

## Supporting Information

### **Silica Core - Polystyrene Shell Nanoparticles Synthesis and Assembly in Three Dimensions**

Hadi Sabouri <sup>a</sup>, Yun Huang <sup>b</sup>, Kohji Ohno, <sup>b</sup> Sébastien Perrier <sup>c,d</sup>

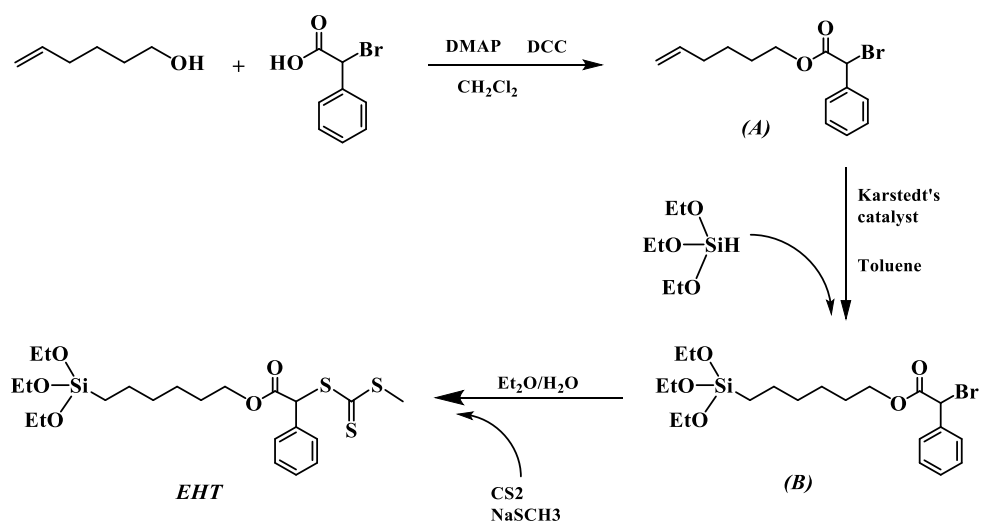
<sup>a</sup> *Key Centre for Polymers & Colloids, School of Chemistry, The University of Sydney, NSW, Australia*

<sup>b</sup> *Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan.*

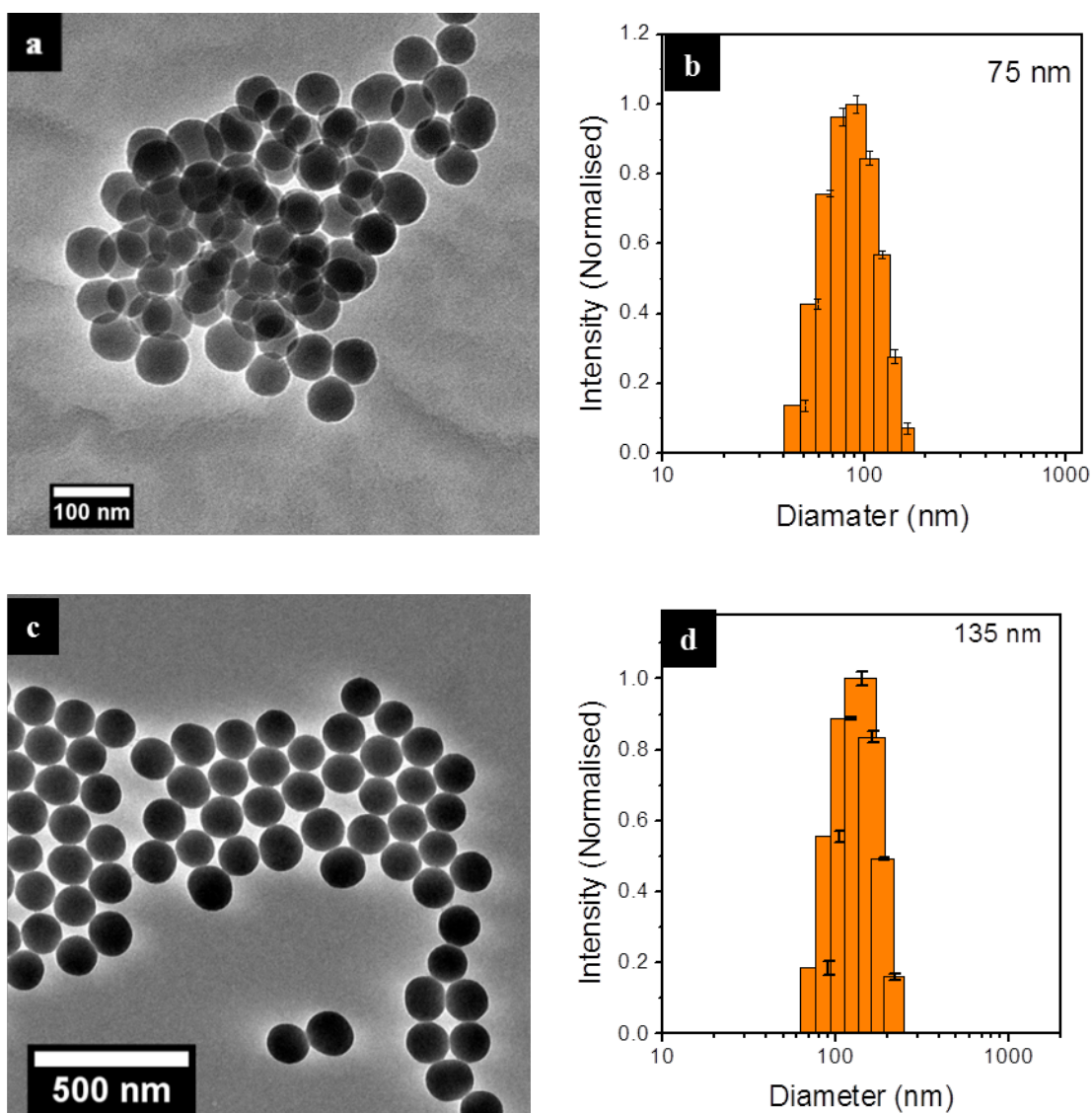
<sup>c</sup> *Department of Chemistry, The University of Warwick, Gibbet Hill, Coventry, CV4 7AL, United Kingdom*

