Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supporting Information

Investigation of Cucurbit[7]uril Complexation on Photophysical and Acid-Base Properties of an Antimalaria Drug Quinine

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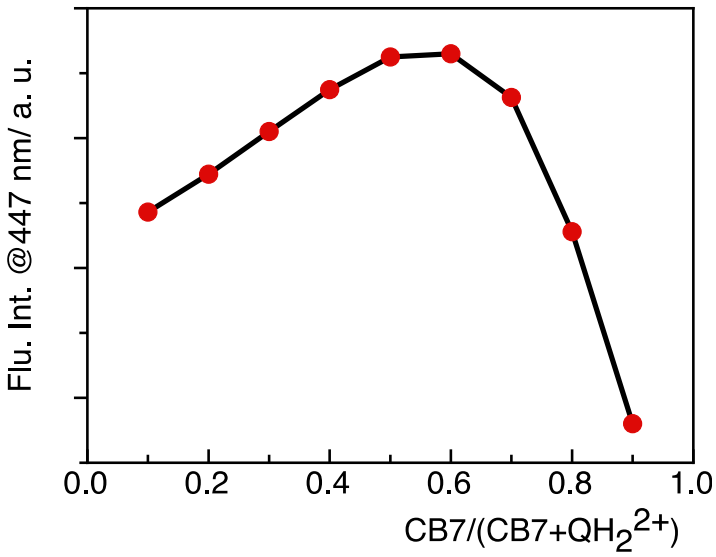


Fig S1: Job's plot showing a maximum around 0.66 mole fraction, corresponds to 2:1 complexation.

