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## COMMUNICATION

# Nano-sized heterometallic macrocycles based on 4-pyridinylboron-capped iron(II) clathrochelates: syntheses, structures and properties

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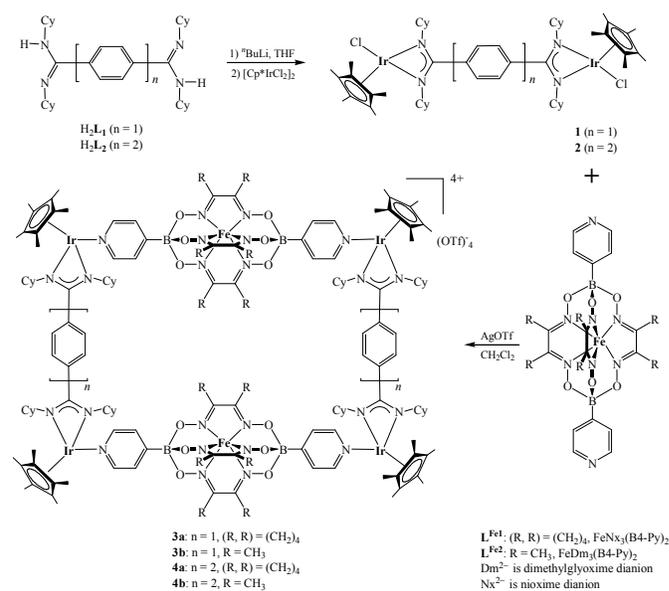
**Ir-Fe heterometallic macrocycles from clathrochelate-based bipyridyl and bis(amidinate) ligands with controllable cavity size have been prepared and characterized.**

The successful applications of well-defined metal-organic coordination macrocycles and cages in various areas, such as host-guest chemistry, photo- and electrochemical sensing, catalysis and so on, has driven the development to systematic and rational approaches for their preparation.<sup>1</sup> Most of the macrocycles and cages synthesized to date are homometallic based on transition metal ions. The synthesis of multimetallic hybrid materials is of special interest because the incorporation of two or more kinds of metal ions can add different functionalities.<sup>2</sup> However, much attention has been focused on the synthesis of homometallic macrocycles, whereas the chemistry, as well as the synthetic strategy toward discrete heterometallic frameworks, has received much less attention.<sup>3</sup> A useful strategy toward heterometallic macrocycles is to use metallaligands as building blocks via stepwise formation approach.<sup>4</sup>

Clathrochelates, cage complexes with an encapsulated metal ion, were first proposed by Busch.<sup>5</sup> Recently, numerous clathrochelate complexes of different types with the encapsulated iron(II), ruthenium(II) and cobalt(I, II and III) ions, which display interesting chemical, physical and physicochemical properties, have been obtained and characterized.<sup>6</sup> One of the main pathways for functionalization of these clathrochelates is to use various substituents in both their ribbed chelate  $\alpha$ -dioximate fragments<sup>7</sup> and the apical capping groups.<sup>8</sup> The cage complexes with two apical 4-pyridinyl substituents are linear bipyridyl ligands, which has been widely used as a bridging ditopic  $N,N'$ -ligand for the preparation of countless discrete supramolecules,<sup>9</sup> as well as coordination polymers.<sup>10</sup> In this paper, we choose 4-pyridinylboron-capped iron clathrochelates as metallaligands and bis(amidinate) as organic ligands to construct heterometallic macrocycles.

As shown in Scheme 1,  $[\text{Cp}^*\text{IrCl}_2]_2$  was first treated with dilithium salt (formed by the addition of 2 equiv. of  $^t\text{BuLi}$  at  $-78\text{ }^\circ\text{C}$ ) of the bis(amidinate) ligand  $\text{H}_2\text{L}_1$  in THF at  $0\text{ }^\circ\text{C}$  to afford the bis(amidinate) bridged dinuclear complex  $[\text{Cp}^*\text{IrCl}]_2(\text{L}_1)$  (**1**), to which 4-pyridinylboron-capped clathrochelates  $\text{L}^{\text{Fe1}}/\text{L}^{\text{Fe2}}$  was added in the presence of 2 equiv.  $\text{AgOTf}$  at  $-78\text{ }^\circ\text{C}$ . After the mixture was stirred at low temperature for 2 h and kept stirring for additional 6 h

