**Homochiral Self-Sorted and Emissive Ir$^{	ext{III}}$ Metallo-Cryptophanes**

Victoria E. Pritchard,[a] Diego Rota Martir,[b] Samuel Oldknow,[a] Shumpei Kai,[c] Shuichi Hiraoka,[c] Nikki J. Cookson,[a] Eli Zysman-Colman,[b] and Michael J. Hardie[a]

In memory of Dr. Julie Fisher

**Abstract:** The racemic ligands (±)-tris(isonicotinoyl)-cyclo-triguiacylene (L1), or (±)-tris(4-pyridyl-methyl)-cyclo-triguiacylene (L2) assemble with racemic (Δ,Δ)-(Ir-ppy)$_3$(MeCN)$_2$ in which ppy = 2-phenylpyridinato, to form ([Ir(ppy)$_3$]$_2$(L)$_2$)$_{3+}$ metallo-cryptophane cages. The crystal structure of ([Ir(ppy)$_3$]$_2$(L1)$_2$)$_{3+}$BF$_4$$_2$ has MM-ΔΔΔ and PP-ΔΔΔ isomers, and homochiral self-sorting occurs in solution, a process accelerated by a chiral guest. Self-recognition between L1 and L2 within cages does not occur, and cages show very slow ligand exchange. Both cages are phosphorescent, with ([Ir(ppy)$_3$]$_2$(L2)$_2$)$_{3+}$ having enhanced and blue-shifted emission when compared with ([Ir(ppy)$_3$]$_2$(L1)$_2$)$_{3+}$.

Metallo-cages are discrete 3D-coordination assemblies with a hollow interior and have applications as hosts and nanoscale vessels. [1] They form through the self-assembly of multideterminate ligands with metals, or with metal complexes with controlled available coordination sites (“metallo-tectons”). Luminescent metallo-cages are known,[2-4] with many examples exhibiting fluorescence-active ligands,[5] alongside rarer examples of cages with pendant metal-complex emissive groups.[6] There are very few examples of metallo-cages constructed from inherently phosphorescent structural components.[4-6] Cyclometalated Ir$^{	ext{III}}$ complexes bearing either two N-donor ligands or one NN chelating ligand represent an important subclass of phosphorescent materials.[7] Lusby and co-workers reported the enantiopure Ir$^{	ext{III}}$ metallo-cage ([Ir(ppy)$_3$]$_2$(tbcb)$_2$)(OTf)$_6$ (tbcb = 1,3,5-tricyanobenzene),[8] which self-assembly, despite the inertness of the d$^8$ Ir$^{	ext{III}}$ centre, as the C,C-cis-N,N-trans arrangement of the ppy ligands has a trans-labilising effect. The cage shows red-shifted emission compared with a monomeric analogue, and enhanced photoluminescence quantum yields ($\Phi_{PL}$). To date, this is the only report of a 3D metallo-cage that utilizes ([Ir(ppy)$_3$]$_2$) as the sole metal centre, although mixed metal examples are known.[9]

Here, we report two metallo-cages of the type ([Ir(ppy)$_3$]$_2$(L)$_2$)$_{3+}$, in which L is a chiral tripodal ligand related to the molecular host cyclotrimeratylene (CTV). [M(chelatel)]$_2$L$_2$ cages with CTV-type ligands are known as metallo-cryptophanes, and most examples feature square planar metals.[10] The ([Ir(ppy)$_3$]$_2$(L)$_2$)$_{3+}$ cages reported here show homochiral sorting on crystallization and in solution, and slow ligand exchange behaviour is observed.

Cages ([Ir(ppy)$_3$]$_2$(L1)$_2$)$_{3+}$ 1 and ([Ir(ppy)$_3$]$_2$(L2)$_2$)$_{3+}$ 2 are formed from nitromethane mixtures of (Δ,Δ)-(Ir-ppy)$_3$(MeCN)$_2$X (X = PF$_6^-$, BF$_4^-$) and (±)-L1 or (±)-L2 in 3:2 stoichiometry (Scheme 1). Electrospray ionization mass spectrometry (ESI-MS) gives a triply charged m/z peak at 983.1120 (cage 1) or at 955.2853 (cage 2), along with ([Ir(ppy)$_3$]$_2$L)$_{3+}$ and ([Ir(ppy)$_3$]$_2$(L)$_2$)$_{3+}$ fragment species (Figures S3 and S4 in the Supporting Information). Initial $^1$H NMR spectra of ([Irppy)$_3$(NCMe)$_2$)X and L in [D$_3$]_MeNO$_2$ show considerable broadening of the resonances and chemical shift changes, most saliently the ppy protons ortho to the coordinating N (H$_{1}$) and C (H$_{1}$) move upfield and downfield, respectively. For cage 2, the previously sharp CH$_2$ bridge singlet of L2 at 5.19 ppm becomes a complex multiplet as free rotation is hindered (Figure S15). ROESY spectra of 1 and 2 give the expected couplings, including between H$_{1}$ on the ppy ligands and the ortho pyridyl protons of L (Figures S8 and S16). Diffusion ordered NMR spectroscopy in [D$_3$]_MeNO$_2$ for 1-3PF$_3$ (Figure S9) gave a hydrodynamic radius of 18.99 Å.