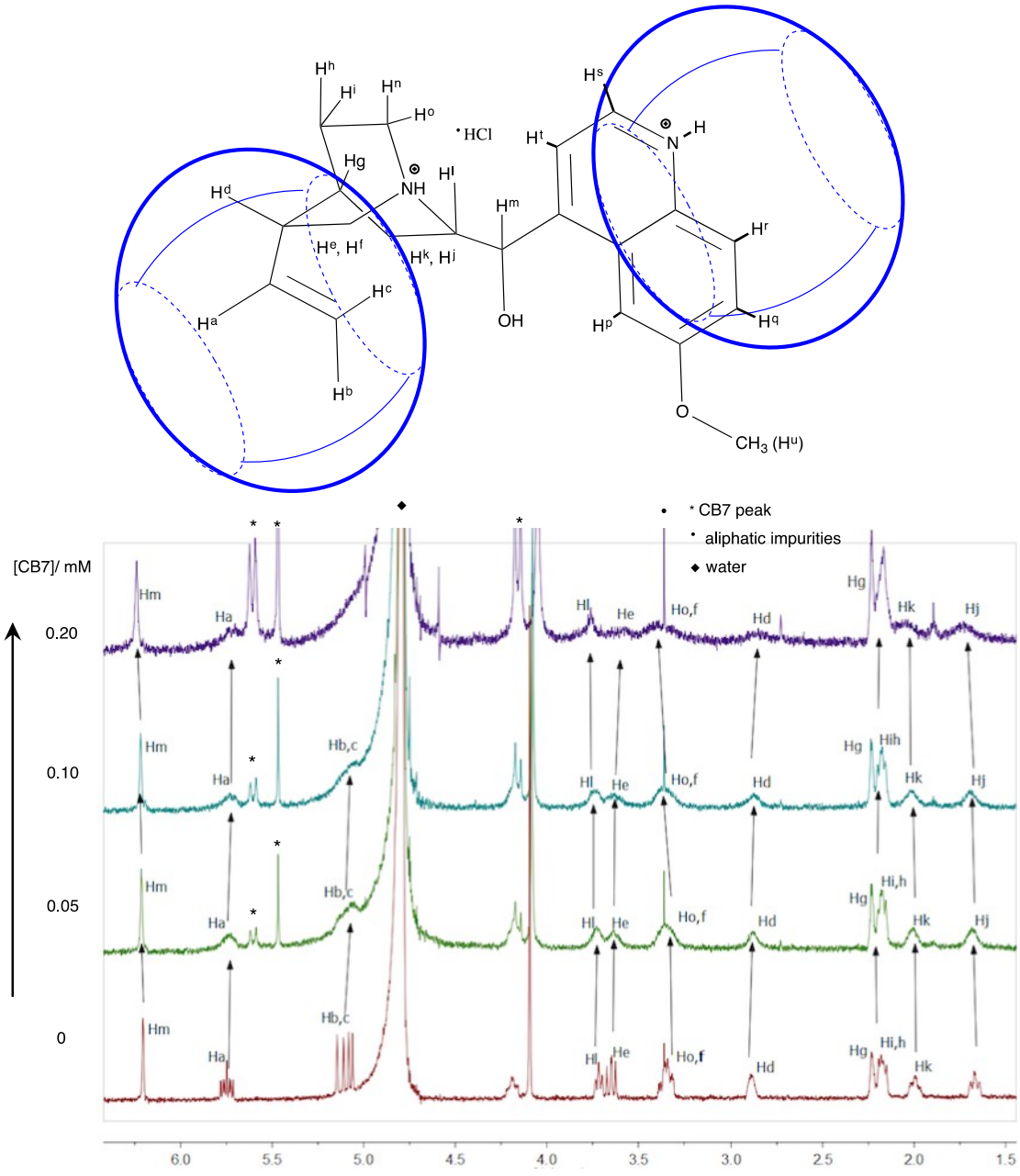


Fig S2: Aliphatic part of ^{1}H signal $\mathbf{QH_2^{2+}}$ from the NMR titration between 0.5 mM $\mathbf{QH_2^{2+}}$ and increasing concentration of CB7. Arrow shows complexation-induced chemical shift upon complexation with CB7.

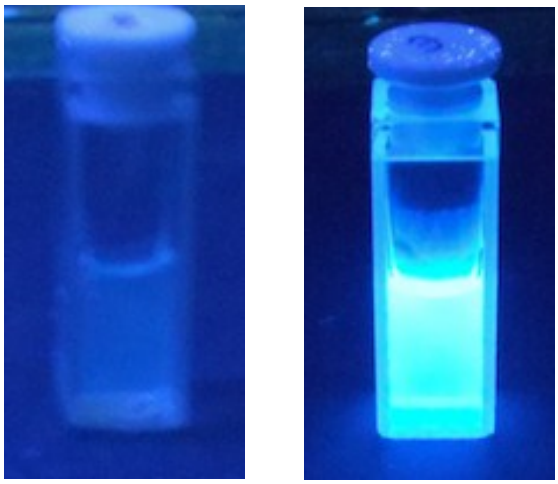


Fig S3: Digital photograph of 0.8 mM Quinine Hydrochloride at 0.1 (N) HCl and the solution containing 1.3 mM CB7 at pH 3.0 showing complexation induced fluorescence enhancement under hand-held UV (365 nm) light.

