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Luminescent, Enantiopure, Phenylatopyridine Iridium-Based Coordination Capsules**

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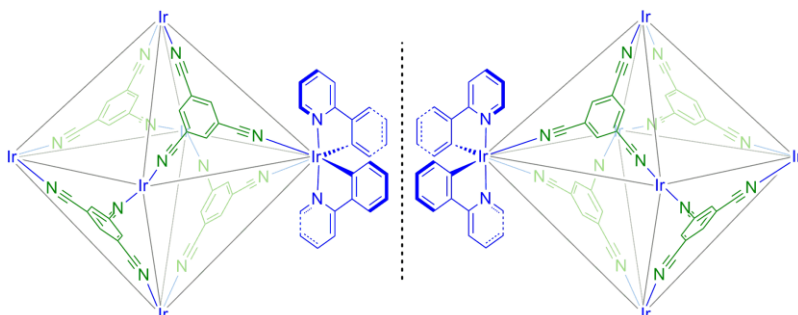
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Supporting information:

For full synthetic details and compound characterisation, crystallographic results in cif format, details of IMMS calculations, volume calculations, see the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>

Graphical abstract:



Abstract

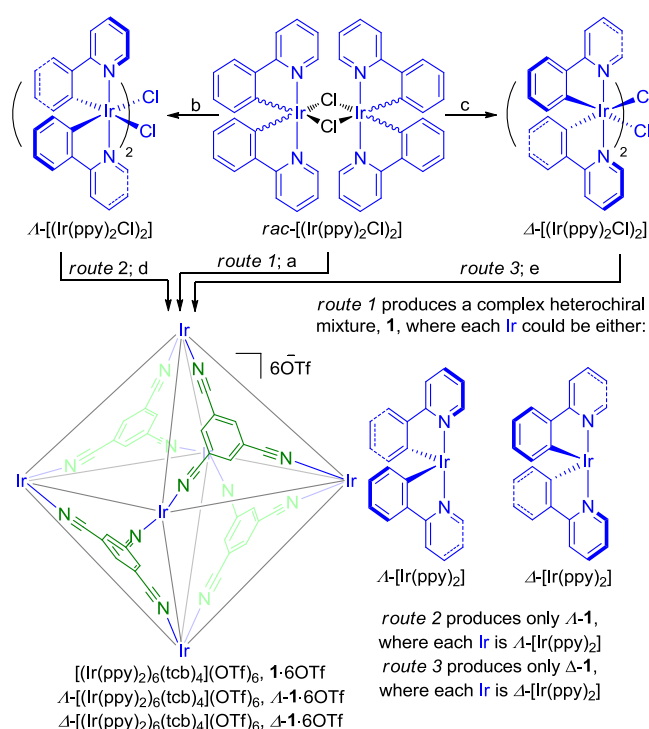
The first molecular capsule based on an $[\text{Ir}(\text{ppy})_2]^+$ unit (ppy = 2-phenylatopyridine) has been prepared. Following the development of a method to resolve *rac*- $[(\text{Ir}(\text{ppy})_2\text{Cl})_2]$ into its enantiopure forms, homochiral Ir_6L_4 octahedra were obtained with the tritopic 1,3,5-tricyanobenzene. Solution studies and XRD show that these capsules encapsulate four of the six associated counteranions and that these can be exchanged for other anionic guests. Initial photophysical studies have shown that an ensemble of weakly coordinating ligands can lead to luminescence not present in comparative, mononuclear systems.

