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## A bright tetranuclear iridium(III) complex†

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**A cyclic tetranuclear cyclometallated iridium(III) complex using cyanide anions as bridging ligands and displaying a tetrahedrally distorted square geometry has been obtained with high yield; photo- and electrochemical characterizations show that most interesting properties of mononuclear cyclometallated iridium complexes are retained in the tetranuclear assembly.**

Molecular two- and three-dimensional transition-metal polynuclear complexes have attracted a great deal of attention in recent years.<sup>1,2</sup> High yields of molecules with highly complex structures are obtained by taking advantage first of the thermally labile nature of a heteroatom–metal bond and second of the formation of the most thermodynamically favourable structure.<sup>3</sup> Most often, the metal centres have purely an architectural role and the main interest resides in the host properties of the assembly.<sup>1</sup> When the aim is specifically at the study of photoinduced processes,<sup>2</sup> the preparation of the cyclic assemblies ultimately relies on transition metals with favourable labile character. Therefore complexes of transition metals with less labile character but important photo-physical properties like polyimine ruthenium and osmium complexes are rarely directly made during the self-assembling processes.<sup>4</sup> While a wide range of different transition-metals have been used to build such defined small clusters, surprisingly we found only few examples using iridium.<sup>1d</sup> However, these complexes use half-sandwiched iridium complexes and do not take advantage of the unique photophysical properties of cyclometallated iridium complexes.<sup>5</sup>

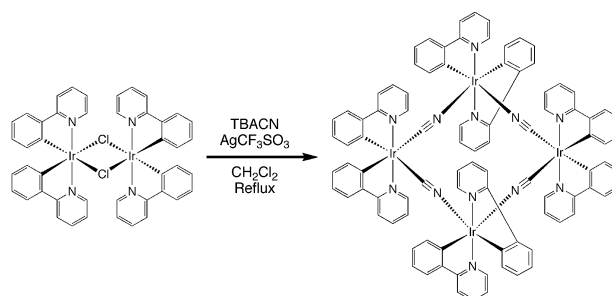
Cyclometallated iridium(III) complexes are intensively studied due to their high emission quantum efficiency, tunable emission color over the entire visible spectrum, and chemical stability. These compounds are suitable for a wide range of applications such as oxygen sensors,<sup>6</sup> biological labelling agents,<sup>7</sup> photocatalysts for hydrogen production,<sup>8</sup> sensitizers for solar cells,<sup>9</sup> and as dopants for organic light-emitting devices.<sup>10</sup> In all these applications, mononuclear complexes

are commonly used. While cyclometallated iridium(III) complexes have been already used as building blocks in linear or branched one dimensional multinuclear assemblies to study photoinduced energy and electron transfer,<sup>11</sup> they have not been employed yet for the construction of discrete two- and three-dimensional transition-metal polynuclear complexes. We believe that having a framework with widely tunable photoactivity will expand the practical applications of such nanoscale molecular devices beyond the sole architectural aspect.

Here we report our first success in building a discrete two-dimensional polynuclear complex incorporating highly luminescent cyclometallated iridium groups. We show that this multinuclear complex qualitatively retains the advantageous photo-physical properties of mononuclear cyclometallated iridium(III) complexes, which makes these complexes promising in view of building more complex photoactive discrete multinuclear assemblies.

In this work, we aimed for one of the simplest structures, namely a square, suited by the 90° directing angle of the bis-cyclometallated iridium complex. For our final design, we chose cyanide as a bridging ligand. Cyanides are linear ambidentate ligands and lead to complexes suitable for acting as a ditopic angular subunit with 90° directing angle.<sup>12</sup> This geometry is expected to favour a tetranuclear cyclic square.

The tetranuclear complex **EB91**, *e.g.*  $[\{\text{Ir}(\text{2-phenyl-pyridine})_2(\text{CN})\}_4]$ , was synthesized in one step by reacting the dimeric complex  $[\{\text{Ir}(\text{2-phenyl-pyridine})_2\text{Cl}\}_2]$  with one equivalent of tetrabutyl ammonium cyanide (TBACN) for each iridium atom in the presence of a small excess of silver(I) trifluoromethane sulfonate in dichloromethane as depicted in Scheme 1. Purification was achieved by a silica gel chromatography column leading to a surprisingly high yield of 74% of a yellow



