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Fraternal twin iridium hemicage chelates[†]

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The synthesis and complete photophysical characterization of rigidified neutral hemicage iridium complexes are presented. The hemicage ligands were obtained *via* a modular synthesis, which will facilitate the expansion of future hemicage syntheses. Slight variations in structure between the two iridium hemicage podates reveal subtle differences in photophysical behavior, which will aid in the design of functional materials. A parallel computational investigation corroborates the experimental findings. The insight gleaned from this study will have an impact for the design of iridium-based luminophores for OLED-type applications.

Introduction

Tripodal structures, which are nominally formed from a benzene skeleton equipped with three pendant ligand arms flexibly attached to the arene with *meta* dispositions with respect to each other, serve as important scaffolds used within a variety of applications. When a guest analyte is introduced, the C_3 -symmetric podand host, or hemicage (HC), adopts an all *syn* conformation wherein the three arms of the host act to complex the guest on the same face. Hexasubstitutued analogs are particularly effective, though not necessary, for sterically preorganizing the host. The arms of the host are staggered thus preorienting the three ligand-containing arms onto the same face of the central arene.¹ The hemicage architecture has been exploited towards the generation of fluorescent chemosensors for heparin,² as logic gates,³ as siderophores,⁴ as selective hosts for both cations⁵ and anions⁶ and as air-stable lanthanide catalysts for Diels–Alder reactions.⁷

In particular, metals such as In, Al and Ga have been complexed with 8-hydroxyquinoline-derived HCs,⁸ while Fe,⁹ Ru⁹⁻¹⁰ and Zn^{10e} complexes have formed from bipyridine-derived HCs. Notably, there is but one report of an Ir–HC complex,¹¹ the ligand arms being derived from phenylpyridine with the Ir situated *ca*. 10 Å above the plane of the arene. Recently, Velders and co-workers reported the first Ir^{III} caged complex, bearing tris(2-aminoethyl)amine caps.¹² Owing to their structure, metal complexes of HCs are endowed with several advantages: they are more chemically inert than their acyclic congeners;^{10b,10e} nonradiative decay processes are inhibited as a result of increased rigidity of the ligand framework resulting in greater luminescence.^{8,10f}

Herein we report the modular synthesis of two HC ligands, HC1 (Scheme 1) and HC2 (Scheme 2), and their complexation with iridium(III), and compare the photophysical properties of these podates to that of *fac*-Ir(ppy)₃ (ppyH = 2-phenylpyridine) (1) and the chiral iridium hemicage constructed by Von Zelewski.¹¹



Scheme 1 Synthesis of HC1: (a) 1. 1.05 equiv. *t*BuLi/THF, -78 °C, 30 min, 2. 1.05 equiv. ZnCl₂/THF, -78-0 °C, 150 min, 3. 0.95 equiv. 2,5-dibromopyridine, 5 mol% Pd(PPh₃)₄/THF, reflux, 18 h; (b) 2.4 equiv. TMSA, 16 mol% CuI, 6 mol% Pd(PPh₃)₄/3 : 1 THF/*i*-Pr₂NH, reflux, 16 h; (c) 2.30 equiv. K₂CO₃/MeOH, RT, 30 min; (d) 0.25 equiv. **5**, 3 mol% CuI, 2.5 mol% Pd(PPh₃)₄/1 : 1 PhMe/NEt₃, reflux, 18 h; (e) H₂, 10 mol% Pd(C/THF, RT, 3 d.

Results and discussion

The modular synthetic approach undertaken enabled a facile and convergent construction of the desired podands. 2-Phenyl-5-bromopyridine **2** was quickly accessed in excellent

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[†] Electronic supplementary information (ESI) available: Complete experimental section and compound characterization including ¹H assignment for ligands and complexes. Summary of crystallographic parameters for **Ir.HC2**. Methodologies used for photophysical characterization. Details of computational methodology. Full computational output, including figures of calculated absorption spectra, tables of 50 lowest energy transitions calculated by TD-DFT and tables of calculated emission energies and isodensity surface plots for selected orbitals of **Ir.HC1** and **Ir.HC2**. CCDC reference number 831090. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11236h



yield *via* a Negishi¹³ reaction between bromobenzene and 2,5-dibromopyridine (Scheme 1). Sonogashira¹⁴ coupling with trimethylsilylacetylene (TMSA) followed by base deprotection afforded 5-ethynyl-2-phenylpyridine **4** in excellent yield. Three equivalents of **4** were efficiently coupled with 1,3,5-tribromobenzene **5** to afford **6**, which was subjected to hydrogenation conditions over 3 days to cleanly and efficiently afford **HC1** (7).

