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ACCEPTED MANUSCRIPT The synthesis of brominated heteroleptic *tris*-cyclometallated Ir(III)-complexes as photoactive building blocks on polyaryl backbones.

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Abstract: Luminescent facial *tris*-cyclometallated iridium complexes of generic structure $Ir(L)_2(dbppy)$ with one 2-(4-bromophenyl)-5-bromopyridyl (dbppy) ligand {where L represents the cyclometallating ligands [2-phenylpyridyl (ppy), 2-(4,6-

difluorophenyl)pyridyl] (dfppy), [1-phenylpyrazole] (ppz) or [1-(4,6-difluorophenyl)pyrazole] (dfppz)} were synthesized. The bromine substituents allow the further incorporation of the iridium complexes into a polyaryl backbone. The route starts from μ -chloro-bridged dimers L₂Ir(μ Cl)₂IrL₂. Further reaction of these precursors with an excess of dbppyH at temperatures of 95–120 °C leads to the target complexes only in the case of the phenylpyridine based precursors (L = ppy and dfppy). All complexes were characterized via 1D- and 2D NMR spectroscopic methods. All the facial *tris*-cyclometallated complexes exhibited strong absorptions between 200 and 320 nm typical of a $\pi \rightarrow \pi^*$ transition together with weaker MLCT absorptions below 320 nm. The emission spectra of all these luminescent Ir(III)-complexes cover the region between approximately 500 to 700 nm. This strongly supports the hypothesis that the luminescent properties are controlled mainly by the dbppy ligand. The lifetimes of the complexes are quite different relative to each other and are much shorter than their homoleptic Ir(L)₃ counterparts.

Keywords: Iridium complex, Phosphorescence, Triplet emitting polymer, Copolymerization, OLED, triplet emitter

1 Introduction

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Organic Light Emitting Diodes (OLEDs) and Organic Light Emitting Electrochemical Cells (LECs) are of high interest due to the advantages they offer compared to classical light sources or commonly used display techniques. Thus, they have use in the development of extremely flat, flexible and energy saving displays and in energy saving substitutes for conventional light bulbs.

Typical materials used as light emitters are those in which the light formation arises from fluorescence. When using such materials in OLEDs, one big problem is the limited internal quantum efficiencies of only a maximum 25%. This arises from classical spin statistics where three excited triplet states and only one singlet state are formed during device [1, 2, 3, 4, 5, 6]. In fluorescent molecules, only singlet states can relax into the ground state under emission of light. Excited triplet states cannot relax to ground state easily [7]. These persisting excited triplet states may damage the emitter material and, for example, cause a loss of light producing efficiency and limit the lifetimes of the OLED devices. To eliminate the problems caused by the excited triplet states, devices were developed that are composed of triplet emitting materials or devices which contain such substances as a dopant in the emitter base materials [8]. As triplet harvesters are typically complexes of rare earth metals, mainly Eu³⁺ or complexes based on third row transition metals such as platinum or iridium are used [9, 10, 11, 12, 13, 14, 15, 16, 17, 18]. These complexes possess a high spin-orbit coupling and associated short lifetimes of the excited states. 6d-metals emit a broad band caused by MLCT-transitions. In spite of the disadvantage of the 6d-metal complexes emission properties, platinum-, and even more commonly iridium-complexes, are predominantly used for OLED-devices. This is due to the potential for tuning the emission color of the complexes [19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29].

Until recently, most research into triplet emitters and triplet harvesting has been carried out on small molecules based OLED-devices [30]. The combination of semiconducting polymer based organic light emitting devices with triplet emitters has been attained mainly by simply blending the metal complexes into polymer matrices [31, 32]. This methodology has the disadvantage of the quenching of the phosphorescence of the embedded complexes by the polymer [33]. The first structural combination of transition-metal complexes with semiconducting polymers was made by attaching them onto the polymer via specially designed side chains [34, 35, 36, 37, 38]. This approach contains, electronically, the same disadvantages as simple blending, but the immobilization of the complex prevents its migration through the polymer matrix, which would lead to depletion and

enrichment of complexes in several areas within the light emitting layer. During the last years in was tried by several groups to combine the advantages of semiconducting luminescent oligomer [39, 40, 41, 42, 43], polymers [44, 45, 46, 47, 48] or dendrimers [49, 50] and triplet emitters by incorporation of triplet emitters into the polymer system in such a way that the π -electron systems of both the ligands of the complexes and the backbone can interact. In our approach, we have synthesized several heteroleptic coordinated charge neutral iridium-phenylpyridine based complexes containing bromine functionalities which can therefore be easily used as building blocks for the design of triplet emitter containing macromolecular systems via homo- and cross-coupling reactions using Suzuki or Yamamoto protocols.

We report here the synthesis and characterization of various heteroleptic *tris*-cyclometallated Ir(III)complexes with 2-(4-Bromophenyl)-5-bromopyridine ligand (dbppy) and unsubstituted and fluorine substituted 2-phenylpyridine (ppy, dfppy) and 1-phenylpyrazole (ppz, dfppz) ligands. The optical behavior of the Ir(III)-complexes was investigated.

2 Experimental

2.1 General

All chemicals and solvents were purchased from Acros, Aldrich or Strem Inc. and used without further purification unless noted otherwise. Deuterated solvents for NMR measurements were purchased from Eurisotop GmbH. 2-(2,4-Difluorophenyl)pyridine was prepared according to literature procedures [51]. 1-(2,4-Difluorophenyl)pyrazole was prepared following the procedure reported by Ainsworth and Jones [52]. The cyclometallated Ir(III)- μ -chlorobridged dimers tetrakis(2-phenylpyridyl-C²,N')(μ -dichloro)diiridium **5**, tetrakis(2-(4,6-difluorophenyl)pyridyl-C²,N')(μ -dichloro)diiridium **6**, tetrakis(2-phenylpyrazol-C²,N')(μ -dichloro)diiridium **7** and tetrakis(2-difluorophenylpyrrazolyl-C²,N')(m-dichloro)diiridium **8** were synthesized via the Nonoyama route [53, 54, 55]. Synthesis of 2-(4-Bromophenyl)-5-bromopyridine **9** was according literature method [48].

UV/Vis-spectra were measured on a TIDAS II spectrometer from J&M. Photoluminescence spectra were measured with a Varian Cary-Eclipse spectrometer. NMR were recorded on a Bruker Avance 500 spectrometer (500 MHz, ¹H-NMR and 125 MHz, ¹³C-NMR in CDCl₃ or acetone-D₆. NMR spectra are reported in δ from CDCl₃ ($\delta_{1H} = 7.24$ ppm and $\delta_{13C} = 77.2$ ppm) or from acetone-D₆ ($\delta_{1H} = 2.05$ ppm and $\delta_{13C} = 29.92$ ppm). The ¹H-NMR chemical shifts and coupling constants were determined assuming first-order behaviour. Multiplicities are reported using the following

abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad) or a suitable combination. The assignments of proton resonances were based on DQF-COSY, TOCSY and ROESY experiments. The ¹³C-NMR signals were recorded and assigned by gs-HSQC and gs-HMBC spectra. For the time resolved luminescence measurements, the samples were dissolved in degased methylene chloride and excited at 355 nm via the third harmonic of a Nd:YAG-laser at room temperature. The time resolution and the integration time were both set to ten nanoseconds.

2.2 Synthesis

2.2.1 2-(4-Bromophenyl)-5-bromopyridine (dbppyH) 9

To a solution of 10.2 g (43.2 mmol, 1.02eq.) p-dibromobenzene in 150 mL of dry THF at -78 °C was added, dropwise, 28.25 mL of a solution of BuLi in n-hexane (1.6M). Stirring was continued for one hour at this temperature after which the solution was transferred into a solution of freshly fused ZnCl₂ (5.9 g, 43.4 mmol, 1.02eq.) in 80 mL of dry THF via a double needle. The solution was then allowed to warm to room temperature. In a 1L Schlenk flask, 0.6g (0.85 mmol, 0.02eq.) of bistriphenylphosphine palladium dichloride were suspended in 80mL of dry THF and 1.7mL of a solution of diisobutylaluminium hydride in toluene (1M) was added. After 15 minutes, 10g (42.4 mmol, 1 eq.) 2,5-dibromopyridine was added, followed by the organozinc solution prepared above. The reaction mixture was stirred at room temperature for 18h, after which time the solvent was removed on a rotary evaporator and the residue dissolved in 200 mL ethylacetate. The solution was washed successively with water (2200 mL) and saturated NaCl-solution (2200 mL). The separated organic phase was dried over MgSO₄ and filtered through a small pad of silica gel and the filtrate reduced to dryness in vacuo. The resulting raw product was purified via flash chromatography on silica gel with hexane/ethylacetate (95/5) as eluent. After removal of the solvent 2-(4bromophenyl)-5-bromopyridin was obtained as a colorless solid (10.2 g 82%, mp. 124 °C). ¹H-NMR (300 MHz, CDCl₃): δ = 8.72 (d, 1H); 7.88-7.83 (m, 3H); 7.61–7.58 (m, 3H).

¹³C-NMR (75 MHz, CDCl₃): δ = 154.6; 150.8; 139.4; 137.1; 132.0; 128.3; 123.9; 121.3; 119.7.

2.2.2 fac-Bis(2-phenylpyridyl-C²,N')[2-(p-bromophenyl)-5-bromopyridyl-C²,N']iridium 1

686 mg (0.64 mmol, 1eq.) $Ir_2(ppy)_4Cl_2$ and 329 mg (1.28 mmol, 2 eq.) silver triflate were suspended in 7 mL of degassed 2-ethoxyethanol and 1.2g of 2-(4-Bromophenyl)-5-bromopyridine were added and the mixture heated to 120 °C for 18h. After cooling to room temperature, a yellow solid formed and was collected by filtration. The residue was washed successively water, methanol, diethylether and hexane until the filtrate remained clear. The raw product was purified via column chromatography with methylene chloride as eluent affording *fac*-bis(2-phenylpyridine-C²,N')[2-(*p*-

bromophenyl)-5-bromopyridine- C^2 ,N']iridium as a yellow powder (841 mg, 81%).

¹H-NMR (500 MHz, acetone-D₆): $\delta =$ ¹H-NMR (500MHz, acetone): $\delta = 8.13$ (d, 2H, ³J=8,5Hz); 8,10 (d, 1H, ³J=9,1Hz); 7.97 (dd, 1H, ³J=8.7Hz, ⁴J=2.2Hz); 7.85–7.80 (m, 2H); 7,78 (d, 1H, ³J=5,5Hz); 7.71 (d, 1H, ³J=8,3Hz); 7,70 (d, 2H, ³J=7.4Hz); 7.67 (d, 1H, ⁴J=2,2Hz); 7.65 (d, 1H, ³J=5.5Hz); 7.11 (t, 2H, ³J=6.5); 7.02 (dd, 1H, ³J=8,4Hz, ⁴J=2.2Hz); 6.95 (d, 1H, ⁴J=2.1Hz); 6.85 (m, 2H); 6.75 (m,4H).

¹³C-NMR (HSQC-500 MHz, acetone-D₆): δ = 149.5 (d); 149.3 (d); 149.1 (d); 140.1 (d); 138.4 (d); 138.3 (d); 125.7 (d); 124.3 (d); 124.1 (d); 121.8 (d); 120.4 (d); 120.3 (d)..

MS(ESI): $m/z = 813 (M^+; Ir(ppy)_2(dbppy)^+, 100\%); 734.1 (M^+-Br, 6\%); 658.9 (M^+-ppy, 7\%);$ 501.1 (M⁺-dbppy, 24%).

2.2.3 *fac*-Bis[2-(4,6-difluorophenyl)pyridyl-C²,N'][2-(p-bromophenyl)-5-bromopyridyl-C²,N']iridium 2

455 mg (0.374 mmol, 1 eq.) $Ir_2(dfppy)_4Cl_2$, 550 mg (1.758 mmol, 6 eq.) 2-(4-Bromophenyl)-5bromopyridine and 260 mg (1.01 mmol, 2.7 eq.) silver triflate were suspended in degassed 2ethoxyethanol and the mixture heated to 120 °C overnight. After cooling to room temperature the reaction mixture was extracted twice with 20 mL 2M hydrochloric acid followed by extraction with 2 × 50mL methylene chloride. The aqueous phase was extracted with 20 mL methylene chloride and the combined organic phases washed with water, dried over Na₂SO₄ and the solvent evaporated to dryness. The crude product was purified via column chromatography on silica gel with methylene chloride as eluent. *fac*-bis[2-(4,6-difluorophenyl)pyridine-C²,N'][2-(p-bromophenyle)-5bromopyridine-C²,N']iridium was obtained as a lemon yellow powder in a yield of 130 mg (20%).