Introduction

The combination of transition metal ions and geometrically complementary, multitopic bridging organic ligands has led to the preparation of numerous molecular capsules and cages.¹ These assemblies possess well-defined internal cavities that promote the ingress of guest molecules so that interesting functions, such as catalysis or the stabilisation of reactive species, may be observed.^{1,2} By and large, the transition metal ions within these systems have played solely a structural role, offering advantages such as predictable, well-defined coordination preferences and bond strength.³ However, transition metals and their complexes often possess many other notable features, such as interesting photophysical properties; arguably the most well-known class are the poly(pyridyl) complexes of ruthenium(II),⁴ while more recently, analogous cyclometallated C^N iridium(III) complexes have found widespread use as luminescent biological probes⁵ and as dopants in OLEDs.⁶ Although Newkome has described the synthesis of several very elegant metallocycles which feature $[\text{Ru}(\text{terpy})_2]^{2+}$ connections,⁷ the use of Ru poly(pyridyl) or cyclometallated Ir complexes as structural components in metallosupramolecular assemblies, in particular polyhedral architectures, remains rare.^{7,8} Herein, we report the first molecular capsule based on an $[\text{Ir}(\text{ppy})_2]^+$ (ppy = 2-phenylatopyridine) motif, and demonstrate that incorporation of this unit into a multimetallic array leads to a significant luminescence enhancement with respect to a comparative mononuclear complex, thus paving the way to capsules with light-harvesting function and the development of devices with emergent luminescent properties.

It was initially envisaged that $[\text{Ir}(\text{ppy})_2]^+$ could be used in an analogous fashion to *cis*-protected square planar complexes, such as either $[\text{Pd}(\text{en})]^{2+}$ or $[\text{Pt}(\text{dppp})]^{2+}$,⁹ and that the ppy ligands, arranged in a *C,C-cis-N,N-trans* orientation, would sufficiently labilise the exchangeable sites to facilitate self-assembly.¹⁰ Targeting an M_6L_4 octahedron,¹¹ at first we chose to explore the reaction of tris(4-pyridyl)triazine with the known iridium compound, $[\text{Ir}(\text{ppy})_2(\text{CH}_3\text{CN})_2]\text{OTf}$. As no evidence could be gathered for the formation of the intact architecture, we decided to instead investigate the self-assembly of the same Ir starting material with 1,3,5-tricyanobenzene (tcb). While it was anticipated that acetonitrile substitution from $[\text{Ir}(\text{ppy})_2(\text{CH}_3\text{CN})_2]\text{OTf}$ by tcb to generate the M_6L_4 assembly should be entropically, if not enthalpically, favoured, initial experiments suggested only partial displacement. Instead, what is presumed to be $[(\text{Ir}(\text{ppy})_2\text{OTf})_2]$,¹² prepared by treating

$[(\text{Ir}(\text{ppy})_2\text{Cl})_2]$ with silver triflate in $\text{C}_2\text{H}_4\text{Cl}_2$, was reacted with tcb in the same solvent (Scheme 1, step a). While the product gave a relatively complex ^1H NMR spectrum (see the Supporting Information, Figure S1a), Nanoelectrospray Mass Spectrometry (n-ESI-MS) showed an intense 2+ peak at 2106 m/z (see the Supporting Information, Figure S2a), which matched the predicted isotope pattern for $[\mathbf{1}\cdot 6\text{OTf}]^{2+}$. A ^1H DOSY NMR spectrum of the product also showed that the multiple aromatic signals possessed similar diffusion coefficients (see the Supporting Information, Figure S3a). This led us to postulate that $\mathbf{1}\cdot 6\text{OTf}$ is formed as a complex mixture of diastereoisomers¹³ when the synthesis commences from racemic $\text{rac}-[(\text{Ir}(\text{ppy})_2\text{Cl})_2]$ (Scheme 1, route 1) and thus tcb does not efficiently transmit stereochemical information between adjacent metal centres.¹⁴



Scheme 1. Synthesis of heterochiral and homochiral hexanuclear iridium assemblies. Conditions: a) (i) AgOTf , $\text{C}_2\text{H}_4\text{Cl}_2$, RT, 2 h; (ii) tcb, $\text{C}_2\text{H}_4\text{Cl}_2$, RT, 4 h, 48% (starting from $\text{rac}-[(\text{Ir}(\text{ppy})_2\text{Cl})_2]$). b) (i) *D*-serine, NaOMe, MeOH, 313 K, 16 h; (ii) 1M HCl, MeOH, RT, 10 min, 50% (from $\text{rac}-[(\text{Ir}(\text{ppy})_2\text{Cl})_2]$). c) *L*-serine, NaOMe, MeOH, 313 K, 16 h; (ii) 1M HCl, MeOH, RT, 10 min, 37% (from $\text{rac}-[(\text{Ir}(\text{ppy})_2\text{Cl})_2]$). d) (i) AgOTf , $\text{C}_2\text{H}_4\text{Cl}_2$, RT, 2 h; (ii) tcb, $\text{C}_2\text{H}_4\text{Cl}_2$, RT, 5 h, 57% (starting from $\Delta-[(\text{Ir}(\text{ppy})_2\text{Cl})_2]$). e) (i) AgOTf , $\text{C}_2\text{H}_4\text{Cl}_2$, RT, 2 h; (ii) tcb, $\text{C}_2\text{H}_4\text{Cl}_2$, RT, 4 h, 68% (starting from $\Lambda-[(\text{Ir}(\text{ppy})_2\text{Cl})_2]$).

To eliminate the problem of mixed stereoisomer formation, we have developed a preparative method to resolve *rac*-[(Ir(ppy)₂Cl)₂] into its enantiopure forms,¹⁵ which involves chromatographic resolution of serine complexes (Scheme 1, steps b and c).¹⁶ We have found that the most efficient method to obtain both enantiomers (which, as expected, exhibit mirror image CD spectra, see the Supporting Information, Figure S4), is to resolve with both *D* and *L*-serine, as the similarity in *R_f* values on silica ensure that only the faster running diastereoisomer can be obtained in significant quantities. Both enantiomers crystallize in the chiral space group *P*2₁2₁2₁ upon diethyl ether diffusion into saturated dichloromethane solutions; the solid-state structures (see the Supporting Information, Figure S5) reveal that the compound isolated following resolution with *D*-serine is *Δ*-[(Ir(ppy)₂Cl)₂] and from *L*-serine, *Λ*-[(Ir(ppy)₂Cl)₂] is obtained (Scheme 1, steps b and c).¹⁷

When the self-assembly was commenced from either *Δ* or *Λ*-[(Ir(ppy)₂Cl)₂] (Scheme 1, routes 2 and 3), a precipitate was observed shortly after the addition of tcb to what are presumed to be *Δ* and *Λ*-[(Ir(ppy)₂OTf)₂], which was then isolated after a few hours stirring at room temperature. We were delighted to find that not only were the ¹H NMR spectra of the two products indistinguishable (see the Supporting Information, Figure S1b and c), but also clearly single species with the number and ratio of tcb to ppy signals consistent with the sole formation of *Δ* and *Δ*-1. CD confirmed that the two compounds were enantiomers (see the Supporting information, Figure S4). The mass spectra also showed essentially single species at 2106 *m/z*, which correspond to the doubly charged [1·4OTf]²⁺ (see the Supporting information, Figure S2b and c). The surprising lack of other charge states in the MS of *Δ* and *Δ*-1·6OTf prompted us to look at the ¹⁹F NMR spectra (see the Supporting Information, Figure S6a), which showed two distinct signals at -77.45 and -79.04 ppm in a ratio of 1:2, respectively. Addition of excess NBu₄OTf resulted in an increase in the intensity of the peak at -77.45 (see the Supporting Information, Figure S6b), strongly suggesting that the peak at -79 is due to encapsulated triflates. A combination of other NMR techniques (HOESY and DOSY, see the Supporting information, Figure S7 and 8) confirm this assignment and thus support the solution structure [4OTf⊂*Δ*-1]·2OTf. Further EXSY NMR experiments have shown that the *exo* and *endo* triflates are in slow exchange and that the activation barrier for this process is 18 kcal mol⁻¹ (see the Supporting information, Figure S9).