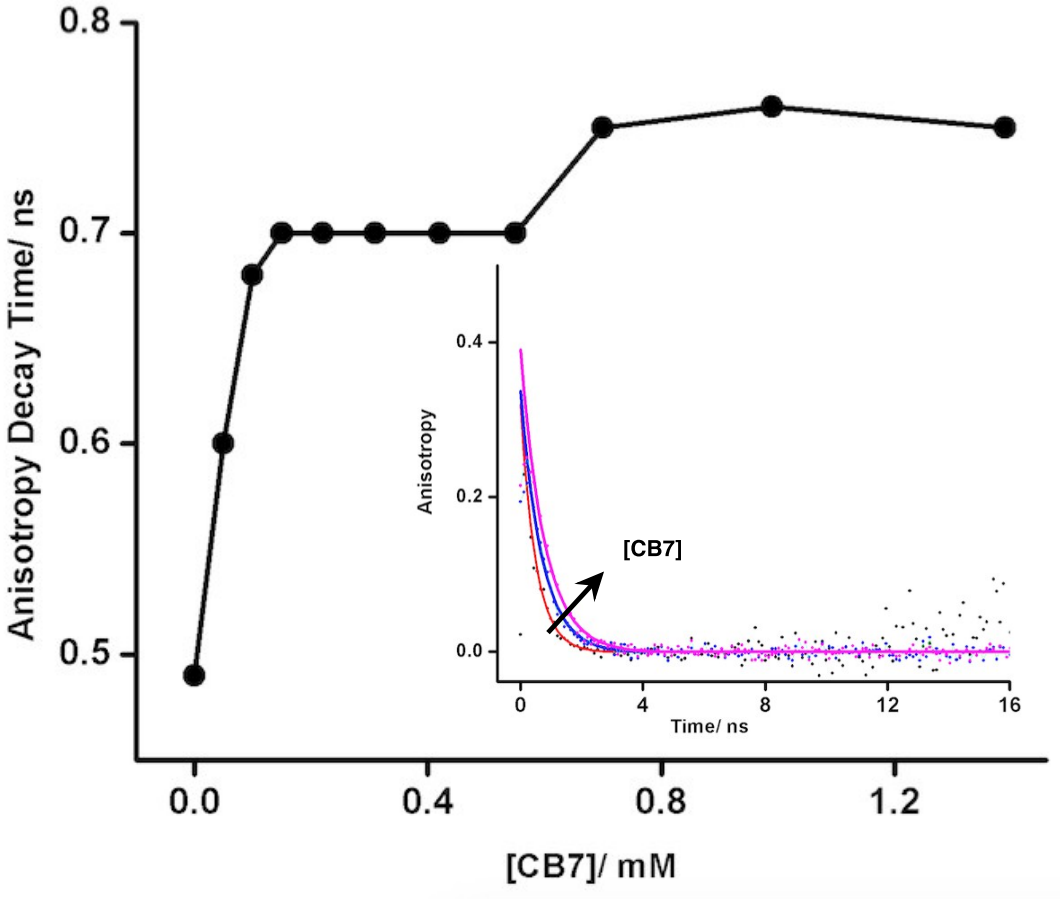


Fig S4: Plot of time-resolved fluorescence anisotropy decay time with increasing concentration of CB7 at pH 2.7 Stepwise changes in fluorescence anisotropy decay time indicate a 2:1 complexation with Quinine and CB7. Inset shows time-resolved anisotropy decay with increasing concentration of CB7.

2:1 equation for the determination of binding constants using UV-Vis and fluorescence titration

$OD = \varepsilon_Q[Q] + \varepsilon_{CB7\cdot Q}[CB7\cdot Q] + {}^{\varepsilon_{[(CB7)_2\bullet Q]}}[(CB7)_2\cdot Q]$

and

$Intensity = {}^{I_Q}[Q] + I_{CB7\cdot Q}\,[CB7\cdot Q] + {}^{I_{(CB7)_2\bullet Q}}[(CB7)_2\cdot Q]$,

Where $[Q]= \dfrac{[Q]_0}{1 + K_1[CB7] + K_1K_2[CB7]^2}$

$[CB7\cdot Q]= \dfrac{K_1[CB7][Q]_0}{1 + K_1[CB7] + K_1K_2[CB7]^2}$

$[(CB7)_2\cdot Q]= \dfrac{K_1K_2[CB7]^2[Q]_0}{1 + K_1[CB7] + K_1K_2[CB7]^2}$

$K_1K_2[CB7]^3 + K_1(2K_2[Q]_0 - K_2[CB7]_0 + 1)[CB7]^2 + (K_1[Q]_0 - K_1[CB7]_0 + 1)[CB7] - [CB7]_0 = 0$

by solving this cubic equation we can find out K_1 and K_2

Estimating pK_a shift from the binding constant values of protonated and non-protonated dye with host molecule.

$log[(K_1K_2)_{pH=2.7}/(K_1K_2)_{pH=9.0}] = \Delta pK_a$, K_1K_2= overall binding strength, $(K_1K_2)_{pH=2.7}$ = overall binding strength of the doubly protonated Quinine and $(K_1K_2)_{pH=9.0}$ = overall binding strength of the mono-protonated Quinine

Fluorescence lifetime values of Quinine with and without CB7 along with fitting parameters

Table S1: Fluorescence lifetime of QH_2^{2+} at pH ~ 2.2 by exciting at 280 nm

λ_{mon} (nm)	τ_1 (ns)	τ_2 (ns)	a_1	a_2	τ_{av} (ns)	χ^2
430	1.5	4.7	5.0	95.0	4.6	1.1
460	-	4.9	-	100	4.9	1.1
490	0.4	4.8	-7.0	107.0	4.8	1.2

Table S2: Fluorescence lifetime of QH^+at pH ~ 9.0 by exciting at 280 nm

λ_{mon} (nm)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	a_1	a_2	a_3	τ_{av} (ns)	χ^2
380	2.3	0.2	5.0	55.0	-5.0	50.0	4.1	1.2
460	5.1	0.4	16.4	52.3	-4.3	52.0	13.7	1.0

Table S3: Fluorescence lifetime of QH_2^{2+} in presence of 1.5 mM CB7 at pH 2.2 by exciting at 375 nm