¹H-NMR (500 MHz, acetone-D₆): $\delta = 8.22$ (d, 1H, ³J=8.2 Hz); 8.20 (d, 1H, ³J=8.2 Hz); 8.04 (d, 1H, ³J=8.8 Hz); 7.92 (dd, 1H, ³J=8.7 Hz, ⁴J=2.3 Hz); 7.80 (1H, t, ³J\approx8.0 Hz); 7.78 (1H, t, ³J\approx8.0 Hz); 7.74 (d, 1H, ³J=5.6 Hz); 7.64 (d, 1H, ³J=8.4 Hz); 7.62 (d, 1H, ³J=5.6 Hz); 7.51 (dd, 1H, ⁴J=2.2 Hz, ⁵J=0.6); 7.09 (t, 1H, ³J=6.6 Hz); 7.05 (t, 1H, ³J=6.6 Hz); 6.97 (dd, 1H, ³J=8.4Hz, ⁴J=2.1 Hz); 6.7 (d, 1H, ⁴J=2.0 Hz); 6.41 (dt, 1H, ³J=11.2 Hz, ⁴J=2.5 Hz); 6.40 (dt, 1H, ³J=11.2 Hz, ⁴J=2.5 Hz); 6.12 (dd, 1H, ³J=4.2 Hz, ⁴J=2.5 Hz); 6.10 (dd, 1H, ³J=4.2 Hz, ⁴J=2.5 Hz).

¹³C-NMR (125 MHz, acetone-D₆): $\delta = 165,12$ (s); 164,5 (d); 163,09 (s); 162,5 (d); 149,29 (d); 148,9 (d); 148,9 (d); 143,43 (s); 141,43 (d); 139,19 (d); 139,0 (d); 128,89 (d); 127,64 (d); 126,3 (s); 124,89 (d); 124,25 (d); 124,15 (d); 124,07 (d); 123,96 (d); 121,98 (d); 118,84 (s); 118,70(dd); 118,44 (dd); 97,59 (t); 97,41 (t).

¹⁹F-NMR (282 MHz, acetone-D₆): δ = 110.45 (q, 1F); 110.54 (q, 1F); 111.31 (t, 1F); 111.51 (t, 1F); MS (LDI): m/z = 884,2 (M⁺, Ir(dfppy)₂(dbppy)⁺, 44%); 865.2 (M-F, 8%); 805.1 (M⁺-Br, 13%); 694.3 (M⁺-dfppy, 80%); 675.1 (M ⁺-dfppy-F, 5%); 614.6 (M⁺-dfppy-Br, 8%); 572.5 (M⁺-dbppy, 100%); 554.8 (M⁺-dbppy-F, 9%).

2.2.4 *fac*-Bis[2-(4-bromophenyl)-5-bromopyridyl-C²,N'][1-phenylpyrazolyl-C²,N']iridium 10

850 mg (0.83 mmol, 1eq.) $Ir_2(ppz)_4Cl_2$, 1.553 g (4.96 mmol, 6 eq.) 2(4-Bromophenyle)-5bromopyridine and 425 mg (1.62 mmol, 2eq.) silver triflate were suspended in 10 mL of 2ethoxyethanol and heated to 110 °C overnight. The suspension was allowed to cool to room temperature and the solid filtered off. The filter cake was successively washed with water, ether, ethanol and hexane until the filtrate remained clear and the solid then dissolved in acetone (100 mL) and filtered. The solvent was reduced in volume until precipitation began to occur and then methanol (15mL) was added to afford a yellow precipitate. Further purification was by column chromatography on silica gel with chloroform as eluent results yielding 1016 mg (64 %) of *fac*bis[2-(4-bromophenyl)-5-bromopyridine-C²,N'][1-phenylpyrazole-C²,N']iridium as a yellow powder.

¹H-NMR (500 MHz, acetone-D₆): $\delta = 8.44$ (d, 1H, ³J=2.7 Hz); 7.99 (d, 1H, ³J=8.3 Hz); 7.89 (dd, 1H, ³J=8.5 Hz, ⁴J=2.2 Hz); 7.88 (dd, 1H, ³J=8.5 Hz, ⁴J=2.2 Hz); 7.78 (d, 1H, ⁴J=2.4 Hz); 7.62 (d, 1H, ³J=8.4 Hz); 7.58 (d, 1H, ⁴J=2.4 Hz); 7.38 (dd, 1H, ³J=7.9 Hz, ⁴J=1.3 Hz); 7.15 (d, 1H, ³J=2.0 Hz); 6.95 (dd, 1H, ³J=8.4 Hz, ⁴J=2.3 Hz); 6.94 (dd, 1H, ³J=8.4 Hz, ⁴J=2.3 Hz). 6.81 (d, 1H, ⁴J=2.1 Hz); 6.78 (dt, 1H, ³J=7.5 Hz, ⁴J=1.4 Hz); 6.75 (d, 1H, ⁴J=2.1 Hz); 6.60 (dt, 1H, ³J=7.5 Hz, ⁴J=1.4 Hz); 6.47 (dd, ³J=2.7 Hz, ³J=2.2 Hz).

¹³C-NMR (125 MHz, acetone-D₆): δ = 165.7 (s); 165.1 (s); 162.2 (s); 150.0 (d); 148.82 (d); 144.77 (s); 141.08 (d); 141.0 (d); 140.16 (s); 139.41 (d); 139.10 (d); 138.92 (d); 138.07 (d); 127.88 (d); 127.38 (d); 127.06 (d); 124.49 (d); 122.53 (d); 121.71 (d); 121.38 (d); 12.52 (d); 118.7 (s); 118.2 (s); 112.69 (d); 108.88 (d);

MS (ESI): $m/z = 960 (M^+, Ir(dbppy)_2(ppz)^+, 25\%)$; 879 (M⁺-Br, 17%); 817 (M⁺-ppz, 100%); 648 (M⁺-dbppy, 41%).

