Supplementary Information

A latent photoreaction predominates within water soluble calixarenes: Photochemistry of benzoin alkyl ethers

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Experimental Protocol:

The benzoin alkyl ethers (3a-c) are sparingly soluble in water. For complex preparation, the required equivalents of the guest was added to an aqueous solution of the host and stirred for 6 hours. The complex formation was confirmed by $^1$H NMR. The pH of the solution was ~ 7.7. The complexes were irradiated for ~ 10 minutes using a 450W medium pressure mercury arc lamp. The photoproducts were extracted with ethyl acetate. A known amount of benzophenone was added as an internal standard before GC analysis. The mass balance was 65-70% excluding benzaldehyde. Photoproducts were analysed by HP 5890 series-II GC using an SE-30 capillary column, error limit ± 3%.

Determination of host-guest association constants: $^1$

The association constants were calculated for the following equilibrium,

$$ G + H \rightleftharpoons H.G $$. 

![Figure S1. Structures of host 1 and 2 and guest 3a.](image)

Binding of benzoin methyl ether with hosts 1 and 2 was fast on the NMR time scale (400 MHz) and the determination of $K$ required titration studies. The shift of the aromatic proton (H$_a$) signals of benzoin methyl ether (Figure S1) was recorded after each addition (~1.7 mg, 1.02x10$^{-6}$ moles) of the host. The plot of 1/Δ vs 1/[Host] is shown in Figure S2.
$K$ according to equation (1) is given by

$$K = \frac{[H.G]}{[H][G]}$$

$$\frac{1}{\Delta} = \frac{1}{(\Delta_{11}K[H])} + \frac{1}{(\Delta_{11})}$$

Where,

$K =$ association constant,

$\Delta = \delta_{\text{complex}} - \delta_{\text{guest}}$ and $\Delta_{11} = \delta_{\text{complex}} - \delta_{\text{guest}}$

the observed chemical shift $\delta$ is the average of the chemical shifts of the guest and the complex, $\delta_{\text{complex}}$ is the chemical shift of the complex, $\delta_{\text{guest}}$ is the chemical shift of the guest and $[H]$ = concentration of host.

For host 1 (with guest 3a), $K = 386 \text{ M}^{-1}$, and for host 2 (with guest 3a), $K = 137 \text{ M}^{-1}$

![Graph](image)

**Figure S2.** (a) Plot of $1/\Delta$ vs $1/[\text{Host 1}]$  (b) Plot of $1/\Delta$ vs $1/[\text{Host 2}]$.

**Determination of the concentration of H.G complex at a given concentration of host and guest:**

$$G + H \rightleftharpoons H.G$$
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\[ K = \frac{[H \cdot G]}{[G][H]} \]

\[ K = \frac{[H \cdot G]}{([G] - [H \cdot G])([H] - [H \cdot G])} \]

\[ [H \cdot G] = 0.5[H] \left\{ 1 + R + \frac{1}{[H]}K \pm \left( (1 + R + \frac{1}{[H]}K)^2 - 4R \right)^{0.5} \right\} \quad \text{where} \ R = \frac{[G]}{[H]} \]

For complex of host 1 with guest 3a, the values are as follows, \([G] = 3.4 \times 10^{-3}\)M, \([H] = 1.2 \times 10^{-2}\)M and \([H \cdot G] = 2.6 \times 10^{-3}\)M, percentage of guest 3a complexed to host 1 = 76

For complex of host 2 with guest 3a, the values are as follows, \([G] = 4.76 \times 10^{-3}\)M, \([H] = 2.13 \times 10^{-2}\)M and \([H \cdot G] = 3.38 \times 10^{-3}\)M, percentage of guest 3a complexed to host 2 = 70

**Percentage relative yield of deoxybenzoin at infinite concentration of host:**

Percentage relative yields of deoxybenzoin at infinite concentration of the hosts 1 and 2 were calculated by extrapolating the plot of (100 - %yield) vs 1/[Host] as shown in Figure S3. At infinite concentration of the respective host, the percentage yield is given below,

For host 1, percentage yield = 100 and for host 2, percentage yield = 84
Figure S3. (a) Plot of (100 - %yield) vs 1/\([\text{Host 1}]\) (b) Plot of (100 - %yield) vs 1/\([\text{Host 2}]\).

References:
