Hemicages and bis(hemicages) as luminescent chemosensors

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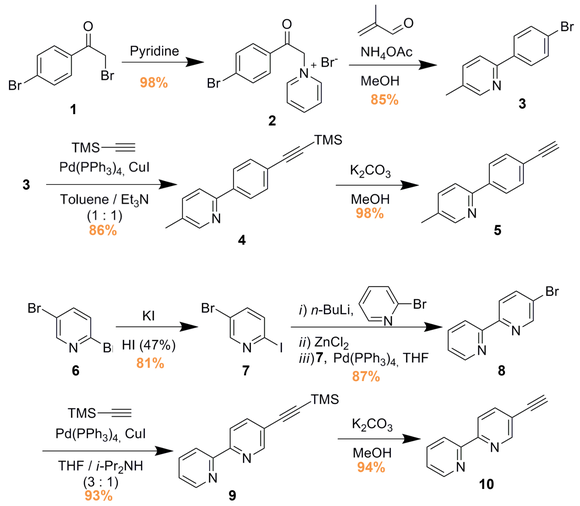
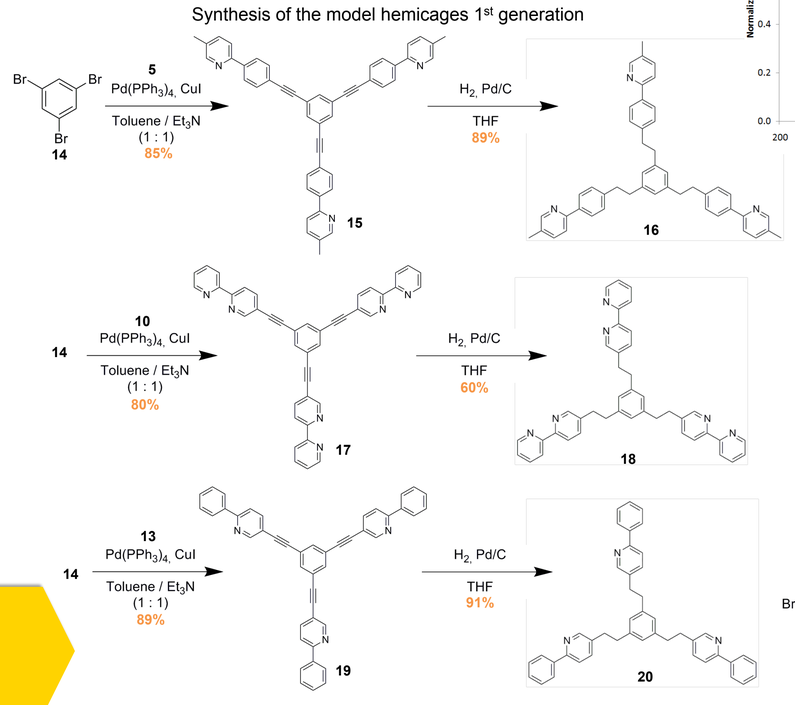
Introduction

The interest of the hemicage (**HC**) structure, employing a 1,3,5-trisubtituted benzene scaffold, is through the pre-orientation of its "arms" in the presence of an analyte. Like active sites of enzymes, these constructs can trap small organic molecules or metals. By themselves, the **HC** ligands under investigation are fluorophores and the incorporation of a metal analyte (*e.g.*, Ru, Ir) changes greatly the absorbance and fluorescence properties of the adduct. The large changes in these properties make the material a potential sensitive detector of metals. The **HC** serves as our model compound for the study of the bis(hemicage) (**BHC**). With the additional complexation site, the **BHC** can complex up to two analytes. The cyclophane plays two roles: it's a good chromophore and fluorophore; it mediates electronic communication from one side of the cyclophane to the other. The **BHC** can thus be seen as a logic gate. The current report shows the synthesis and photophysical analysis of **HC** models system and our efforts toward the construction of a **BHC**.