2.2.5 [2-(4-Bromophenyl)-5-bromopyridyl][1-difluorophenylpyrazolyl-C²,N']iridium 11 852 mg (0.73 mmol, 1eq.) Ir₂(dfppz)₄Cl₂, 683 mg (2.18 mmol, 3 eq.) 2-(4-Bromophenyl)-5bromopyridine and 347 mg (1.46 mmol, 2 eq.) silver triflate are suspended in degased 2ethoxyethanol and heated at reflux overnight. The suspension was allowed to cool to room temperature, the solid was filtered off and washed successively with water, ethanol, ether and hexane until the remaining solution stayed clear. The solid was dissolved in acetone (100 mL), filtered and the solvent removed until precipitation started, at which time methanol (15 mL) was added and the resultant precipitate collected. The crude product was purified by column

¹H-NMR (500 MHz, acetone-D₆): $\delta = 8.62$ (dd, 1H, ⁴J=2.4 Hz, ⁵J=0.7 Hz);8.55 (d, 1H, ³J=3.0 Hz); 7.94 (dd, ³J=8.5 Hz, ⁴J=2.4 Hz); 7.93 (m, 1H); 7.93 (m, 1H); 7.81 (dd, 1H, ³J=8.5 Hz, ⁴J=0.8 Hz); 7.72 (d, 1H, ³J=2.3 Hz); 7.54 (m, 1H); 7.54 (m, 1H); 6.85 (dd, 1H, ³J=3.0 Hz, ³J=2.3 Hz); 6.52 (ddd,1H, ³J=11.8 Hz, ³J=9.0 Hz, ⁴J=2.5 Hz); 5.26 (ddd,1 H, ³J=8.7 Hz, ⁵J=2.5 Hz, ⁴J=0.9 Hz).

¹³C-NMR (125 MHz, acetone- \underline{D}_6): $\delta = 155.29$ (s); 151.50 (d); 141.47 (d); 140.6 (d); 138.22 (s); 132.91 (d); 132.84 (d); 132.84 (d); 129.49 (d); 129.49 (d); 122.62 (d); 120.42 (s); 115.03 (dd); 109.17 (d); 99.01 (dd).

3 Results and discussion

chromatography on silica gel with acetone as eluent.

The route described here, leading to heteroleptic coordinated Ir(III)-complexes with a generic structure shown in Figure 1, starts from µ-chloro-bridged dimer complexes with a general structure $(L)_2 Ir(\mu-Cl)_2 Ir(L)_2$ (where L=ppz, dfppz, ppy or dfppy). The compounds can be easily prepared with a variety of ligands using the method of Nonoyama [48, 49, 50]. The third ligand, dbppyH 5, is then inserted separately in a subsequent step as shown in Figure 2.



Figure 1. Target structures with one dibromopyridine ligand and two further 2-phenylpyridine or 1phenylpyrazole ligands, unsubstituted or with fluorine substituents in 4- and 6-positions.



Figure 2. The desired two step reaction pathway. First: formation of the μ -chloro complex via the Nonoyama-method. Second: insertion of the dbppyH ligand with supporting base and 200 °C [56] or by breaking the μ -chloro bridges with silver triflate [57].

As a first attempt for the synthesis of *fac*-Ir(ppy)₂(dbppy) **1**, we tried the method described by Thompson [56] in which the third ligand is inserted by heating the μ -chloro-precursor with excess of cyclometallating ligand to 200 °C in glycerol. Using this protocol, by reacting the Ir₂(ppy)₄Cl₂ complex with six equivalents of dbpyyH, no heteroleptic complex Ir(ppy)₂(dbppy) was formed. Under the harsh reaction conditions, ligand exchange occurred forming the homoleptic complex Ir(ppy)₃ exclusively. The spectroscopic data of the product are identical to those for the Ir(ppy)₃complex described in the literature [56, 57].

8



Figure 3. The observed reaction pathway of the reaction of the μ -chloro complex with dbppyH **9** depends on the cyclometallating ligand of the μ -chloro complex. A: ppy and dfppy ligands leading to the desired products Ir(ppy)₂(dbppy) **1** and Ir(dfppy)₂(dbppy) **2** B: ppz ligand leads to ligand exchange of one ppz ligand against one dbppy ligand and hence to the complex Ir(dbppy)₂(ppz) **10**. C: one dfppz ligand is lost and the dbppHy ligand is coordinated via the pyridine nitrogen only (structure **11** Ir(dfppz)(dbppy)).

In a modified strategy, we used the protocol of Güdel [57] to insert the dbppy-ligand under much milder conditions than in the Thompson route described above. Thus, the μ -chloro-bridges of the Ir₂(ppy)₄Cl₂ **5** complex were replaced by the weak coordinating triflate anion by adding two equivalents of silver triflate to the reaction mixture. The complex thus activated is cyclometallated by a sixfold excess of the dbppyH ligand **9**. For the thermal rearrangement from the meridional to the more stable facial isomer, temperatures of at least 90 °C are necessary. The complete reaction was carried out as a one-pot reaction by heating the reactants overnight in 2-ethoxyethanol at a temperature of 95–120 °. The target complex Ir(ppy)₂(dbppy) **1** was obtained in a yield of 80%.



Figure 4 Two step reaction to facial Ir(dfppy)₂(dbppy) 2 complex via meridional Ir(dfppy)₂(dbppy)12 and its subsequent rearrangement via UV-light.

The fac-Ir(dfppy)₂(dbppy) 2 compound was initially synthesized using a method similar to that for fac-Ir(ppy)₂(dbppy) **1** described above, but it afforded a lower yield of only 20%. To achieve higher yields, we decided to follow a two-step process, first synthesizing a meridional Ir(dfppy)₂(dbppy)complex at lower temperature, which could then be converted into the facial isomer in a second step by a photoinduced rearrangement according to reference [58] (Figure 4). Following this procedure, the first the meridional isomer was synthesized from the reaction of Ir₂(dfppy)₄Cl₂ 6, dbppyH 9, silver triflate, and triethylamine as base, in refluxing acetone leading to a very air-sensitive yellow powder, which formed dark decomposition products within a few minutes in non-deoxygenated solvents. For the second step, the photoinduced rearrangement of the meridional complex into the facial isomer, the complex was dissolved in nitrogen purged acetonitrile and irradiated with UV light. After removal of the solvent, a yellow powder was obtained which showed the same sensitivity as the meridional complex to air and oxygen containing solvents and which was much more sensitive to oxygen than the facial complex synthesized directly via the thermal route. This behavior leads to the conclusion, that no photoinitiated rearrangement took place and only meridional starting material was isolated. Further experiments to achieve a photoinduced rearrangement were not carried out.

