stirring at −25 °C, Bu_3SnCl (8.5 mL, 31.19 mmol) was slowly added. The reaction mixture was warmed up to rt and stirred overnight. After dilution with CH_2Cl_2 (40 mL), the organic phase was successively washed with saturated aqueous

NH_4Cl and water and dried over Na_2SO_4, and the solvent was removed under reduced pressure. The colorless oil **6** (12.9 g, 95%) was directly used in the next step without further purification. Product **6** (1.13 g, 2.48 mmol) was combined in an oven-dried vacuum flask with compound **4** (0.48 g, 1.03 mmol), *tetrakis*(triphenylphosphine)palladium(0) (0.12 g, 10 mol%), and 20 mL of dry toluene (20 mL). The flask was deaerated for 5 min with argon, sealed, and brought to 140 °C for 12 h. The solvent was removed by reduced pressure. The crude product was purified by silica column chromatography (*n*-hexane/ethyl acetate, 10:3, v/v) to give a gray solid. Yield: (0.37 g, 56%). Anal. Calcd for $C_{40}H_{49}NO_2S_2$: C 75.07, H 7.72, N 2.19. Found: C 75.10, H 7.69, N 2.20. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.92^{q} (s, 6H), 0.99^{h} (s, 9H), 1.35−1.44^{n,o,p} (m, 12H), 1.75^{m} (m, 4H), 2.86^{i} (t, ^3J = 8.6 and 7.6 Hz, 4H), 4.97^{g} (s, 2H), 5.34^{f} (s, 1H), 6.78^{e} (d, ^3J = 3.5 Hz, 2H), 7.17^{d} (d, ^3J = 3.6 Hz, 2H), 7.29^{c} (d, ^3J = 8.6 Hz, 2H), 7.69^{b} (dd, ^3J = 8.6 Hz, 2H), 8.29^{a} (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 14.1^{1}, 22.6^{2}, 27.1^{22}, 28.8^{3}, 30.3^{4}, 31.6^{5}, 31.7^{6}, 38.9^{21}, 48.8^{19}, 92.7^{17}, 108.9^{16}, 117.6^{13}, 121.8^{12}, 123.6^{8}, 124.9^{4}, 127.3^{11}, 140.2^{15}, 142.5^{10}, 144.8^{7}, 190.7^{18}, 200.4^{20}. IR (cm^{-1}): 3078, 3044 (C═C−H), 2956, 2924, 2869 (C−H), 1728, 1587 (C═C), 1364, 1325, 1252, 1159, 1141, 884, 861, 832,789, 759, 726, 680. HRMS (ESI) *m*/*z* calcd for $C_{40}H_{49}NO_2S_2$ $(M + H)^+$ 639.95, found 639.60.

General Procedure of (C^N)$_4$Ir$_2$Cl$_2$ Complexes. Iridium(III) trichloride hydrate was combined with the respective C^N ligand ppy or npy, dissolved in a mixture of 2-ethoxyethanol (30 mL) and water (10 mL). The mixture was stirred for 24 h under reflux. The solution was cooled to room temperature, and the precipitate was collected on a glass filter frit. The precipitate was washed with ethanol (30 mL) and dichloromethane (20 mL).

(npy)$_4$Ir$_2$Cl$_2$ (8(npy)). Iridium(III) trichloride hydrate (233 mg, 0.78 mmol) and compound **2** (400 mg, 1.95 mmol) afforded an orange-red powder. Yield: (327 mg, 76%). Anal. Calcd for $C_{60}H_{40}C_{l2}Ir_2N_4$: C 56.64, H 3.17, N 4.40. Found: C 56.22, H 3.21, N 4.42. ^{1}H NMR (400 MHz, dimethylsulfoxide-d_6, ppm): δ 5.74−5.76^{j} (d, ^3J = 8.6 Hz, 2H), 6.42−6.44$^{j'}$ (d, ^3J = 8.5 Hz, 2H), 7.14−7.16^{i} (d, ^3J = 8.5 Hz, 2H), 7.26−7.33$^{i',g,g'}$ (m, 6H), 7.46−7.52$^{f,f'}$ (m, 4H), 7.58−7.69$^{b,b',h,h'}$ (m, 8H), 8.06−8.11^{c} (t, ^3J = 9.2 and 7.6 Hz, 2H), 8.14−8.18$^{c'}$ (t, ^3J = 9.2 and 7.6 Hz, 2H), 8.49−8.55$^{d,e,e'}$ (m, 6H), 8.63−8.65$^{d'}$ d(d, ^3J = 8.5 Hz, 2H), 9.70−9.72^{a} (d, ^3J = 5.6 Hz, 2H), 9.89−9.91$^{a'}$ (d,^3J = 5.1 Hz, 2H). IR (cm^{-1}): 3048 (C═C−H), 1637, 1610, 1468, 1419 (C═C, C═N), 1312, 1263, 1241, 1074, 762, 740, 720, 667. APLI-MS *m*/*z* calcd for $C_{60}H_{40}C_{l2}Ir_2N_4$ 1272.19, found 1271.90.

