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Organoiridium Quinolinolate Complexes: Synthesis, Structures, Thermal Stabilities and Photophysical Properties

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The syntheses, solid-state structures, thermal properties and photophysics of a series of heteroleptic iridium(III) complexes with phenylpyridine as the cyclometalating ligands and quinolinolates are reported. The title compounds were formed by reaction of di-μ-chloro-tetrakis[$\kappa^2(C^2,N)$-2-phenylpyridine]-diiridium(III) with the corresponding 8-hydroxyquinolines in 56 to 86 % yield. The crystal structures of two of the complexes have been determined. Both complexes show the two carbon ligands in a *cis* disposition and the 2-phenylpyridine nitrogen atoms in a *trans* disposition. Assessment of the thermal stabilities of the compounds revealed huge differences depending on the substituents on the quinolinolato ligand. Most complexes are poor emitters in solution, in films and in OLEDs. Substitution of the quinolinolato ligand with electron-withdrawing functional groups in the 5-position caused additional absorption features in the visible region facilitating the finding of appropriate host materials for OLEDs and gave emission properties governed by the quinolinolato ligand.

Introduction

The design, synthesis and characterisation of phosphorescent light-emitting materials have received considerable attention in the last couple of years due to a series of possible practical applications such as in organic light-emitting diodes (OLEDs),[1] light-emitting electrochemical cells (LECs)[2] or for sensing purposes.[3] Although tremendous improvements concerning device lifetimes, efficiencies, brightness and device structures[4] have been made for phosphorescent metal complexes containing platinum, osmium and iridium,[1,5] there is still a great demand for stable emitter materials that cover the entire visible spectrum.[6]

Among this class of materials, cyclometalated iridium(III) complexes have emerged as very promising candidates because of the powerful colour-tuning from blue to red brought about by variations in the cyclometalating ligands or extension of the corresponding conjugated ligand systems.[4] However, the drawbacks of this approach are the cumbersome synthesis of the μ-chloro-bridged precursor material. Harsh conditions are needed for the preparation of tris(cyclometallated) iridium(III) complexes and the formation of several by-products also occurs.[4,7] In contrast to the difficulties with the preparation of these homoleptic iridium(III) complexes, an alternative approach is based on the incorporation of ancillary ligands such as acetylacetonato, picolinato, triazolato or tetrazolato derivatives with clearly facilitated synthetic procedures.[4a] On the other hand, only a few examples of heteroleptic iridium(III) complexes with emission properties dominated by the third ligand have been reported[4,8] which is clearly disadvantageous for a fast and versatile approach to colour-tuneable phosphorescent emitter materials.

During the last two decades a large number of reports have been published concentrating on the design and characterisation of luminescent metal complexes bearing 8-hydroxyquinoline and its derivatives as ligands.[9] 8-Hydroxyquinolines are of particular interest because of the possibility of tuning the energy gap by the simple attachment of electron-donating or electron-withdrawing groups and the commercial availability of many 8-hydroxyquinoline derivatives.[6,9] Although considerable scientific efforts have been focused on studying luminescent metal complexes of aluminium, platinum, palladium or boron containing 8-hydroxyquinolines as ligands, corresponding investigations on the impact of ligand modifications on the materials properties of organoiridium quinolinolate complexes are rare.[10]

Recently we reported on heteroleptic iridium(III) complexes bearing 8-hydroxyquinolines as ligands for the preparation of white organic light-emitting diodes (WOLEDs)

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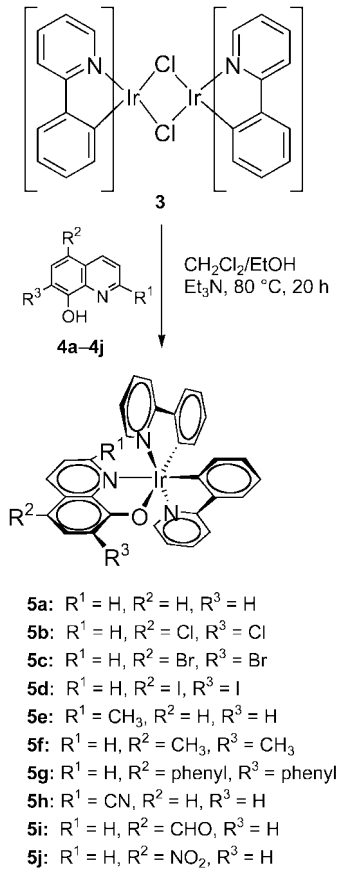
and communicated our first results on the colour-tuning of organoiridium quinolinolate complexes with emission properties controlled by the quinolinolato ligand.[11] In this work we wish to present the synthesis, structures, thermal and photophysical properties of a series of derivatives of bis[κ²(*C*²,*N*)-2-phenylpyridine][κ²(*N*,*O*)-8-quinolinolato]iridium(III). The presented systematic study on the influence of functional groups on materials properties corresponds to recent reports on iridium(III) complexes tailored towards particular needs[1c,11] and provides a step towards a general toolbox for realising low-cost and colour-tuneable iridium(III) compounds for, e.g., OLED applications. Parts of this work have been communicated briefly.[11b]

Results and Discussion

The compounds under investigation were prepared as depicted in Scheme 1. According to a literature procedure starting from $IrCl_3 \cdot nH_2O$ (**1**) and 2-phenylpyridine (**2**),[12] the μ-chloro-bridged precursor material di-μ-chloro-tetrakis[κ²(*C*²,*N*)-2-phenylpyridine]diiridium(III) (**3**) could be obtained by heating the black coloured reaction mixture to reflux, in 2-ethoxyethanol and water, at 120 °C for 24 h. Purification of **3** was achieved by filtration of the greenish precipitate which formed during the reaction and repeated washing of the solid residue with hot MeOH. The various derivatives of bis[κ²(*C*²,*N*)-2-phenylpyridine][κ²(*N*,*O*)-8-quinolinolato]iridium(III) (**5a**–**5j**; for nomenclature see Exp. Sect.) were synthesised by treating **3** with 2.1 to 2.5 equiv. of the corresponding 8-hydroxyquinoline (**4a**–**4j**) in CH_2Cl_2, EtOH and Et_3N at 80 °C for 20 h.[11] Work-up of the organoiridium(III) complexes **5a**–**5j** turned out to be straightforward and was achieved by filtration and subsequent washing of the yellow to deeply red solids with hot MeOH several times affording yields between 56 and 86% of the pure products. It is worth noting that with the exception of **4g** all 8-hydroxyquinoline derivatives were obtained from commercial sources. Compound **4g** was prepared by means of a Suzuki cross-coupling reaction of 8-benzyloxy-5,7-dibromoquinoline and phenylboronic acid in a solvent mixture of toluene, EtOH and water with Na_2CO_3 as a base and $[Pd(PPh_3)_4]$ as catalyst. Removal of the benzyloxy protecting group was achieved by treatment with $BF_3 \cdot Et_2O$ and KI in CH_3CN as reported recently.[13]



Scheme 1. Synthesis of bis[κ²(*C*²,*N*)-2-phenylpyridine][κ²(*N*,*O*)-8-quinolinolato]iridium(III) derivatives **5a**–**5j**.