<sup>d</sup> *Faculty of Pharmacy and Pharmaceutical Sciences, Monash University, 381 Royal Parade, Parkville, VIC 3052, Australia*

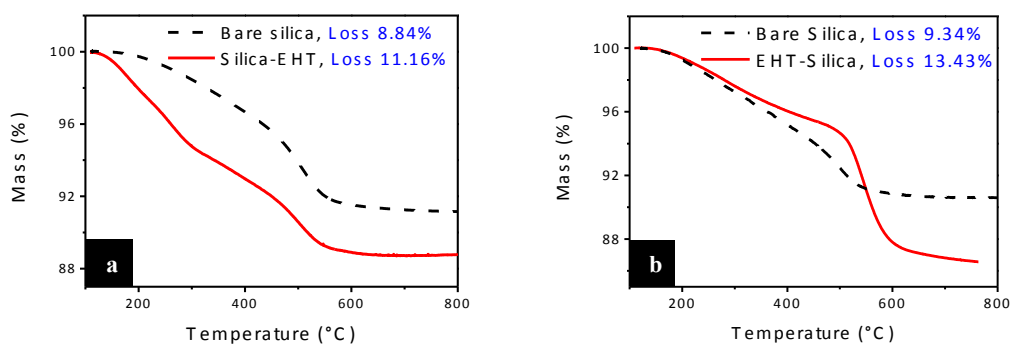
\* *email: s.perrier@warwick.ac.uk; Tel: +44 (0)2476 528085; Fax: +44 (0)2476 524112*



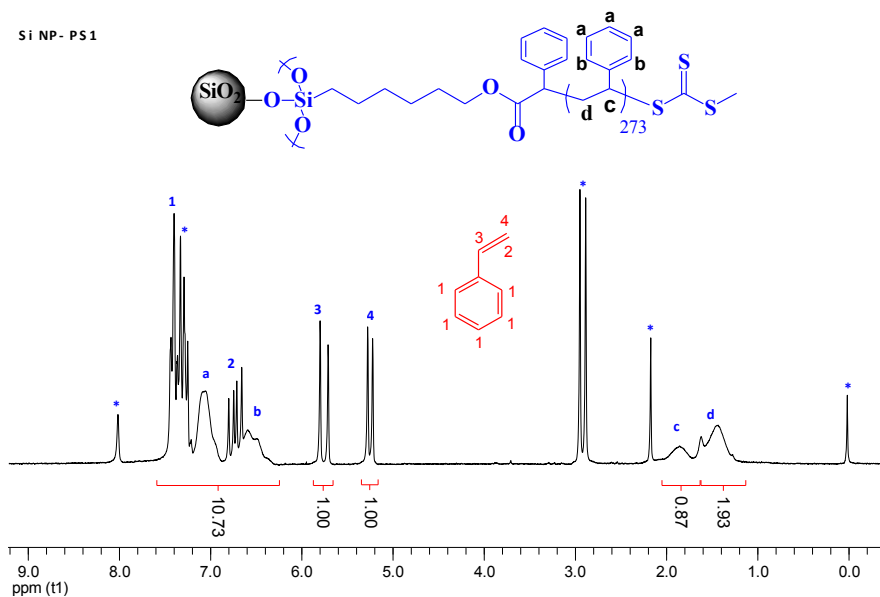
**Scheme S1. Synthetic route of RAFT Agent 6-(Triethoxysilyl)hexyl 2-(((Methylthio)- carbonothioyl)thio)-2-phenylacetate (EHT)**



