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Meso- and axially-modified Ir^{III}triarylcorroles with tunable electrocatalytic properties

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ABSTRACT

The synthesis of three A_2B type Ir(III)triarylcorroles with *meso*-aryl substituents that provide electron donating (push) and withdrawing (pull) properties and three A_3 type Ir^{III} triphenylcorroles with differing pyridine axial ligands is reported, along with their structural characterization. An analysis of the structure-property relationships in the optical and redox properties has been carried out by comparing their optical spectroscopy and electrochemistry to trends predicted in DFT and TD-DFT calculations. The results demonstrate that A_2B type Ir^{III} triarylcorroles are highly efficient electrocatalyzed oxygen reduction reactions (ORRs) and that their reactivity can be modulated by modulating the electronic structure by changing the nature of the *meso*-substituent at the B-positions, and even axial pyridine ligands.

1. Introduction

Corroles are tetrapyrrolic ligands that provide sterically constrained environments for coordinating central atoms because in contrast with porphyrins they have three inner N–H protons, since a trianionic ligand is required to form an 18 π -electron system on the inner perimeter when there are only three *meso*-carbons [1–4]. Various groups can be introduced at the *meso*-, β -, and/or axial positions to modify the structures of the corrole ligands and their metal complexes [5–8]. Interest in corrole coordination chemistry is not only driven by their unusual structures and topologies, but also by their interesting properties. The trianionic corrole ligand stabilizes numerous metals in high oxidation states, making them suitable for use in bioimaging and biosensors, optical and magnetic materials, and in catalysis [9–12].

The use of renewable energy sources can be balanced with demand through the use of fuel cells to decrease the environmental pollution and greenhouse effect. This has many advantages and is widely considered to be the energy source that is most likely to replace the use of fossil fuels in the decades ahead [13–15]. Molecular electrochemical catalysis has received considerable attention due to its low cost, and its renewable

and environmentally friendly properties [16–18]. Recent research has identified the coordination complexes of transition metal ions as being potentially suitable for electrocatalysis, but their low catalytic efficiencies and insufficient stability in the concentrated acid environments that are used in this context has limited further development in this field. For this reason, researchers are currently trying to combine these compounds with inorganic and/or organic nanomaterials to create suitable catalytic nanocomposites, such as reduced graphene oxides (rGOs), carbon nanotubes and γ -C₃N₄, due to their large surface area, high mechanical strength, structural flexibility and electrical conductivity [19–21].

Herein, the synthesis of three A_2B type Ir^{III} triarylcorroles with pushpull *meso*-aryl substituents is reported, and characterization of their properties has been carried out using optical and redox measurements. Large shifts in the wavelengths of the main spectral bands and in the redox potentials have been observed for synthetic metallocorroles. In addition, three A_3 type Ir(III)triphenylcorroles with differing *p*substituted pyridine axial ligands have also been prepared. The trends predicted in the frontier MO energies by theoretical calculations are compared to those observed experimentally to provide information that

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can guide the design of future group 9 corrole electrocatalysts for use in ORRs. The electrocatalytic behavior of Ir^{III} triarylcorrole/rGO-graphene (Ir^{III} corrole/rGO) composites prepared using the three A_2B type, and three A_3 type Ir^{III} triarylcorroles will be described in the context of electrochemically catalyzed redox reactions.

2. Results and discussion

2.1. Structural characterization

Free base corrole compounds **1** and **3** were synthesized according to the reported literature procedures [18]. Ir^{III} triphenylcorroles with *p*-functionalized pyridines as axial ligands were prepared through metalation and were purified by silica gel column chromatography and recrystallization. The isolated yield of Ir^{III} triphenylcorroles are slightly lower than other first-transition metallocorroles, due to the final products were partially decomposed during purification processes. MALDI-TOF MS data for **2a** contains an intense parent peak at m/z =1010.44 (Calcd. $[M]^+ = 1010.40$) providing direct evidence that the (py)₂Ir(III)-5,15-(*p*-trifluoromethylphenyl)-10-phenylcorrole was successfully synthesized. Similar MALDI-TOF MS peaks were observed for Ir^{III}triarylcorroles **2b-c** and **4a-c**. The proton signals for the *meso*-substituents and pyrrole rings of **4a** mainly lie beyond 7.40 ppm in the aromatic region.

