

Electronic Supplementary Information for

Direct synthesis of hollow polymeric nanocapsules of variable shell thickness and rigidity

Ramjee Balasubramanian,* Sangbum Han and Christian Chamberlayne

General remarks: All solvents used in this study were dried and distilled by following standard procedures prior to their use.

Monomers and photopolymerization: Resorcinarene cavitand thiol (**1**)¹ and alkene (**4**)² were prepared by adopting literature procedures. Alkenes **2** and **3** were obtained from commercial sources and used as received. The details of the photopolymerization have been described elsewhere.²

Characterization methods: TEM analysis was carried out in a JEOL JEM-2100F field emission microscope operating at 200 kV equipped with a Gatan SC1000 ORIUS CCD camera (11 megapixel), with stained samples on a carbon coated copper grid. Photoproducts in chloroform were stained (with OsO₄) by mixing them with an equal volume of an aqueous solution of OsO₄ (0.2 % v/v) for at least 45 min, with occasional mixing. Such OsO₄ stained samples were placed on a grid and the excess sample was wicked dry after 10 s. Photoproducts were stained with uranyl acetate in the following manner. Samples were initially drop cast on a TEM grid and almost immediately an aqueous dispersion of uranyl acetate (0.1 % w/v) was placed on the grid. After a min, the excess liquid was wicked dry. The stained sample was washed with a drop of water and dried under ambient conditions. Atomic force microscopy of samples drop cast on glass coverslips was carried out on a Veeco diNanoscope 3 under tapping mode.

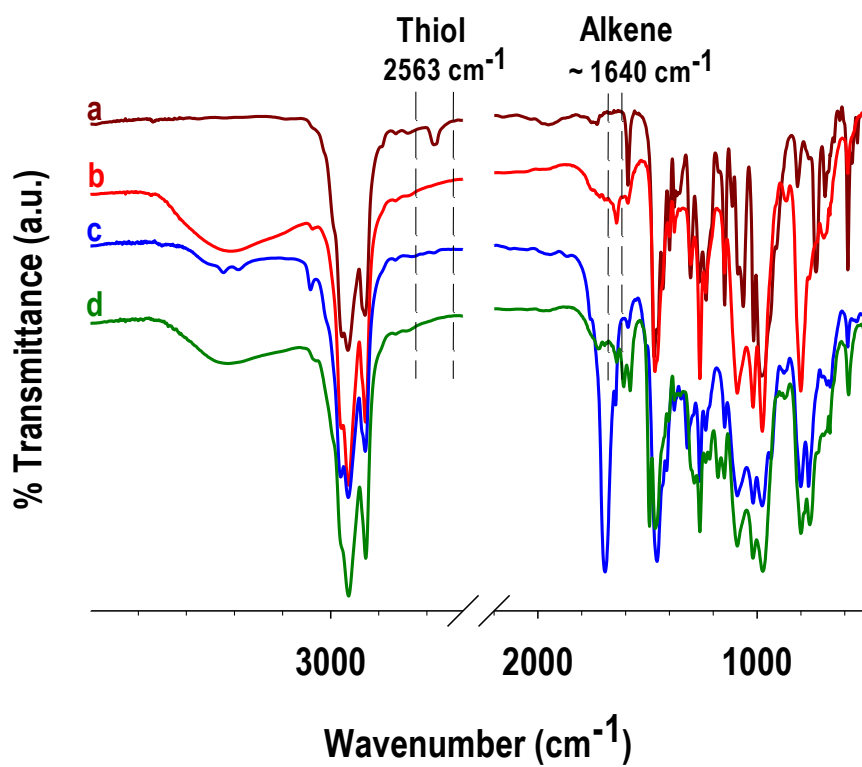


Fig. S1 FTIR spectra of (a) resorcinarene thiol monomer and its photopolymers with (b) diene **2**, (c) triene **3**, and (d) tetraene **4**. These samples were photopolymerized by UV irradiation for 3 h in degassed, sealed quartz tube.