**Scheme 1** Synthetic path for **EB91**.

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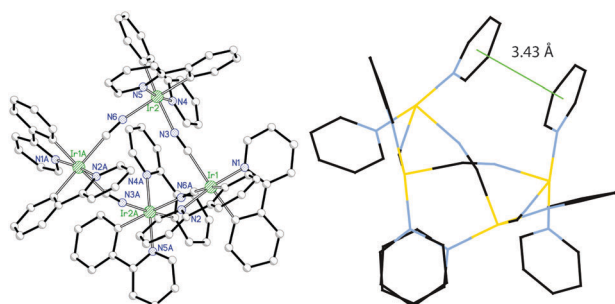
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soft solid with formula **EB91**·2H<sub>2</sub>O and showing bright green luminescence under a UV lamp. The proton NMR spectrum looks highly complex. However, 16 groups of signals could be broadly identified pointing to a material having two slightly different groups of cyclometallated phenyl pyridine ligands. In addition, peaks corresponding to the bis-cyano mononuclear complex, including the signals for the TBA counter cation, are not observed ruling out the presence of the bis-cyano mononuclear complex.<sup>12</sup> Mass spectrometry was not enough to identify the material as only two peaks are observed, one corresponding to the protonated fragment [Ir(ppy)<sub>2</sub>(CN)<sub>2</sub>H]<sup>+</sup> at *m/z* 554.1077 and a second at *m/z* 1054.1054 corresponding to a dinuclear fragment [{Ir(ppy)<sub>2</sub>(CN)<sub>2</sub>]<sub>2</sub><sup>+</sup> that is only half of the expected complex. Elemental analysis resulted in the expected CHN ratios, which however corresponds to any cyclic oligomer of the form [{Ir(ppy)<sub>2</sub>(CN)<sub>2</sub>]<sub>*n*</sub>. The infrared spectrum of the compound in solid-state showed the band for the cyanide at higher energy (2133 cm<sup>-1</sup>) than in the mononuclear bis-cyano complex (2092 cm<sup>-1</sup>).<sup>12</sup> This shift is expected for bridging cyanide ligands when compared to the terminal cyanide anion coordinated through the carbon.<sup>13</sup> Finally the compound obtained after recrystallization in acetonitrile, **EB91**·9CH<sub>3</sub>CN, could be unambiguously identified by an X-ray crystal structure as shown in Fig. 1. It shows the expected cyclic tetranuclear complex, [Ir(ppy)<sub>2</sub>(CN)<sub>4</sub>], which exhibits a tetrahedrally distorted square geometry.

The complex **EB91** is composed of two types of iridium centres. One type coordinates to two cyanide bridges through the carbon atom, named Ir<sub>C</sub>, and the other type of iridium centre coordinates through the nitrogen, and it is named Ir<sub>N</sub>. The complex can then be defined as a cyclic tetramer of the form [-Ir<sub>C</sub>-Ir<sub>N</sub>-Ir<sub>C</sub>-Ir<sub>N</sub>]. On each iridium center, the *trans* configuration of the phenylpyridine ligand of the starting dichloro-bridged dimer is retained. An intramolecular π-π stacking interaction is observed between one pyridine of each similar iridium centres. The tetranuclear iridium square is deformed in such a way that the cyano-bridge does not make a straight linear arrangement with two iridium centres, but a bent one more distorted than in ref 14. As a consequence, the four iridium centres and the four cyanide anions form a chiral structure (see Fig. S3, ESI<sup>†</sup>). Interestingly, while each iridium unit could be the Δ or Λ isomer, giving a total of 9 possible optical isomers due to the cyclic structure, only two isomers are observed in the crystal structure, namely the [-Δ-Λ-Δ-Λ] and the mirror image [-Λ-Δ-Λ-Δ]. In the crystal structure, two

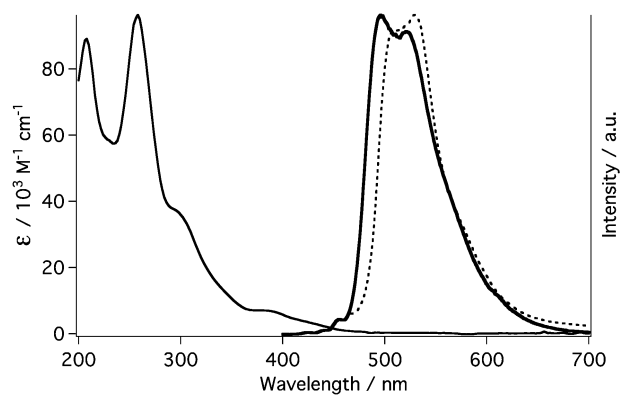


**Fig. 1** X-Ray crystal structure of **EB91**. Hydrogen atoms are omitted for clarity. (right) Phenyl rings are removed for clarity.

enantiomers form pairs interacting through the phenyl-pyridine ligand, one from each tetranuclear complex (see Fig. S4, ESI<sup>†</sup>), similar to mononuclear complexes.<sup>15</sup>

DOSY NMR experiments have been performed to gain further insight into the structure of the assembly in solution (see ESI<sup>†</sup>). First, in CDCl<sub>3</sub> as the non-coordinating solvent, it showed that all the protons have similar diffusion coefficient pointing to a single species in solution. The hydrodynamic radius (6.63 Å) nicely compares with the size of the molecule as determined by X-ray. Deuterated acetonitrile, CD<sub>3</sub>CN, has been used to assess the stability of the edifice in a coordinating solvent. Similar results as for CDCl<sub>3</sub> have been obtained (single species in solution with hydrodynamic radius 6.74 Å) showing that the tetranuclear complex is indeed stable in acetonitrile. For comparison, DOSY has been performed with the mononuclear complex [Ir(ppy)<sub>2</sub>(CN)<sub>2</sub>]<sup>-</sup> in CD<sub>3</sub>CN at the same concentration as **EB91**. It shows a single species with *R*<sub>H</sub> = 4.79 Å, which corresponds to a spherical volume ~1/3 of the one obtained for **EB91**. This is expected due to **EB91** having only four cyano groups and a more compact structure than four mononuclear complexes. To rule out any aggregation effect, we performed as well DOSY on the mononuclear complex at a concentration 4 times the one of **EB91**, corresponding to a similar concentration in iridium centres. Again it shows a single species in solution with *R*<sub>H</sub> = 4.70 Å. Therefore no aggregation can be invoked for the DOSY results of **EB91**. Overall, these DOSY experiments confirm the tetranuclear structure of the complex in solution, both in coordinating and non-coordinating solvents.