2.2. Electrochemical and electrocatalytic characterizations

The redox properties of a large number of group 9 metallocorrole derivatives have been reported previously, including those with Co(III), Rh(III) and Ir(III) central ions [29–31]. The investigation of the structural chemistry of group 9 corroles has usually provided results that are consistent with a classic low-spin d^6 configuration description with low-energy open-shell states also readily accessible for many of these complexes, and the four-coordinate group 9 corroles are only observed as intermediates in solution [32–34]. In order to gain further insight into the electronic structures of the *meso-* (**2a-c**) and axially-modified Ir(III)

corroles (4a-c), cyclic voltammetry (CV) measurements were carried out in low-polar o-dichlorobenzene (o-DCB) containing 0.1 M tetra-n-butylammonium perchlorate ([NBu]ClO₄; TBAP) as a supporting electrolytes (Fig. 5). As shown in Fig. 5 and Table 1, the voltammogram of (py₂) Ir^{III}triarylcorrole **4a** contains a reversible reductive process which can be assigned as the ring reduction of [Ir^{III}triarylcorrole/[Ir^{III}triarylcorrole]⁻, while two reversible oxidation processes are also observed at +0.52 and +1.27 V, respectively. These two oxidation processes can be assigned to corrole ring oxidation and a valence change of Ir^{III}/Ir^{IV}, respectively [35].

Broadly similar redox potential changes are observed for the three meso-modified Ir^{III}triarylcorroles 2a-c and the three axially modified Ir^{III}triphenylcorroles **4a-c** with the exception of the reductive potential for **4b** at -1.37 and -1.59 V which can be assigned to the reduction of *p*cvanopyridine. The change of reduction curves of 4b could be assigned as back-donation from p-cyanopyridine ligand to Ir^{III} center. This was also spectroscopic observed by expanded soret-band absorption and usual stabilization of LUMO orbitals from TD-DFT calculations. This is consistent with the MO energy predictions for the axial ligands of this complex (Fig. 3). The trends observed in the gaps between the first reduction and oxidation steps are consistent with the relatively minor shifts of the main Q and B bands that are observed spectroscopically for 2a-c and 4a-c (Fig. 1) and are predicted in theoretical calculations (Fig. 4), since the inductive effects of the meso-aryl rings on the energies of the frontier MOs are similar in each case. Cyclic voltammograms for 2a-c and 4a-c were recorded at scan rates of 50-500 mV/s, and this demonstrates that the oxidation and reduction processes are diffusion controlled (Figs. S2-S4, see Supporting Information).

A series of Ir^{III} corrole/rGO composites were prepared and examined as electrocatalysts for ORRs (Fig. 6). Firstly, in the case of electrocatalyzed ORRs, it is noteworthy that the voltammograms of the standard **4a**/rGO composites contain significant catalytic peaks beyond the Ir^{III} corrole/[Ir^{III} corrole]⁻ step with an overpotential of -393 mV. Upon introducing electron-withdrawing trifluoromethylphenyl groups at 5,15-positions, there is a clear positive shift of the catalytic peak for the Ir^{III} corrole/rGO for **2a** with an overpotential of -285 mV. More positive



Fig. 1. Magnetic circular dichroism (top) and UV-vis absorption spectra (bottom) of 2a-c and 4a-c in CH₂Cl₂.



