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Homochiral self-sorted and emissive Ir(III) metallo-cryptophanes

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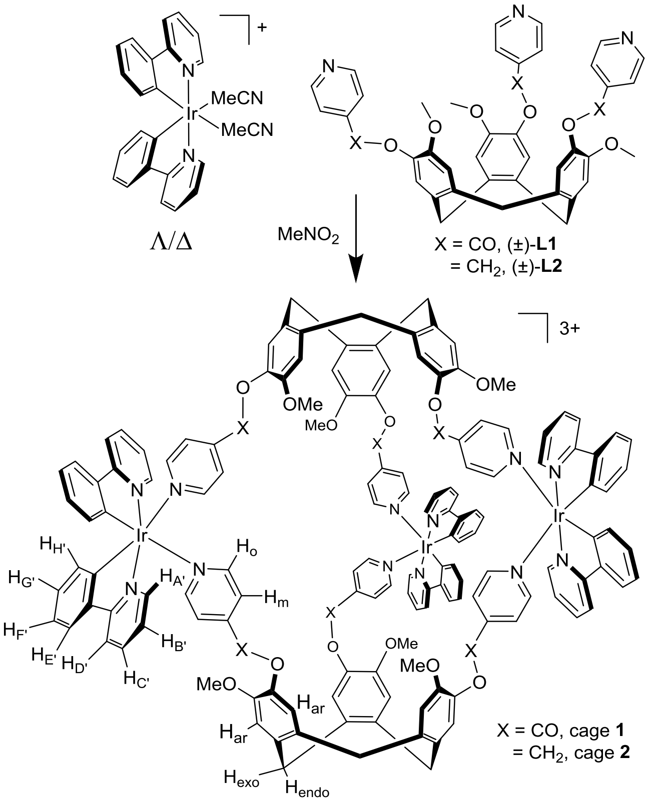
Dedicated to the memory of Dr Julie Fisher.

Abstract: The racemic ligands (±)-*tris*(isonicotinoyl)-cyclotriguaiacylene (L1), or (±)-*tris*(4-pyridyl-methyl)-cyclotriguaiacylene (L2) assemble with racemic (Λ,Δ)-$[Ir(ppy)_2(MeCN)_2]^+$ where ppy = 2-phenylpyridinato to form $[\{Ir(ppy)_2\}_3(L)_2]^{3+}$ metallo-cryptophane cages. The crystal structure of $[\{Ir(ppy)_2\}_3(L1)_2]\cdot 3BF_4$ has *MM*-ΛΛΛ 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 $[\{Ir(ppy)_2\}_3(L2)_2]^{3+}$ having enhanced and blue-shifted emission when compared with $[\{Ir(ppy)_2\}_3(L1)_2]^{3+}$.

Metallo-cages are discrete 3-D coordination assemblies with a hollow interior with applications as hosts and nanoscale vessels.[1] They form through the self-assembly of multidentate ligands with metals, or with metal complexes with controlled available coordination sites ("metallo-tectons"). Luminescent metallo-cages are known,[2-6] with most examples exhibiting fluorescence-active ligands,[2] alongside rarer examples of cages with pendant metal-complex emissive groups.[3] There are very few examples of metallo-cages constructed from inherently phosphorescent structural components.[4-6] Cyclometalated Ir(III) complexes bearing either two N-donor ligands or one N^N chelating ligand represent an important subclass of phosphorescent materials.[7] Lusby et al reported the enantiopure Ir(III) metallo-cage $[\{Ir(ppy)_2\}_6(tcb)_4]\cdot(OTf)_6$ (tcb = 1,3,5-tricyanobenzene) [4] which self-assembles, despite the inertness of the d^6 Ir(III) center, as the *C,C-cis-N,N-trans* arrangement of the ppy ligands has a *trans* labilising effect. The cage show red-shifted emission compared with a monomeric analogue, and enhanced photoluminescence quantum yields (Φ_{PL}). To date, this is the only report of a 3-D metallo-cage that utilizes $[Ir(ppy)_2]$ as the sole metal centre, although mixed metal examples are known.[5]

We report herein two metallo-cages of the type $[\{Ir(ppy)_2\}_3(L)_2]^{3+}$ where L is a chiral tripodal ligand related to the molecular host cyclotriveratrylene (CTV). $\{M(chelate)\}_3L_2$ cages with CTV-type ligands are known as metallo-cryptophanes, and most examples feature square planar metals.[8] The $[\{Ir(ppy)_2\}_3(L)_2]^{3+}$ cages reported here show homochiral sorting on crystallization and in solution, and slow ligand exchange behavior is observed.