The structure of 1-3BF$_4$(MeNO$_2$)$_2$ was confirmed by crystallography (Figure 1).[9] There are two independent cage 1 cations that show minor structural differences. Anions and additional solvent were not located due to significant disorder. Each cage has three pseudo-octahedrally coordinated Ir$^{	ext{III}}$ centres, each with two ppy ligands and the pyridyl groups from two L1 ligands in a cis arrangement. The two L1 ligands bridge between three Ir$^{	ext{III}}$ centres. The average torsion angle between cis-pyridyl groups is 38.04°, typical for ([Ir(ppy)$_3$]$_2$(pyridyl)$_2$)-type
complexes with the bowl shape of CTV-type ligands being able to accommodate these torsion angles within the cage structure.

Both L1 ligands within each cage are the same enantio-mer, giving the chiral anti-cryptophane isomer. Each [Ir(ppy)$_2$] unit within a cage has the same chirality, such that only the enantiomeric MM-LLL and PP-DDD cage isomers are observed in the structure. Given that the $\Lambda$ and $\Delta$ enantiomers of the [Ir(ppy)$_2$]$^+$ moieties and the $M$ and $P$ enantiomers of the L-types ligands are present in the reaction mixture, there are twelve possible stereoisomers of the cage. The $^1$H NMR spectra of both cages 1 and 2 undergo significant sharpening upon standing (Figures S7 and S15 in the Supporting Information), and fully equilibrate after several months. The $^1$H NMR spectrum of cage $1\cdot3$PF$_6$, collected after 3 months of standing, is virtually identical to that of the single crystals of $1\cdot3$BF$_4\cdot$3(CH$_3$NO$_2$) re-dissolved in [D$_3$]MeNO$_2$ (Figure 2a, b). ($\pm$)-L1 was resolved into its constituent enantiomers by chiral HPLC$^{[10]}$ and each L1 enantiomer reacted with each of $\Lambda$-[Ir(ppy)$_2$](MeCN)$_2$BF$_4$ and $\Delta$-[Ir(ppy)$_2$](MeCN)$_2$BF$_4$. As expected, the two combinations that were mis-matched pairs of enantiomers gave poorly resolved $^1$H NMR spectra (Figures S10 and S11), whereas the two combinations that were matched pairs (presumably $M$-$\Delta$ and $P$-$\Lambda$) gave sharp spectra in short timeframes that were similar to the fully sorted cage mixture (Figures 2d, S12, S13). ESI-MS of matched and mis-matched pairs are similar with all combinations showing cage formation (Figure S14). The observed $^1$H NMR spectral sharpening is therefore indicative of equilibration involving chiral self-sorting of an initial mixture of cage stereoisomers; this was also seen in our previous studies of a $[\text{Pd}_6(L1)_8]^{12+}$ cage but only the ligand was a chiral component.$^{[12]}$ We could not resolve the sorted cages by analytical chiral HPLC.

Homochiral metallo-cages with tris-chelate metal coordination are known both from achiral$^{[13a,b]}$ and resolved chiral ligands.$^{[13c-e]}$ Metallo-cages that show homochiral self-sorting from a racemic mixture of ligand enantiomers observed in so-
olution are rare,[14] although these include Pd[II] metallo-cryptophanes.[8a] The simultaneous chiral self-sorting of both ligand and pre-formed inert metallo-tecton as reported here have not been previously reported. In a preliminary investigation of the influence of chiral guests on the self-assembly of cage 1, globular additives were included in 3:2 mixtures of (A,Δ)-[Ir-(ppy),](MeCN)3·PF6 and (±)-L1. Addition of chiral R-camphor or S-camphor led to noticeably faster sharpening of the 1H NMR spectra than in their absence, but this was not observed for the addition of achiral adamantane (Figures S15–S20 in the Supporting Information). Interestingly, addition of the related anionic species R-(or S)-10-camphorsulfonic acid to the reaction mixture prevents cage formation presumably as carboxylate is a competing ligand for the iridium (Figures S21 and S22).