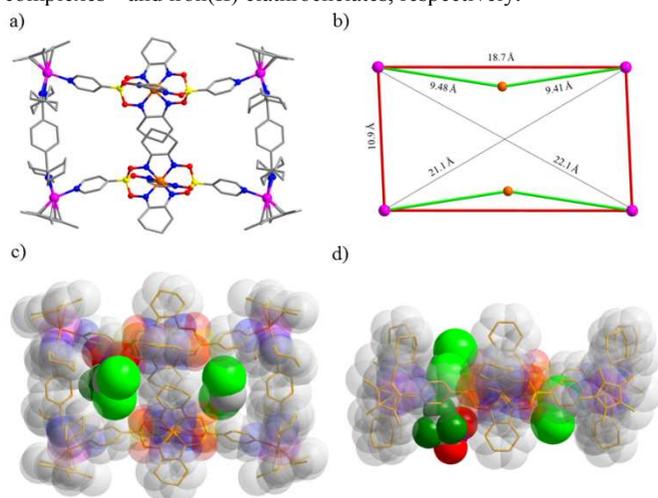
at room temperature. Macrocycles  $[(\text{Cp}^*\text{Ir})_4(\text{L}_1)_2(\text{L}^{\text{Fe1}})_2][\text{OTf}]_4$  (**3a**) and  $[(\text{Cp}^*\text{Ir})_4(\text{L}_1)_2(\text{L}^{\text{Fe2}})_2][\text{OTf}]_4$  (**3b**) were obtained simply by removal of the precipitation. The  $^1\text{H}$  NMR spectra for **3a** and **3b** had similar signals at almost the same chemical shifts except for that of the substituents in the metallaligands, which suggest that the structures of **3a** and **3b** are similar.



**Scheme 1** The syntheses of the heterometallic macrocycles (**3a**, **3b**, **4a** and **4b**).

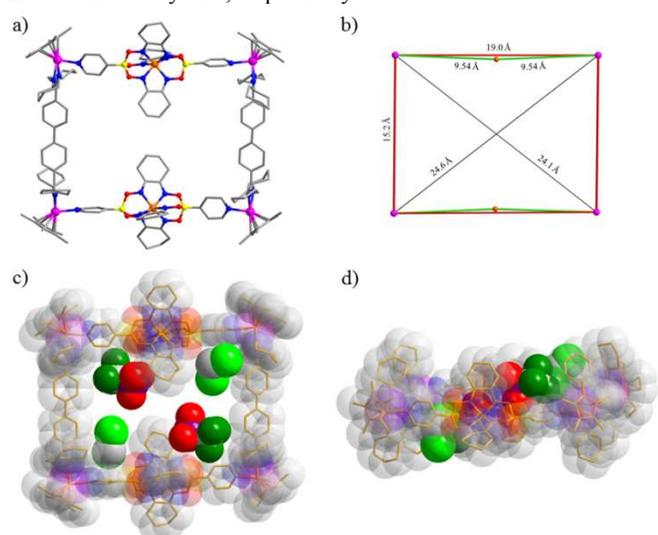
The structure of **3a** was confirmed by X-ray crystallography at 193 K. As shown in Fig. 1, the cation of complex **3a** adopts a slightly distorted rectangular structure based on the  $[4\text{Ir} + 2\text{Fe}]$  nuclear core with a nano-scaled cavity of  $18.7 \times 10.9\text{ \AA}$ , which accommodates several solvent molecules ( $\text{CH}_2\text{Cl}_2$ ) and a part of triflate anions. The three coordination sites of the half-sandwich Ir fragment are occupied by pyridyl donor  $\text{L}^{\text{Fe1}}$  and chelating group  $\text{L}_1$ . The coordination geometry of Fe(II) center is intermediate between a trigonal prism (TP, distortion angle  $\varphi = 0^\circ$ ) and a trigonal antiprism (TAP, distortion angle  $\varphi = 60^\circ$ ); the distortion angle  $\varphi$  values are equal to 22.1, 22.0 and 21.7°, respectively. The heights  $h$  of their

TP-TAP coordination polyhedra are approximately 2.3 Å. The average Ir-N and Fe-N distances (Table S1) are equal to 2.126 and 1.904 Å, which are similar to the observed six-coordinated iridium complexes<sup>11</sup> and iron(II) clathrochelates, respectively.<sup>12</sup>



**Fig. 1** (a) Molecular structure of **3a**. All hydrogen atoms and guest molecules were omitted for clarity. (b) The dimensions of cavity for **3a**. (c) Top view of **3a** and (d) side view of **3a** in space-filling mode. Triflate anions and solvent molecules outside the framework, as well as hydrogen atoms are omitted for clarity. Color code: N, blue; O, red; B, yellow; C, gray; Cl, light green; F, green; S, violet; Fe, orange; Ir, pink.