Scheme 1. Synthesis of metallo-cryptophane cage species.

Cages $[\{Ir(ppy)_2\}_3(L1)_2]^{3+}$ **1** and $[\{Ir(ppy)_2\}_3(L2)_2]^{3+}$ **2** are formed from nitromethane mixtures of (Λ,Δ)-$[Ir(ppy)_2(MeCN)_2]\cdot X$ ($X = PF_6^-$, 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 $[\{Ir(ppy)_2\}(L)]^{3+}$ and $[\{Ir(ppy)_2\}_2(L)_2]^{3+}$ fragment species (SI Figs. S3, S4). Initial ^1H NMR of $[Ir(ppy)_2(NCMe)_2]\cdot X$ 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 ($H_{A'}$) and C ($H_{H'}$) move upfield and downfield, respectively, and 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 (Fig. S15). ROESY spectra of **1** and **2**

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give expected couplings, including between $H_{H'}$ on the ppys and the *ortho* pyridyl protons of L (Figs. S8, S16). Diffusion ordered NMR in d_3-MeNO$_2$ for **1**·3PF$_6$ (Fig. S9) gave a hydrodynamic radius of 18.99 Å.

The structure of **1**·3BF$_4$·n(MeNO$_2$) was confirmed by crystallography, Fig. 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(III) centers, 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(III) centers. Average torsion angle between *cis* pyridyl groups is 38.04°, typical for [Ir(ppy)$_2$(pyridyl)$_2$]-type complexes [10] with the bowl shape of CTV-type ligands able to accommodate these torsion angles within the cage structure.

Both L1 ligands within each cage **1** are the same enantiomer, giving the chiral *anti*-cryptophane isomer. Each [Ir(ppy)$_2$] unit within a cage has the same chirality, such that only the enantiomeric *MM*-ΛΛΛ and *PP*-ΔΔΔ cage isomers are observed in the structure. Given the Λ and Δ 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.

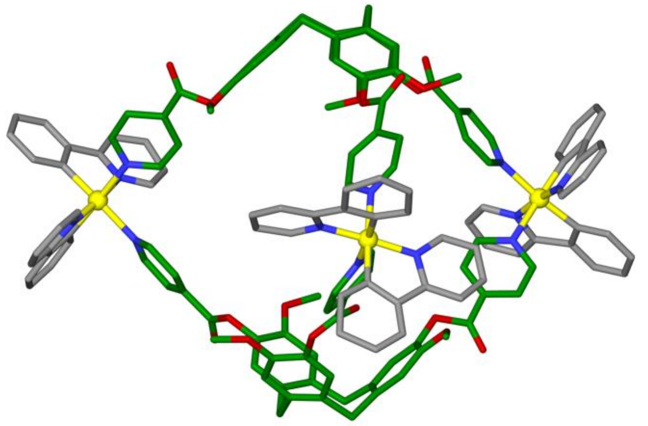

Figure 1. A [{Ir(ppy)$_2$}$_3$(L1)$_2$]$^{3+}$ cage from the crystal structure of **1**·3BF$_4$·n(CH$_3$NO$_2$), L1 and ppy ligands shown in green and grey respectively.

The ^{1}H NMR spectra of both cages **1** and **2** undergo significant sharpening upon standing (Figs. S7 and S15), and fully equilibrate after several months. The ^{1}H NMR spectrum of cage **1**·3PF$_6$ collected after 3 months of standing is virtually identical to that of the single crystals of **1**·3BF$_4$·n(CH$_3$NO$_2$) re-dissolved in d_3-MeNO$_2$, Fig. 2a/b. (±)-L1 was resolved into its constituent enantiomers by chiral HPLC,[11] and each L1 enantiomer reacted with each of Λ-[Ir(ppy)$_2$(MeCN)$_2$]·BF$_4$ and Δ-[Ir(ppy)$_2$(MeCN)$_2$]·BF$_4$. As expected, two combinations were mis-matched pairs of enantiomers that gave poorly resolved ^{1}H NMR spectra (Figs. S10-11) while two combinations were matched pairs (presumably *M*-Δ and *P*-Λ) gave sharp spectra in short timeframes that were similar to the fully sorted cage mixture (Figs. 2d, S12-13). ESI-MS of matched and mis-matched pairs are similar with all combinations showing cage formation (Fig. S14). The observed ^{1}H NMR spectral sharpening is therefore indicative of equilibration involving chiral self-sorting of an initial mixture of cage stereoisomers, as was also seen in our previous studies of a [Pd$_6$(L1)$_8$]$^{12+}$ cage but where only the ligand was a chiral component.[12] We could not resolve the sorted cages by analytical chiral HPLC.

