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Luminescent, Enantiopure, Phenylatopyridine Iridium-Based Coordination Capsules

Oleg Chepelin,[†] Jakub Ujma,[†] Xiaohua Wu,[†] Alexandra M. Z. Slawin,[‡] Mateusz B. Pitak,[§] Simon J. Coles,[§] Julien Michel,[†] Anita C. Jones,[†] Perdita E. Barran,[†] and Paul J. Lusby*,[†]

[†]EaStCHEM School of Chemistry, University of Edinburgh, The King's Buildings, West Mains Road, Edinburgh EH9 3JJ, U.K.
[‡]EaStCHEM School of Chemistry, University of St. Andrews, Purdie Building, St. Andrews, Fife KY16 9ST, U.K.
[§]UK National Crystallography Service, School of Chemistry, University of Southampton, Southampton, SO17 1BJ, U.K.

Supporting Information

ABSTRACT: The first molecular capsule based on an $[Ir(ppy)_2]^+$ unit (ppy = 2-phenylatopyridine) has been prepared. Following the development of a method to resolve *rac*-$[(Ir(ppy)_2Cl)_2]$ into its enantiopure forms, homochiral Ir_6L_4 octahedra where obtained with the tritopic 1,3,5-tricyanobenzene. Solution studies and X-ray diffraction 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 comparable mononuclear systems.

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 stabilization 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 cyclometalated C^N iridium(III) complexes have found widespread use as luminescent biological probes[5] and as dopants in organic light-emitting devices.[6] Although Newkome has described the synthesis of several very elegant metallocycles which feature $[Ru(terpy)_2]^{2+}$ connections,[7] the use Ru poly(pyridyl) or cyclometalated 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 $[Ir(ppy)_2]^+$ (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 comparable 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 $[Ir(ppy)_2]^+$ could be used in an analogous fashion to *cis*-protected square planar complexes, such as $[Pd(en)]^{2+}$ or $[Pt(dppp)]^{2+}$,[9] and that the ppy ligands, arranged in a *C,C-cis-N,N-trans* orientation, would sufficiently labilize 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, $[Ir(ppy)_2(CH_3CN)_2]OTf$. 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 $[Ir(ppy)_2(CH_3CN)_2]OTf$ by tcb to generate the M_6L_4 assembly should be entropically, if not enthalpically, favored, initial experiments suggested only partial displacement. Instead, what is presumed to be $[(Ir(ppy)_2OTf)_2]$,[12] prepared by treating $[(Ir(ppy)_2Cl)_2]$ with silver triflate in $C_2H_4Cl_2$, 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 ionization mass spectrometry (n-ESI-MS) showed an intense 2+ peak at 2106 *m*/*z* (see Figure S2a), which matched the predicted isotope pattern for $[\mathbf{1}\cdot 4OTf]^{2+}$. A ^1H DOSY NMR spectrum of the product also showed that the multiple aromatic signals possessed similar diffusion coefficients (see Figure S3a). This led us to postulate that $\mathbf{1}\cdot 6OTf$ is formed as a complex mixture of diastereoisomers[13] when the synthesis commences from racemic $[(Ir(ppy)_2Cl)_2]$ (Scheme 1, route 1), and thus tcb does not efficiently transmit stereochemical information between adjacent metal centers.[14]

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 circular dichroism (CD) spectra; see Figure S4) is to resolve with both D- and L-serine, as the similarity in R_f values on silica ensures that only the faster-running diastereoisomer can be obtained in significant quantities. Both enantiomers crystallize in the chiral space group $P2_12_12_1$ upon diethyl ether