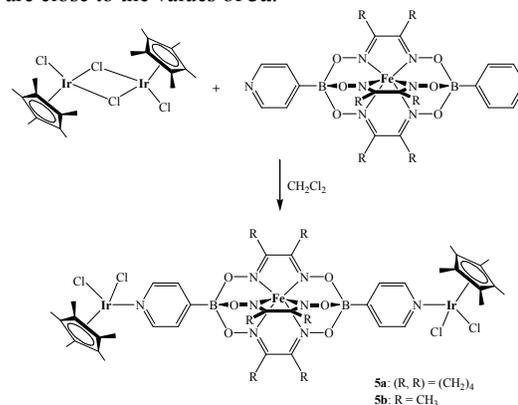
With the intent of exploring the scope of our synthetic approach and improving the cavity size of the rectangles, xenyl-linked bis(amidine) ligand  $H_2L_2$  was introduced to these reactions. Complexes  $[(Cp^*Ir)_4(L_2)_2(L^{Fe1})_2][OTf]_4$  (**4a**) and  $[(Cp^*Ir)_4(L_2)_2(L^{Fe2})_2][OTf]_4$  (**4b**) were obtained by treatment of  $[Cp^*IrCl]_2(L_2)$  (**2**) with iron(II) clathrochelates  $L^{Fe1}/L^{Fe2}$  used the previously conditions in 88% and 85% yields, respectively.



**Fig. 2** (a) Molecular structure of **4a**. All hydrogen atoms and guest molecules were omitted for clarity. (b) The dimensions of cavity for **4a**. (c) Top view of **4a** and (d) side view of **4a** in space-filling mode. Triflate anions and solvent molecules outside the framework, as well as hydrogen atoms are omitted for clarity.

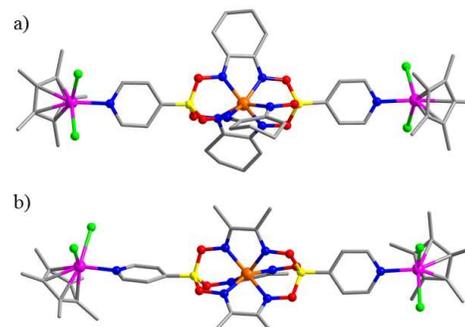
The structure of **4a**, which contains four iridium and two iron metal centers, was established by X-ray structure analysis (Fig. 2). The complex cation of **4a** is quite similar to that of **3a** and has a rectangular cavity with dimensions of  $19.1 \times 15.2$  Å according to Ir...Ir non-bonding distances, which is much larger than that of **3a**, as well as the known molecular rectangles.<sup>13</sup> Two triflate anions and

several solvent molecules found as guests are contained in the rectangular framework. A remarkable feature of the structure is that both of the metallaligands and the organic ligands are almost in the normal configuration compared with the twisted ones in complex **3a**. The Ir-N and Fe-N distances are in the range of 2.084(15) to 2.198(12) Å and 1.872(13) to 1.936(13) Å (Table S2), respectively, which are close to the values of **3a**.



**Scheme 2** Formation of complexes **5a** and **5b**.

We attempted to use the reported synthetic methodology<sup>4</sup> to obtain the same matallarectangles, but the crude products are complicate and difficult to purify so that only the heterometallic dinuclear complexes were obtained. A stoichiometric (1:1) mixture of  $[Cp^*IrCl_2]_2$  and the corresponding clathrochelate-based bipyridyl ligands  $L^{Fe1}/L^{Fe2}$  in  $CH_2Cl_2$  at room temperature gave the dinuclear complexes **5a** and **5b** in almost quantitative yields (Scheme 2). The  $^1H$  NMR spectra of **5a** and **5b** display a similar signal pattern of the  $Cp^*$  protons and pyridyl protons ( $H_\alpha$  and  $H_\beta$ ). However, with respect to the macrocycles above, in **5a** and **5b**, the  $H_\alpha$  signal is shifted to higher frequencies ( $\delta = 8.85$  ppm for **5a** and 8.88 ppm for **5b**), whereas both of the  $Cp^*$  signal and  $H_\beta$  signal are shifted to lower frequencies ( $\delta = 1.56, 7.57$  ppm for **5a** and 1.57, 7.58 ppm for **5b**) (Fig. S1).