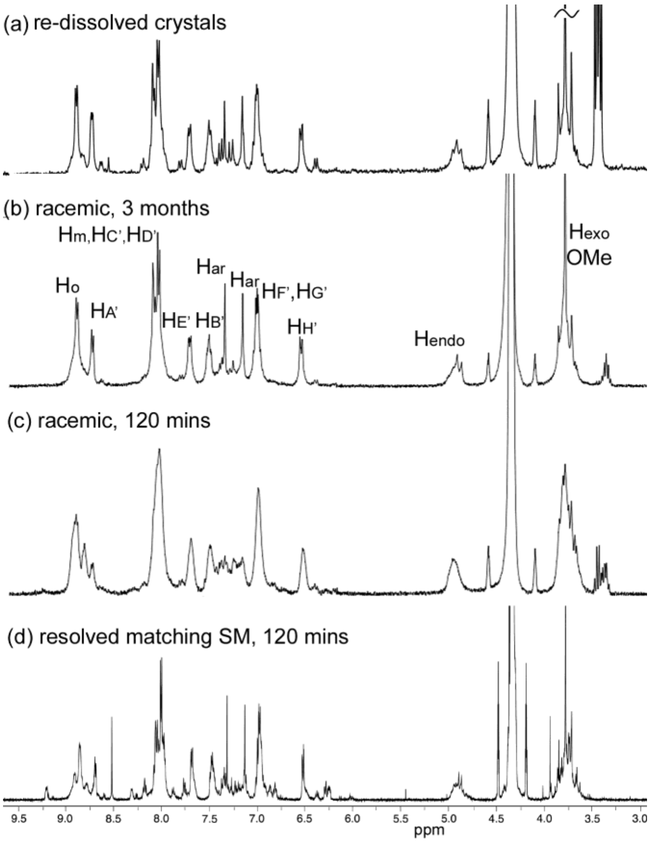

Figure 2. ^{1}H NMR spectra of cage **1** in CD$_3$NO$_2$ of (a) re-dissolved racemic single crystals of *MM*-ΛΛΛ and *PP*-ΔΔΔ cages of **1**·3BF$_4$; (b) (Λ,Δ)-[Ir(ppy)$_2$(MeCN)$_2$]·PF$_6$ and (±)-L1 3 months after mixing; (c) (Λ,Δ)-[Ir(ppy)$_2$(MeCN)$_2$]·PF$_6$ and (±)-L1 two hours after mixing; (d) matched pair of Δ-[Ir(ppy)$_2$(MeCN)$_2$]$^+$ and one L1 enantiomer after 2 hrs.

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 solution are rare,[14] though include Pd(II) metallo-cryptophanes.[8a] The simultaneous chiral self-sorting of both ligand and pre-formed inert metallo-tecton as reported here has 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 (Λ,Δ)-[Ir(ppy)$_2$(MeCN)$_2$]·PF$_6$ and (±)-L1. Addition of chiral *R*-camphor or *S*-camphor led to noticeably faster sharpening of the ^{1}H NMR spectra than in their absence, but this was not observed for addition of achiral adamantane (Fig. S15-S20). 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 (Fig. S21-22).

The cages do not show self-recognition of L-ligand species. ESI-MS of a MeNO$_2$ solution of L1, L2 and [Ir(ppy)$_2$(MeCN)$_2$]·BF$_4$ shows a statistical mixture of **1**:[{Ir(ppy)$_2$}$_3$(L1)(L2)]$^{3+}$:**2** cage species, Fig. 3. Mixing **1**·3BF$_4$ and **2**·3BF$_4$ in MeNO$_2$ results in very slow exchange between L1 and L2 with appreciable ligand

Table 1. Photophysical properties of complexes **1**·3(BF_4) and **2**·3(BF_4).