For the synthesis of complex $Ir(ppz)_2(dbppy)$, we tried to follow the same method as described for the complex $Ir(ppy)_2(dbppy)$ **1**. Surprisingly, after the reaction of $Ir_2(ppz)_4Cl_2$ **7** with six equivalents of dbppyH **9** and two equivalents of silver triflate in 2-ethoxyethanol at 95 °C, none of the desired product, $Ir(ppz)_2(dbppy)$ **3**, was isolated. Instead, a product of formulation $Ir(dbppy)_2(ppz)$ **10** was produced exclusively in a yield of 62% due to an unexpected ligand exchange of one ppz ligand by a dbppyH 9 ligand. After this unpredicted reaction pathway, we decreased the amount of dbppyH 9 from six to three equivalents. In spite of these changes, the only product which was isolated was a complex $Ir(dbppy)_2(ppz)$ 10. To avoid any ligand exchange, the amount of dbppyH 9 was decreased to the minimal equivalents needed for the reaction $Ir_2(ppz)_4Cl_2$ 7 to $Ir(ppz)_2(dbppy)$ 3 (two equivalents). After workup only dark brown non-crystalline products could be isolated. The structural analysis did not show any defined product which could not be charaterized.

For the synthesis of $Ir(dfppz)_2(dbppy)$ **4**, the μ -chloro-precursor $Ir_2(dfppz)_4Cl_2$ **8** was heated with silver triflate and three equivalents dbppyH **9** in 2-ethoxyethanol at 95 °C overnight. The color of the suspension changed from white to yellow. The solid was separated and purified via column chromatography on silica with acetone as eluent. Unexpectedly, the compound formed was not the desired product $Ir(dfppz)_2(dbppy)$ **4**. Instead, the isolated product was Ir(dbppyH)(dfppz) **11** (for details in structural analysis see analytical section below). Futher experimental setups led only to instable products. Due to the unexpected instability of the obtained products we decided to discontinue further experiments for the synthesis of $Ir(dfppz)_2(dbppy)$.

4 Structural analysis of the Ir(III)-complexes

Attempts to obtain single-crystals for X-ray diffraction analysis of the products have so far resulted only in powders. However, the nature and coordination of the ligands around the metal may be unequivocally elucidated using detailed 1D and 2D NMR spectroscopic analyses.

Table 1: ¹ H- and ¹³ C-NMR signals, multiplicity and ³ J and ⁴ J-coupling constants of the complexes $Ir(ppy)_2(dbppy)$ 1 and $Ir(dfpy)_2(dbppy)$ 2 . ^{<i>a</i>} Two different signals, caused by
asymmetry of the complex. ^b Signal not detectable (eventually caused by quadrupole moment of the iridium core). ^c Signals not detectable due to low solubility. *) The signal
can be assigned to both positions.

Position	Ir-ppy2-dbppy (1)							Ir-dfppy2-dbppy (2)					
	1H	mult	13C	mult	³ J-	⁴ J-	1H	mult	13C	mult	³ J-	⁴ J-	⁵ J-
					coup	coup					coup	coup	coup
Α	-	-	b				-	-	b				
В	6,95	d	140,1	D		2,1	6,7	d	139,19	D		2,0	
С	-	-	С				-	-	126,3	S			
D	7,02	dd	124,3	D	8,4	2,2	6,97	dd	124,89	D	8,4	2,1	
E	7,71	d	С		8,3		7,64	d	127,64	D	8,4		
F	-	-	С				-	-	143,43	S			
G	-	-	С				-	-	165,12	S			
Н	8,10	d	120,3	D	9,1		8,04	d	121,98	D	8,8		
I	7,97	dd	С		8,7	2,2	7,92	dd	141,43	D	8,7	2,3	
J	-	-	С				-	-	118,84	S			
К	7,67	d	149,5	D		2,2	7,51	dd	148,9	D		2,2	0,6
L						Pyridinic	Nitrogen						
1	-	-	b				_	-	b				
2	6,74	m	138,3*	D			6,10;6,12	dd	118,44;118,70	DD	4,2	2,5	
3	6,77	m	138,3*	D			-	-	164,5	D			
4	6,85	m	121,8	D			6,40;6,41	dt	97,41;97,59	Т	11,2	2,5	
5	7,77	d	125,7	D	7,4	7	-	-	162,5	D			
6	-	-	С				-	-	128,89	D			
7	-	-	С	C			-	-	163,09	S			
8	8,13	d	120,4	D	8,5		8,20;8,22	d	123,96;124,07	D	8,2		
9	7,80 bis 7,85	m	138,4	D			7,78;7,80	t	139,0	D	~8,0		
10	7,11	t	124,1	D	6,5		7,05;7,09 ^a	t	124,15;124,25ª	D	6,6		
11	7,65;7,78 ^a	d	149,1;149,3 ^{<i>a</i>}	D	5,5		7,74;7,62 ^a	d	149,29;148,9 [°]	D	5,6		
12	Pyridinic Nitrogen												

Table 2:¹H- and ¹³C-NMR signals, multiplicity and ³J and ⁴J-coupling constants of the complexes $Ir(ppz)(dbppy)_2$ **10** and Ir(dfppz)(dbppy) **11**. ^{*a*}Two different signals, caused by asymmetry of the complex. ^{*b*}Signal not detectable (caused by quadrupole moment of the iridium core). ^{*c*}Signals not detectable. *) and **) The close proximity of labeled peaks in the spectrum makes full assignment difficult. However, a tentative assignment is shown in the table.

Position	Ir-dbppy2-ppz (10)						Ir-dbppyH-dfppz (11)						
	1H	mult	13C	mult	³ J-coup	⁴ -coup	1H	mult	13C	mult	³ J-coup	⁴ J-coup	⁵J-coup
Α	-	-	165,1*	S			-	-	b				
В	6,5	dd	138,07	D	7,5	1,4	5,26	ddd	115,03	DD	8,7	2,5	0,9
С	6,60	dt	127,06	D	7,5	1,3	-	-	c				
D	6,78	dt	122,53	D	7,5	1,4	6,52	ddd	99,01	DD	11,8; 9,0	2,5	
E	7,38	dd	112,69	D	7,9	1,3	-	-	c				
F	-	-	144,77***	S			-	-	С				
G						Pyrrazo	lic Nitr	ogen					
н	8,44	d	127,88	D	2,7		8,55	d	132,91	D	3,0		
I	6,47	dd	108,88	D	2,7	2,2	6,85	dd	109,17	D	3,0; 2,3		
J	7,15	d	138,92	D		2,0	7,72	d	141,47	D	2,3		
К						Pyrrazo	lic Nitr	ogen					
L					Positi	on not exi	sting ir	n PPZ-li	gands				
1	-	-	165,7*	S			7,93	m	129,49	D			
2	6,81;6,75 [°]	d	139,10;139,41 ^a	D	2,1		7,54	m	132,84	D			
3	-	-	118,7**	S			-	-	С				
4	6,95;6,94	dd	124,49	D	8,4	2,3	7,54	m	132,84	D			
5	7,62	d	12,52;127,38	D	8,4		7,93	m	129,49	D			
6	-	-	140,16	S			-	-	138,22	S			
7	-	-	162,2*	S			-	-	155,29	S			
8	7,99	d	121,38;121,71	D	8,3		7,81	dd	122,62	D	8,5		0,8
9	7,89;7,88	dd	141,0;141,08	D	8,5	2,2	7,94	dd	140,6	D	8,5	2,4	
10	-	-	118,2**	S			-	-	120,42	S			
11	7,58;7,78 ^ª	d	148,82;150,0 [°]	D		2,4	8,62	dd	151,50	D		2,4	0,7
12						Pyridir	ic Nitro	gen					