HC2 was constructed in an analogous sequence in excellent yield (Scheme 2). The methyl group was incorporated into 10 as the yield for the Kröhnke¹⁵ condensation of 9 with methacrolein was superior to that with acrolein. The methyl group should have little impact upon the photophysical properties of metal complexes of HC2.

Treatment of each of **HC1** and **HC2** with Ir(acac)₃ in refluxing ethylene glycol over 24 h produced the homoleptic complexes with facial geometries **Ir.HC1** and **Ir.HC2** in 33% and 37%, respectively. The ¹H NMR spectrum of the hemicaged complexes **Ir.HC1** and **Ir.HC2** reveal a single set of phenylpyridine protons, thus establishing the three-fold symmetry of the complexes (Fig. 1).

Exact structural assignment was determined through a series of 1D- and 2D-NMR experiments (DQCOSY, COSY, HMBC NOESY). Notably, protons H_1 and $H_{3'}$ are significantly shifted upfield (*ca.* 2 ppm) upon complexation. In fact, H_1 in **Ir.HC1** and $H_{3'}$ in **Ir.HC2** are oriented to reside in the anisotropic cone of two aryl rings and within the d_{z^2} orbital of the iridium metal, resulting in extensive shielding of the proton; aromatic $H_{3'}$ in **Ir.HC2** for example is shifted to *ca.* 5.4 ppm.

The crystal structure of **Ir.HC2** was obtained by slow evaporation of a chloroform solution and crystallizes as a distorted octahedron within a centrosymmetric trigonal space group (*R*-3), where each unit cell contains six molecules as three enantiomeric dimeric pairs (Fig. 2a).¹⁶ Bond lengths and bond angles (Ir–C_{ppy} = 2.01 Å; Ir–N_{ppy} = 2.14 Å; N_{ppy}–Ir–C_{ppy} = 80°) are unremarkable when compared to those in 1¹⁷ or in Von Zelewski's iridium hemicage.¹¹ Thus, the presence of short 2-carbon methylene arms does not unduly impact complex formation nor significantly distort the octahedral geometry about the iridium center. The



Fig. 1 Complexation of $Ir(acac)_3$ with (a) HC1 and (b) HC2. ¹H NMR of ligand in red and complex in blue in CD_2Cl_2 , with peak assignments. Computed structures are shown for the complexes. * indicates non-deuterated DCM solvent.



Fig. 2 Crystal structure of **Ir.HC2**. (a) Crystal packing of dimeric pair of complexes; (b) ORTEP perspective representation (ellipsoids at 50% probability). A molecule of CHCl₃ has been removed for clarity. The red spheres represent calculated centroids of the aromatic rings.

iridium metal resides 5.47 Å above the centroid of the central arene while there are C–H– π interactions between H_{3'} and the two proximal arenes (Fig. 2). There are no intermolecular interactions between hemicages in the unit cell.

The photophysical properties for **Ir.HC1** and **Ir.HC2** are summarized in Table 1 and Fig. 3 and are compared to archetypal fac-Ir(ppy)₃ (1).

Absorption and emission profiles for **Ir.HC1** are quite similar to those of **Ir.HC2**, exhibiting only a slight bathochromic shift of

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 Table 1
 Photophysical properties of hemicage complexes

			Absorbance 298 K (nm)	Phosphorese	cence	Stokes shifts		Quantum Yi	eld ^b	Lifetime			
Complex		Solvent	[Molar Absorptivities (×10 ⁴ M ⁻¹ cm ⁻¹)]	77 K (nm) ^a	298 K (nm)	77 K (cm ⁻¹)	298 K (cm ⁻¹)	Degassed (%)	in air (%)	77 Κ (μs) ^a	298 K (ns)	$k_{\mathrm{r}} = (\times 10^5 \mathrm{ s}^{-1})$	$k_{ m ur} \over (imes 10^5 \ { m s}^{-1})$
fac-Ir(ppy)3	Ref. 19 and 26	2-MeTHF ^e	244 [4.6], 283 [4.5], 341 [0.9], 377 [1.2], 405 [0.8], 455 [0 31 488 [0 21	491	508	125	807	97	3.6	4.0	1600	6.1	1.9
	This study	2-MeTHF	250 [3.37]; 285 [4.20]; 380 [1.33]; 410 [0.87]; 455 [0.37]: 485 [0.15]	493	512	335	1087	97	2.9	3.7	1660	5.8	0.2
		CHCI ₃	290 [4:33], 345 [0.99], 380 [1.19], 410 [0.79], 455 [0 30], 490 [0 12]	(496)	518	247	1103	41	2.9	(4.8)	879	3.1	6.7
		ACN	240 [4.70]; 280 [4.42]; 340 [0.91]; 375 [1.10]; 405 [0.69]; 450 [0.25]; 480 [0.11]	(496)	531	672	2001	78	2.1	(4.8)	1322	3.9	1.7
lr.HC1	This study	CHCI ₃	250 [4.13]; 285 [4.36]; 375 [0.92]; 410 [0.85]; 450 [0.60]: 485 [0.11]	(491)	508	252	934	17	1.4	(4.0)	443	3.8	19
		BuCN	245 [3.99]; 285 [3.74]; 245 [3.99]; 285 [3.74]; 345 [0.80]; 375 [0.86]; 410 [0.56]; 450 [0.22]; 485 [0.03]	490	510	210	1011	76	2.4	3.9	1482	3.4	1.6
lr.HC2	This study	CHCI ₃	245 [4.04]; 275 [3.80]; 290 [4.07]; 355 [1.23]; 410 [0 76]: 485 [0 12]	(494)	503	376	738	10	2.3	(3.9)	888	1.2	10
		ACN	245 [4.6]; 290 [4.57]; 380 [1.34]; 410 [0.95]; 455 [0.31]: 490 [0.11]	(494)	524	165	1324	79	2.3	(3.9)	887	8.9	2.4
		BuCN	245; 290; 380; 410; 455; 490		521		1214				1445		
A-Ir(pppy) ³	Ref. 11	ACN [€]	242 [5.37]; 286 [3.92]; 342 [1.21]; 382 [0.92]; 408 [0.68]; 452 [0.31]; 487 [0.15]	507	505	810	732	64	1.3 [0.9] ^y	2.1	1400	4.6	2.6
fac-A-Ir-L		ACN ^e	245 [0.82]; 288 [3.97]; 245 [0.99]; 379 [0.93]; 408 [0.64]; 453 [0.22]; 487 [0.11]	507	508	810	849	51	1.4 [1.0] ^y	1.9	1200	4.2	4.1
^{<i>a</i>} Spectra and spectra were 1 properties for of 2.8% in aer	values in parenthes measured in DCM the Δ isomer are ve ated water). The da	s were measured in see ref. 19, emissio ry similar see ref. 11 ta originally report	MeOH/EtOH (1/1) glass sta on spectra, quantum yield ar 1. * Absorption spectra were : ed from ref. 11 are in square	tte. ⁴ Using [Ru nd lifetime we measured in D brackets.	ı(bpy),](PF re measure 0CM. / Valı	(b)2 as the stanc d in 2-Me-TH Les reported ha	lard ($\Phi_{PL} =$ IF see ref. ave been re	: 9.5% in deara 26. ^d Only val calculated usi	ted ACN, ues for th ng [Ru(bp:	4.0% in aer e A isomer y)3](PF ₆)2 a	rated wate r are show is the stane	r) see ref. 21 ^e . In but the ph dard ($\Phi_{PL} = 4$	Absorption otophysical 0% instead



Fig. 3 Photophysical properties of hemicage podates. (a) Photos of N_2 -degassed solutions in CHCl₃ and nitrile solvents of 1, Ir.HC1 and Ir.HC2, irradiated at 325 nm; (b) Absorption (solid) and emission (dashed) for 1, Ir.HC1 and Ir.HC2 at 298 K in ACN (the spectra for Ir.HC1 were obtained in BuCN).

5 nm for λ_{em} in CHCl₃. Intense bands found at wavelengths inferior to 300 nm were assigned to ligand-centred (¹LC) π – π^* transitions of the ppy ligand.¹⁸ The mixed ¹LC and ¹MLCT d– π^* band at *ca.* 380 nm is more intense for **Ir.HC2** compared to either **Ir.HC1** or **1** and this difference in intensity is more marked in CHCl₃ than in nitrile solvents (see ESI†). The small absorption bands at longer wavelengths have been assigned to spin-forbidden mixed ³LC and ³MLCT transitions and are of similar amplitudes for the three complexes under investigation. The assignments for these transitions are similar to those reported by Hofbeck and Yersin^{18a} for **1** and are corroborated by our computational investigation (see below).

The phosphorescence emission spectrum is broad and essentially featureless for both podates at 298 K and are not dissimilar from that of 1, exhibiting a hypsochromic shift by ca. 12 nm in CHCl₃ compared to the spectrum of 1 ($\lambda_{em} = 518$ nm). The shape of the emission spectrum implies that the origin of the emission is in part characteristic of a ³MLCT transition. It is generally accepted that emission from complexes such as 1 can be described as an admixture of ³MLCT and ³LC transitions.¹⁹ Remarkably, though there is a pronounced red shift of 21 nm for Ir.HC2 when migrating from CHCl₃ to the more polar nitrile solvents ACN and BuCN,²⁰ similar to that found for 1, there is little observed change in λ_{em} for **Ir.HC1** (there is also essentially no change in absorption and emission energies between ACN and BuCN for Ir.HC2; see Fig. S5[†]). For Ir.HC1, BuCN was necessary to solubilize the complex. Based on the behavior of Ir.HC2 in nitrile solvents, the surprising lack of solvatochromism inherent in **Ir.HC1** is thus not due to the identity of the alkyl group on the nitrile solvent. One possible explanation for the lack of solvatochromism is based on an analysis of the orientation and magnitude of the dipole moments of each of the hemicages. The orientation of the dipole should emanate from the iridium center and be projected towards the three nitrogen atoms. Ir.HC1 would thus have a dipole directed towards the central benzene while Ir.HC2's dipole is projected to

the periphery of the hemicage. Based on this electronic analysis, solvent molecules should stabilize less **Ir.HC1** than **Ir.HC2**. A quantification and corroboration of the assignment of dipoles is discussed below. Emission spectra for the three complexes in this study obtained at 77 K in the glass state in 1 : 1 EtOH/MeOH were found to be blue shifted and displayed fine vibrational structure compared to those taken at 298 K (see ESI[†]).

