Electronic Supplementary Material (ESI) for Dalton Transactions

SUPPLEMENTARY INFORMATION

Strong enhancement of luminescence from an iridium polypyridyl complex via encapsulation in cucurbit[10]uril

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Contents:

1. Experimental

Materials: Cucurbit[10]uril (Q[10]) was prepared in our laboratory according to the method described previously.[1,2] [Ir(ppy-CHO)$_2$(bpy)](Cl or PF_6) (IrCHO) was synthesised by the method of Lo et al.[3] and its purity was confirmed by NMR and UV spectra. Sodium acetate buffer (0.05 M, pH 4.7) was prepared from d_4-acetic acid and anhydrous sodium carbonate in deuterium oxide according to standard procedures. This was not corrected to pD. All samples were prepared in this buffer for all spectroscopic measurements.

Equipment: NMR spectra were recorded on a Varian Unity *plus*-400 spectrometer (operating at 400 MHz for the ^{1}H nuclei), and analysed using Varian's VNMR software. All NMR experiments were conducted at 25 °C.

UV-visible absorption spectra were recorded on a Cary 50 Bio UV-vis spectrometer in quartz cuvette (1 cm pathlength). The molar extinction coefficient of IrCHO was calculated as 3.8 x 10^4 $dm^3mol^{-1}cm^{-1}$ in sodium acetate buffer solution.

Steady-state fluorescence spectra were recorded using a FluoroMax-3 fluorimeter, HORIBA Jobin Yvon, with slit widths of 5 nm (excitation) and 1 nm (emission). Samples were excited at 360 nm. Fluorescent lifetimes were determined using an Edinburgh Instrument FLS980 fluorescence spectrometer equipped with a pulsed EPLED excitation source (360 nm). This spectrometer was also used to measure temperature dependence of emission intensity. All samples were prepared in sodium acetate buffered prepared with MilliQ water (0.05M, pH 4.7) and were deoxygenated by purging with argon. 4 window quartz cuvettes were used (1 cm path length).

2. Absorption spectra

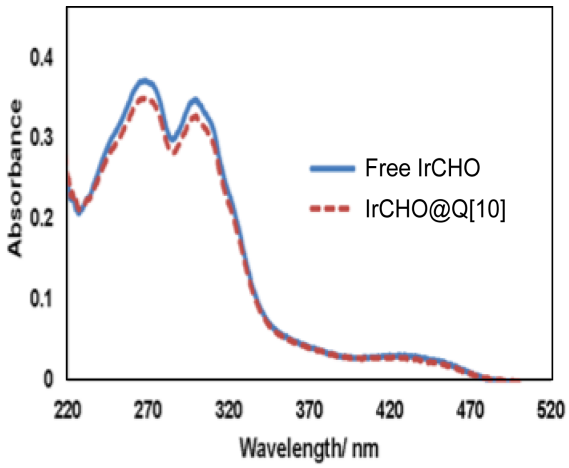

Fig S1. Absorption spectra of IrCHO (solid blue line) and IrCHO@Q[10] (dashed red line) in sodium acetate buffer solution (pH =4.7).

3. Binding constant

The binding constant (K_a) of IrCHO with Q[10] was calculated with the modified Benesi-Hildebrand equation (1), assuming a 1:1 molar ratio of host to guest, using the fluorescence data. Aliquots of Q10] stock solution were added to a known volume of IrCHO stock solution (1.02 x10^{-5} M) at 22 ºC, and the fluorescence spectrum collected after each addition.

$$\frac{1}{F-F0} = \frac{1}{[\mathbf{Q[10]}]K_a\alpha} + \frac{1}{\alpha} \qquad (1)$$

F and F_0 are the fluorescence intensity in the presence and absence of Q[10] respectively. [Q[10]] is the total concentration of Q[10] in the solution, and α is a constant. K_a is obtained from the slope and intercept of the double reciprocal plot of $1/(F-F_0)$ vs. $1/[Q[10]]$[4].

4. Temperature effect on the luminescence of IrCHO@Q[10]

Table S1. Emission lifetimes (fit to dual exponential) detected at 543 nm, with pulsed excitation at 360 nm.

	6°C	21 °C	32 °C	40 °C	51°C	62°C
τ_1 (ns)*	3260	2690	2110	1750	1460	1150
τ_2 (ns)*	230	160	130	100	80	70
% τ_2 component[#]	2	5	10	14	20	24

* *Standard deviation in τ values obtained from the fits was approximately ±40 ns*
[#]*From the dual exponential fits, numerical value only.*

5. NMR Studies

The ^{1}H NMR spectra of IrCHO and IrCHO@Q[10] were recorded separately in D_2O buffered solutions referenced to HDO (4.78 ppm). The IrCHO@Q[10] was prepared by the addition of IrCHO to a solution or suspension of Q[10] in buffer to produce a mole ratio of 1:1. The aqueous solubility of IrCHO is increased by encapsulation in Q[10] and no unbound IrCHO is visible in solutions of IrCHO@Q[10].