The UV-visible absorption spectrum of **EB91** in acetonitrile solution shows bands in the UV at 208, 258 and 296 and the visible at 386 extending up to 486 nm, due to intra-ligand (π-π\*) and metal-to-ligand charge transfer (MLCT) transitions, respectively (Fig. 2). When the solution is excited within the π-π\* and MLCT absorption bands, bright green luminescence with a maximum at 496 nm and a second peak at 521 nm is observed with a photoluminescence quantum yield of 0.66. The excited state lifetime (τ) in non-degassed solution is 40 ns and 2.32 μs in solution de-aerated with argon. The emission maximum is 26 nm red-shifted when compared to the bis-cyano mononuclear complex which shows maxima at 470 and 502 nm in acetonitrile with a photoluminescence quantum



**Fig. 2** UV-visible absorption (left solid line), and photo-luminescence (right solid line) spectra of **EB91** in acetonitrile solution; emission from the neat film (dotted line).

yield of 0.79. This further confirms the absence of the mononuclear complex. In addition the emission maximum is quasi-independent of the solvent used (Fig. S10, ESI†). Emission from a neat film of **EB91** is very similar to emission from solution. The emission spectrum measured at 77 K shows maximum at 492 and 526 nm only slightly hypsochromatically shifted from liquid solution (Fig. S11, ESI†). Overall **EB91** has qualitatively similar photophysical properties than general mononuclear iridium complexes. Interestingly it shows only limited red shift in the neat film. Such red shift is often observed for mononuclear iridium complexes and it is actually an issue hindering the development of blue emitting electrochemical devices.<sup>16</sup> The emission being quasi independent of the medium is attributed to the very compact and rigid structure of the complex and the  $\pi$ - $\pi$  interaction of the ppy ligands.<sup>15,17</sup>

The cyclic voltammogram measured in acetonitrile solution shows a first reversible oxidation at 0.64 V vs. ferrocene and a second irreversible oxidation at 0.90 V vs. ferrocene (Fig. S12, ESI†). These two oxidations are tentatively attributed to the two types of iridium centres. Irreversible reduction is observed around -2.45 V vs. ferrocene. In the case of bis-cyano mononuclear complex, TBA[Ir(ppy)<sub>2</sub>(CN)<sub>2</sub>], oxidation is observed at 0.55 V vs. ferrocene and reduction at -2.69 V vs. ferrocene in acetonitrile.<sup>12a</sup> Therefore the HOMO, based on oxidation potential  $E_{\text{ox}}$ , and LUMO, based on  $E_{\text{ox}}$  and  $E_{0-0}$ , energy levels are stabilized in the tetranuclear complex compared to the mononuclear complex.

The data show that the photo- and electrochemical properties of the tetranuclear complex are qualitatively similar to that of mononuclear complexes. To further support this view, we have fabricated green emitting OLED devices using a non-optimized architecture with **EB91** as a phosphorescent emitter. The electroluminescent spectrum shows maximum at 497 nm, similar to emission from solution. The device reached a fair maximum External Quantum Efficiency (EQE) of 10.2% (Fig. S14, ESI†).

In conclusion, we presented the synthesis of a discrete two-dimensional polynuclear complex based on the cyclometallated iridium(III) building block. The resulting complex is a tetrahedrally distorted square-shaped tetranuclear iridium(III) obtained in a high yield with a simple procedure. The photo- and electrochemical properties of this tetranuclear complex are in the same range as the mononuclear complex, in particular high photoluminescence quantum yield and electrochemical activity. Due to the characteristics of mononuclear complexes being retained in the multinuclear assembly, tuning the photo- and electrochemical properties should be achievable by donor and acceptor substitution on the phenylpyridine ligand as commonly done with mononuclear cyclometallated complexes.† This shows for the first time that bis-cyclometallated iridium complexes can be successfully used as building blocks for the construction of discrete and photoactive two- and three-dimensional transition metal polynuclear complexes. This is promising for incorporating into more complex architectures and taking advantage of their particular photophysical properties.

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## Notes and references

‡ Initial results show that bright blue and orange emitting products can be obtained following the procedure described in this manuscript for the green **EB91** using different starting chloro-bridged iridium dimers (see Fig. S16). As some doubts about the structure still remain due to a lack of X-ray crystal structure, full results will be reported in due course.

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