Compounds **5a**–**5j** were characterised by ^{1}H- and ^{13}C-NMR spectroscopy, absorption and fluorescence measurements as well as matrix-assisted laser desorption ionisation time-of-flight (MALDI-TOF) MS. Furthermore, the thermal behaviour and the impact of ligand modifications on the thermal stability were probed by combined DSC/TGA measurements.

NMR spectroscopy has been shown to be a powerful tool for the characterisation of homo- and heteroleptic iridium(III) complexes.[14] Because organoiridium quinolinolate complexes have hitherto rarely been studied,[10,11] we herein present our interpretation and assignment of the proton NMR spectroscopic peaks of **5b** (Figure 1). Based on these results, the interpretation of the NMR spectra of the other studied compounds can also be easily performed as given in the Experimental Section.[11]

As shown in Figure 1 for **5b** in $[D_6]$DMSO, there are considerable differences in the shift values of the protons of the two phenylpyridine ligands resulting from the asymmetrical character of the quinolinolato ligand. Thus, different shifts especially for the protons of Py^6 (δ = 8.39 and 7.59–7.55 ppm), Py^3 (8.21 and 8.16 ppm) and Py^5 (7.30 and 7.10 ppm) can be observed. Less drastic differences may be found for the protons of the phenyl rings. While the peaks of Ph^6 are located at low-field around 7.91–7.80 ppm, the peaks for Ph^5 (6.93–6.87 ppm), Ph^4 (6.79 and 6.74 ppm) and Ph^3 (6.26 and 6.11 ppm) are shifted towards higher fields with an increased proximity to the metalation centre. For the quinolinolato ligand, the protons of Q^4, Q^6, Q^2 and Q^3 are located at 8.35, 7.74, 7.71 and 7.59–7.55 ppm, respectively. It is worth noting that for these complexes metalation causes a shift to higher-fields for Q^2, while for other metal complexes of quinolinolates, e.g. for organoboron quinolinolates, significantly higher shift-values are obtained.[9d]

For the corresponding carbon NMR spectra, similar results caused by the asymmetrical character of the quinolinolato ligand can be found for **5b** in $[D_6]$DMSO. Consequently, slightly different shift-values were obtained for all

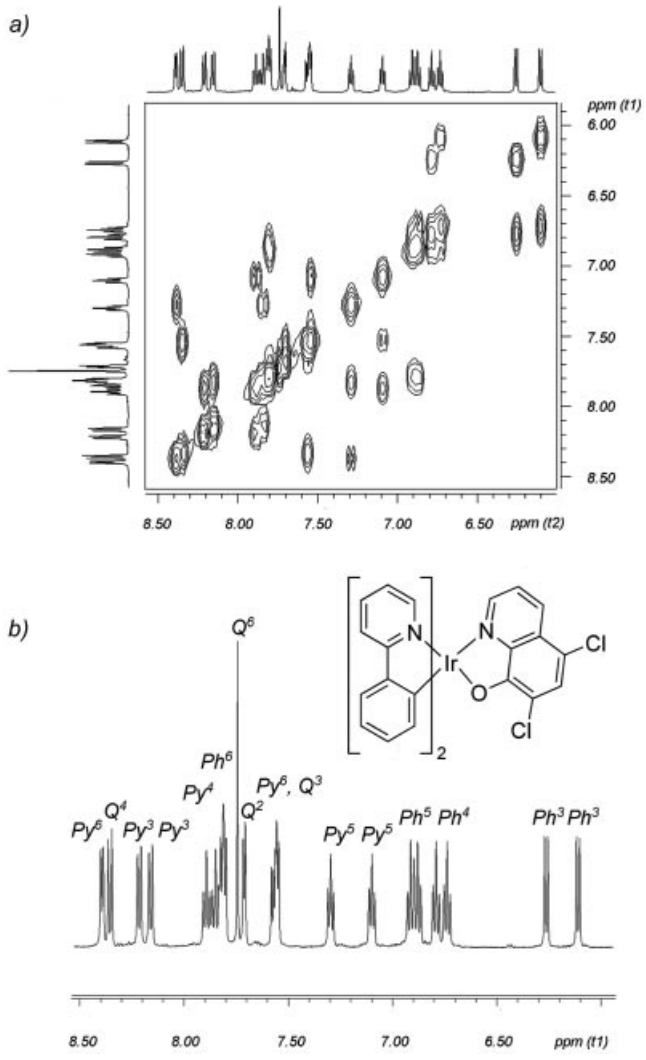


Figure 1. a) H,H-COSY NMR spectrum of **5b** and b) assignment of the ^{1}H NMR spectroscopic peaks based on the proton-correlation experiment (spectra recorded in [D$_6$]DMSO).

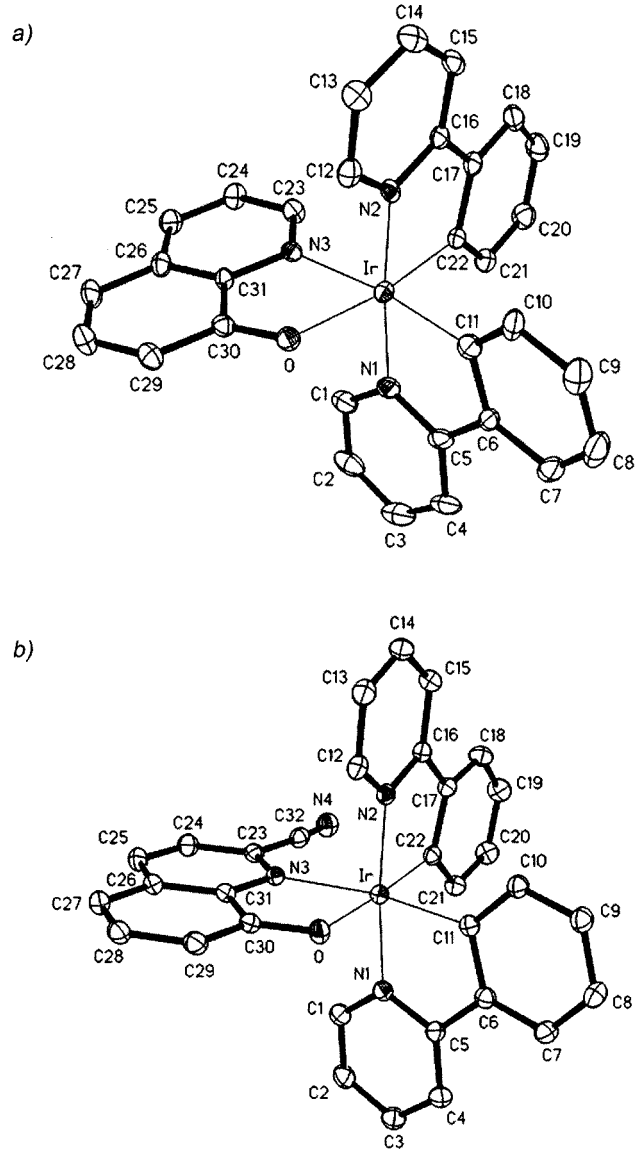


Figure 2. Structural views of a) **5a** and b) **5h** (40% ellipsoids, H atoms and cocrystallised diethyl ether in **5h** omitted). Key bond lengths and angles are given in Table 1.

carbon atoms of the phenylpyridine ligands as they are listed in the Experimental Section. For the other compounds under investigation, no unexpected NMR spectroscopic features were observed and all spectra are in accordance with the proposed structures.[11]

To further confirm the structural identities of the described organoiridium quinolinolate complexes, we tried to grow single-crystals from ether diffusion into saturated CH_2Cl_2 solutions and by layering CH_2Cl_2 solutions with *n*-pentane. Although all complexes could be crystallised by these methodologies, single-crystals suitable for X-ray diffraction were obtained only for **5a**, **5c**,[11a] **5g**,[11a] **5h** and **5j**.[11b] Structural views of the complexes **5a** and **5h** are shown in Figure 2. Key bond lengths and angles for all five complexes are shown for comparison in Table 1.