Figure 5. Aromatic region of the 500 MHz ¹H NMR-spectrum of the $Ir(ppy)_2(dbppy)$ 1 complex in acetone-D₆ with structural assignments

related to the schematic illustration.

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Figure 6. Aromatic region of the ¹H NMR-spectrum of the $Ir(dfppy)_2(dbppy)$ 2 complex in acetone-D₆ with structural assignments related to the

schematic illustration

The proton NMR spectrum of $Ir(dfppy)_2(dbppy)$ **2**, (Figure 6), is much clearer compared to the spectrum of $Ir(ppy)_2(dbppy) \mathbf{1}$ (Figure 5), having fewer protons together with a wider spread of the resonances (8.2–6.1 ppm). Due to this and its higher solubility which leads to a better signal to noise ratio, we choose complex 2 as reference system for a general structural assignment. The resonances were assigned by 2D-method COSY. The C_3 -symmetry related structure of complex 2 results in a relative simple spectrum over a range from 6.1 to 8.2 ppm. The pyridine resonances in the dfppy and dbppy ligands show only slight differences. Only the proton signals neighbored to the pyridine nitrogen, positions 11, 11'and K differ significantly (7.74, 7.62 ppm and 7.51 ppm). The further resonances of all three phenyl pyridine ligands occur at similar chemical shifts of the aromatic region except the proton meta to the pyridine nitrogen of the dffppy ligand (10 and 10'). The resonances are split into two distinguishable triplets at 7.09 and 7.05 ppm. The protons neighboring the carbon-iridium bond show the strongest high field shift of all protons of the corresponding ligand system. The bromine neighbored proton encounters a weaker high field shift (6.7 ppm) than both protons of the fluoro substituted phenyl rings (6.41 ppm, 6.40 ppm and 6.12 ppm, 6.10 ppm). All resonances show the expected multiplicity, dependent on their position in the ring, resulting from coupling with the surrounding fluorine atoms and/or a ⁴J-coupling with other protons in *meta* position. The protons *ortho* to the phenyl-pyridyl bond (positions 8, H and E in figure 5) show a strong low field shift, occurring at 8.20, 8.22, 8.04 and 7.51 ppm respectively. This might be a result of the influence of the neighboring in plane aromatic ring system. Complex 2 shows generally a much higher solubility in common solvents and allows a carbon NMR spectrum to be measured. The spectrum shows 25 resonances in line with that expected due to the presence of two fluorine atoms in the phenyl ring and the asymmetry of the complex. Due to the low intensity of the phenyl centered correlations in the HMBC-correlation spectrum, the signals generated by quarternary phenyl carbons could not be completely assigned to their corresponding position in the ring. For the ¹³C-NMR spectrum and the signal-resonance assignment see the Supporting Information. Also, due to the complex asymmetry, the fluorine spectrum shows two quartets resulting from the substituents at the *para*-positions at -110.45 and -110.54 ppm and two triplets two triplets generated by the atoms in *ortho*-position to the phenyl-pyridyl bond at -111.31 and -111.51 ppm. To confirm the existence of the facial structure of the complex Ir(dfppy)₂(dbppy) 2 the 2D-ROESY NMR method was used. The spectrum shows the expected correlation resonances for the *fac* configuration between the hydrogen atoms (position 2) of the dfppy ligands neighbouring the iridium-carbon bond and also the hydrogen (position B) of ligand dbppy. In contrast, no cross signals between the pyridine and the phenyl signals can be seen, which must occur in case of the meridional structure. An LDI-TOF mass spectrum was measured, which shows the molecular ion

peak at 884 m/z and expected fragmentation pattern from loss of one dfppy ligand (694 m/z) or one dbppy ligand (573 m/z). The remaining peaks are formed by halogen loss and fragments combining ligand and halogen loss. A full assignment of all signals may be found in the Supporting Information.



Figure 7: 2D-Matrix COSY and ROESY spectra assignment of the Ir(dfppy)₂(dbppy) complex 2.



Figure 8: 2D-Matrix HSQC and HMBC spectra assignment of the Ir(dfppy)₂(dbppy) complex 2.

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Figure 5 shows the proton NMR spectrum of the $Ir(ppy)_2(dbppy)$ complex 1 and denominates the assignments used in this discussion. As in case of complex 2 all resonances were assigned by the 2D methods COSY and TOCSY. The spectrum covers the aromatic range from 6.5 to 8.0 ppm a smaller span as in the spectrum of $Ir(dfppy)_2(dbppy)$. As compound 2 the spectrum of 1 shows a relatively simple spectrum as its facial complex structure is C_3 -symmetry related. The sectioning of the signals is also comparable to that of complex 2. In case of the phenyl pyridine ligands, only the signals of the protons next to the pyridine nitrogen (positions 11 and 11' in figure 5) differ significantly (7.78 and 7.65 ppm respectively) whereas the protons in position 10 are undistinguishable and display only one common triplet at 7.11 ppm. Analogously to substance 2 the signals of the protons ortho to the phenyl-pyridyl bond of both ring systems (position 4, 5 and C, D in Figure 4) expectedly experience a strong lower field shift compared to the other protons. It was not possible to measure ¹³C-NMR spectra directly due to the low solubility of the complex in all solvents and we therefore used indirect measurement via the HSQC method to determine the tertiary aromatic carbons. Use of the HMBC method to detect the quaternary carbons was not possible as the quadrupole moment of the iridium core causes line broadening, and this represses the correlation signals within the phenyl ring system. With the indirect HSQC method, twelve signals can be seen, where the resonance at 138.3 ppm is generated by two carbon. The splitting of the resonances for the atoms neighboring the nitrogen atom in the ppy-ligands (position 11 and 11'), which appear in the proton spectrum, is also detectable in the ¹³C spectrum. The ROESY-correlation method was used to confirm the facial structure of the $Ir(ppy)_2(dbppy)$ complex 1. This shows the correlation between the protons in the ppy and dbppy ligands neighboring the nitrogen atom (positions 11, 11' and K) ligands and the protons next to the iridium-carbon bond (positions 2 and B). No correlation signal between phenyl and pyridyl protons appears, as would be expected in a meridional structure. The molecular formulation deduced from NMR spectroscopy is confirmed in the ESI-MS spectrum, which shows a fragmentation pattern consistent with the proposed formulation, with four masses at 813, 734, 659 and 501 m/z. The molecular ion peak of the $Ir(ppy)_2(dbppy)$ complex 1 appears with the highest intensity (see supplementary information). The fragmentation pattern can be assigned to structures with the loss of bromine atoms and/or entire ppy or dbppy ligands.