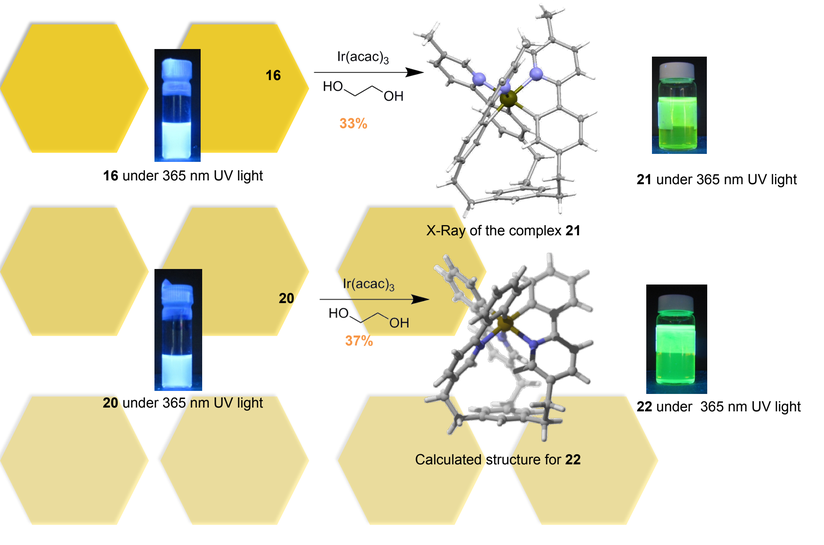
Preparation of the alkynes (arms)



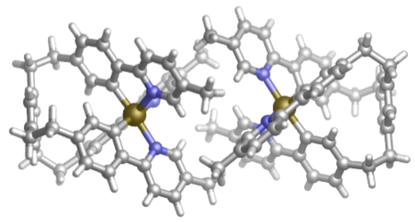
Synthesis of the model hemicages 1st generation



Formation of the Iridium complexes



Crystal packing of iridium complexe **22**



Each unit cell contains six molecules as three enantiomeric (Λ and Δ) dimeric pairs like shown