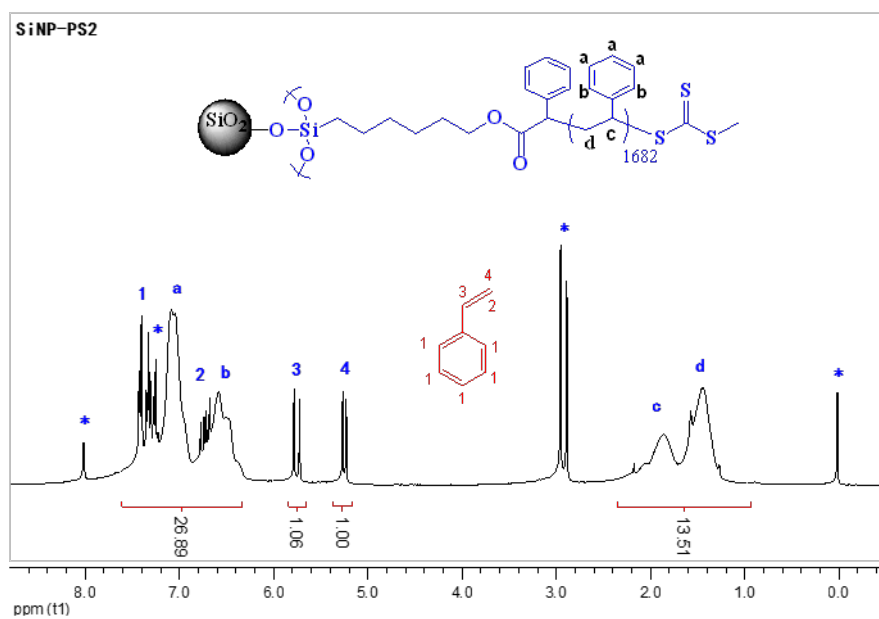
**Figure S1. (a) TEM image and (b) DLS size distribution of synthetic SiNP with mean diameter of 75 nm and polydispersity index of 0.08, (c) TEM image and (d) DLS size distribution of commercial SiNP with average diameter of 135 nm and polydispersity index of 0.05.**



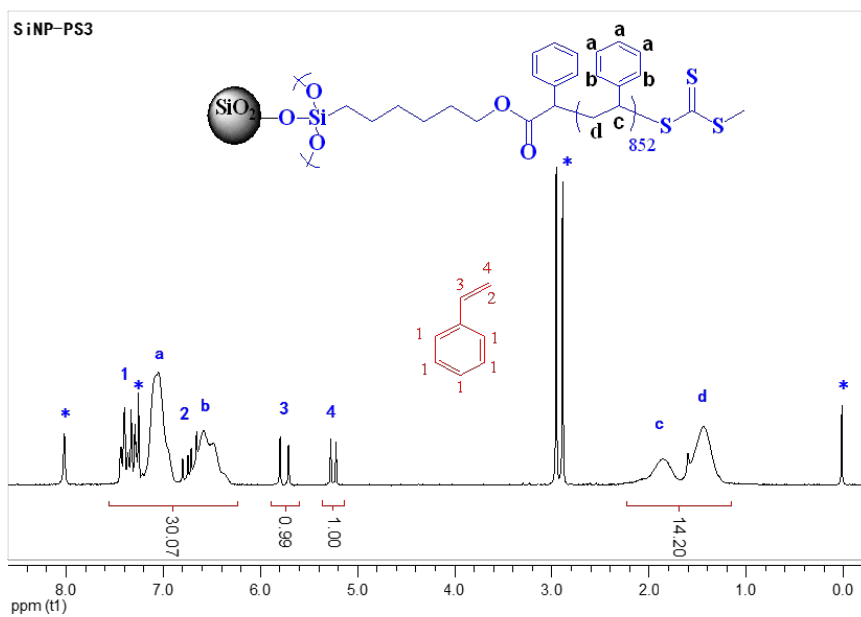
**Figure S2. (a) and (b) Thermogravimetric analysis of SiNP with average diameters of 75 and 135 nm, respectively.**