Figure 9. ¹H NMR spectrum in the aromatic region of the complex $Ir(dbppy)_2(ppz)$ 10 in acetone-D₆ together with structural assignments related to the schematic illustration.

etc.



10. ¹H NMR spectrum in the aromatic region of Ir(dfppz)(dbppyH) 11 in acetone-D₆ with structural assignments related to the schematic illustration.

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The proton spectrum of Ir(dbppy)₂(ppz) 10 (Figure 9 with enumeration of the atom positions which are used in the discussion below), shows the pyridine and the phenyl signals occurring in same shift ranges as the other *tris*-cyclometallated iridium complexes. A complete signal assignment was made via COSY and TOCSY methods analogously to Ir-complexes described above. The pyridine signals of both dbppy ligands occur between 7.78 and 8.0 ppm, the nitrogen neighboring protons exhibit the expected two resonances at 7.58 and 7.78 ppm. The phenylic proton signals of all ligands also show the expected pattern. The resonances of the protons next to the phenyl-pyridyl or -pyrazole bond (positions E+5) are shifted to lower field (7.61 ppm for dbppy; 7.38 ppm for ppz). Remarkably, the Ir-C neighboring protons (2 and 2') of the both dbppy ligands experience a different shift showing two signals occurring at 6.75 and 6.82 ppm instead of one common signal as in case of complexes 1 and 2. The main difference between the spectrum of Ir(dbppy)₂(ppz) 10 compared to those of the complexes 1 and 2 are in the resonances of the pyrazole ring. The protons therein show strong shifts over the whole aromatic region from 6.40 ppm (position I) to 8.44 ppm (position H) and 7.16 ppm (position J) with a relatively small ³J-coupling constants of 2.0 and 2.7 Hz. The ESI mass spectrum of Ir(dbppy)₂(ppz) 10 shows the molecular ion peak at 960m/z with further peaks at 817 and 648 m/z that may be assigned to fragments with ligand losses, viz. (Ir(dbppy)²⁺ and Ir(dbppy)(ppz)⁺. Mass, and further spectra are shown in the Supporting Information.

A structural analysis of Ir(dfppz)(dbppyH) **11** (Figure 10), which was formed unexpectedly, is crucial as the ESI mass spectrum shows that the desired complex $Ir(dfppz)_2(dbppy)$ **4** was synthesized successfully. Peaks at 864 and 551 m/z, which can be assigned to the expected molecular ion $Ir(dfppz)_2(dbppy)^+$ and its fragment $Ir(dbppz)^{2+}$, confirms the formation of the target complex. Surprisingly, NMR studies showed a completely different structure (Figure <u>8</u>) which reveals, that a ligand exchange occurred under the conditions of the mass analysis. The ¹H-NMR spectrum shows resonances due to 12 protons and this is fewer than the 16 that would be expected for $Ir(dfppz)_2(dbppy)$ **4**. The two resonances at 5.27 and 6.52 ppm arising from protons neighboring the fluorine atoms show the expected multiplicity and the shift to higher field caused by the fluorine atoms. Consequently, we hypothesized a structure of formulation Ir(dfppz)(dbppy) **11**. However, this assumes that the structure contains 11 protons. A further detailed NMR-analysis using the 2D methods COSY, TOCSY and HSQC indicated a formulation Ir(dfppz)(dbppyH) **11**, where only the dfppz ligand was *ortho*-metallated to the iridium center. Here, the dbppyH ligand is bound only via the pyridine nitrogen and the iridium-phenyl bond to the dbppy-ligands had been cleaved (Route C

in Figure 3). This single bond through the Ir-N-bond causes an inverted signal order of the pyridine resonances compared to the *tris*-cyclometallated Ir(III)complexes. Due to the coordination of the dbppyH ligand through the pyridine nitrogen only, the signal order is different from cyclometallating ligands. The nitrogen proton neighboring the pyridine nitrogen experiences the strongest shift to lower field and occurs at 8.62 ppm, whereas the proton in the *meta* position to the nitrogen (position 8) shows a shift of 0.82 ppm to higher field at 7.81 ppm. The signals of the pyrrazole ring of the dfppz ligand occurring in the same order as the pyrrazole ring of the complex Ir(dbppy)₂(ppz) **10** and are spread over the hole aromatic region (8.55 ppm (position H), 7.72 ppm (position J), 6.85 ppm (position I)). The 4-bromophenyl group, due to its symmetrical position, generates two doublets in the ¹H-NMR spectrum at 7.54 and 7.93 ppm showing a AA'-BB' pattern. This might be a result of steric hindrance of the rotation of the 4-bromophenyl group around the pyridyl-phenyl bond.

5 Optical properties of the tris-cyclometallated complexes



Figure 11. Solution absorption spectra (200–400 nm) and emission spectra (500–700 nm) (both in methylene chloride) of the *tris*-cyclometallated Ir(III) complexes.

Table 1. Absorption and emission maxima and phosphorescence lifetimes of the *tris*-cyclometallated Ir(III)-complexes. All measurements were carried out in methylene chloride at ambient temperature.