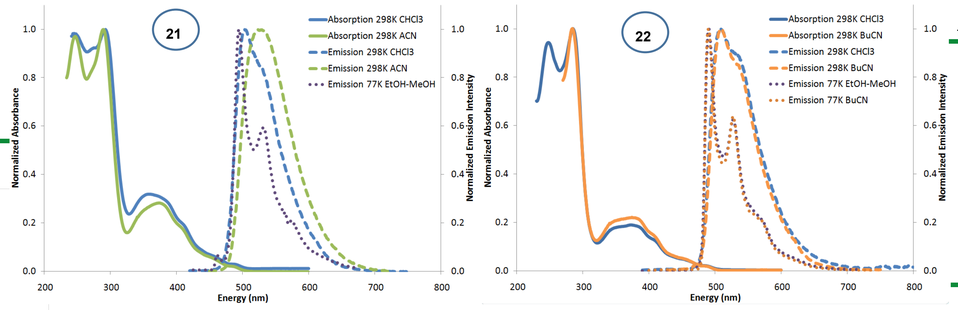
Photophysical data

Table 1 : photophysical characterisation

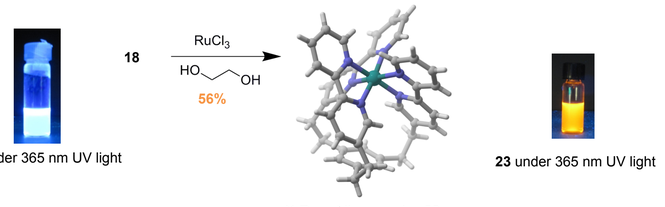
Complex		Solvent	Absorbance 298 K (nm) [Molar Absorptivities (x10^4 M^{-1}cm^{-1})]	Phosphorescence 77 K (nm)[a]	Phosphorescence 298 K (nm)	Stokes shifts 77 K (cm^{-1})	Stokes shifts 298 K (cm^{-1})	Quantum Yield degassed (%)	Quantum Yield in air (%)	Lifetime 77 K (μs)[a]	Lifetime 298 K (ns)	k_r (x10^{5}s^{-1})	k_{nr} (x10^{5}s^{-1})
fac-Ir(ppy)$_3$	ref. 18	2-MeTHF [b]	244 [4.6], 283 [4.5], 341 [0.9], 377 [1.2], 405 [0.8], 455 [0.3], 488 [0.2]	492	510	167	884	40	-	3.6	1900	2.1	3.2
	this study	2-MeTHF	250 [3.37]; 285 [4.20]; 380 [1.33]; 410 [0.87]; 455 [0.32]; 485 [0.15]	493	512	335	1087	63	2.0	3.7	1660	3.8	2.2
		$CHCl_3$	290 [4.33], 345 [0.99], 380 [1.19], 410 [0.79], 455 [0.30], 490 [0.12]	(496)	518	247	1103	27	2.0	(4.8)	879	3.1	8.3
		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	51	1.5	(4.8)	1322	3.9	3.7
Ir.HC1	this study	$CHCl_3$	250 [4.13]; 285 [4.36]; 375 [0.92]; 410 [0.85]; 450 [0.60]; 485 [0.11]	(491)	508	252	934	11	1.0	(4.0)	443	2.5	20.1
		BuCN	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	50	1.7	3.9	1482	3.4	3.4
Ir.HC2	this study	$CHCl_3$	245 [4.04]; 275 [3.80]; 290 [4.07]; 355 [1.23]; 410 [0.76]; 485 [0.12]	(494)	503	376	738	6.7	1.6	(3.9)	888	0.8	10.5
		ACN	245 [4.46]; 290 [4.57]; 380 [1.34]; 410 [0.95]; 455 [0.31]; 490 [0.11]	(494)	524	165	1324	52	1.6	(3.9)	887	5.9	5.4
Λ-Ir(pppy)$_3$ [c]	ref. 11	ACN [b]	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	0.9	2.1	1400	4.6	2.6
fac- Λ-Ir-**L**		ACN [b]	245 [4.82]; 288 [3.97]; 348 [0.99]; 379 [0.93]; 408 [0.64]; 453 [0.22]; 487 [0.11]	507	508	810	849	51	1.0	1.9	1200	4.2	4.1

[a] Spectra and values in parentheses were measured in MeOH/EtOH (1/1) glass state. [b] Absorbance and molar absorptivities were measured in DCM. [c] Only values for Λ isomer are shown but photophysical properties for the Δ isomer are very similar and can be found in the corresponding litterature.

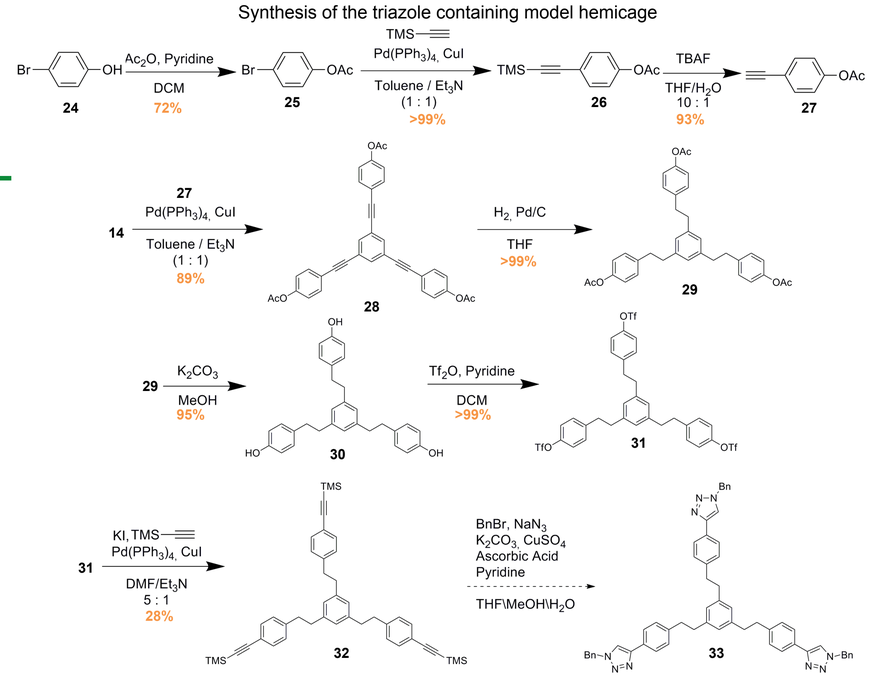
Absorption (298K) and Emission (298 and 77K) spectra