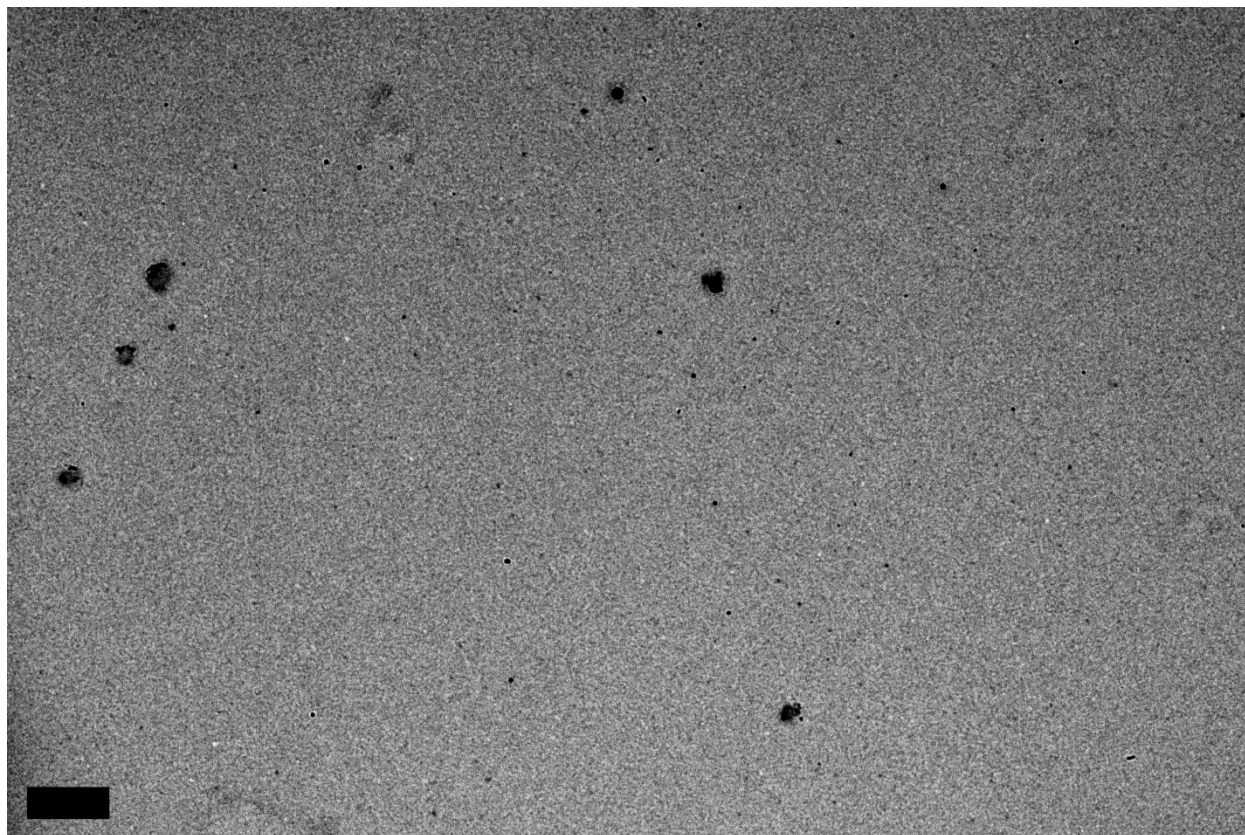


Fig. S2 TEM image (scale bar = 500 nm) of the photopolymer obtained from resorcinarene thiol cavita nd **1** and diene **2**. This sample was stained with OsO_4 .