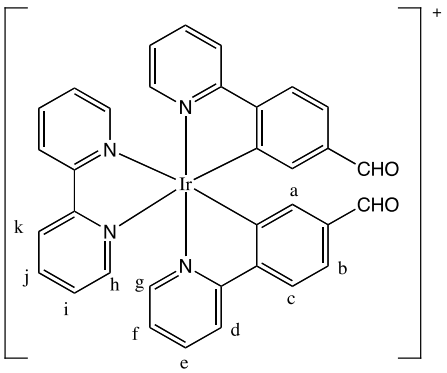

Fig S2 The structure of IrCHO with proton labels used in the NMR assignment.

Table S2 Chemical shift differences of the ^{1}H resonances of the free IrCHO complex compared to the encapsulated complex (IrCHO@Q[10] in buffer solutions.

Ring	H	Free IrCHO (δ)	IrCHO@Q[10] (δ)	Δδ
Phenyl	*CHO*	9.58	9.06	0.52
	a	6.88	6.08	0.80
	b	7.53	6.89	0.64
	c	7.98	7.31	0.67
Pyridine	*d*	8.24	7.45	0.79
	e	7.99	7.71	0.28
	f	7.19	7.09	0.11
	g	7.82	7.81	0.01
Bipyridine	*h*	8.04	7.99	0.05
	i	7.46	7.81	-0.35
	j	8.16	8.17	-0.01
	k	8.60	8.56	-0.04

The chemical shift differences are calculated as **Free IrCHO – IrCHO@Q[10] = Δ*δ***

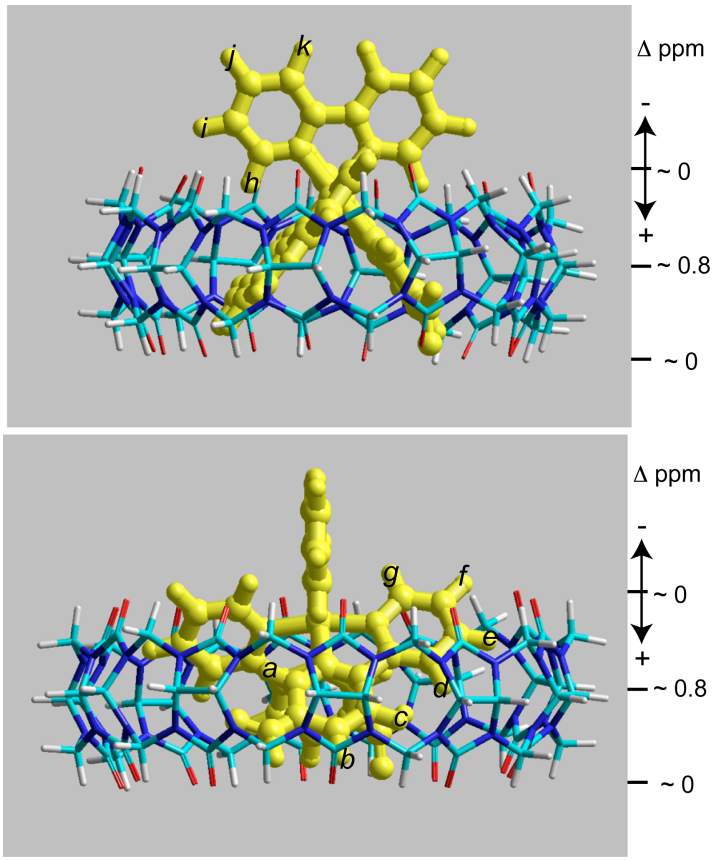

Fig S3. Models showing the encapsulation of IrCHO in Q[10] which demonstrates the observed relationship between the location of individual protons ***a*** – ***g*** (ppy-CHO) and ***h*** – ***k*** (bpy) and the chemical shift effect on these proton resonances relative to the depth of

encapsulation.[5] The position of the guest IrCHO within the cavity and the degree of chemical shift upfield and downfield is consistent with its positioning as represented.

IrCHO Assignment:

Assignments of the IrCHO resonances were made by identifying the two separate ring systems using COSY NMR (Fig. S3), supported by 1D ROESY correlations between protons of C**H**O to ***a*** and ***b*** confirming the phenyl proton resonances. Strong 1D ROESY correlations between ***g*** to ***f*** as well as ***k*** to ***j*** were also identified, with further confirmatory correlations from ***f*** to ***g*** and ***f*** to ***e*** (Table S2). The coupling patterns of the protons of each ring systems in conjunction the cross correlations in support of the assignments.