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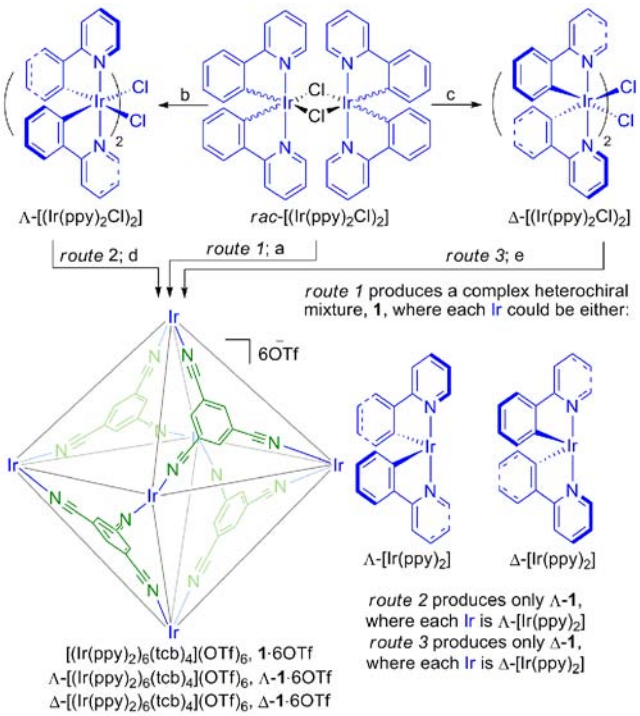
Scheme 1. Synthesis of Heterochiral and Homochiral Hexanuclear Iridium Assemblies[a]



[a] Conditions: (a) (i) AgOTf, $C_2H_4Cl_2$, RT, 2 h; (ii) tcb, $C_2H_4Cl_2$, RT, 4 h, 48% (starting from *rac*-[$(Ir(ppy)_2Cl)_2$]). (b) (i) D-Serine, NaOMe, MeOH, 313 K, 16 h; (ii) 1 M HCl, MeOH, RT, 10 min, 50% (from *rac*-[$(Ir(ppy)_2Cl)_2$]). (c) L-Serine, NaOMe, MeOH, 313 K, 16 h; (ii) 1 M HCl, MeOH, RT, 10 min, 37% (from *rac*-[$(Ir(ppy)_2Cl)_2$]). (d) (i) AgOTf, $C_2H_4Cl_2$, RT, 2 h; (ii) tcb, $C_2H_4Cl_2$, RT, 5 h, 57% (starting from Λ-[$(Ir(ppy)_2Cl)_2$]). (e) (i) AgOTf, $C_2H_4Cl_2$, RT, 2 h; (ii) tcb, $C_2H_4Cl_2$, RT, 4 h, 68% (starting from Δ-[$(Ir(ppy)_2Cl)_2$]).

diffusion into saturated dichloromethane solutions; the solid-state structures (see Figure S5) reveal that the compound isolated following resolution with D-serine is Λ-[$(Ir(ppy)_2Cl)_2$], and that from L-serine is Δ-[$(Ir(ppy)_2Cl)_2$] (Scheme 1, steps b and c).[17]

When the self-assembly was commenced from either Λ- or Δ-[$(Ir(ppy)_2Cl)_2$] (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 of stirring at room temperature. We were delighted that the ^{1}H NMR spectra of the two products not only were indistinguishable (see Figure S1b,c) but also clearly showed single species with the number and ratio of tcb-to-ppy signals consistent with the sole formation of Λ- and Δ-**1**. CD confirmed that the two compounds were enantiomers (see Figure S4). The mass spectra also showed essentially a single species at 2106 *m*/*z*, which corresponds to the doubly charged [**1**·4OTf]$^{2+}$ (see Figure S2b,c). The surprising lack of other charge states in the mass spectra of Λ- and Δ-**1**·6OTf prompted us to look at the ^{19}F NMR spectra (see Figure S6a), which showed two distinct signals at −77.45 and −79.04 ppm in a ratio of 1:2, respectively. Addition of excess NBu_4OTf resulted in an increase in the intensity of the peak at −77.45 ppm (see Figure S6b), strongly suggesting that the peak at −79 ppm is due to encapsulated triflates. Other NMR techniques (HOESY and DOSY; see Figures S7 and S8) 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 Figure S9).