**Fig. 3** Molecular structures of complex **5a** (a) and **5b** (b). All hydrogen atoms and guest molecules were omitted for clarity. Color code: N, blue; O, red; B, yellow; C, gray; Cl, light green; Fe, orange; Ir, pink.

X-ray analysis indicated that all of the  $Cp^*Ir$  fragments in complexes **5a** and **5b** are coordinated to two chlorine atoms and one nitrogen atom from the pyridine ligand. Despite the fact that these two complexes in some respects are alike, the details of their crystal structures are significantly different. Obviously, the  $Cp^*$  groups in **5a** are positioned *trans* to each other while neither *trans* nor *cis* in **5b**.

The UV-vis spectra of the complexes containing 4-pyridinylboron-capped iron(II) clathrochelates obtained contain one metal-to-ligand  $Fed \rightarrow L\pi^*$  charge transfer (MLCT) band in the visible region with maxima at about 450 nm (Fig. S2), which is characteristic of the macrobicyclic iron(II) tris-dioximates.

Meanwhile, the bands of the intraligand  $\pi$ - $\pi^*$  transitions are observed in the UV region from 227 to 283 nm.

The electrochemical characteristics of the dichloromethane solutions of the heterometallic complexes obtained were studied by cyclic voltammetry (CV) using a glassy carbon (GC) working electrode. All of the CVs have similar shapes and exhibit one redox pair and one oxidation wave in the potential range from -1.5 to +1.7 V (Fig. S3 and Table S3). The CVs for all of the complexes in their cathodic ranges contain only one peak of the oxidation, which is apparently irreversible and may correspond to the one-electron process of  $\text{Fe}^{2+/+}$ . However, the anodic ranges of these CVs contain quasi-reversible one-electron waves assigned to the  $\text{Fe}^{2+/\beta+}$  oxidations. The  $\Delta E$  values for complexes **5a** and **5b** are higher than those of the macrocycles (**3a**, **3b**, **4a** and **4b**) (170-230 mV), which might be because of the slight effect of the electron-withdrawing chloride ions.

## Conclusions

In summary, we have reported a series of iridium(III)-iron(II) heterometallic complexes with clathrochelate-based bipyridyl and bis(amidine) ligands. Single-crystal X-ray diffraction indicated that they have rectangular structures with different nano-sized cavities, in which some small molecules and anions were found, such as dichloromethane molecules, triflate anions, and so on. The cyclic voltammograms exhibits one redox pair and one oxidation wave. Our results further confirmed that 4-pyridinylboron-capped iron(II) clathrochelates can be used as building blocks to construct the nano-sized multicentered hybrid systems.

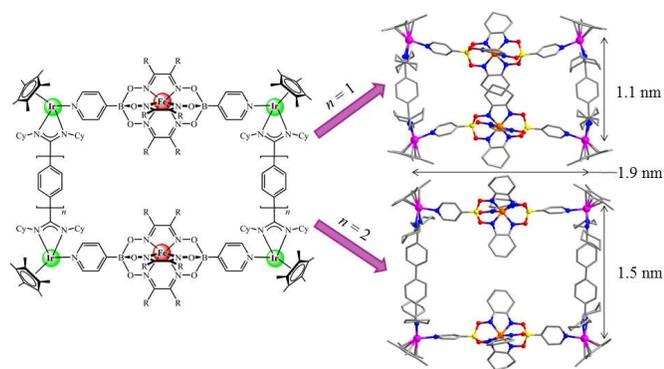
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## Notes and references

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† Electronic supplementary information (ESI) available: Experimental details, UV-Vis spectra, cyclic voltammogram curves and other materials. CCDC 973498 (**3a**), CCDC 973499 (**4a**), CCDC 973500 (**5a**), and CCDC 973501 (**5b**). For ESI and crystallographic data in CIF or other materials see DOI: 10.1039/c000000x/.

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**Toc Graphic:****Text:**

A series of nano-scaled Ir-Fe heterometallic rectangles were prepared from 4-pyridinylboron-capped iron(II) clathrochelates and bis(amidine) ligands. The cavity size could be controlled easily by the length of the organic ligand.