In all complexes the iridium exhibits a moderately distorted octahedral coordination environment with relatively uniform bond lengths and angles with mean bond lengths of 2.000(8) Å for the Ir–C distance, 2.037(8) Å for the Ir–

Table 1. Comparison of key bond lengths [Å] and angles [°] in the solid-state structures of **5a**, **5c**, **5g**, **5h** and **5j**.

	5a[a]	**5c**[b,c]	**5g**[b]	**5h**[a]	**5j**[d]
Ir–N(1)	2.038(5)	2.046(2)	2.045(2)	2.040(3)	2.044(5)
Ir–N(2)	2.020(5)	2.039(2)	2.025(2)	2.038(3)	2.030(5)
Ir–N(3)	2.127(5)	2.137(2)	2.143(2)	2.189(3)	2.131(5)
Ir–C(11)	2.010(6)	2.014(3)	2.008(2)	1.994(3)	1.997(6)
Ir–C(22)	1.996(5)	2.000(3)	1.988(2)	2.005(3)	1.989(6)
Ir–O	2.151(4)	2.163(2)	2.152(2)	2.130(2)	2.181(5)
O–C(30)	1.309(7)	1.293(3)	1.302(3)	1.301(4)	1.266(8)
N(1)–Ir–C(11)	81.0(2)	80.5(1)	80.7(1)	80.7(1)	81.0(3)
N(2)–Ir–C(22)	81.2(2)	80.8(1)	80.8(1)	81.0(1)	80.9(3)
N(3)–Ir–O	78.3(2)	77.5(1)	77.1(1)	77.7(1)	76.8(2)
C(11)–Ir–C(22)	91.9(2)	88.9(1)	85.9(1)	88.7(1)	88.0(2)
N(1)–Ir–N(2)	174.4(2)	175.1(1)	174.3(1)	174.4(1)	174.5(2)

[a] This work. [b] Data from the literature.[11a] [c] Mean values of two independent Ir complexes. [d] Data from the literature.[11b]

$N_{pyridine}$ distance, 2.145(22) Å for the Ir–$N_{quinoline}$ distance and 2.155(17) Å for the Ir–O distance. Characteristic for all complexes is that the two carbon ligands are in a *cis* disposition and that the 2-phenylpyridine nitrogen atoms are in a *trans* disposition. No indication for a reversal of this geometry was found and this is consistent with related bis(phenylpyridine)(acetylacetonato)iridium(III) [$ppy_2Ir(acac)$] complexes or similar compounds for which no bond breaking or spatial rearrangement of the phenylpyridine ligands was observed during complex formation from the precursor **3**.[4d,4e] Compared with the O–Ir–O bite angles of the acetylacetonato complexes, the N–Ir–O bite angles of the quinolinato complexes are systematically smaller by about 5°.

Whereas the quinolinato ligands are in all cases practically perfectly planar, the 2-phenylpyridine ligands occasionally show larger deviations from planarity by being either curved or twisted, e.g. in **5a** or **5g**,[11a] due to crystal packing effects. In the case of **5h** it is interesting to note that the 2-cyano group is in close intramolecular contact with the second 2-phenylpyridine ligand showing π-π interactions with comparatively short distances of C(32)–C(22) 3.112 Å and N(4)–C(21) 3.259 Å. This contact appears to be responsible for the slightly aberrant Ir–N(3) and Ir–O bond lengths of **5h** (Table 1).

To determine the thermal stabilities of **5a**–**5j**, heat flux DSC/TGA measurements were performed. For practical applications such as in OLEDs, materials with good thermal stabilities are very desirable due to the resultant improved device lifetimes.[15] For comparison of the compounds under investigation, a weight loss of 5% was chosen as a measure for the thermal stability. As depicted in Figure 3 and summarised in Table 2, a significant impact on the corresponding thermal stabilities can be observed as a result of ligand modifications.

While the unmodified organoiridium quinolinolate complex **5a** exhibits a 5% weight-loss at 136 °C,[11] the halogen-substituted derivatives **5b**–**5d** show noticeably increased thermal stabilities with temperature values of 380 °C, 347 °C and 328 °C, respectively.[11] Note that the thermal stabilities of the complexes **5b**–**5d** increase within the series I < Br < Cl which is presumably a result of steric effects of the halogen substituents. Also, for the alkyl and aryl-substituted derivatives **5e**–**5g**, a considerably higher thermal stability can be observed. While **5g** bearing phenyl rings at the 5 and 7 positions of the quinolinolato ligand shows only a slightly increased temperature value for a 5% weight loss at 211 °C, the 2-methyl- and 5,7-dimethyl-substituted derivatives **5e** and **5f** are thermally stable up to 380 and 357 °C, respectively. The most striking impact on the thermal properties is exhibited by **5h** with a weight loss of 5% at 422 °C. As reported recently,[11] significantly increased thermal stabilities compared with **5a** are also found for the formyl- and nitro-substituted derivatives **5i** and **5j** at 354 and 395 °C, respectively.

From these data, the significant influence of ligand modifications on the thermal stabilities of the organoiridium(III) complexes becomes evident. While electron-donating as well as electron-withdrawing groups improve the thermal properties of this class of materials, the cyano substituent in position 2 of the quinolinolato ligand causes the highest thermal stability.

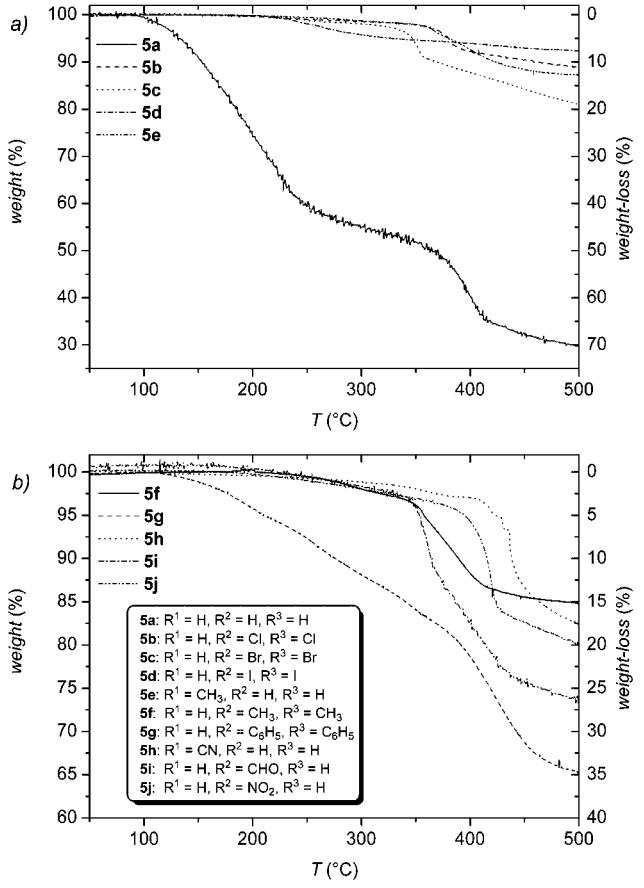


Figure 3. TGA runs of a) compounds **5a**–**5e** and b) **5f**–**5j** indicate increased thermal stability compared with **5a**.