Fig. 2. Angular nodal patterns and MO energies of the frontier-MOs of model complex 5 at the CAM-B3LYP/SDD level of theory.

overpotentials are also observed for the Ir^{III}corrole/rGO composites of **2b** and **2c** at -243 and -178 mV, respectively. When the electronic structure was modulated by introducing *p*-functionalized pyridines at the axial positions, modified electrocatalyzed ORR behavior was also observed. In the presence of electron-withdrawing *p*-cyanopyridine was introduced, the significant stabilization of the π -MOs causes an overpotential at -387 mV, while introducing electron donating *p*-



methoxypyridine causes a significant negative shift of the overpotential to -446 mV due to the destabilization of the π -MOs.

It is clear from the investigation of the electrocatalytic properties of the nanocomposites that the introduction of electron donating and/or withdrawing substituents at the *meso-* and axial positions of group 9 corroles has a much larger effect on the electrocatalytic properties than it does on their optical and redox properties. In the context of nanocomposites, such as porphyrinoid-functionalized rGOs, electron transfer



Fig. 4. TD-DFT calculated spectral of model complex **5, 2a-c** and **4a-c** at the CAM-B3LYP/SDD level of theory. Red and black diamonds are used to highlight the Q and B bands and MLCT bands, respectively. The green and blue diamonds denote transitions into MOs localized on the axial ligands and *meso*-aryl rings, respectively. The Chemcraft program was used to generate the simulated spectra by using a fixed bandwidth of 2000 cm⁻¹ [25–28]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Fig. 3. MO energies of the frontier-MOs of model complex **5, 2a-c** and **4a-c** at the CAM-B3LYP/SDD level of theory. The **a, s, -a** and **-s** MOs are highlighted with thicker black lines, while blue lines are used for the $3d_{xz}$ and $3d_{yz}$ MOs. The other unoccupied MOs shown are localized on the axial or phenyl rings. Small black diamonds denote occupied MOs, while black circles are used to highlight the **s** and **-s** MOs. The average HOMO–LUMO gap values that take into account all four frontier π -MOs are highlighted with red diamonds and are plotted against a secondary axis. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



Fig. 5. Cyclic voltammograms for Ir^{III}triarylcorroles 2a-2c and Ir^{III}triphenylcorroles 4a-c in *o*-dichlorobenzene (*o*-DCB) containing 0.1 M TBAP as a supporting electrolyte.

channels may be the most important factor [36,37].

3. Conclusions

In summary, the synthesis and characterization of the optical and

redox properties of three A_2B type Ir^{III} triarylcorroles with push-pull *meso*-aryl substituents and three A_3 type Ir^{III} triphenylcorroles with differing pyridine axial ligands have been described. An analysis of the electronic structure and structure-property relationships has been carried out by comparing their optical spectroscopy and electrochemistry to

Table 1

Redox potentials observed for Ir^{III}triarylcorroles **2a-c** and **4a-c** in volts.

	-		-		
	$E_{1/2} \operatorname{Ox}^{II}$	$E_{1/2} \operatorname{Ox}^{\mathrm{I}}$	$E_{1/2} \operatorname{Red}^{\mathrm{I}}$	$E_{1/2} \operatorname{Red}^{II}$	$E_{1/2} \operatorname{Ox}^{\mathrm{I}} - \operatorname{Red}^{\mathrm{I}}$
2a	+1.26	+0.58	-1.71	_	2.29
2b	+1.29	+0.59	-1.68	-	2.27
2c	+1.22	+0.57	-1.71	-	2.28
4a	+1.27	+0.52	-1.95	-	2.47
4b	+1.21	+0.59	-1.37	-1.59	-
4c	+1.25	+0.51	-1.99	_	2.50



Fig. 6. CV measurements for the 2a-c/rGO and 4a-c/rGO nanocomposites in 0.1 M NaOH aqueous solution.

trends predicted in DFT and TD-DFT calculations. Further investigations with Ir^{III}corrole/rGO composites demonstrated that while push-pull A₂B type Ir^{III}triarylcorroles and axially-modified A₃ type Ir^{III}triphenylcorroles have broadly similar redox and optical properties, large differences are observed in their electrocatalytic properties of the rGO nanocomposites. Their reactivity in this regard can be modulated by changing the nature of the *meso*-substituent at the B-positions or by changing the axial pyridine ligands in the context of A₃ type Ir^{III}triphenylcorroles. These properties suggest that the electrocatalytic properties of group 9 corrole nanocomposites merit further in-depth study since it is apparent that a fine-tuning of the electrocatalytic properties of ORRs can be achieved in a rational manner on this basis once the key structure-property relationships have been identified.