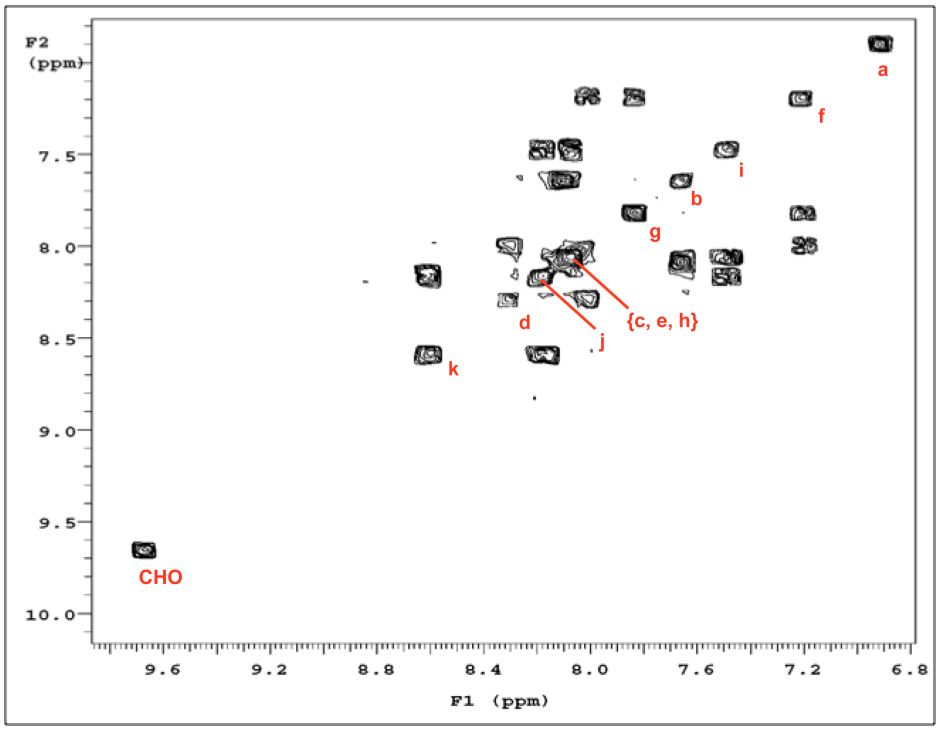

Fig S4. COSY NMR spectrum of IrCHO (acquired using 2048 complex data points in t_2; spectral width of 3360 Hz; 128 increments in t_1; recycle time = 1.3 s; 256 scans per fid.

Table S3 1D ROESY results for IrCHO (acquired using 49152 complex data points in t_2; spectral width of 6410 Hz; recycle time = 5.3 s; 8248 scans per fid. Mixing times of 400 ms were used.)

Irradiated peak (ppm)		Correlated peaks (ppm)			
C**H**O	(9.58)	***a***	(6.88)	***b***	(7.53)
k	(8.60)	***j***	(8.16)		
f	(7.19)	***g***	(7.82)	***e***	(7.99)

IrCHO@Q[10] Assignment

Assignments were made based upon NOESY and COSY NMR spectra (Fig S4 and S5 respectively). Strong correlations were found between the C**H**O and protons ***a*** and ***b***. In addition, a strong correlation between ***c*** and ***d***. COSY NMR was used to identify the separate ring systems in conjunction with the NOESY correlations (refer to annotated spectra).

