Cyclometalated red iridium(III) complexes containing carbazolylacetylacetonate ligands: efficiency enhancement in polymer LED devices†

Nan Tian,^{*a,c*} Yaroslav V. Aulin,^{*b*} Daniel Lenkeit,^{*a*} Simon Pelz,^{*a*} Oleksandr V. Mikhnenko,^{*b,c*} Paul W. M. Blom,^{*b,c*} Maria Antonietta Loi*^{*b,c*} and Elisabeth Holder*^{*a,c*}

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The design, synthesis, photophysical and significantly improved electrooptical properties of a series of red emitting cyclometalated iridium(III) complexes containing carbazolylacetylacetonate ligands are described.

Cyclometalated iridium(III) complexes are of major interest in a series of optical applications like organic light-emitting diodes,¹ sensors,² or biomedical imaging applications.³ In all of these applications the favorable and general properties such as high quantum yields, short lifetimes, or color-tunability of the iridium(III) complexes⁴ are in the focus. In red light-emitting diodes one particular interest is the enhancement of luminous and power efficiencies of the heteroleptic iridium(III) complexes while keeping the phosphorescence lifetimes short. One successful strategy is the variation of the iridium(III) triplet emitters by introducing functional groups to potentially enhance the charge recombination at the emitter site and to increase the miscibility with the polymer matrix.

One thriving approach is the use of hole-accepting moieties like carbazolyl functions. In such systems, the ligands have a significant impact on the charge acceptor properties. Directed charge recombination shall avoid recombination at non-emitting sites within the light-emitting device. We anticipated that the presence of carbazolyl moieties in the ancillary ligand will provide a measurable enhancement of the light-emitting efficiency of the complexes while moreover reducing the lifetime but keeping the emission color of the iridium(III) complexes unchanged. In order to keep a deep red emission color the use of 1-phenylisoquinoline cyclometalating ligands should be beneficial.

In this contribution we describe the synthesis of deep red emitting cyclometalated iridium(III) complexes 1 and 2 (Chart 1) by using this design strategy based on carbazolyl-based ancillary ligands and 1-phenylisoquinoline cyclometalating ligands.

These deep red emitting Ir(III) complexes are compared to a very well-known and commonly used iridium dye [(btp)₂Ir(III)(acac)]⁵ (Chart 1) in order to benchmark their properties with respect to application in light-emitting devices. For this, the Ir(III) compounds were mixed in specific ratios into blends of PVK:PBD polymer matrixes. Such active layer blends were utilized determining their favorable photoluminescence and electroluminescence properties, their significantly reduced phosphorescence lifetimes as well as their enhanced luminous efficiencies and power efficiencies.

Neutral, cyclometalated iridium(III) complexes of a heteroleptic architecture were formed using 1-(9*H*-carbazol-9-yl)-5,5-dimethylhexane-2,4-dione (**3**) or 1-(3,6-*bis*(4-hexylphenyl)-9*H*-carbazol-9-yl)-5,5-dimethylhexane-2,4-dione (**4**) as ancillary ligands^{1e,2e} and 1-phenylisoquinoline cyclomatalating ligands. Prior to this, a dimeric μ -chloro-bridged iridium(III) complex carrying 1-phenylisoquinoline ligands was prepared in 78% yield according to previously introduced procedures.^{1e,2e} Ancillary ligand **3** (yield: 62%) or ancillary ligand **4** (yield: 80%) were synthesized according to modified procedures introduced previously^{1e,2e} (Scheme 1) and were subsequently coordinated to the precursor complex. The resulting red light emitting iridium(III) complexes **1** and **2** were obtained in yields of 67% and 72%, respectively.

The intense absorption bands of **1** and **2** below 300 nm were attributed to spin-allowed $\pi \rightarrow \pi^*$ transitions of the cyclometalating ligand 1-phenylisoquinoline (Table 1).

The spin-allowed singlet ¹MLCT transitions were located in the visible part of the spectrum at around 400 nm, these were visible as a shoulder overlapping with the ligand $\pi \rightarrow \pi^*$ transitions. The slight absorptions typically at wavelengths above 400 nm were



Chart 1

^aFunctional Polymers Group and Institute of Polymer Technology, University of Wuppertal, Gaußstr. 20, D-42097, Wuppertal, Germany. E-mail: holder@uni-wuppertal.de; Fax: +49-202-439-3880; Tel: +49-202-439-3879 ^bUniversity of Groningen, Zernike Institute for Advanced Materials, Groningen, The Netherlands. E-mail: M.A.Loi@rug.nl; Fax: +31-50-363-8751; Tel: +31-50-363-4119

^cDutch Polymer Institute (DPI), P.O. Box 513, NL-5600 AX, Eindhoven, The Netherlands

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Table 1Spectroscopic properties of 1 and 2 (see also Fig. S1 and Fig. S2,ESI)

	Absorbance/nm (log $\epsilon/L \text{ mol}^{-1} \text{ cm}^{-1}$)	Maximum of emission/nm	Quantum yield ^a (%)	$T_{d}{}^{b}/^{\circ}C$
1	247 (5.33), 291 (5.20)	624	31	356
2	264 (3.97), 299 (3.98) 359 (3.40), 481 (2.79)	625	30	340

 a Determined according to the method of Demas and Crosby.⁶ b @ 5% weight loss.

reasonable to arise as spin-forbidden triplet ³MLCT excited states. However, the absorptions in the far-UV, at about 270 nm, were found to be most likely due to β -diketonate-based transitions, analogous to the absorptions of the free β -diketone. The phosphorescence of complexes 1 and 2 was obtained at maximum emission wavelengths of 624 nm and 625 nm, correspondingly. Iridium(III) complexes 1 and 2 reveal favorably high quantum yields of 31% and 30%, respectively. Note these high quantum yields were even obtained in aerated chloroform solutions. In addition, 1 and 2 were remarkably temperature stable revealing 5% weight loss at 340 °C and 356 °C, correspondingly.