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Complex	Absorption max. [nm]	Emission max. [nm]	Lifetime [µs]							
$Ir(dfppy)_2(dbppy)$ 2	247; 278; 353	518	0.85							
$Ir(ppy)_2(dbppy)$ 1	247; 284; 347	535	0.2							
	240 255 200 251	52.4	0.01							
$Ir(dbppy)_2(ppz)$ 10	248; 275; 299; 371	524	0.31							

The emission properties of the complexes $Ir(ppy)_2(dbppy)$ **1**, $Ir(dfppy)_2(dbppy)$ **2**, and $Ir(dbppy)_2(ppz)$ **10** (spectra shown in Figure <u>11</u>) are almost identical and are dominated by the ligand with the lowest HOMO-LUMO-distance, which is similar for dbppy and ppy. The emission wavelengths reach from around 450 up to 700 nm in all three cases. Ligands with a higher HOMO-LUMO-distance (ppz in **10** or dfppy in **2**) exhibit only a minor influence on the emission spectra. Thus the emission maximum of the $Ir(dfppy)_2(dbppy)$ **2** complex (518nm) is shifted only slightly to shorter wavelength compared to the emission maximum of $Ir(ppy)_2(dbppy)$ **1** (536nm). In the case of homoleptic *tris*-cyclometallated Ir(III)-complexes, the influence of relatively electron poor (dfppy) to electron rich (ppy) ligands leads to much stronger differences in the luminescence characteristics [56]. Furthermore, the emission maximum of the $Ir(dbppy)_2(ppz)$ **10** complex of 512nm occurs at a much higher wavelength then expected compared to the homoleptic complex $Ir(ppz)_3$ (414nm at 77K) described in the literature [56]. This shows that electronic structure of the non-brominated ligand not only has an influence on the emission spectrum but also the number of these ancillary ligands in the complex affects the luminescence properties.

The lifetimes of the exited states of all three *tris*-cyclometallated complexes $Ir(ppy)_2(dbppy)$ **1**, $Ir(dfppy)_2(dbppy)$ **2** and $Ir(dbppy)_2(ppz)$ **10** show many differences (see table <u>1</u>) compared to each other and compared to their homoleptic counterparts [57, 59, 56]. In all three cases, the lifetimes are much shorter than described in the literature for facial homoleptic Ir(III) complexes and lie in the ranges that are typical for meridional cyclometallated Ir(III)-complexes. More interesting than the absolute τ -values are the extreme differences of the lifetimes between the three complexes. Thus, the lifetimes of the excited states in $Ir(dfppy)_2(dbppy)$ **2** are four times longer than in $Ir(ppy)_2(dbppy)$ **1**.

The absorption spectra of Ir(ppy)₂(dbppy) **1**, Ir(dfppy)₂(dbppy) **2** and Ir(dbppy)₂(ppz) **10** were

assigned analogously to similar facial phenylpyridine based Ir(III)-complexes [57, 59]. The spectra of Ir(ppy)₂(dbppy) and Ir(dfppy)₂(dbppy) are nearly equal and show the typical, very intense, spin allowed ${}^{1}\pi \rightarrow \pi$ transitions for the ligands containing two maxima in the range of 235–330 nm (Figure <u>8</u>). The lower lying MLTC transitions ranging from 330 to 500 nm consists of both spin allowed ${}^{1}MLCT$ and spin forbidden ${}^{3}MLCT$ transitions. The intersection from the ${}^{1}MLCT$ and ${}^{3}MLCT$ can be seen as a small bend at around 400nm. This shows that the intense yellowish color of the complexes has its origin mainly in the ${}^{3}MLCT$ -transitions.

6 Conclusion

In this paper we report on the synthesis of charge-neutral tris-cyclometallated Ir(III) complexes with 2-phenylpyridine- and 1-phenylpyrazol-based ligands and at least one 2-(4-Bromophenyl)-5bromopyridine ligand of general structure $Ir(C,N)_2(C',N')$. The presence of bromine substituents on the ligands allows the complexes to be used as building blocks for further synthesis via Suzuki- or Yamamoto-coupling reactions in complexes containing, for example, aryl-based polymers such as polyparaphenylenes [60, 61, 62, 63]. Our pathway to heteroleptic Ir(III) complexes reveals that the bromine substituents on the dbppy ligand exhibit a strong influence on the coordinative reactivity of the ligand as well as on the stability of the complexes formed. Thus, the straightforward replacement of 2-phenylpyridine based ligands by dbppy is not possible in a simple manner and leads to undesired products due to unexpected ligand exchanges or reduction of the metal centre or coordinative bond-cleavage. However, reaction of Ir(L)₂(dbppy) (L=2-phenylpyridine, 2-(4,6difluorophenylpyridine)) via the route described by Güdel [57], through activation of a precursor complex $Ir_2(L)_4Cl_2$ via silver triflate followed by reaction with excess dbppyH leads to the expected products. When attempting to adapt this methodology to *tris*-cyclometallated complexes with L=ppz or dfppz, none of the expected Ir(ppz)₂(dbppy) or Ir(dfppz)₂(dbppy) products could be obtained. In the case of the ppz, a product with the structure Ir(dbppy)₂(ppz) was formed exclusively instead. Similarly, the dfppz-coordinated iridium-complex led to Ir(dbppyH)(dfppz). Trials to obtain the facial complexes Ir(dfppy)₂(dbppy) and Ir(dfppz)₂(dbppy) by a photoinduced rearrangement from the meridional isomers failed in both cases.

Photophysical analysis showed that all the *tris*-cyclometallated Ir(III) complexes are highly luminescent and all show a yellow-greenish emission color (maxima approximately around 525 nm). This reveals that the emission properties are mainly dominated by the ligands with the lowest HOMO-LUMO-distance. This is in case of Ir(dbppy)₂(ppz) and Ir(dfppy)₂(dbppy) the dbppy ligand, in case of Ir(ppy)₂(dbppy) the ppy ligand. The UV/Vis analysis shows spectra typical for facial *tris*-

cyclometallated iridium complexes with 2-phenylpyridine based ligands with very intense ${}^{1}\pi \rightarrow \pi$ transitions in typical regions below 330nm and strong MLCT transitions above 330nm.

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Conflicts of Interest

none

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Highlights

- A synthesis of Ir(III)-complexes for use in cross-coupling reactions is described.
- Conversion of the complex geometry is possible only via thermal rearrangement.
- Complexes having Phenylpyrrazole ligands exhibits a different reaction pathway.
- Optical properties of luminescent complexes are determined by the dibromophenylpyridine ligand.