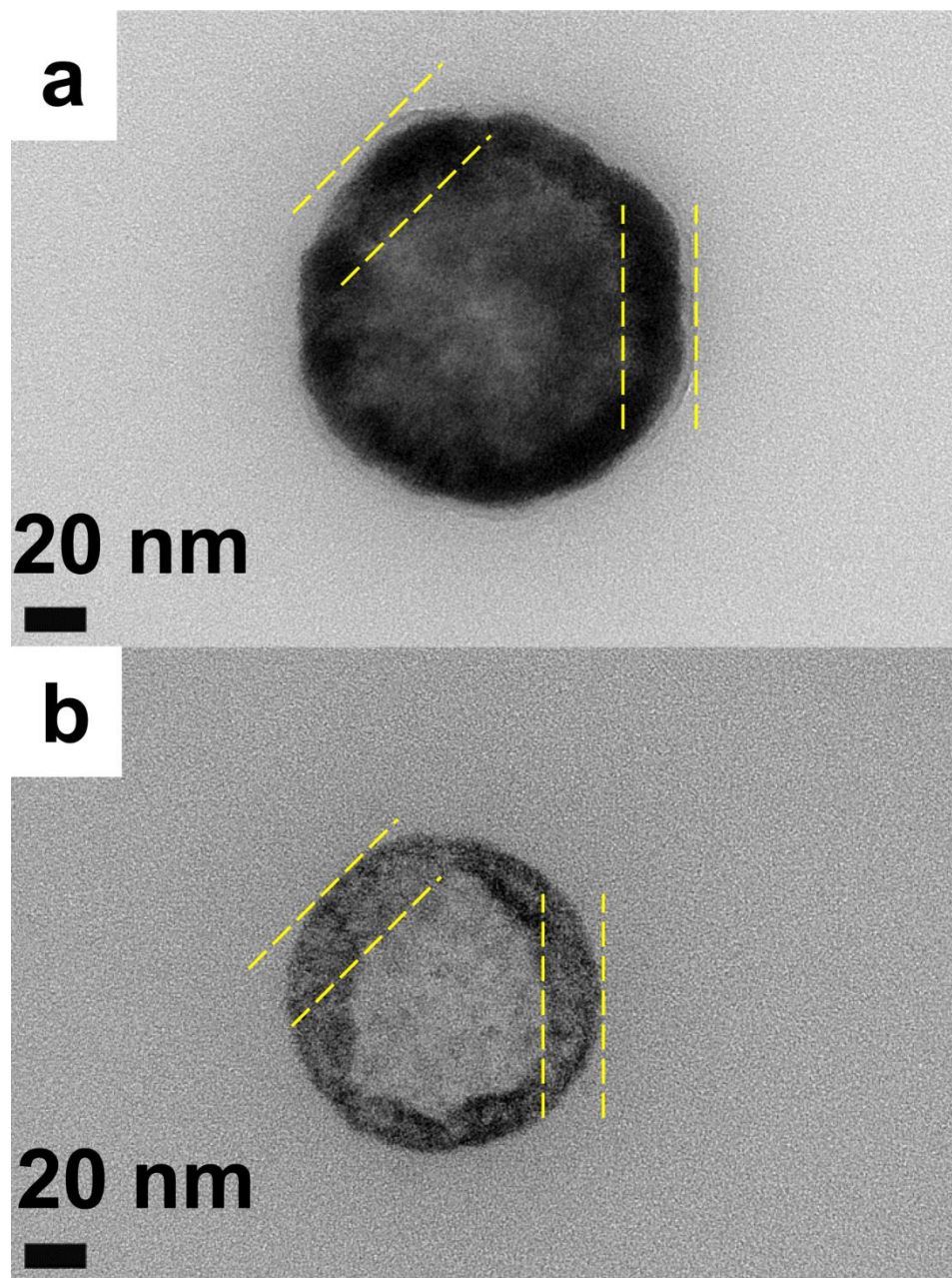


Fig. S3 TEM images of the photopolymers obtained from resorcinarene cavita nd thiol **1** and diene **2** (a), triene **3** (b).

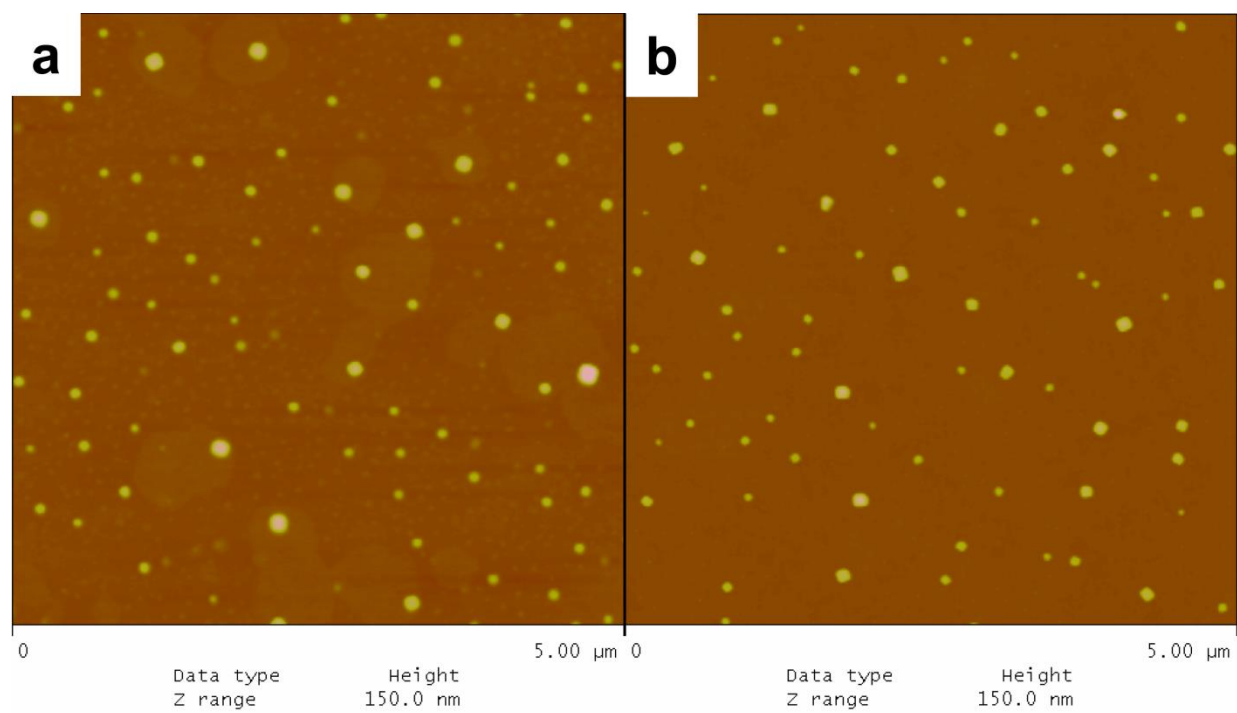


Fig. S4 AFM analysis of photopolymers obtained from resorcinarene cavitand thiol **1** and alkenes **3** (a) and **4** (b).