General Procedure of (C^N)$_2$Ir(acac) Complexes. In a 50 mL flask, the μ-chloride-bridged dimer Ir(III) complex, the acac ligand, and K_2CO_3 were mixed with 2-ethoxyethanol (30 mL), and the mixture was stirred under reflux for 2−12 h. After cooling to room temperature, 2-ethoxyethanol was removed under reduced pressure. The crude product was dissolved in dichloromethane (20 mL), and the obtained solid was filtered off. The dichloromethane solution (20 mL) was concentrated under reduced pressure. Subsequently, *n*-hexanes were utilized in order to precipitate the complexes, and the obtained solid was filtered off. The residue was purified by silica column chromatography (*n*-hexane/ethyl acetate, 5:1, v/v), if needed, a purification on a BioBeads SX-1 column (dichloromethane) followed additionally.

(npy)$_2$Ir(acac) (9a). Compound **8(npy)** (200 mg, 0.157 mmol), compound **4** (183 mg, 0.393 mmol), and K_2CO_3 (152 mg, 1.100 mmol) afforded after reaction and purification a deep-red powder. Yield: (137 mg, 41%). Anal. Calcd for $C_{50}H_{39}Br_2IrN_3O_2$: C 56.34, H 3.69, N 3.94. Found: C 56.39, H 3.67, N 3.93. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.59 (s, 9H), 4.61(s, 1H), 5.13 (s, 2H), 6.35−6.38^{j} (d, ^3J = 8.3 Hz, 1H), 6.44−6.46$^{j'}$ (d, ^3J = 8.3 Hz, 1H), 6.85^{g} (t, ^3J = 7.6 and 7.1 Hz, 1H), 7.00−7.05$^{g',i,i'}$ (m, 3H), 7.15−7.30$^{c,c',m,m',d,d'}$ (m, 6H), 7.41−7.44^{b} (t, ^3J = 8.6 and 7.1 Hz, 1H), 7.48−7.53$^{b'}$ (t, ^3J = 8.1 and 8.6 Hz, 1H), 7.61−7.63^{l} (d, ^3J = 8.1 Hz, 1H), 7.66−7.68$^{l'}$ (t, ^3J = 7.6 Hz, 1H), 7.71−7.75^{f} (t, ^3J = 8.6 and 6.7 Hz, 1H), 7.81−7.85$^{f'}$ (t, ^3J = 8.6 and 6.7 Hz, 1H), 8.03−8.05$^{k,k'}$ (d, ^3J = 8.1 Hz, 2H), 8.32−8.33^{h} (d, ^3J = 5.6 Hz, 1H), 8.35−8.37$^{h'}$ (d, ^3J = 5.6 Hz, 1H), 8.42−8.45^{e} (d, ^3J = 8.5 Hz, 1H), 8.47−8.49^{a} (d, ^3J = 8.6 Hz, 1H), 8.54−8.56$^{e'}$ (d, ^3J = 8.5 Hz, 1H), 8.57−8.59$^{a'}$ (d, ^3J = 8.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 27.5, 41.0, 51.3, 92.4, 109.1, 119.0, 119.8, 120.1, 120.2, 120.9, 121.2, 121,9, 122.0, 122.1, 122.3, 123.0, 125.5, 126.2, 126.3, 128.1, 128.5, 129.6, 129.8, 131.0, 131.2, 131.6, 131.8, 132.5, 132.8, 136.8, 136.9, 137.8, 137.9, 140.7, 148.6, 148.7, 155.5, 155.7, 169.0, 169.4, 181.1, 196.8. IR (cm^{-1}): 3043 (C═C−H), 2948, 2922, 2863 (C−H), 1705, 1569, 1500 (C═C, C═N, C═O), 1354, 1272, 1153, 1118, 897, 862, 813, 744, 669, 659. UV−vis [$CHCl_3$, λ_{max}, nm, (log ε, L × mol^{-1} × cm^{-1})]: 260 (4.67), 297 (4.61), 342 (4.27), 400 (3.59), 488 (3.57). Emission ($CHCl_3$, λ_{max}, nm): 595. T_d (5% weight loss): 207 °C. APLI-MS *m*/*z* calcd for $C_{50}H_{39}Br_2IrN_3O_2$: 1063.10, found 1063.10.