4. Experimental section

4.1. General considerations

¹H NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (400.03 MHz). Residual solvent peaks were used to provide internal references ($\delta = 7.26$ ppm for CDCl₃). All reagents and solvents used were of reagent grade and were used as received unless noted otherwise. Cyclic voltammetry was carried out on a Chi-730D electrochemistry station with a three-electrode cell. A glassy carbon disk, a platinum wire and an Ag/AgCl electrode were used as the working, counter and reference electrodes, respectively. An inert nitrogen atmosphere was introduced during all of the electrochemical measurements, which were carried out at room temperature. The UV and visible regions of the electronic absorption spectra were recorded with an HP 8453A diode array spectrophotometer. A JASCO J-815 spectrodichrometer equipped with a JASCO permanent magnet (1.6 T) was used to measure magnetic circular dichroism (MCD) spectra. Spectra were recorded using both parallel and antiparallel fields. The conventions

recommended by Piepho and Schatz are used to describe the sign of the Faraday terms, so the sign of the B_0 terms matches that of the MCD signal [22].

4.2. Preparation of modified electrodes

1.0 mg of rGO was mixed with 1 mL of isopropyl alcohol containing 0.2% Nafion and the mixture sonicated in an ultrasonic bath for 30 min to produce a homogeneous mixture of concentration 1 mg/mL. The surface of the glassy carbon electrode (GCE) was polished with 0.05 μ m alumina and rinsed with doubly distilled water in the ultrasonic bath to remove any adhered Al₂O₃ particles. The electrodes were rinsed with ethanol and dried under room temperature for ca. 5 min. Three 3 μ L of the rGO/isopropyl alcohol/Nafion suspensions was drop cast on the surface of the GC electrode and allowed to dry at room temperature. 10 μ L aliquots of 0.2 mM dichloromethane solutions of **2a-c** and **4a-c** were added dropwise to the rGO/Nafion-coated electrodes and dried at room temperature for 1 h. The electrodes were stored in MilliQ water in the dark.

4.3. Computational methods

The Gaussian 09 software package [23] was used to carry out DFT geometry optimizations for **2a-c** and **4a-c** and a model complex **5** (Scheme S1, *see ESI*) with *meso*-trifluoromethylphenyl rings at both the B- and A₂-positions by using the B3LYP functional with SDD basis sets. TD-DFT calculations were carried out by using CAM-B3LYP functional, which includes a long-range correction of the exchange potential, since this provides more accurate results for complexes that have excited states with significant intramolecular charge transfer character. The Chemcraft program [24] was used to generate simulated spectra.