Corroboration of the capsule's structure (Figure 1) was obtained from X-ray diffraction (XRD) using single crystals grown from benzene diffusion into a saturated dichloroethane solution of Δ-**1**·6OTf.[17,18] 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 toward the center of these vacant windows (or, if viewed as a truncated tetrahedron, toward 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 in the ^{19}F NMR spectrum at room temperature.

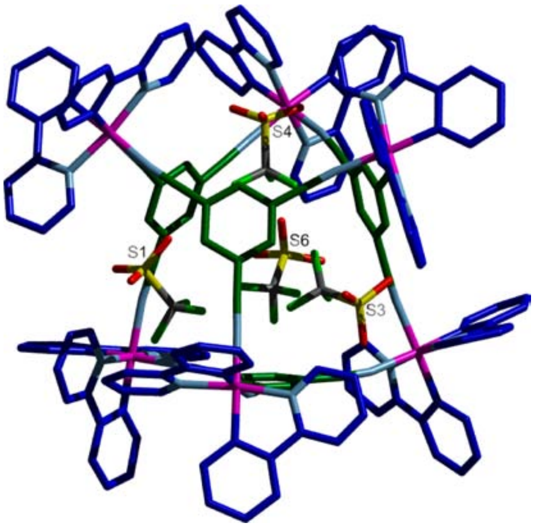


Figure 1. X-ray crystal structures of [4OTf⊂Δ-**1**]$^{2+}$. Color code: Ir, magenta; C(ppy), dark blue; C(tcb), dark green; C(OTf), gray; N, light blue; O, red; S, yellow; F, light green.

To explore whether the structure and, in particular, the encapsulated anions are preserved under MS conditions, ion-mobility measurements have been undertaken.[19] For the ions at 2106 *m*/*z*, both samples gave superimposable arrival time distributions, consistent with a single species/conformation (see Figure S10). The observed rotationally averaged collision cross sections for Λ- and Δ-**1** were found to be 551 and 543 Å^2, 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 or trajectory method, 555 and 551 Å^2, respectively, agree remarkably well with the experimental data, suggesting that the counteranions remain within the capsule upon ionization into the gas phase.

Examples of metallocapsules which encapsulate multiple species of the same charge are very rare.[20] Clearly, the strong Coulombic attraction between the positively charged Ir vertices and negative counteranions, alongside the series of CH···X (X

= O, F) hydrogen bonds (*vide supra*), is enough to overcome the repulsion between same-charge ions. It could also be that the CF_3 groups, which are "meshed" together within the center of the cavity (C−C distances between encapsulated OTf counteranions range from 4.93 to 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 $Å^3$, of which the triflate counteranions occupy 280 $Å^3$, which equates to 55% filled cavity space, in line with previous observations made by Rebek.[21]

Held under a standard long-wavelength UV lamp, tetrachloroethane (TCE) solutions of Λ- and Δ-**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, $[Ir(ppy)_2(PhCN)_2]OTf$.[22] Placed next to the samples of Λ- and Δ-**1** under UV light (Figure 2, inset), there is no visible luminescence from $[Ir(ppy)_2(PhCN)_2]OTf$ in the same solvent (at equivalent [Ir]). The absorption and emission spectra of these samples confirm these visual observations (Figure 2). Even with a vast excess of benzonitrile, $[Ir(ppy)_2(PhCN)_2]OTf$ is only weakly luminescent (Figure 2). The emission of Λ- and Δ-**1**·6OTf is also broadened and red-shifted with respect to $[Ir(ppy)_2(PhCN)_2]OTf$ (in the presence of excess benzonitrile), signifying increased charge-transfer character of the emitting state. While the quantum yields for Λ- and Δ-**1**·6OTf, found to be 0.04 in air-equilibrated TCE (see the Supporting Information), are comparable to those for many cyclometalated Ir complexes under similar ambient conditions,[23] these often utilize either bidentate or strongly coordinating (and high ligand strength) monodentate ligands.[24] As far as we are aware, this is the first time a collection of weakly coordinating ligands has been used to inhibit nonradiative ligand dissociation pathways.[25] Interestingly, the emission intensity of Λ- and Δ-**1**·6OTf increases only marginally (by a factor of 1.1) when the samples are thoroughly degassed, in contrast to many other such Ir complexes,[23] suggesting that the metallosupramolecular architecture may also in some way inhibit collisional O_2 quenching.[23b] Alternatively, the presence of four desolvated anions located within the cavity of the capsule may provide such an efficient, alternative nonradiative decay pathway (e.g., via electron transfer) that the capsule is insensitive to the presence of O_2.