Table 2. Temperatures at 5% weight loss $T_{5\%}$, absorption wavelengths λ_{abs}, molecular coefficients of extinction ε, emission wavelengths λ_{em} in solution and emission wavelengths λ_{77K} of films recorded at 77 K. Note that the spectra of **5a**, **5c**, **5g**, **5i** and **5j** have already been communicated elsewhere.[11]

	$T_{5\%}$ /°C	λ_{abs} (ε) /nm ($L\ mol^{-1}\ cm^{-1}$)	λ_{em} (λ_{77K}) /nm
5a	136	258.9 (53200)	– (640)
5b	380	252.0 (52600)	– (664)[c]
5c	347	254.0 (54070)	– (658)[c]
5d	328	263.0 (42230)[a]	– (654)[c]
5e	380	272.0 (22190)[a]	– (647)
5f	357	270.0 (39070)	521 (–)
5g	211	264.0 (51030)	– (680)
		299.9 (43830)[a]	
5h	422	263.9 (54670)[b]	– (–)
5i	354	261.0 (52960)	603, 645 (602, 655)
		427.0 (11750)	
5j	39	266.0 (69060)	670[d] (623, 678)
	5	459.0 (34270)	

[a] Broad absorption peak. [b] The onset of absorption is significantly red-shifted to approximately 615 nm. [c] The emission intensity is decreased presumably because of the heavy-atom effect. [d] Broad emission peak.

To investigate the photophysical properties of the studied compounds (see Table 2), UV/Vis absorption and photoluminescence (PL) spectra were recorded in dilute solutions of $CHCl_3$ at room temperature. In Figure 4 the UV/Vis absorption spectra of **5a**–**5j** are shown. The complexes **5a**–**5g** exhibit comparably weak absorption bands in the range of approximately 530 to 350 nm which can be assigned to spin-allowed and spin-forbidden metal–ligand charge transfer (MLCT) transitions. Significantly stronger absorption peaks resulting from π-π* transitions can be found in the higher energy region around 250 nm for all complexes.

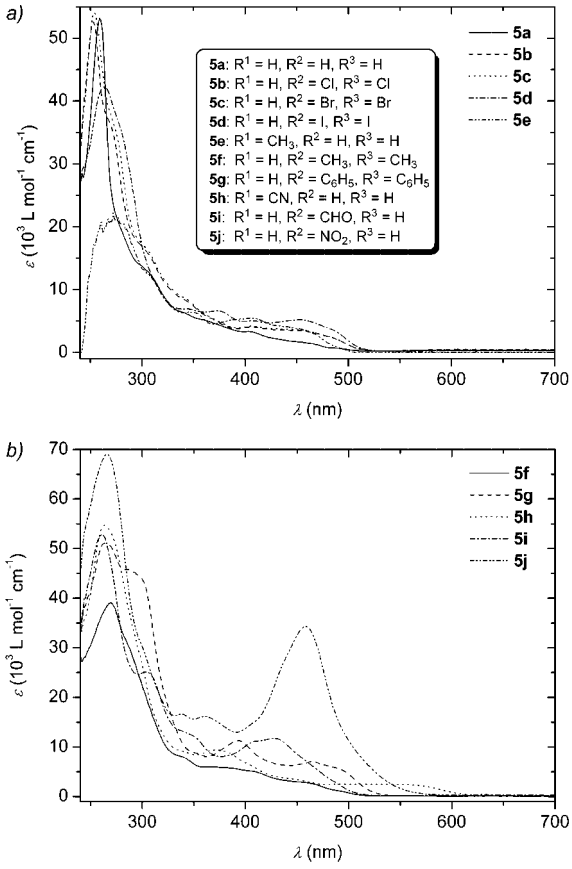


Figure 4. Absorption spectra of a) compounds **5a**–**5e** and b) **5f**–**5j** recorded in dilute $CHCl_3$ solutions.

Although the cyano, formyl and nitro modified compounds **5h**–**5j** exhibit, in general, the same spectroscopic features, the corresponding functional groups lead to additional absorption bands. Whereas for **5h** a shift of the onset of absorption towards longer wavelengths can be observed (i.e. approx. 615 nm), **5i** and **5j** feature distinct new absorption bands at 427 and 459 nm, respectively.

For practical applications, iridium(III) complexes with emission properties controlled by the "ancillary ligand" are desirable. Although this description can be frequently found in the literature, it is important to note that in such compounds this ligand is certainly not ancillary and therefore this term should be avoided. In any case, only a few successful examples of heteroleptic iridium(III) complexes with photophysical properties controlled by the third ligand have been reported.[4] Organoiridium quinolinolate complexes are known to be red phosphorescent emitter materials and thus the emission characteristics are dominated by the quinolinolato ligand.[10,11] From this point of view it is surprising that a systematic investigation of the impact of ligand modifications on the emission characteristics is missing since there is a significant demand for phosphorescent materials with easily tuneable photophysical properties.

To study the photoluminescence of the compounds under investigation, we tried to record the corresponding PL spectra of dilute $CHCl_3$ solutions at room temperature in aerated as well as degassed solutions (Figure 5). Among the studied complexes only **5f**, **5i** and **5j** gave weak photoluminescence with quantum yields (Φ) smaller than 1% (apparent lifetimes at room temperature $\tau = 3 \pm 1$ μs for **5f** and 20 ± 4 μs for **5i** and **5j**)[11] while the other compounds were not found to be luminescent in solution (even in degassed solutions) indicating an unfavourable mixing of singlet and triplet excited states for these complexes when compared with, for example, $ppy_2Ir(acac)$ ($\Phi = 34\%$; $\tau = 1.6$ μs).[4]

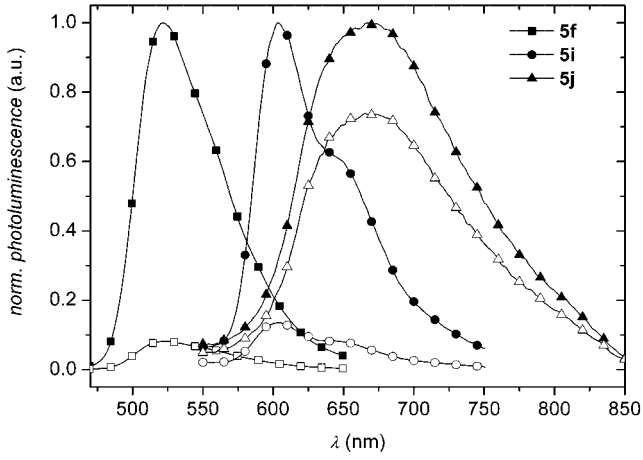


Figure 5. Photoluminescence spectra of **5f**, **5i** and **5j** in aerated (open symbols) and degassed (filled symbols) $CHCl_3$ solutions.

As depicted in Figure 5, significantly different emission wavelengths were achieved with these three luminescent compounds. While **5f** exhibits its emission maximum at 521 nm (λ_{exc} = 390 nm), a structured PL spectrum with the maximum at 603 nm and a shoulder at 645 nm (λ_{exc} = 400 nm) may be obtained for **5i**. Compound **5j** gave the most red-shifted spectrum displaying a broad and unstructured emission band peaking at 670 nm (λ_{exc} = 450 nm). Although most of the studied materials were not luminescent in solution, film spectra of the organoiridium quinolinolate complexes blended into polystyrene were recorded at room temperature and also after cooling with liquid nitrogen to 77 K. With the exception of **5f** and **5h**, all compounds were found to be weakly luminescent in the red spectroscopic region at room temperature. However, cooling the samples gave slightly increased luminescence intensities (see Table 2 and Supporting Information).

From these data a striking impact of the ligand modifications on the emission properties becomes evident. While the

5-formyl- and 5-nitro-substituted complexes emit orange to red light dominated by the quinolinolato ligand in solution, the 5,7-dimethyl derivative gives greenish phosphorescence which is very similar to $ppy_2Ir(acac)$ suggesting a phenylpyridine governed emission in this case [for comparison, green-emitting $ppy_2Ir(acac)$ exhibits its emission maximum at 516 nm].[4c,4d] To further support this hypothesis, the photophysical properties of tris[κ^2(*N*,*O*)-5,7-dimethyl-8-quinolinolato]iridium(III) were investigated.[10b] From the corresponding emission spectrum peaking around 695 nm (see Supporting Information) a phenylpyridine-centred emission for **5f** can be concluded.

The luminescent compounds **5f**, **5i** and **5j** as well as **5a**, **5b**, **5c** and **5h** were tested as emitting materials in OLEDs using various host materials. As communicated recently, efficient light-emitting diodes were obtained from **5i** and **5j**. For example, a maximum luminance of 940 cd m^{-2} was obtained at 13 V for diodes containing 1 wt.-% of **5i** in poly(vinylcarbazole) (PVK) as the host material.[11b] In contrast, attempts to prepare OLEDs from **5a**, **5b**, **5c**, **5f** and **5h** were unsuccessful. Similar to the above mentioned diodes built from **5i**, the herein studied complexes were investigated as the emitting guest using PVK as the host (1 wt.-% complex loading). OLEDs of the configuration ITO/PEDOT:PSS/host-guest emitting layer/Ca/Al gave weak electroluminescence at wavelengths similar to those listed in Table 2 for the 77 K measurements, with low luminescence intensities of 0.8–10 cd m^{-2} at comparably high turn on voltages of more than 8 V (see Supporting Information). These findings distinctly underline the importance of introducing an electron-withdrawing group in the 5-position of the quinolinolato for obtaining efficient OLEDs. In these cases (i.e. **5i** and **5j**) the additional absorption bands with high extinction coefficients in the blue region are beneficial for providing efficient Förster energy transfer from the blue emitting host material. At the same time, the electron-withdrawing groups offer appropriate energy level tuning[11b] so that endothermic Dexter triplet energy back transfer from the phosphorescent iridium complex to the host material is prevented.[16]

Conclusions

Herein we have reported the synthesis, structure, thermal stabilities and photophysical properties of a rarely studied class of materials, namely derivatives of bis[κ^2(*C*^{2},*N*)-2-phenylpyridine][κ^2(*N*,*O*)-8-quinolinolato]iridium(III). Photophysical measurements revealed only minor changes in the absorption characteristics for most derivatives except that bearing electron-withdrawing groups in the 5-position of the quinolinolato ligand. These complexes exhibit absorption features with comparably high extinction coefficients in the visible suitable for finding appropriate host materials for OLED applications.[11] Only the 5-formyl, 5-nitro and 5,7-dimethyl derivatives were found to be luminescent in solution, whereas measurements at 77 K showed red photoluminescence in the solid state for most compounds under investigation. While in the case of **5f** the quinolinolate is rather a spectator ligand similar to acac and emission originates from the ppy_2Ir fragment, the emissions of **5a**–**5e**, **5g**, **5i** and **5j** are quinolinolato-dominated. From the corresponding film measurements, PL spectra in degassed solutions and comparison with the photophysical properties of tris[κ^2(*N*,*O*)-8-quinolinolato]iridium(III) derivatives (see Supporting Information),[10b] an unfavourable mixing of singlet and triplet excited states of these complexes can be concluded rendering most of the described compounds insufficiently luminescent for typical OLED applications. With this information, the rational design of (electro-)luminescent iridium complexes bearing quinolinolato ligands has been revealed and further easily accessible iridium complexes based on 5-electron acceptor-substituted quinolinolato ligands can be foreseen to enter the stage of (electro)luminescent emitter materials.

Experimental Section

General: Unless otherwise noted, materials were obtained from commercial sources (Aldrich, Fluka or Lancaster) and were used without further purification. Solvents for reactions were freshly distilled from appropriate drying agents prior to use (ee = ethyl acetate, cy = cyclohexane). Reactions were carried out under an inert atmosphere of Ar using standard Schlenk techniques. ^{1}H NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer at 500 MHz and ^{13}C{^{1}H} NMR spectra were recorded at 125 MHz. Assignment of the peaks was carried out by DEPT and COSY NMR spectroscopy. Residual solvent peaks were used for referencing the NMR spectra to the corresponding values given in the literature.[17] UV/Vis absorption spectra were recorded on a Cary 50 Bio UV/Vis spectrophotometer and fluorescence spectra on a Perkin–Elmer luminescence spectrometer LS50B. MALDI-TOF mass spectra were recorded on a Micromass TofSpec 2E. The instrument was equipped with a nitrogen laser (337 nm wavelength, operated at a frequency of 5 Hz) and a time lag focusing unit. Spectra were taken in reflection mode at an accelerating voltage of +20 kV. Analysis of data was done with MassLynx 3.4 (Micromass, Manchester, UK). Samples were dissolved in THF (1 mg mL^{-1}). Dithranol or retinoic acid was used as the matrix (10 mg mL^{-1} in THF). Solutions were mixed in the cap of a microtube in the ratio of 1 μL:10 μL. Then, 0.5 μL of the resultant mixture was spotted onto the target and air-dried. Combined DSC/TGA measurements were performed with a Netzsch STA 449C instrument equipped with a Quadrupole MS QMS 403C or with a Polymer Laboratories simultaneous thermal analyser STA 625 (crucibles: aluminium from Rheometric Scientific). The thermal properties were determined in aluminium pans with a heat rate of 10 °C min^{-1} in a helium flow of approximately 50 mL min^{-1} (Netzsch STA 449C) or a nitrogen flow of 20 mL min^{-1} (Polymer Laboratories simultaneous thermal analyser STA 625).

Di-μ-chloro-tetrakis[κ^2(*C*^{2},*N*)-2-phenylpyridine]diiridium(III) (3): $IrCl_3 \cdot nH_2O$ (**1**, 0.2123 g, 0.711 mmol) was suspended in a mixture of 2-ethoxyethanol (6 mL) and water (2 mL) under Ar. After the addition of 2-phenylpyridine (**2**, 270 μL, 1.889 mmol) the dark brown reaction mixture was stirred for 24 h at 120 °C. The greenish suspension formed was cooled to room temperature and the solvent was removed in vacuo. Washing the residue with hot methanol gave rise to 0.2025 g (53.1%) of a yellow-greenish powder of **3**. NMR spectra were found to be identical with that described in the literature.[11]

General Procedure for the Preparation of Organoiridium Quinolinolate Complexes: For the preparation of **5a**–**5j** 1 equiv. of **3** was suspended with 2.1 to 2.5 equiv. of the corresponding 8-hydroxyquinoline derivative **4a**–**4j** in a solvent mixture of degassed CH_2Cl_2/EtOH/Et_3N under Ar and was heated to reflux at 80 °C for 20 h. The solvent was removed in vacuo and the residue was washed with hot methanol. Filtration of the precipitate gave the corresponding product in analytically pure form.

Bis[κ²(C²,*N*)-2-phenylpyridine][κ²(*N*,*O*)-8-quinolinolato]iridium(III) (5a): Compound **5a** was prepared starting from **3** (0.0403 g, 0.038 mmol) and **4a** (0.0126 g, 0.087 mmol) in CH_2Cl_2 (1 mL), EtOH (1 mL) and Et_3N (300 μL) giving 0.0379 g (78.2%) of a yellow-orange powder. R_f(acetone) = 0.86. The recorded NMR and MALDI-TOF MS spectra are in accordance with literature data.[11]

[κ²(*N*,*O*)-5,7-Dichloro-8-quinolinolato]bis[κ²(C²,*N*)-2-phenylpyridine]iridium(III) (5b): Complex **5b** was obtained from **3** (0.0509 g, 0.047 mmol) and **4b** (0.0214 g, 0.100 mmol) in CH_2Cl_2 (2 mL), EtOH (1 mL) and Et_3N (300 μL) yielding 0.0459 g (67.7%) of an orange solid. R_f(cy:ee = 3:1) = 0.27. ^{1}H NMR ([D$_6$]DMSO, 500 MHz): δ = 8.39 (d, J = 5.9 Hz, 1 H, *Py*^{6}), 8.35 (d, J = 8.8 Hz, 1 H, *Q*^{4}), 8.21 (d, J = 7.8 Hz, 1 H, *Py*^{3}), 8.16 (d, J = 8.3 Hz, 1 H, *Py*^{3}), 7.91–7.80 (m, 4 H, *Py*^{4}, *Ph*^{6}), 7.74 (s, 1 H, *Q*^{6}), 7.71 (d, J = 4.9 Hz, 1 H, *Q*^{2}), 7.59–7.55 (m, 2 H, *Py*^{6}, *Q*^{3}), 7.30 (t, J = 7.3 Hz, 1 H, *Py*^{5}), 7.10 (t, J = 7.3 Hz, 1 H, *Py*^{5}), 6.93–6.87 (2 t, J = 7.3 Hz, 2 H, *Ph*^{5}), 6.79 (t, J = 7.3 Hz, 1 H, *Ph*^{4}), 6.74 (t, J = 7.3 Hz, 1 H, *Ph*^{4}), 6.26 (d, J = 7.3 Hz, 1 H, *Ph*^{3}), 6.11 (d, J = 7.3 Hz, 1 H, *Ph*^{3}) ppm. ^{13}C NMR ([D$_6$]DMSO, 125 MHz): δ = 167.8, 167.0 (2 C, *Py*^{2}), 164.3 (1 C, *Q*^{8}), 150.7, 148.4 (2 C, *Ph*^{2}), 148.2, 147.4, 147.3 (3 C, *Py*^{6}, *Q*^{2}), 144.7, 144.3, 143.7 (3 C, *Ph*^{1}, *Q*^{8a}), 138.0, 134.0, 134.0, 132.0, 131.7, 129.7, 129.4, 129.0, 124.7, 124.3, 123.8, 123.3, 123.0, 121.1, 120.9, 119.4, 119.3 (17 C, *Ph*^{3,4,5,6}, *Py*^{3,4,5}, *Q*^{3,4,6}), 127.2 (1 C, *Q*^{4a}), 118.8 (1 C, *Q*^{5}), 110.7 (1 C, *Q*^{7}) ppm. HRMS: calcd. for $C_{31}H_{20}Cl_2IrN_3O$ 711.0590; found 711.0631.

[κ²(*N*,*O*)-5,7-Dibromo-8-quinolinolato]bis[κ²(C²,*N*)-2-phenylpyridine]iridium(III) (5c): The dibromo complex **5c** was synthesised from **3** (0.0520 g, 0.049 mmol) and **4c** (0.0293 g, 0.097 mmol) in CH_2Cl_2 (2 mL), EtOH (1 mL) and Et_3N (300 μL). The product was obtained as orange powder in a yield of 0.0599 g (76.9%). R_f(cy:ee = 3:1) = 0.30. NMR and MALDI-TOF MS characterisation of this compound can be found in the literature.[11]

[κ²(*N*,*O*)-5,7-Diiodo-8-quinolinolato]bis[κ²(C²,*N*)-2-phenylpyridine]iridium(III) (5d): Compound **5d** resulted from the reaction of **3** (0.1000 g, 0.093 mmol) with **4d** (0.0820 g, 0.207 mmol) in CH_2Cl_2 (4 mL), EtOH (2 mL) and Et_3N (600 μL). The complex was isolated in a yield of 0.1437 g (85.9%) as a yellow-brownish powder. R_f(cy:ee = 1:1) = 0.72. ^{1}H NMR ([D$_6$]DMSO, 500 MHz): δ = 8.37 (d, J = 5.8 Hz, 1 H, *Py*^{6}), 8.22 (s, 1 H, *Q*^{6}), 8.20 (d, J = 8.3 Hz, 1 H, *Q*^{4}), 8.15–8.12 (2 d, each J = 8.1 Hz, 2 H, *Py*^{3}), 7.88, 7.85–7.78 (dd, 2 × J = 7.8 Hz, 1 H, m, 3 H, *Ph*^{6}, *Py*^{4}), 7.62 (d, J = 4.6 Hz, 1 H, *Q*^{2}), 7.54–7.52 (m, 2 H, *Py*^{6}, *Q*^{3}), 7.29 (dd, 2 × J = 6.6 Hz, 1 H, *Py*^{5}), 7.09 (dd, 2 × J = 6.6 Hz, 1 H, *Py*^{5}), 6.92–6.86 (2 dd, each 2 x J = 7.5 Hz, 2 H, *Ph*^{5}), 6.78 (dd, 2 × J = 7.4 Hz, 1 H, *Ph*^{4}), 6.73 (dd, 2 × J = 7.4 Hz, 1 H, *Ph*^{4}), 6.22 (d, J = 7.5 Hz, 1 H, *Ph*^{3}), 6.11 (d, J = 7.5 Hz, 1 H, *Ph*^{3}) ppm. ^{13}C NMR ([D$_6$]DMSO, 125 MHz): δ = 169.4 (1 C, *Q*^{8}), 167.7, 167.0 (2 C, *Py*^{2}), 150.9, 148.5 (2 C, *Ph*^{2}), 148.1, 147.2, 147.2, 146.1 (4 C, *Py*^{6}, *Q*^{2,6}), 144.6, 144.2 (2 C, *Ph*^{1}), 142.1 (1 C, *Q*^{8a}), 140.9, 138.0, 137.9, 132.0, 131.6, 129.6, 129.1, 124.7, 124.6, 124.3, 123.2, 123.0, 121.0, 120.9, 119.4, 119.3 (16 C, *Ph*^{3,4,5,6}, *Py*^{3,4,5}, *Q*^{3,4}), 132.2 (1 C, *Q*^{4a}), 86.7 (1 C, *Q*^{5}), 74.3 (1 C, *Q*^{7}) ppm. HRMS: calcd. for $C_{31}H_{20}I_2IrN_3O$ 894.9302; found 894.9327.

[κ²(*N*,*O*)-2-Methyl-8-quinolinolato]bis[κ²(C²,*N*)-2-phenylpyridine]iridium(III) (5e): Complex **5e** was synthesised from **3** (0.0722 g, 0.067 mmol) and **4e** (0.0256 g, 0.161 mmol) in CH_2Cl_2 (4 mL), EtOH (2 mL) and Et_3N (600 μL). The orange solid was isolated in a yield of 0.0669 g (75.4%). R_f(cy:ee = 1:1) = 0.23. ^{1}H NMR ([D$_6$]-DMSO, 500 MHz): δ = 8.48 (d, J = 5.6 Hz, 1 H, *Py*^{6}), 8.18 (d, J = 8.1 Hz, 1 H, *Py*^{3}), 8.13 (d, J = 8.1 Hz, 1 H, *Py*^{3}), 8.11 (d, J = 8.5 Hz, 1 H, *Q*^{4}), 7.86, 7.83–7.81, 7.77, 7.74 (dd, 2 × J = 7.9 Hz, 1 H, m, 2 H, d, J = 7.8 Hz, 1 H, d, J = 7.8 Hz, 1 H, *Ph*^{6}, *Py*^{4,6}), 7.25–7.19 (m, 3 H, *Py*^{5}, *Q*^{3,6}), 7.10 (dd, 2 × J = 6.7 Hz, 1 H, *Py*^{5}), 6.83 (dd, 2 × J = 7.3 Hz, 1 H, *Ph*^{5}), 6.79 (dd, 2 × J = 7.3 Hz, 1 H, *Ph*^{5}), 6.74 (d, J = 7.8 Hz, 1 H, *Q*^{5}), 6.68–6.65 (m, 3 H, *Ph*^{4}, *Q*^{7}), 6.25 (d, J = 7.5 Hz, 1 H, *Ph*^{3}), 5.91 (d, J = 7.5 Hz, 1 H, *Ph*^{3}), 2.00 (s, 3 H, *Q*-*CH*$_3$) ppm. ^{13}C NMR ([D$_6$]DMSO, 125 MHz): δ = 169.6, 167.9, 167.5 (3 C, *Py*^{2}, *Q*^{8}), 158.1, 153.5, 149.2 (3 C, *Ph*^{2}, *Q*^{2}), 148.8, 147.5 (2 C, *Py*^{6}), 144.2, 143.7, 143.4 (3 C, *Ph*^{1}, *Q*^{8a}), 138.1, 137.4, 137.4, 132.4, 130.9, 129.3, 128.8, 128.7, 124.7, 123.9, 123.7, 123.1, 122.0, 120.9, 119.7, 119.3, 118.8, 116.2 (18 C, *Ph*^{3,4,5,6}, *Py*^{3,4,5}, *Q*^{3,4,5,6}), 129.8 (1 C, *Q*^{4a}), 110.1 (1 C, *Q*^{7}), 26.9 (1 C, *Q*-*CH*$_3$) ppm. HRMS: calcd. for $C_{32}H_{24}IrN_3O$ 657.1525; found 657.1474.

[κ²(*N*,*O*)-5,7-Dimethyl-8-quinolinolato]bis[κ²(C²,*N*)-2-phenylpyridine]iridium(III) (5f): The dimethyl complex **5f** was prepared starting from **3** (0.1006 g, 0.094 mmol) and **4f** (0.0362 g, 0.209 mmol) in CH_2Cl_2 (4 mL), EtOH (2 mL) and Et_3N (600 μL). The product was obtained as dark orange solid in a yield of 0.1038 g (82.2%). R_f(cy:ee = 1:1) = 0.56. ^{1}H NMR ([D$_6$]DMSO, 500 MHz): δ = 8.54 (d, J = 5.6 Hz, 1 H, *Py*^{6}), 8.18–8.17 (2 d, each J = 7.8 Hz, 2 H, *Py*^{3}), 8.10 (d, J = 8.3 Hz, 1 H, *Q*^{4}), 7.86, 7.79–7.76 (dd, 2 × J = 7.3 Hz, 1 H, m, 3 H, *Ph*^{6}, *Py*^{4}), 7.58 (d, J = 4.4 Hz, 1 H, *Q*^{2}), 7.51 (d, J = 5.6 Hz, 1 H, *Py*^{6}), 7.30–7.27 (dd, J = 8.5 Hz, J = 4.5 Hz, 1 H, *Q*^{3}), 7.22 (dd, 2 × J = 6.5 Hz, 1 H, *Py*^{5}), 7.19 (s, 1 H, *Q*^{6}), 7.07 (dd, 2 × J = 6.6 Hz, 1 H, *Py*^{5}), 6.89–6.83 (2 dd, each 2 × J ≈ 7.3 Hz, 2 H, *Ph*^{5}), 6.77 (dd, 2 × J ≈ 7.2 Hz, 1 H, *Ph*^{4}), 6.71 (dd, 2 × J ≈ 7.2 Hz, 1 H, *Ph*^{4}), 6.28 (d, J = 7.3 Hz, 1 H, *Ph*^{3}), 6.14 (d, J = 7.3 Hz, 1 H, *Ph*^{3}), 2.46 (s, 3 H, *Q*^{5}-*CH*$_3$), 2.25 (s, 3 H, *Q*^{7}-*CH*$_3$) ppm. ^{13}C NMR ([D$_6$]DMSO, 125 MHz): δ = 168.0, 167.3 (2 C, *Py*^{2}), 165.3 (1 C, *Q*^{8}), 152.8, 151.3 (2 C, *Ph*^{2}), 147.7, 147.4, 145.0 (3 C, *Py*^{6}, *Q*^{2}), 144.6, 144.4 (2 C, *Ph*^{1}), 142.6 (1 C, *Q*^{8a}), 137.5, 137.4, 134.0, 132.8, 132.1, 131.7, 129.5, 128.8, 124.5, 124.2, 122.9, 122.5, 120.6, 120.5, 120.4, 119.2, 118.9 (17 C, *Ph*^{3,4,5,6}, *Py*^{3,4,5}, *Q*^{3,4,6}), 128.0 (1 C, *Q*^{4a}), 123.8 (1 C, *Q*^{5}), 115.0 (1 C, *Q*^{7}), 16.9, 16.7 (2 C, *Q*^{5}-*CH*$_3$, *Q*^{7}-*CH*$_3$) ppm. HRMS: calcd. for $C_{33}H_{26}IrN_3O$ 671.1682; found 671.1752.

[κ²(*N*,*O*)-5,7-Diphenyl-8-quinolinolato]bis[κ²(C²,*N*)-2-phenylpyridine]iridium(III) (5g): The diphenyl-substituted compound **5g** was obtained from **3** (0.0930 g, 0.087 mmol) and **4g** (0.0500 g, 0.168 mmol) in CH_2Cl_2 (3 mL), EtOH (2 mL) and Et_3N (300 μL) giving 0.0768 g (55.5%) of a yellow-orange powder. R_f(cy:ee = 1:1) = 0.77. NMR and MALDI-TOF MS spectra were found to be in accordance with literature.[11]

[κ²(*N*,*O*)-2-Cyano-8-quinolinolato]bis[κ²(C²,*N*)-2-phenylpyridine]iridium(III) (5h): Compound **5h** resulted from reacting **3** (0.0497 g, 0.046 mmol) with **4h** (0.0183 g, 0.108 mmol) in CH_2Cl_2 (2 mL), EtOH (1 mL) and Et_3N (300 μL). From this complex 0.0468 g (75.4%) could be isolated as deeply red solid. R_f(acetone) = 0.9. ^{1}H NMR ([D$_6$]DMSO, 500 MHz): δ = 8.39 (d, J = 8.5 Hz, 1 H, *Q*^{4}), 8.31 (d, J = 5.6 Hz, 1 H, *Py*^{6}), 8.19 (d, J = 8.3 Hz, 1 H, *Py*^{3}), 8.15 (d, J = 8.3 Hz, 1 H, *Py*^{3}), 7.90 (ddd, 2 × J = ca. 7.8 Hz, J = 1.2 Hz, 1 H, *Py*^{4}), 7.85–7.82 (m, 2 H, *Py*^{4,6}), 7.77 (d, J = 7.8 Hz, 1 H, *Ph*^{6}), 7.74 (d, J = 7.8 Hz, 1 H, *Ph*^{6}), 7.69 (d, J = 8.5 Hz, 1 H, *Q*^{3}), 7.51 (dd, 2 × J = 7.8 Hz, 1 H, *Q*^{6}), 7.21–7.18 (ddd, 2 × J ≈

6.6 Hz, J = 1.2 Hz, 1 H, Py^5), 7.12–7.10 (ddd, $2\times J \approx 6.6$ Hz, J = 1.2 Hz, 1 H, Py^5), 6.90, 6.87–6.82 (dd, J = 7.8 Hz, $J \approx 1$ Hz, 1 H, m, 2 H, Ph^5, $Q^{5,7}$), 6.80–6.77 (ddd, $2\times J$ = ca. 7.2 Hz, J = 1.2 Hz, 1 H, Ph^5), 6.71–6.68 (ddd, $2\times J \approx 6.8$ Hz, J = 1.2 Hz, 1 H, Ph^4), 6.64–6.61 (ddd, $2\times J \approx 6.8$ Hz, J = 1.2 Hz, 1 H, Ph^4), 6.20 (d, J = 7.6 Hz, 1 H, Ph^3), 5.93 (d, J = 7.6 Hz, 1 H, Ph^3) ppm. ^{13}C NMR ([D$_6$]DMSO, 125 MHz): δ = 170.6, 168.1, 167.1 (3 C, Py^2, Q^8), 150.5, 147.6 (2 C, Ph^2), 149.0, 147.4 (2 C, Py^6), 144.2, 144.0, 143.8 (3 C, Ph^1, Q^{8a}), 138.8, 138.0, 137.9, 132.7, 132.7, 131.2, 129.4, 128.9, 126.5, 124.7, 124.0, 123.4, 122.1, 121.3, 120.6, 119.5, 119.0, 118.2 (18 C, $Ph^{3,4,5,6}$, $Py^{3,4,5}$, $Q^{3,4,5,6}$), 132.1 (1 C, Q^2), 129.4 (1 C, Q^{4a}), 114.8 (1 C, *Q-CN*), 110.3 (1 C, Q^7) ppm. HRMS: calcd. for $C_{32}H_{21}IrN_4O$ 668.1321; found 668.1302.

[κ²(*N*,*O*)-5-Formyl-8-quinolinolato]bis[κ²(C²,*N*)-2-phenylpyridine]-iridium(III) (5i): The recently reported complex **5i** was synthesised from **3** (0.0500 g, 0.047 mmol) and **4i** (0.0184 g, 0.106 mmol) in CH_2Cl_2 (2 mL), EtOH (1 mL) and Et_3N (300 μL) yielding 0.0474 g (75.5%) of an orange solid. R_f(acetone) = 0.88. NMR and MALDI-TOF MS characterisation can be found in the literature.[11]

[κ²(*N*,*O*)-5-Nitro-8-quinolinolato]bis[κ²(C²,*N*)-2-phenylpyridine]-iridium(III) (5j): The nitro complex **5j** was prepared from **3** (0.1010 g, 0.094 mmol) and **4j** (0.0446 g, 0.235 mmol) in CH_2Cl_2 (4 mL), EtOH (2 mL) and Et_3N (600 μL). The deeply red product was isolated in a yield of 0.1091 g (84.0%). R_f(cy:ee = 1:1) = 0.57. NMR and MALDI-TOF MS spectra have been reported in the literature.[11]

Crystal Structure Determinations of 5a and 5h: X-ray data of **5a** and **5h** (in the form of the diethyl ether solvate **5h**·0.5 $C_4H_{10}O$) were collected on a Bruker Smart APEX CCD area detector diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and 0.3° ω-scan frames. Corrections for absorption, $\lambda/2$ effects and crystal decay were applied.[18] After structure solution with SHELXS-97, refinement on F^2 was carried out with SHELXL-97.[19] Non-hydrogen atoms were refined anisotropically. All H atoms were placed in calculated positions and thereafter treated as riding. Salient crystallographic data are:

5a: $C_{31}H_{22}IrN_3O$, M_r = 644.72, brown prism, 0.54 × 0.14 × 0.05 mm, monoclinic, space group $P2_1/n$ (no. 14), a = 11.3945(7) Å, b = 9.2935(6) Å, c = 22.5274(15) Å, β = 93.013(2)°, V = 2382.2(3) Å^3, Z = 4, μ = 5.635 mm^{-1}, T = 100 K. 25068 reflections were collected up to θ_{max} = 30.05° and, after applying absorption corrections, merged to 5486 independent data (R_{int} = 0.050). Final R indices: R_1 = 0.0468 [6859 reflections with $I > 2\sigma(I)$], wR_1 = 0.0943 (all data), 325 parameters.

5h·0.5 $C_4H_{10}O$: $C_{32}H_{21}IrN_4O$·0.5 $C_4H_{10}O$, M_r = 706.79, brown prism, 0.32 × 0.24 × 0.18 mm, monoclinic, space group $P2_1/n$ (no. 14), a = 11.5085(8) Å, b = 19.7715(14) Å, c = 12.5921(9) Å, β = 110.578(1)°, V = 2682.4(3) Å^3, Z = 4, μ = 5.016 mm^{-1}, T = 100 K. 44953 reflections were collected up to θ_{max} = 30.07° and, after applying absorption corrections, merged to 7760 independent data (R_{int} = 0.034). Final R indices: R_1 = 0.0296 [6669 reflections with $I > 2\sigma(I)$], wR_1 = 0.0628 (all data), 371 parameters. A disorder of the solvent in was taken into account.

CCDC-634415 and -634416 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Film measurements, photophysical measurements of tris[κ²(*N*,*O*)-8-quinolinolato]iridium(III) derivatives and OLED characteristics.

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