4.4. Synthesis and characterizations

4.4.1. Synthesis of bis(pyridine)Ir(III)-5,15-(p-trifluoromethylphenyl)-10-phenylcorrole, 2a

Synthesis of meso-p-trifluoromethylphenyl-dipyrromethane followed the literature reported procedure. meso-p-trifluoromethylphenyl-dipyrromethane (2 mmol, 0.6106 g) and benzaldehyde acid (1 mmol, 0.2 g) were stirred in a mixed methanol/5% HCl acid (v:v = 1:1) solution for 1 h. The organic components were extracted with CH₂Cl₂, and the solvent was fully evaporated. The residue was dissolved in 10 mL CH₂Cl₂ and pchloranil was added and the solution was heated to reflux at 55 °C for 5 h to give the 5,15-(p-trifluoromethylphenyl)-10-phenylcorrole 1a in 67.2% yield (0.1546 g). 1a (0.0331 g, 0.05 mmol), [Ir(cod)Cl]₂ (0.1679 g, 0.25 mmol) and anhydrous K₂CO₃ (0.0691 g, 0.5 mmol) were dissolved in a 40 mL anhydrous THF, and refluxed at 85 °C under N2 for 90 min. Once fluorescence was no longer observed, pyridine (0.4746 g, 0.6 mmol) was added. After removal of the organic solvent, purification by silica gel column chromatography gave the deep purple 2a target compound in 6.9% yield (0.0519 g). MALDI-TOF-mass: m/z = 1010.44(Calcd. $[M]^+ = 1010.40$). ¹H NMR (400 MHz, CDCl₃, 298K): $\delta_{\rm H}$, 8.89 (s, 2H), 8.65 (d, J = 4.9 Hz, 2H), 8.43 (s, 2H), 8.36 (d, J = 7.2 Hz, 4H), 8.20 (s, 5H), 8.01 (d, J = 7.9 Hz, 4H), 7.95 (d, J = 8.0 Hz, 2H), 6.13 (d, J = 7.5 Hz, 2H), 5.19 (d, J = 7.4 Hz, 4H), 1.72 (d, J = 5.8 Hz, 4H).

4.4.2. Synthesis of bis(pyridine)Ir(III)-5,15-(p-trifluoromethylphenyl)-10-pentafluorophenyl-corrole, 2b

The synthetic procedure is the same as for **2a**, with pentafluorobenzaldehyde used instead of benzaldehyde, and the target compound was obtained in a 30.3% yield (0.053 g). MALDI-TOF-MS: m/z =1099.97 (Calcd. [M]⁺ = 1099.99). ¹H NMR (400 MHz, CDCl₃, 298K): $\delta_{\rm H}$, 8.93 (dd, J = 14.4, 4.2 Hz, 2H), 8.70–8.58 (m, 2H), 8.47 (s, 2H), 8.39 (d, J = 7.6 Hz, 2H), 8.34–8.23 (m, 4H), 8.03 (d, J = 8.1 Hz, 2H), 7.97 (d, J =6.5 Hz, 2H), 6.17 (dd, J = 14.6, 7.3 Hz, 2H), 5.23 (dt, J = 10.5, 7.2 Hz, 4H), 1.78 (dd, J = 39.1, 5.5 Hz, 4H).



Scheme 1. Synthesis of Ir(III)corroles 2a-c and 4a-c.

4.4.3. Synthesis of bis(pyridine)Ir(III)-5,15-(p-trifluoromethylphenyl)-10methoxyphenyl-corrole, 2c

The synthetic procedure is the same as **2a**, with 4-methoxybenzaldehyde used instead of benzaldehyde. The target compound was obtained in a 32.5% yield (0.0930 g). MALDI-TOF-MS: m/z = 1040.15 (Calcd. $[M]^+ = 1040.06$). ¹H NMR (400 MHz, CDCl₃, 298K): $\delta_{\rm H}$, 8.88 (d, J = 4.2Hz, 2dcH), 8.64 (d, J = 4.8 Hz, 2H), 8.45 (d, J = 4.8 Hz, 2H), 8.38 (d, J =7.9 Hz, 4H), 8.28 (d, J = 4.2 Hz, 2H), 8.23 (d, J = 7.9 Hz, 2H), 8.00 (d, J =8.0 Hz, 4H), 7.94 (d, J = 8.0 Hz, 2H), 6.13 (t, J = 7.6 Hz, 2H), 5.19 (t, J = 7.2 Hz, 4H), 3.75 (q, J = 7.2 Hz, 6H), 1.70 (d, J = 5.5 Hz, 4H). 4.4.4. Synthesis of bis(pyridine)iridium(III)5,10,15-triphenylcorrole, 4a