(npy)$_2$Ir(acac)Thiophene (9b). Compound **8(npy)** (119 mg, 0.094 mmol), compound **7** (120 mg, 0.188 mmol), and K_2CO_3 (91 mg, 0.819 mmol) afforded after purification a deep-red powder. Yield: (95 mg, 40.7%). Anal. Calcd for $C_{72}H_{72}IrN_3O_2S_2$: C 67.82, H 5.53, N 3.39. Found: C 67.56, H 5.51, N 3.40. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.66 (s, 9H), 0.93 (s, 6H), 1.37 (m, 8H), 1.46 (m, 4H), 1.77 (m, 4H), 2.88 (m, 4H), 4.62 (m, 2H), 5.26 (s, 1H), 6.34−6.36^{j} (d, ^3J = 8.6 Hz, 1H), 6.38−6.40$^{j'}$ (d, ^3J = 8.1 Hz, 1H), 6.80−6.81$^{o,o'}$ (d, ^3J = 3.6 Hz, 2H), 6.82−6.85^{g} (t, ^3J = 7.6 and 6.6 Hz, 1H), 6.93−6.96$^{g'}$ (t, ^3J = 7.6 and 6.1 Hz, 1H), 6.98−7.00$^{i,i'}$ (d, ^3J = 8.6 Hz, 2H), 7.12−7.15$^{c,c',n,n'}$ (m, 4H), 7.20−7.24$^{m,m'}$ (m, 2H), 7.44−7.46$^{b,b',d,d'}$ (m, 4H), 7.60−7.62$^{l,l'}$ (d, ^3J = 8.1 Hz, 2H), 7.70−7.77$^{f,f'}$ (m, 2H), 8.17$^{k,k'}$ (s, 2H), 8.24−8.25^{h} (d,^3J = 4.6 Hz, 1H), 8.29−8.30$^{h'}$ (d,^3J = 4.6 Hz, 1H), 8.42−8.53$^{a,a',e,e'}$ (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 14.1, 22.6, 27.6, 28.9, 29.7, 30.4, 31.7, 41.1, 51.5, 92.8, 109.6, 117.1, 119.8, 120.1, 120.9, 121.1, 121.5, 121.9, 122.0, 122.1, 122.2, 123.3, 124.0, 124.9, 126.3, 126.4, 127.3, 128.1, 128.5, 129.6, 129.8, 131.0, 131.6, 131.7, 132.5, 132.7, 136.8, 140.4, 142.9, 144.5, 148.4, 169.3, 180.4, 202.1. IR (cm^{-1}): 3043 (C═C−H), 2953, 2920, 2852 (C−H), 1725, 1573, 1498 (C═C, C═N, C═O), 1357, 1289, 1156, 862, 808, 790, 740, 657, 640. UV−vis [$CHCl_3$, λ_{max}, nm, (log ε, L × mol^{-1} × cm^{-1})]: 260 (4.95), 308 (4.81), 400 (3.67), 488 (3.57). Emission ($CHCl_3$, λ_{max}, nm): 595. T_d (5% weight loss): 302 °C. APLI-MS *m*/*z* calcd for $C_{70}H_{68}IrN_3O_2S_2$ 1239.65, found.1239.60.

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Supporting Information Available: Experimental details and analysis of the compounds not described and Ir(III) complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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