The cages do not show self-recognition of L-type ligand species. ESI-MS of a MeNO2 solution of L1, L2 and [Ir(ppy)2(MeCN)2]·BF4 shows a statistical mixture of 1:([Ir(ppy)2(L1)(L2)])3:+2 cage species (Figure 3). Mixing 1·3BF4 and 2·3BF4 in MeNO2 results in very slow exchange between L1 and L2 with appreciable ligand exchange only observed after four weeks, and near-statistical mixing reached after ten weeks (Figure S6 in the Supporting Information). Thus, these cages have a high degree of kinetic stability but are not completely inert. It is interesting to note that this speciation behaviour is in contrast with recently reported [Pd3L2]6+ metallo-cryptophanes, which exclusively formed homocages from two different L-type ligands, with no ligand exchange.[8a]

The absorption spectra of 1 and 2 in dichloromethane (DCM) are similar to other [Ir(ppy)2(N)]+ systems,[7] and characterised by two intense ligand centred (1LC) transitions between 260 and 320 nm localised on the ppy and three lower intensity broad bands below 380 nm that consist of spin-allowed and spin-forbidden mixed metal-to-ligand and ligand-to-ligand charge transfer (1MLCT/2LLCT and 3MLCT/2LLCT, respectively) transitions (Figure S26 in the Supporting Information). The weak CT transition observed for 1 at 470 nm was not reported for the monomeric [Ir(ppy)2(4-pyCO2Et)]+ (4-pyCO2Et = 4-ethyl isonicotinate),[10c] suggesting increased conjugation in 1 due to the CTV scaffold. For both 1 and 2, the excitation spectra in DCM match the absorption spectra and indicate a single photophysically active species.

Cages 1 and 2 are emissive in DCM solution and in the solid state. Upon photoexcitation of 1, a broad and unstructured emission is observed both in DCM and in the powder (Figure 4a) due to emission from a mixed 3MLCT/2LLCT state.[7] The photoluminescence spectrum in the powder is red-shifted (λmax = 648 nm) compared to that in DCM (λmax = 604 nm); however, 1 possesses similarly low ϕPL of around 1% and bi-exponential decay kinetics in both media (Table 1). Due to the increased conjugation into the CTV scaffold, cage 1 shows red-shifted emission and similar ϕPL compared to [Ir(ppy)2(4-
Table 1. Photophysical properties of complexes 1-3(BF3) and 2-3(BF3).

| Entry | λ_{max} (nm) | ΔφPL (%) | τ_{em} (ns) | DCM | Film | Powder | DCM | Film | Powder |
|-------|--------------|-----------|-------------|------|------|--------|------|------|--------|
|       |              |           |             | (0.7)| (0.7)| (0.7)  | (0.4)| (0.4)| (0.4)  |
| 1     | 604          | 481       | 648         | 1    | 5.5  | 1.3    | 59   | 634  | 55 (0.6) |
|       |              |           |             | (0.7)| (0.7)| (0.7)  | (1)  | (1)  | (1)    |
|       |              |           |             | 514  | 129  | 2319   | 203  | 203  | 203    |
|       |              |           |             | (1)  | (0.3)| (0.6)  | (0.4)| (0.4)| (0.4)  |
|       |              |           |             | 556  | 887  | 3042   | 1175 | 1175 | 1175   |
|       |              |           |             | (0.8)| (0.8)| (0.8)  | (1)  | (1)  | (1)    |
| 2     | 485          | 486       | 519         | 15   | 10   | 1.6    | 523  | 688  | 141    |
|       |              |           |             | (0.8)| (0.8)| (0.8)  | (1)  | (1)  | (1)    |
|       |              |           |             | 516  | 515  | 887    | 3042 | 1175 | 1175   |
|       |              |           |             | (1)  | (0.6)| (0.3)  | (0.6)| (0.6)| (0.6)  |
|       |              |           |             | 547  | 545  | 545    | 545  | 545  | 545    |

[a] Measurements in degassed DCM at 298 K. [b] Quinine sulfate employed as an external reference (ΦPL = 54.6 %). [c] PMMA-doped films (5 wt% of cage) formed by spin-coating deposition on a quartz substrate. [d] Phosphorescence measurements were carried out under nitrogen (λ_{em} = 360 nm). [e] Values obtained using an integrating sphere. [f] Principal emission peaks listed with values in parentheses indicating relative intensity. [g] λ_{max} = 378 nm; values in parentheses are pre-exponential weighting factors, in relative % intensity, of the emission decay kinetics.

In summary, phosphorescent [(Ir(ppy))2(L)2]+ metallo-cryptophanes can be synthesized in high yields, with the CTV-type ligands being able to accommodate torsion angles typical of [(Ir(ppy))2(L)2] complexes to form rare examples of 3D IrIII cyclometallated coordination cages. These cages undergo ligand exchange processes over months and show a remarkably high degree of homochiral self-sorting of both ligand and metallo-tecton, but not self-recognition between similar L-type ligands. Chiral sorting is enhanced by the presence of neutral chiral additives. For cage 1, chiral self-sorting occurs relatively rapidly upon crystallisation through an induced seeding effect, but on a timescale of months in solution. Luminescence properties of the two cages are quite distinct, pointing to an ability to tune the photophysical properties of these systems. Cage 2 showed an enhanced and blue-shifted emission compared to 1, reaching a ΦPL of 15% in DCM solution and 10% in doped film. These are promising systems for a variety of applications including semicrystalline hosts, photoredox catalysts and in energy conversion materials.

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Conflict of interest

The authors declare no conflict of interest.

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