Electronic Supporting Information

Silica – calix hybrid composite of covalently linked allyl calix[4]arene to MCM-41 nanoparticles for sustained release of doxorubicin to cancer cells

Nilesh Narkhede,^a Bhawna Uttam,^a Ravinder Kandi^a and Chebrolu Pulla Rao^{*a}

^aBioinorganic Laboratory, Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai-400 076, India, *Email: <u>cprao@iitb.ac.in</u>

- S1. (a) 1 H & (b) 13 C NMR and (c) ESI-MS spectra of 1a.
- S2. (a) 1 H & (b) 13 C NMR and (c) ESI-MS spectra of **1b**.
- S3. (a) 1 H & (b) 13 C NMR and (c) ESI-MS spectra of allylCalix.

S4. Flowcytometry analysis of Dox internalization into HeLa cells.

S5. Flowcytometry analysis of Dox internalization into MCF7 cells.

S6. Localization of Dox into HeLa cells upon treating with MCM-allylCalix-Dox.

S7. Fluorescence intensities of Dox internalized into MCF7 & HeLa cells based on microscopy.



S1. (a) 1 H & (b) 13 C NMR and (c) ESI-MS spectra of 1a.



Figure S1. (a) 1 H & (b) 13 C NMR, (c) ESI-MS and (d) Expanded MS [M+K] spectra of 1a.







Figure S2. (a) 1 H & (b) 13 C NMR, (c) ESI-MS and (d) Expanded MS [M+K] spectra of 1b.

According to literature based on ¹H & ¹³C NMR spectra [*J. Am. Chem. Soc.* **1982**, *104*, 2652-2653; *Tetrahedron*, **1983**, 39, 409-426], **1b** is present in the partial cone plus other conformers. Therefore, one will expect a complex pattern & spectrum in 3.0 to 5.0 ppm since the resonances of bridge-CH₂-, arm -O-CH₂- and -CH=CH₂ appear in this region (labelled in the figure). The ¹³C NMR showed the signals in the regions 156-115 (aryl & vinyl), 76-72 (OCH₂) and 37-29 (bridge –CH₂) ppm corresponding to *aryl* and *C*=*C* (vinyl) carbons, OCH₂ and Ar-*C*H₂-Ar, respectively. Thus the obtained NMR spectra are in agreement with the literature reported ones.



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20

S3. (a) ¹H and (b) ¹³C NMR and (c) ESI-MS spectra of allylCalix.

 F2
 Processing parameters

 SI
 32768

 SF
 125.7577890 MHz

 WDW
 EM

 SSB
 0

 LB
 1.00 Hz

 GB
 0

 PC
 1.40

32768 125.7577890 MHz EM

ppm

10 0



Figure S3. (a) 1 H & (b) 13 C NMR, (c) ESI-MS and (d) Expanded MS [M+K] spectra of allylCalix.



S4. Flowcytometry analysis of Dox internalization into HeLa cells.

Figure S4. Flowcytometry analysis of Dox internalization into HeLa cells. Here the controls are simple cells and the cells treated with MCM-allylCalix alone (no Dox loading). 'MD' is MCM-allylCalix-Dox.

S5. Flowcytometry analysis of Dox internalization into MCF7 cells.



Figure S5. Flowcytometry analysis of Dox internalization into MCF7 cells. Here, the controls are simple cells and the cells treated with MCM-allylCalix alone (no Dox loading). 'MD' is MCM-allylCalix-Dox.

S6. Localization of Dox into HeLa cells upon treating with MCM-allylCalix-Dox.



Figure S6. Localization of Dox in HeLa cells upon treating with two concentrations of MCM-allylCalix-Dox for 48 h of incubation.

S7. Fluorescence intensities of Dox internalized into MCF7 & HeLa cells based on microscopy.



Figure S7. Fluorescence intensities measured upon internalization of Dox into MCF7 & HeLa cells when treated with two different concentrations of MD (MCM-allylCalix-Dox) based on microscopy. 'only cells' is a control having no 'MD'.