Synthesis of 5,10,15-triphenylcorrole **3** followed the literature reported procedure. Free base corroles **3** (0.0263 g, 0.05 mmol), [Ir(cod) Cl]₂ (0.1679 g, 0.25 mmol) and anhydrous K₂CO₃ (0.0691 g, 0.5 mmol) were dissolved in 40 mL of anhydrous THF and refluxed at 85 °C under N₂ for 90 min. After the disappearance of fluorescence, pyridine (0.4746 g, 0.6 mmol) was added. After removal of the organic solvent, purification by silica gel column chromatography gave the pure deep solid-state compound **4a** in 25% yield (0.0519 g). MALDI-TOF-MS: *m/z* = 874.72 (Calcd. [M]⁺ = 874.04). ¹H NMR (400 MHz, CDCl₃, 298K): $\delta_{\rm H}$, 8.83 (d, *J* = 4.1 Hz, 2H), 8.66 (d, *J* = 4.8 Hz, 2H), 8.42 (d, *J* = 4.7 Hz,

2H), 8.25 (d, J = 7.1 Hz, 5H), 8.07 (d, J = 7.0 Hz, 2H), 7.74 (t, J = 7.5 Hz, 4H), 7.69–7.50 (m, 6H), 6.08 (ddd, J = 7.6, 4.6, 1.5 Hz, 2H), 5.22–5.12 (m, 4H), 1.81 (dd, J = 6.7, 1.3 Hz, 4H).

4.4.5. Synthesis of bis(4-cyanopyridine)iridium(III)5,10,15triphenylcorrole, 4b

The general synthetic procedure is the same as for **4a**, with 4-cyanopyridine used instead of pyridine, and the target compound was obtained in a 30.3% yield (0.053 g). MALDI-TOF-MS: m/z = 923.65 (Calcd. $[M]^+ = 924.06$). ¹H NMR (400 MHz, CDCl₃, 298K): $\delta_{\rm H}$, 8.92 (d, J = 4.2Hz, 2H), 8.74 (d, J = 4.8 Hz, 2H), 8.53 (d, J = 4.8 Hz, 2H), 8.40 (d, J =4.2 Hz, 2H), 8.31–8.25 (m, 4H), 8.13 (dd, J = 7.9, 1.4 Hz, 2H), 7.82–7.75 (m, 4H), 7.74–7.67 (m, 5H), 5.43 (dd, J = 5.7, 1.4 Hz, 4H), 1.90–1.83 (m, 4H).

4.4.6. Synthesis of bis(4-methoxypyridine)iridium(III)5,10,15triphenylcorrole, 4c

The synthetic procedure is the same as for **4a**, with 4-methoxypyridine used instead of pyridine. The target compound was obtained in a 30.3% yield (0.053 g). MALDI-TOF-MS: m/z = 935.86 (Calcd. $[M]^+ = 935.76$). ¹H NMR (400 MHz, CDCl₃, 298K): $\delta_{\rm H}$, 8.80 (s, 2H), 8.64 (d, J = 4.7 Hz, 2H), 8.42 (d, J = 4.7 Hz, 2H), 8.27 (d, J = 7.1 Hz, 5H), 8.10 (d, J = 7.1 Hz, 2H), 7.74 (t, J = 7.5 Hz, 4H), 7.63 (tt, J = 15.0, 7.3 Hz, 6H), 4.70 (d, J = 7.4 Hz, 4H), 2.92 (s, 6H), 1.66 (d, J = 7.2 Hz, 4H).

Declaration of competing interest

There is no competitive financial interest.

CRediT authorship contribution statement

Xifeng Zhang: Data curation, Formal analysis. Yu Wang: Data curation, Formal analysis. Weihua Zhu: Supervision, Validation, Writing - original draft, Writing - review & editing. John Mack: Data curation, Formal analysis. Rodah C. Soy: Data curation, Formal analysis. Tebello Nyokong: Data curation, Formal analysis. Xu Liang: Supervision, Validation, Writing - original draft, Writing - review & editing.

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Appendix A. Supplementary data

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