Corroboration of the capsule's structure (Figure 1) was obtained from XRD using single crystals grown from benzene diffusion into a saturated dichloroethane solution of *Δ*-1·6OTf.^{18,19} The solid-state structure supports the solution structure, [4OTf⊂*Δ*-1]²⁺, showing triflates located in each of the octahedron 'windows'. For two encapsulated triflates (with S labels 3 and 4), the S-C axis points towards the centre of these vacant windows (or if viewed as a truncated tetrahedron, towards the vertex) forming a series of close contacts between the triflate oxygens and the hydrogen atoms attached to tcb, and the *ortho* pyridyl positions. The other encapsulated anions (with S labels 1 and 6) are positioned in a slightly more "side-on" fashion, with the cage forming short contacts between two of the oxygen atoms and one of the fluorines. It seems probable that in solution these two distinct triflate co-conformations participate in a low energy exchange process, thus explaining the presence of a single "encapsulated" signal by ¹⁹F NMR spectroscopy at room temperature.

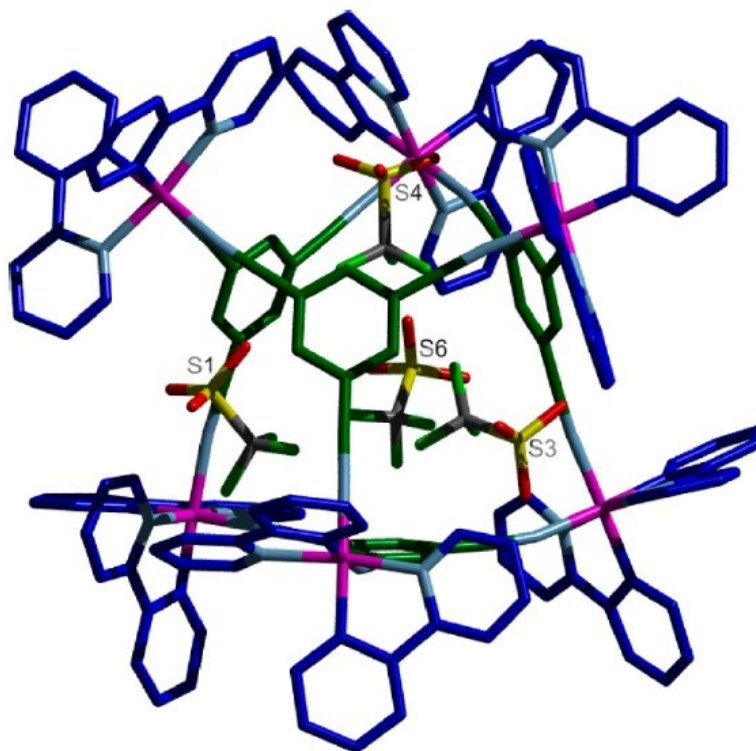


Figure 1. X-ray crystal structures of $[4OTfC-1]^{2+}$. Color code: Ir, magenta; C(ppy), blue; C(tcb), dark green; C(OTf), grey; N, light blue; O, red; S, yellow; F, light green.

To explore whether the structure, and in particular the encapsulated anions, are preserved under MS conditions, Ion-Mobility measurements have been undertaken.²⁰ For the ions at 2106 m/z , both samples gave superimposable arrival time distributions consistent with a single species / conformation (see the Supporting information, Figure S10). The observed rotationally averaged collision cross sections (CCS) for *A* and *A-1* were found to be 551 and 543 Å², respectively, virtually within error of each other. To validate these, ion-mobility simulations have been carried out using structures derived from the XRD data. The values calculated using either the Exact Hard Spheres Scattering (EHSS) or Trajectory Method (TJM), 555 and 551 Å², respectively, agree remarkably well with the experimental data suggesting that the counteranions remain within the capsule upon ionisation into the gas phase.