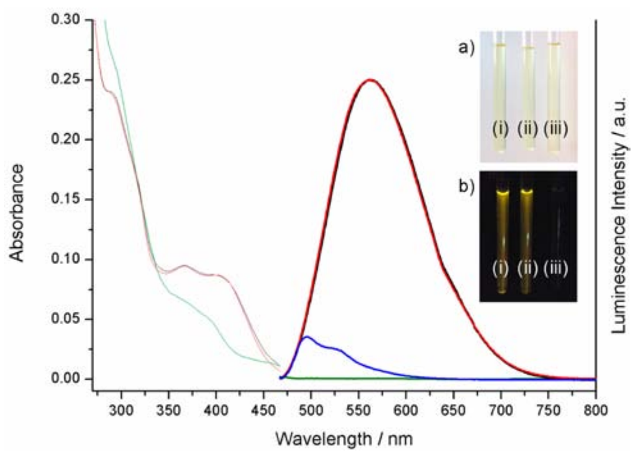


Figure 2. Absorption and emission (excitation at 413 nm) spectra of Λ- and Δ-**1**·6OTf. Λ = black line; Δ = red line; TCE, 2 μM. For comparison, the spectra of the mononuclear $[Ir(ppy)_2(PhCN)_2]OTf$ are also shown (Ir only = green line; Ir + 3000 equiv PhCN = blue line; TCE, 12 μM). Inset: Photographs of (i) Λ-**1**·6OTf, (ii) Δ-**1**·6OTf, and (iii) $[Ir(ppy)_2(PhCN)_2]OTf$ in NMR tubes held (a) in ambient lighting and (b) under a long-wavelength UV lamp.

A preliminary investigation into the host−guest chemistry of $[4OTf\subset\Delta/\Lambda\text{-}\mathbf{1}]^{2+}$ indicates that the encapsulated triflates can be exchanged for other anionic species. When NBu_4PF_6 is titrated into a sample of $[4OTf\subset\Delta\text{-}\mathbf{1}]\cdot 2OTf$ in $C_2D_2Cl_4$, ^{19}F NMR spectroscopy (see Figure S12) shows multiple OTf and PF_6 signals at low $[PF_6]$, indicative of mixed PF_6−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 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 NBu_4BF_4 and $NBu_4CF_3BF_3$, and additional titrations into Λ-**1**·$6BF_4$ (see Figures S14−S23), have ascertained that the overall affinity of perfluorinated anions for the cavity of $[\Delta/\Lambda\text{-}\mathbf{1}]^{6+}$ follows the sequence $PF_6 > OTf \approx CF_3BF_3 > BF_4$.[21c] While at present we are unable to rationalize 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 that there is communication between the luminescent properties of $[\Delta/\Lambda\text{-}\mathbf{1}]^{6+}$ 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 $[\Delta/\Lambda\ \text{-}\mathbf{1}]^{6+}$ acts as a luminescent anion sensor, this also suggests that 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 Λ/Δ-**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 comparable 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.

■ ASSOCIATED CONTENT

S Supporting Information

Full synthetic details and compound characterization, crystallographic results in CIF fomat, details of IMMS calculations, and volume calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

Paul.Lusby@ed.ac.uk

Notes

The authors declare no competing financial interest.

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