Quantum yields are highly solvent dependent. Ir.HC1 was poorly soluble in most organic solvents and exhibited low quantum efficiency in chloroform ($\Phi = 17\%$), which is considerably lower than that obtained for 1 ($\Phi = 41\%$ – standard: $[Ru(bpy)_3](PF_6)_2; \Phi_{PL} = 9.5\%)$.²¹ Ir.HC2 was even less luminescent in CHCl₃. Each, however were highly luminescent in polar aprotic solvents ($\Phi_{BuCN}(Ir.HC1) = 78\%$; $\Phi_{ACN}(Ir.HC2) = 79\%$), exhibiting quantum yields comparable to that found for 1 (Φ_{ACN} = 78%) but superior to that found for Von Zelewski's hemicage $(\Phi_{ACN} = 51\%)$.¹¹ By contrast, A-Ir(pppy)₃ (pppyH = (8*R*,10*R*)-2-(2'-phenyl)-4,5-pinenopyridine) was found to be less luminescent than the corresponding hemicage ($\Phi_{ACN} = 64\%$), perhaps due to the flexibility inherent in the structure of the podand.¹¹ As first elucidated by Watts and co-workers,²² the lower quantum yields and shorter lifetimes (see below) found in CHCl₃ are most probably due to the photoreactivity of the solvent that leads to quenching of the emission of the complexes, similar to that observed for the behavior of 1 in DCM. The relative quantum yield for 1 in 2-MeTHF ($\Phi = 97\%$) was found to be much greater than that first reported by Thompson and co-workers (Φ = 40%).²³ More recently, the room temperature quantum efficiency of 1 has been measured using the absolute method²⁴ in solid matrix hosts such as 4,4'-N,N'-dicarbazole-biphenyl (CBP) and polymethylmethacrylate (PMMA) to be in excess of 90%,25 while RT measurements in degassed 2-MeTHF and DCM were found to be 97%²⁶ and 90%, ^{18a,25b} respectively. The quantum yield for 1 in deaerated toluene using the relative method with quinine sulphate dehydrate as the reference compound was recently reported to be 73%.27 From our internally reproducible results we can conclude that in nitrile solvents that Ir.HC1 and Ir.HC2 are just as brilliant phosphors as 1.²⁸ Quantum efficiencies in air-equilibrated solution were comparable to that found by Von Zelewski and co-workers.

Lifetimes at 77 K in the glass state were on the microsecond timescale while those at 298 K were on the submicrosecond time scale. Whereas Ir.HC2 has a room temperature lifetime ($\tau = 888$ ns) in chloroform solution similar to that of 1, Ir.HC1 possesses a lifetime that is half as long ($\tau = 443$ ns). Room temperature lifetimes obtained in polar aprotic nitrile solvents reveal a different behavior. In BuCN, Ir.HC1 exhibits a lifetime of 1482 ns, longer than that found for either 1 or the hemicaged iridium complex under investigation by Von Zelewski. The lifetime for Ir.HC2 in BuCN is similar (1445 ns) to that of Ir.HC1 but decreases somewhat in ACN (887 ns), a similar value to that obtained in chloroform. The increased lifetime observed in BuCN compared to ACN is most likely due to the increased viscosity of the former, which limits molecular movement that can lead to non-radiative dissipation of energy.²⁹ The lifetime of Ir.HC2 in ACN is noticeably shorter than that measured for 1 (1322 ns).

Radiative $(k_r = \Phi_{PL}/\tau)$ and non-radiative $(k_{nr} = k_r(1 - \Phi_{PL})/\tau)$ were determined for the three complexes under study. Of particular note are the large non-radiative (k_{nr}) decay constants in CHCl₃, which are particularly significant for the two hemicage podates being of an order of magnitude larger than their corresponding $k_{\rm r}$.

A combined DFT and TD-DFT computational study was performed without imposition of symmetry in order to elucidate the photophysical behavior of each. These results are summarized in Fig. 4 (see ESI for details[†]).



Fig. 4 Calculated absorption (HOMO \rightarrow LUMO) and emission energies, assigned transition type and isodensity surface plots for each of the ³HSOMO and ¹HOMO for (a) **Ir.HC1** and (b) **Ir.HC2**.

For each of the hemicage complexes, electron density in the ground state (S₀) is found principally on the iridium (d_{z^2}) , extending onto the phenyl fragment of the ppy-type ligand. In the case of Ir.HC2, this results in the preponderance of the electron density being sterically shielded by the central arene whereas in the case of Ir.HC1, the electron density is mainly on the periphery of the complex. This is due to the difference in the placement of the pyridine ring in each of the complexes. For Ir.HC1, the principle low energy absorption transition predicted by TD-DFT (f = 0.011) is found to be at 415 nm (see ESI[†]) and results mainly from a HOMO \rightarrow LUMO transition and can be characterized as mixed ¹MLCT/¹LC/¹ILCT transition. Analogously, for Ir.HC2, the HOMO \rightarrow LUMO transition at 420 nm is significant (f = 0.013) and can similarly be characterized as mixed ¹MLCT/¹LC/¹ILCT transition. By contrast for 1, nearly degenerate transitions occurring at 401 nm from HOMO-1 \rightarrow LUMO (f = 0.022) and HOMO-2 \rightarrow LUMO (f = 0.022) are dominant.