λ_{mon} (nm)	τ_1 (ns)	τ_2 (ns)	a_1	a_2	τ_{avg} (ns)	χ^2
430	4.9	30.6	4.6	95.4	30.4	1.1
460	11.7	31.2	6.9	93.1	30.7	1.0
490	16.8	31.8	13.5	86.5	30.6	1.0

Table S4: Fluorescence lifetime of QH^+ in presence of 1.5 mM CB7 at pH 10.5 by exciting at 375 nm

λ_{mon} (nm)	τ_1 (ns)	τ_2 (ns)	a_1	a_2	τ_{avg} (ns)	χ^2
380	3.3	8.3	88.8	11.2	4.5	1.0
460	4.3	20.7	23.0	77.0	19.7	1.1

Table S5: Fluorescence lifetime of QH_2^{2+} at pH ~2.2 by exciting at 340 nm

λ_{mon} (nm)	τ_1 (ns)	a_1	τ_{av} (ns)	χ^2
460	4.9	100	4.9	1.1

Table S6: Fluorescence lifetime of QH_2^{2+} in presence of 1.4 mM CB7 at pH ~ 2.2 exiting at 340 nm

λ_{mon} (nm)	τ_1 (ns)	τ_2 (ns)	a_1	a_2	τ_{avg} (ns)	χ^2
460	6.8	30.3	6.5	93.5	30.1	1.1

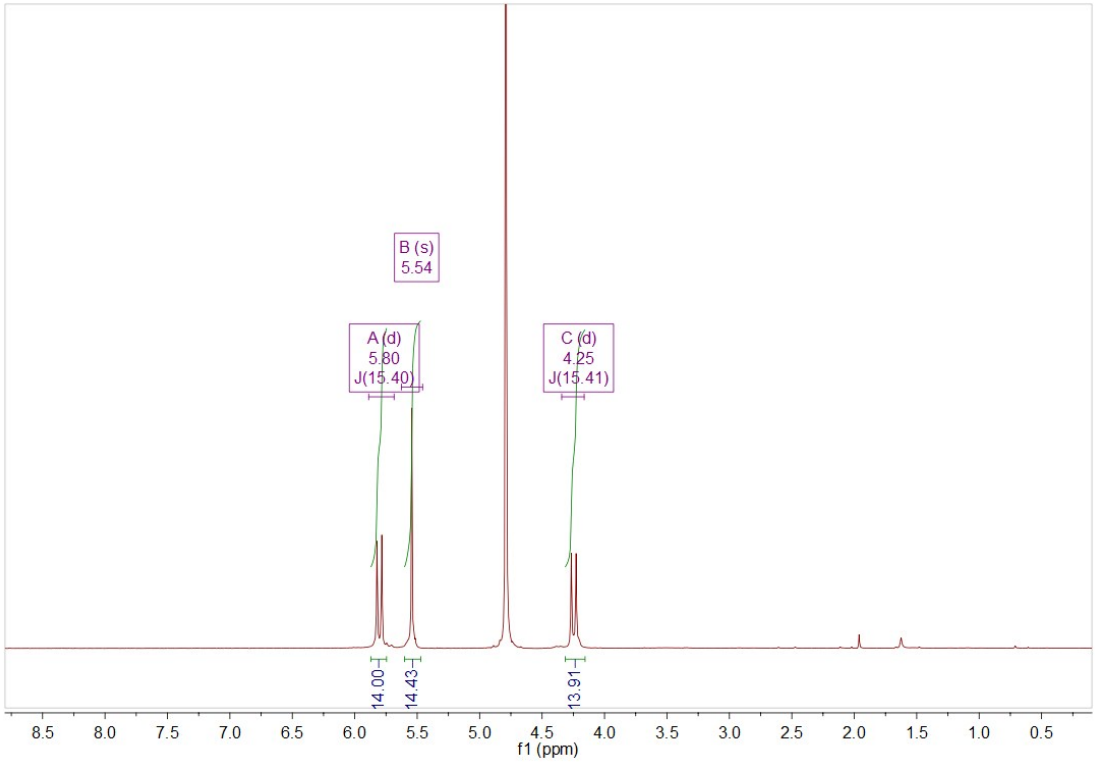
Table S7: Fluorescence lifetime of QH^+ at pH 12.5 by exciting at 340 nm

λ_{mon} (nm)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	a_1	a_2	a_3	τ_{av} (ns)	χ^2
460	0.8	7.0	0.2	19.6	29.6	50.8	6.3	1.1