Examples of metallocapsules which encapsulate multiple species of the same charge are very rare.²¹ Clearly, the strong coulombic attraction between the positively charged Ir vertices and negative counteranions, alongside the series of CH \cdots X (X = O, F) hydrogen bonds (*vide supra*), are enough to overcome the repulsion between same-charge ions. It could also be that the CF₃ groups, which are “meshed” together within the centre of the cavity (C-C distances between encapsulated OTf counteranions range from 4.93-6.05 Å, with an average distance of 5.55 Å), act to insulate this charge. To probe further, we have calculated the capsule’s occupancy. Based on an irregular hexadecahedron model (see Supporting Information for details), the volume

of the empty cavity has been calculated to be 506 \AA^3 of which the triflate counteranions occupy 280 \AA^3 , which equates to 55% filled cavity space, in line with previous observations made by Rebek.²²

Held under a standard longwave UV lamp, tetrachloroethane (TCE) solutions of *A* and *A*-1.6OTf luminesce orange (Figure 2, inset). As most literature Ir complexes are luminescent, the significance of the capsules photophysical properties only becomes apparent when compared against the representative mononuclear bis(benzonitrile) complex, $[\text{Ir}(\text{ppy})_2(\text{PhCN})_2]\text{OTf}$.²³ Placed next to the samples of *A* and *A*-1 under UV light (Figure 2, inset), there is no visible luminescence from $[\text{Ir}(\text{ppy})_2(\text{PhCN})_2]\text{OTf}$ in the same solvent (at equivalent $[\text{Ir}]$). The absorption and emission spectra of these samples confirm these visual observations (Figure 2). Even with a vast excess of benzonitrile, $[\text{Ir}(\text{ppy})_2(\text{PhCN})_2]\text{OTf}$ is only weakly luminescent (Figure 2). The emission of *A* and *A*-1.6OTf is also broadened and red-shifted with respect to $[\text{Ir}(\text{ppy})_2(\text{PhCN})_2]\text{OTf}$ (in the presence of excess benzonitrile), signifying increased charge transfer character of the emitting state. While the quantum yields for *A* and *A*-1.6OTf, found to be 0.04 in air-equilibrated tetrachloroethane (see the Supporting Information) are comparable to many cyclometallated Ir complexes under similar ambient conditions,²⁴ these often utilise either bidentate or strongly coordinating (and high ligand strength) monodentate ligands.²⁵ As far as we are aware, this is the first time a collection of weakly coordinating ligands has been used to inhibit non-radiative ligand dissociation pathways.²⁶ Interestingly, the emission intensity of *A* and *A*-1.6OTf only increases marginally (by a factor of 1.1) when the samples are thoroughly degassed, in contrast to many other such Ir complexes,²⁴ suggesting that the metallosupramolecular architecture may also in some way inhibit collisional O_2 quenching.^{24b} Alternatively, the presence of four desolvated anions located within the cavity of the capsule may provide such an efficient, alternative non-radiative decay pathway (e.g. via electron transfer) that the capsule is insensitive to the presence of O_2 .

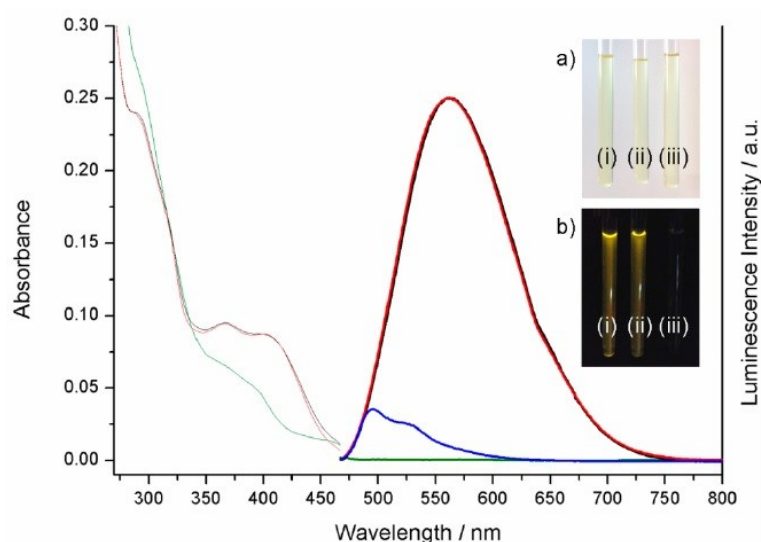


Figure 2. Absorption and emission (excitation at 413 nm) spectra of *A* and *A*-1.6OTf. *A* = black line; *A* = redline; TCE, 2 μM . For comparison, the spectra of the mononuclear $[\text{Ir}(\text{ppy})_2(\text{PhCN})_2]\text{OTf}$ are also shown (Ir