In order to benchmark the carbazolyl-containing iridium(III) emitters 1 and 2 for their suitability in polymer light-emitting diodes (PLEDs), one needs to compare the new compounds to the commonly used red emitter [(btp), Ir(III)(acac)].⁵ Thus, all of these complexes were doped in a polymer matrix of hole conducting poly(vinylcarbazole) (PVK) and electron conducting oligomer 2-(biphenyl-4-yl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD). The blend ratio of PVK to PBD was kept constant at 70:30 wt.%, respectively, in order to serve as active layers in PLEDs. The dopant ratio was varied from 4 to 16 molecules of 1, 2 and [(btp), Ir(III)(acac)]⁵ per 1000 monomer units of PVK translating to a range of about 1-4 wt.%. The simple benchmarking test device architecture7 for each series of dopants consisted of the following layout: ITO/PEDOT:PSS (60 nm)/active layer (80 nm)/Ba (5 nm)/Al (100 nm). Fig. 1 shows the luminous and power efficiencies as a function of the respective dopant concentration for each series of test devices operating at 10 V. For the whole range of concentrations the novel red emitting and carbazolylcontaining Ir(III) complexes 1 and 2 revealed better luminous efficiencies then the standard red iridium(III) phosphorescent emitter [(btp)₂Ir(III)(acac)].⁵ As depicted in Fig. 1 the best PLED



Fig. 1 Luminous and power efficiencies of **1**, **2** and **[(btp)**₂**Ir(III)(acac)]** as a function of the relative dopant amount in PVK:PBD blends of a 70:30 wt.% ratio (see also Fig. S3, ESI†).

devices were comprised of 8–12 molecules of 1 or 2 per 1000 monomer units of PVK. In these molar concentration ranges both newly designed iridium(III) complexes 1 and 2 revealed a superior luminous efficiency enhancement of about 30% compared to the commonly used triplet emitter [(btp)₂Ir(III)(acac)].⁵ Subsequently, the photophysical properties of the devices active layers were studied. Time resolved photoluminescence measurements were performed exciting the samples with 150 fs pulses at 380 nm, and revealing the decays with a Hamamatsu Streak Camera working in single sweep mode.

The steady state photoluminescence and electroluminescence spectra of compounds **1**, **2** and **[(btp)_2Ir(III)(acac)]**⁵ in the active layers of the devices are shown in Fig. 2. The emission intensity of PVK (not shown) is negligible compared to the emission intensity



Fig. 2 Normalized steady state photoluminescence and electroluminescence spectra of the PLEDs active layers at various dopant compositions.



Scheme 1 Synthetic route to ligand 4 (ligand 3^{2e} is obtained in a similar fashion when starting from 9*H*-carbazole). (i) K₂CO₃, ethyl-2-bromoacetate, DMF, 70 °C, (62%). (ii) KHMDS, 3,3-dimethylbutan-2-one, THF, RT, (80%).

of the triplet emitting compounds **1**, **2** and **[(btp)**₂**Ir**(**III)(acac)]⁵** indicating efficient energy transfer from the PVK matrix to all red triplet emitters. The photoluminescence reveals two maxima at 590 nm and 650 nm, respectively, for both of the compounds **1** and **2**. These emission maxima are 10 nm and 25 nm blueshifted compared to **[(btp)**₂**Ir**(**III)(acac)].⁵** The electroluminescence of the triplet emitter series compounds **1**, **2** and **[(btp)**₂**Ir**(**III)(acac)]⁵ are typically about 40 nm and 20 nm red-shifted for each of the emission maxima compared to the observed photoluminescence spectra. This is a typical finding for systems with a charge trapping mechanism of exciton formation at dopant sites, which are characterized by inhomogeneous broadening of the density of states.⁸ Preferably, the electroluminescence emission spectra of 1**, **2** and **[(btp)**₂**Ir(III)(acac)]**⁵ would be almost congruent in shape.

The observed decay curves were identical for every dopant concentration in the studied range, indicating the absence of concentration quenching. The monoexponential fit curves shown in Fig. 3 reveal decay times of 1.2 μ s for complexes 1 and 2 and 5.1 μ s for [(btp)₂Ir(II)(acac)].⁵ Thus, the phosphorescence decay times of the newly designed triplet emitters 1 and 2 are significantly shorter making them thus attractive candidates in advanced light-emitting diode applications.



Fig. 3 Normalized phosphorescence decays of **1**, **2** and **[(btp)_2Ir(III)(acac)]** in PVK:PBD blends with a 70:30 wt.% ratio.

In summary, we prepared newly designed, red emitting, carbazolyl-containing cyclometalated iridium(III) emitters that were compared to a commonly used reference emitter. The introduced triplet emitters revealed excellent performance in benchmarking devices and are additionally furnished with preferably

short phosphorescence lifetimes making them promising lightemitting candidates for a series of applications in advanced organic and polymer light-emitting devices.

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