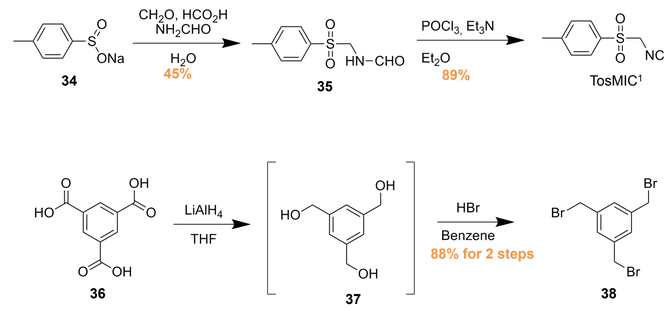
Formation of the Ruthenium complexes



Synthesis of the triazole containing model hemicage

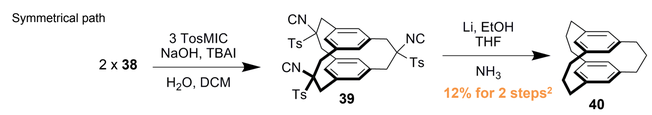


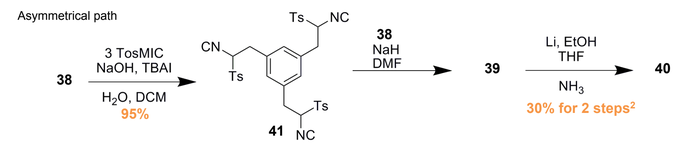
Preparation of cyclophane precursor



1 : *Organic Synthesis*, Coll. Vol.6, **1988**, p. 987.

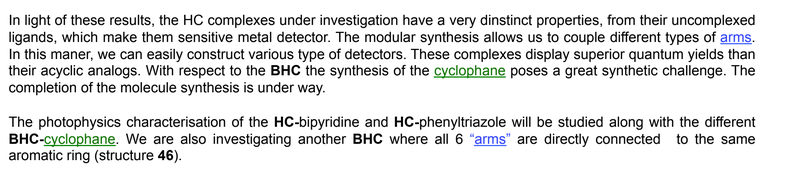
Synthesis of the cyclophane





1 : conversion calculated by GCMS

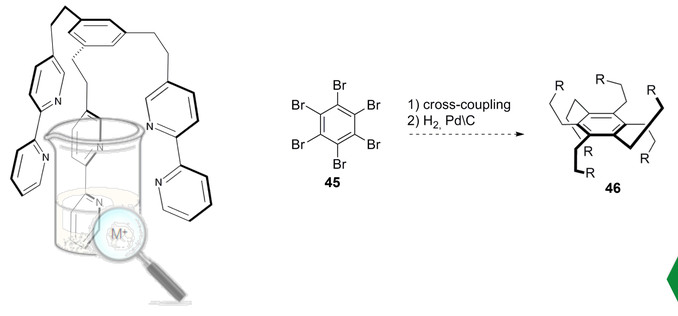
Plan for the synthesis of the bis(hemicage)-cyclophane BHC-Cy



Conclusion

In light of these results, the HC complexes under investigation have a very dinstinct properties, from their uncomplexed ligands, which make them sensitive metal detector. The modular synthesis allows us to couple different types of arms. In this maner, we can easily construct various type of detectors. These complexes display superior quantum yields than their acyclic analogs. With respect to the **BHC** the synthesis of the cyclophane poses a great synthetic challenge. The completion of the molecule synthesis is under way.

The photophysics characterisation of the **HC**-bipyridine and **HC**-phenyltriazole will be studied along with the different **BHC**-cyclophane. We are also investigating another **BHC** where all 6 "arms" are directly connected to the same aromatic ring (structure **46**).



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