only = green line; Ir + 3000 eq. PhCN = blue line; TCE, 12 μ M). Inset: A photograph of i) *A*-**1.6**OTf, ii) *A*-**1.6**OTf and iii) [Ir(ppy)₂(PhCN)₂]OTf in NMR tubes held a) in ambient lighting and b) under a longwave UV lamp.

A preliminary investigation into the host-guest chemistry of [4OTf@*A/A*-**1**]²⁺ indicates that the encapsulated triflates can be exchanged for other anionic species. When NBu₄PF₆ is titrated into a sample of [4OTf@*A/A*-**1**]₂OTf in C₂D₂Cl₄, ¹⁹F NMR spectroscopy (see the Supporting information, Figure S12) shows multiple OTf and PF₆ signals at low [PF₆], indicative of mixed PF₆-OTf host-guest complexes. At equimolar anionic concentrations, encapsulated OTf has mostly been displaced. This process has also been monitored by ¹H NMR spectroscopy (see the Supporting information, Figure S13), which shows that while the overall symmetry is preserved, the proton signals closest to the anion binding sites (the tcb hydrogen atom and the *ortho* and *meta* pyridyl sites) are noticeably shifted. Similar experiments with NBu₄BF₄ and NBu₄CF₃BF₃, and additional titrations into *A*-**1.6**BF₄ (see the Supporting information, Figure S14 to S23), have led us to ascertain that the overall affinity of perfluorinated anions for the cavity of [*A/A*-**1**]⁶⁺ follows the sequence PF₆>OTf \approx CF₃BF₃>BF₄.^{22c} While at present we are unable to rationalise this affinity, due to the fast exchange of some of the anionic species (even at low temperatures), additional DOSY measurements show that the cage remains intact following guest exchange. We have also ascertained there is communication between the luminescent properties of [*A/A*-**1**]⁶⁺ and the cavity-bound guests, as evidenced by changes to the emission spectra during anion titration experiments (see the Supporting information). As well as showing that [*A/A*-**1**]⁶⁺ acts as a luminescent anion sensor, this also suggests it may be possible to tune luminescent properties of multimetallic Ir assemblies through supramolecular means rather than via conventional covalent modification. Our initial attempts to expand host-guest chemistry to neutral organic species have so far been hampered by the low solubility / stability of *A/A*-**1** in more polar solvents.

In summary, the first molecular capsule based on an [Ir(ppy)₂]⁺ unit has been assembled using a multitopic nitrile ligand and enantiopure Ir starting materials. This incorporation leads to luminescence not present in a comparative mononuclear complex. In addition, we have shown that the same capsule is capable of binding multiple same-charge species and that these can be swapped for other anionic guests. We are currently exploring further aspects of this system, in particular how guest-binding features and photophysical properties relate, and whether the light-harvesting properties can be exploited in relation to potential substrate binding.

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[23] In C₂D₂Cl₄, [Ir(ppy)₂(PhCN)₂]OTf appears to be in a 3:1 equilibrium with a mono benzonitrile species; addition of a small excess of PhCN (10 eq) shifts the equilibrium so that [Ir(ppy)₂(PhCN)₂]OTf is the sole complex in solution (see the Supporting information, Figure S5).

[24] There are only a few reported air-equilibrated quantum yields for Ir complexes, see (a) Plummer, E. A.; Hofstraat, J. W.; De Cola, L. *Dalton Trans.* **2003**, *22*, 2080. This is because they exhibit strong O₂ quenching, e.g. for the ubiquitous [Ir(ppy)₃], Φ = 0.71; Φ_{air} = 0.03, see (b) Ruggi, A.; Berenguel Alonso, M.; Reinhoudt, D.N.; Velders, A. H. *Chem. Commun.* **2010**, *46*, 6726.

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