In the excited triplet state for each of the hemicage complexes the electronic density of the ³HSOMO, (see ESI for other ground and excited state MOs[†]) is found to be localized on a single arm of the hemicage, distributed equally about the ppy-type moiety, similar to that described by Koseki and co-workers.³⁰ There is also a small contribution from the metal in the form of a d_{vz} orbital. Inspection of the ³HSOMO and ³LUMO orbitals in the triplet state for each of the complexes reveals that their superposition mirrors the ¹LUMO found for their corresponding S_0 ground states. The majority of the electron density found in the ³HSOMO is localized on the ppy ligands whereas in the ground state HOMO, it is found on both the metal and on the phenyl fragment of the ppy ligand. Thus, the nature of the emission in 1 can be generally characterized as an admixture of ³MLCT and ³LC transitions, consistent with experimental analyses (see above). This conclusion mirrors those found in other theoretical investigations.³¹

Emission energies were determined as the difference between the total energy of the triplet state (T_1) and the total energy of the ground state (S_0) for each of the complexes, with structures optimized at their respective states.^{13b,32} Emission energy predictions of 473 nm and 479 nm for **Ir.HC1** and **Ir.HC2** are nearly identical and reflect quite well the experimental values obtained at 77 K of 491 nm and 494 nm, respectively. The emission energy prediction for **1** is 480 nm, hypsochromically shifted by 16 nm compared that measured in the EtOH/MeOH glass state.

The magnitude of the calculated ground state dipole moments for **1**, **Ir.HC1** and **Ir.HC2** were found to be 6.52, 13.51 and 10.29 Debye, respectively. The magnitude of the corresponding calculated excited triplet state dipole moments for **1**, **Ir.HC1** and **Ir.HC2** were found to be 5.80, 11.82 and 8.79 Debye, respectively. Inspection of the orientation of the dipole moments in each of the hemicages reveals that they are aligned principally along the *x*-axis of the molecule. Whereas both the ground and excited state dipole moments for **Ir.HC2** are oriented away from the central ring, the orientation of the ground and excited state dipole moments towards the central benzene ring of **Ir.HC1** explains the absence of solvatochromism for this complex compared to the other two in the study. In this latter case, dipole–dipole interactions will be weaker despite an overall larger magnitude for the dipole moments in both the ground and the excited state.

Conclusions

In summary, we have synthesized two hemicage podands via a modular synthetic approach. The facial iridium(III) podates subsequently formed exhibit similar photophysical characteristics with two stark exceptions: their lifetime behavior and emission maxima in disparate solvents. Whereas Ir.HC2 emits with a lifetime of about 888 ns in each of CHCl₃ and ACN and exhibits a large bathochromic shift of 21 nm between the two solvents, the lifetime for Ir.HC1 in BuCN was found to be four times longer at 1.5 µs than in CHCl₃ with λ_{em} being essentially solventinsensitive. The long lifetime and lack of solvatochromism in BuCN for Ir.HC1 may be attributed to the increased steric bulk of the butyl group, which impedes a significant stabilization of the polar excited state and thus the observed red shift. In all other respects, Ir.HC1 behaves similarly to 1. The large bathochromic shift in emission maxima for Ir.HC2 is due to a combination of its electronically shielded ground state and electronically exposed excited state (Fig. 4). The polar ACN solvent can preferentially stabilize the excited state more than the ground state leading to the larger red shift. The similar lifetimes observed in CHCl₃ and ACN for Ir.HC2 seem to primarily be due to an increased $k_{\rm nr}/k_{\rm r}$ ratio in chloroform (8.3 for Ir.HC2 vs. 5.0 for Ir.HC1). Upon irradiation, reactive chlorinated species can more easily attack the exposed $Ir(d_{z^2})$ orbital (S₀ state) in Ir.HC2 than in Ir.HC1. The incorporation of these two complexes into OLED devices is currently under investigation and results thereof will be reported elsewhere.

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