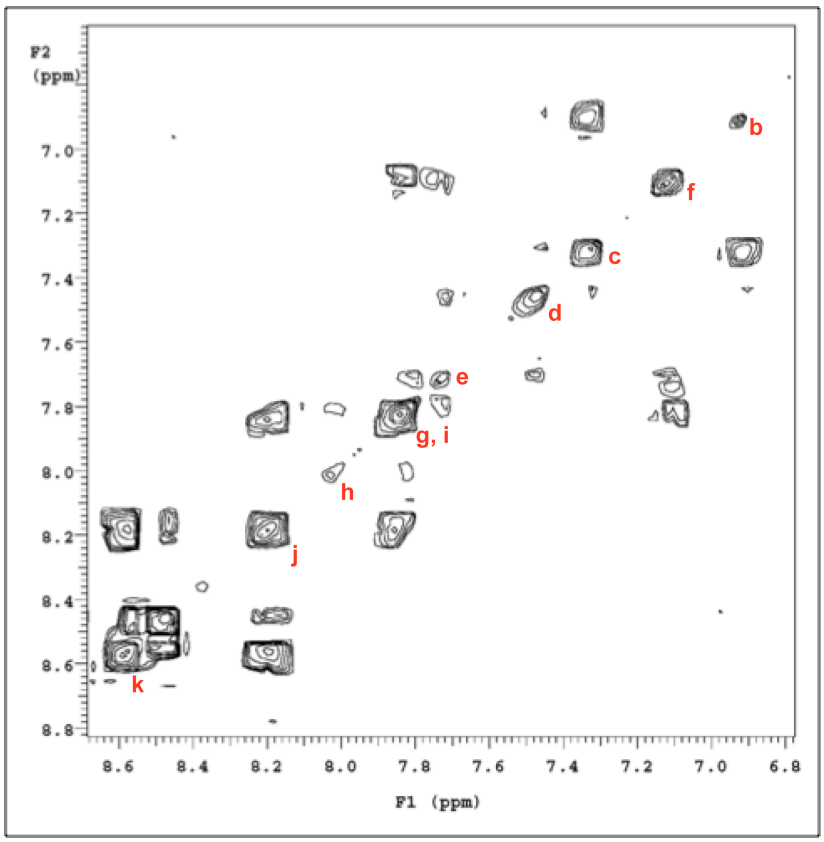

Fig S5. Annotated COSY spectrum of IrCHO@Q[10] showing guest proton resonances with cross correlations. The protons of the C**H**O and ***a*** are not shown as there were no correlations as is consistent with the assignment. (Acquired using 2056 complex data points in t_2; spectral width = 3205 Hz; 128 increments in t_1; recycle time = 1.3 s; 256 scans per fid).

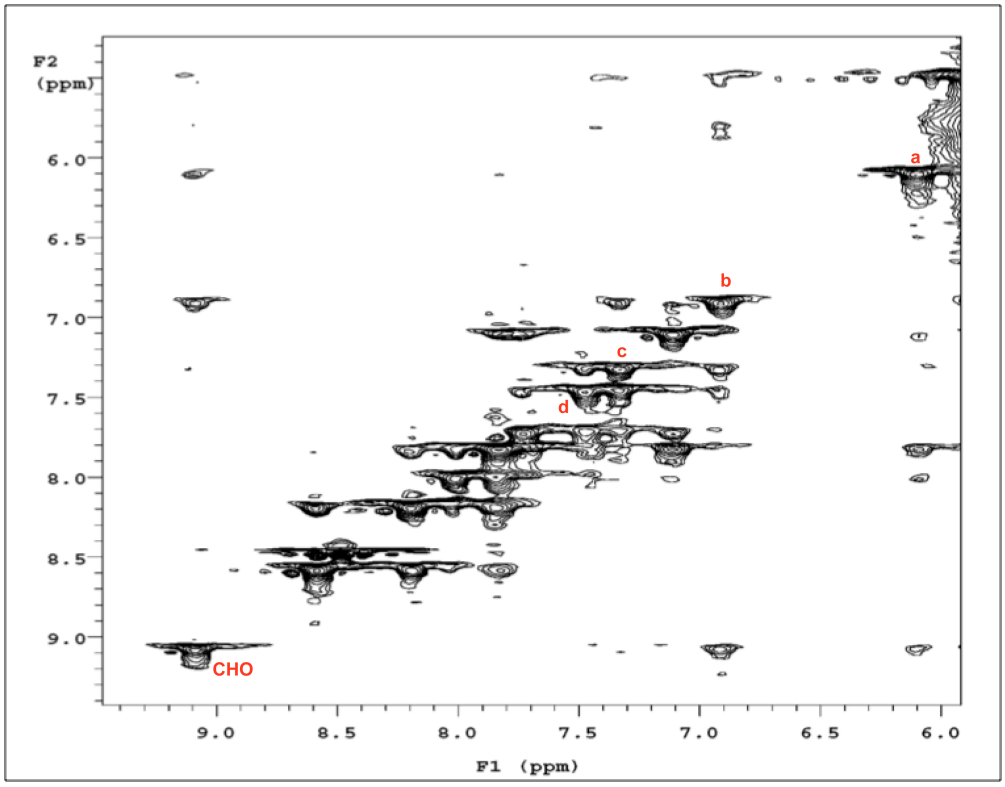

Fig S6. The annotated NOESY spectrum, showing the strong correlations between ***a, b*** and C**H**O. In addition, a strong correlation of the nuclei ***c*** and ***d*** as indicated. (Acquired using 2056 complex data points in t_2; spectral width = 6410 Hz; 128 increments in t_1; recycle time = 1.2 s; 128 scans per fid. Mixing times of 200 ms were used).

References

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