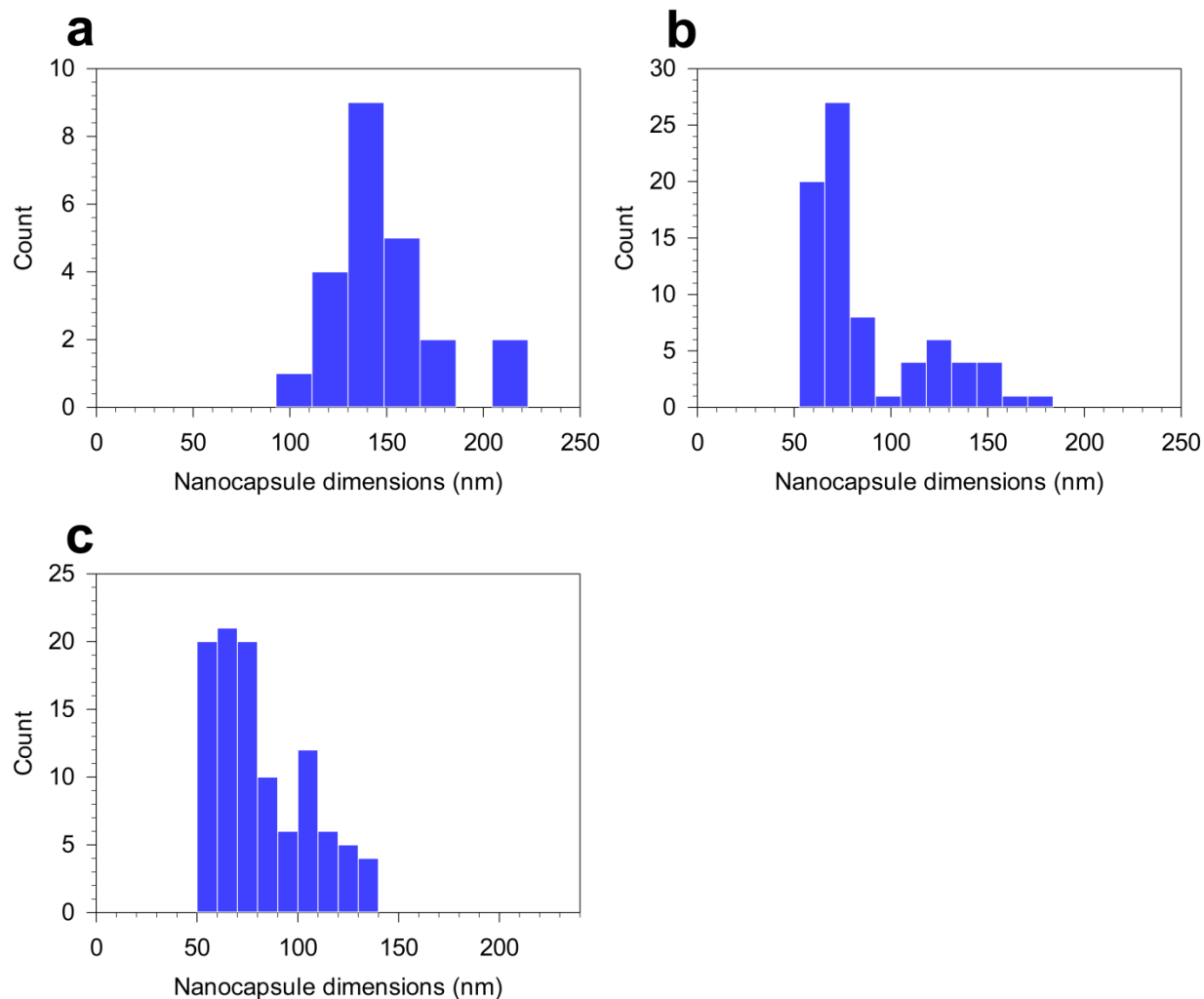


Fig. S5 Histogram of dimensions obtained from AFM analysis of nanocapsules prepared from resorcinarene cavitand thiol **1** and alkenes **2** (a), **3** (b) and **4** (c).

References

1. R. Balasubramanian, B. Kim, S. L. Tripp, X. J. Wang, M. Lieberman and A. Wei, *Langmuir*, 2002, **18**, 3676-3681.
2. R. Balasubramanian, Z. M. Kalaitzis and W. Cao, *J. Mater. Chem.*, 2010, **20**, 6539-6543.