Table S8: Fluorescence lifetime of QH^+ in presence of 1.5 mM CB7 at pH 12.5 by exciting at 340 nm

λ_{mon} (nm)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	a_1	a_2	a_3	τ_{av} (ns)	χ^2
460	3.7	19.6	0.1	16.8	70.8	12.4	18.9	1.1

^{1}H NMR of Cucurbit[7]uril



^{1}H NMR (400MHz, D_2O) : δ (ppm) 5.80 (d, 14H, J=15.40Hz), 5.54 (s, 14H), 4.25 (d, 1H, J=15.41Hz)

Low Resolution Mass Spectrometry of Cucurbit[7]uril

LC-MS REPORT
IISER - BHOPAL

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Sample Name     : ALK-AA-CBN                                Injection vol   : 5.00 ul
Acq Method      : D:\DATA\02-9-2015_6 2015-09-02 16-29-33\DIRECT INJECTION_BO
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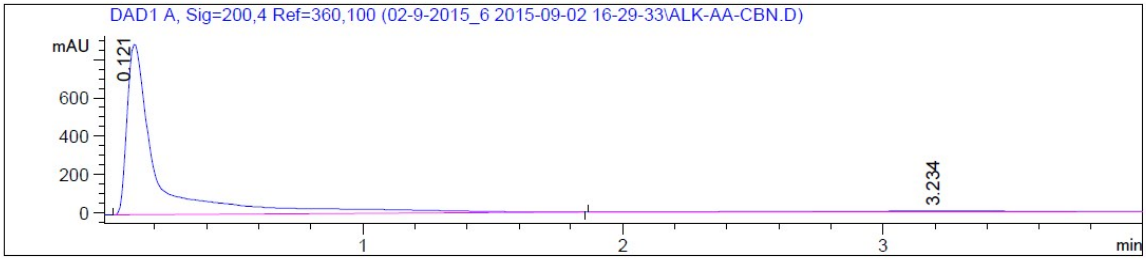

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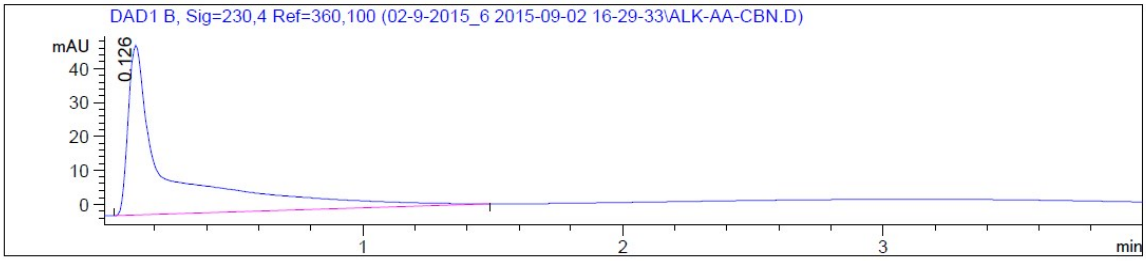

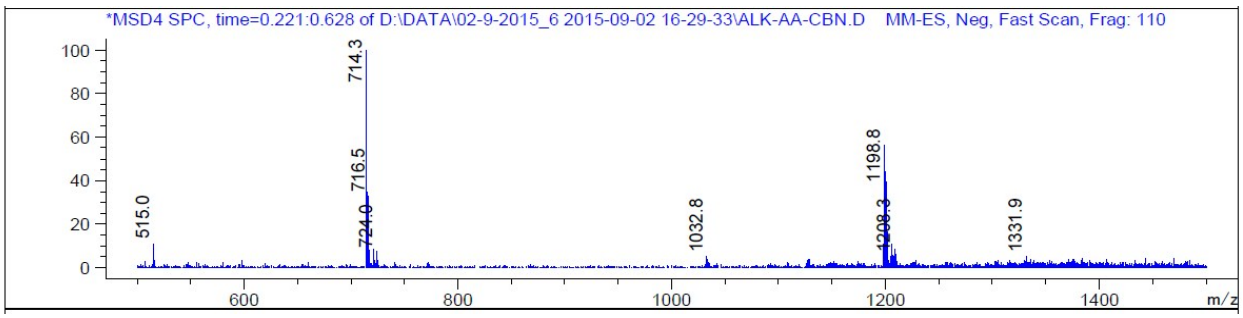

Molecular mass [M] calculated for Cucurbit[7]uril = 1162.34,

mass obtained = 1198.8 [M+2H_2O]