	λ_{em} (nm)			**Φ_{PL}(%)**[d]			**τ_e (ns)**[g]		
	DCM [a,b,f]	film [c,f]	powder	DCM [a]	Film [c,e]	powder [e]	DCM [a]	film [c]	powder
1	604	481 (0.7), 514 (1), 556 (0.8)	648	1	5.5	1.3	59 (0.7), 129 (0.3)	634 (0.4), 2319 (0.6)	55 (0.6), 203 (0.4)
2	485 (0.8), 516 (1), 547 (0.6)	486 (0.8), 515 (1), 545 (0.6)	519	15	10	1.6	523 (0.4), 887 (0.6)	688 (0.7), 3042 (0.3)	141 (0.4), 1175 (0.6)

[a] Measurements in degassed DCM at 298 K. [b] Quinine sulfate employed as the external reference (Φ_{PL} = 54.6% in 0.5 M H_2SO_4 at 298 K). [c] PMMA doped films (5 wt % of cage) formed by spin-coating deposition on quartz substrate. [d] Φ_{PL} measurements were carried out under nitrogen (λ_{exc} = 360 nm). [e] values obtained using an integrating sphere. [f] Principal emission peaks listed with values in brackets indicating relative intensity. [g] λ_{exc} = 378 nm; Values in parentheses are pre-exponential weighting factor, in relative % intensity, of the emission decay kinetics.

exchange only observed after 4 weeks, and near-statistical mixing reached after 10 weeks (Figure S6). Thus these cages have a high degree of kinetic stability but are not completely inert. It is interesting to note that this speciation behavior is in contrast with recently reported $[Pd_3L_2]^{6+}$ metallo-cryptophanes, which exclusively formed homocages from two different L-type ligands, with no ligand exchange.[8a]

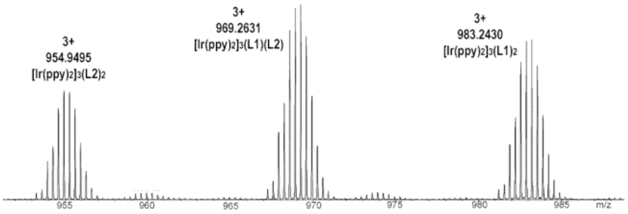

Figure 3. ESI-MS of a 1:1:3 mixture of L1:L2: $[Ir(ppy)_2(MeCN)_2]$·BF_4 in $MeNO_2$ showing formation of statistical mixture of homoleptic and heteroleptic cages.

The absorption spectra of **1** and **2** in dichloromethane (DCM) are similar to other $[Ir(ppy)_2(N^\wedge N)]^+$ systems,[7] and characterised by two intense ligand centered (^{1}LC) transitions between 260 and 320 nm localised on the ppy and three lower intensity broad bands at below 380 nm that consist of spin-allowed and spin-forbidden mixed metal-to-ligand and ligand-to-ligand charge transfer (^{1}MLCT/^{1}LLCT and ^{3}MLCT/^{3}LLCT) transitions (Fig. S26). The weak CT transition observed for **1** at 470 nm was not reported for the monomeric $[Ir(ppy)_2(4\text{-}pyCO_2Et)_2]^+$ (4-$pyCO_2Et$ = 4-ethyl isonicotinate),[10c] pointing to 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, Fig. 4a**,** due to emission from a mixed ^{3}MLCT/^{3}LLCT state.[7] The photoluminescence spectrum in the powder is red-shifted (λ_{max} = 648 nm) compared to that in DCM (λ_{max} = 604 nm); however, **1** possesses similarly low Φ_{PL} 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 Φ_{PL} compared to $[Ir(ppy)_2(4\text{-}pyCO_2Et)_2]^+$ (λ_{max} = 560 nm; Φ_{PL} = 2%).[10c] Lusby's $[\{Ir(ppy)_2\}_6(tcb)_4]^{6+}$ cage also showed red-shifted emission (λ_{max} = 575 nm) when compared with the corresponding $[Ir(ppy)_2(NCPh)_2]OTf$ complex (λ_{max} = 525 nm); however, unlike for cage **1** and other $Ir(ppy)_2$ discrete supramolecular systems,[15] the Φ_{PL} for the Lusby cage was enhanced compared with that of the mononuclear complex (Φ_{PL} = 4% cf. Φ_{PL} = < 1%).[4]

In order to mitigate non-radiative vibrational motion in the cage we spin-coated 5 wt % of **1** in polymethyl methacrylate (PMMA), which serves as an inert matrix. The emission in the thin film was blue-shifted and more structured (λ_{max} = 514 nm) compared to both the powder and solution spectra. The Φ_{PL} of 5.5% was enhanced as a result of the rigidification conferred by the PMMA host and the emission lifetimes were significantly longer (τ_e = 634 and 2319 ns).

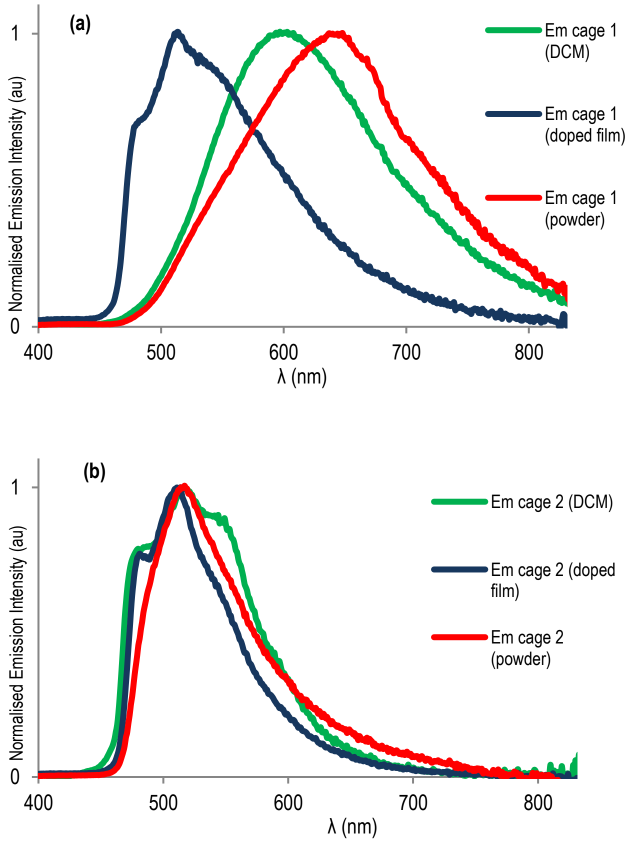

Figure 4. Normalised photoluminescence spectra of a) **1**·3BF_4 and b) **2**·3BF_4. Dotted lines de-areated DCM solution; dashed lines PMMA doped films with 5 wt % of cages spin-coated on a quartz substrate; red lines bulk powders.

The photoluminescence spectrum of cage **2** in DCM is more structured and blue-shifted (λ_{max} = 516 nm) compared to **1**, indicating emission that is more predominantly ligand-centered (^{3}LC) (Fig. 4(b)). The blue-shifted emission of **2** compared to **1** was expected considering the presence of the electron-withdrawing ester moieties located on L1 in **1**, which stabilise the LUMO.[10c] Cage **2** shows a significantly enhanced Φ_{PL} and longer τ_e compared to **1** in DCM (Φ_{PL} = 15%, τ_e = 523, 887 ns).

Unlike for **1**, as a powder the emission of **2** is not significantly red-shifted (λ_{max} = 519 nm) though the emission profile is less structured, showing less well-resolved vibrational bands as shoulders of the main emission peak. The emission profile for **2** in PMMA doped thin film is likewise very similar to that in DCM. Though Φ_{PL} values are low in the powder (Φ_{PL} = 1.6%), in doped film they are higher (Φ_{PL} = 10 %). Emission lifetimes are expectedly longer in doped films than in powder, Table 1. Attempts to synthesize an analogous mononuclear complex of 4-phenoxymethylpyridine for comparison were not successful due to ligand oligomerization.

In summary, phosphorescent $[\{Ir(ppy)_2\}_3(L)_2]^{3+}$ metallo-cryptophanes can be synthesized in high yields, with the CTV-type ligands able to accommodate torsion angles typical of $[Ir(ppy)_2(L)_2]$ complexes to form rare examples of 3-D Ir(III) 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 crystallization 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 Φ_{PL} of 15% in DCM solution and 10% in doped film. These are promising systems for a variety of applications: as semiochemical hosts, photoredox catalysts and in energy conversion materials.

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Data accessibility. Data supporting this work can be accessed at DOI:###########.

Keywords: supramolecular chemistry; cage compounds • homochiral self-sorting • phosphorescence

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