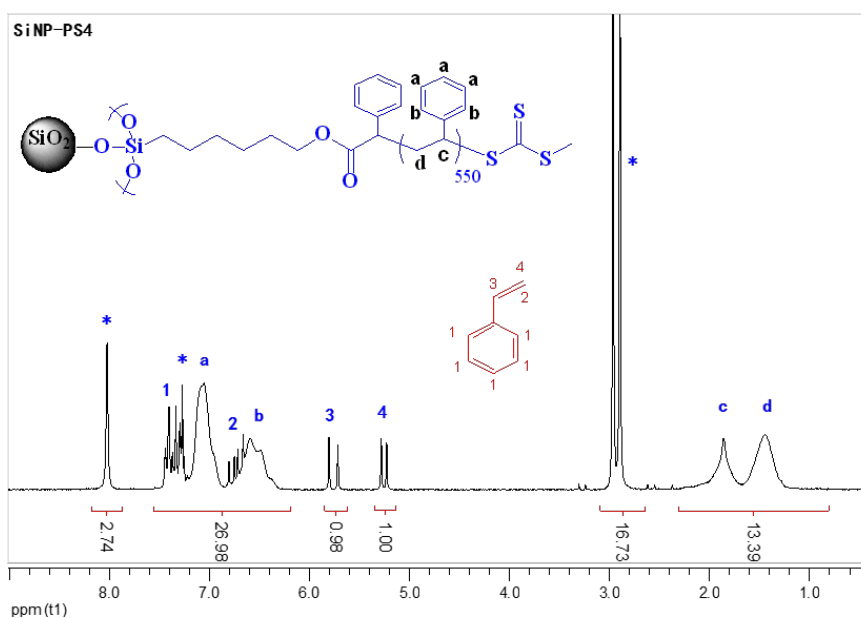
**Figure S3.  $^1\text{H}$  NMR spectrum of grafted polystyrene obtained from self-initiated polymerization. Monomer conversion is 49 %. \* represents solvent peaks.**



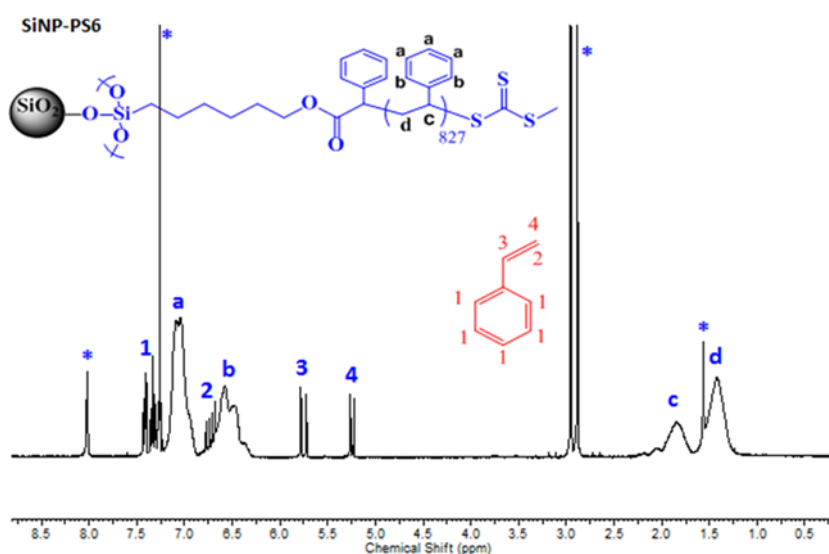
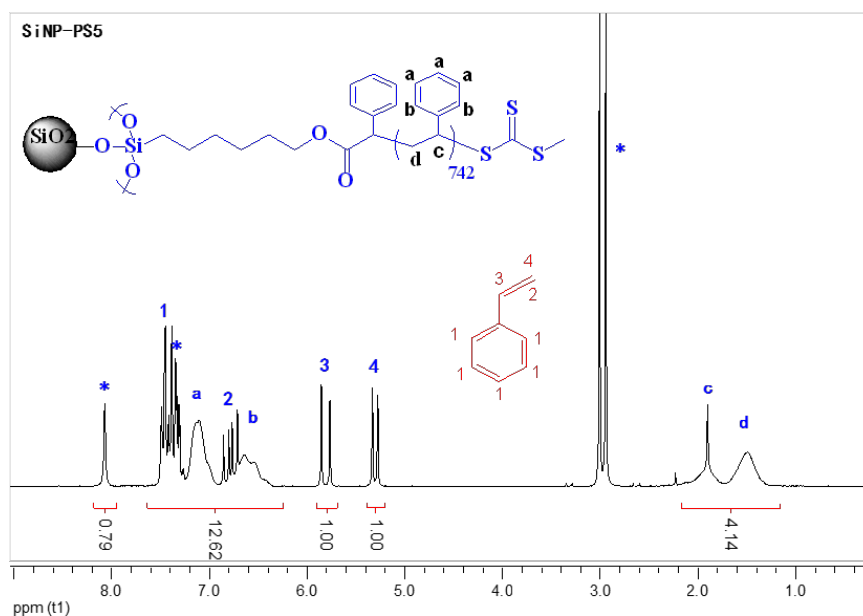
**a**



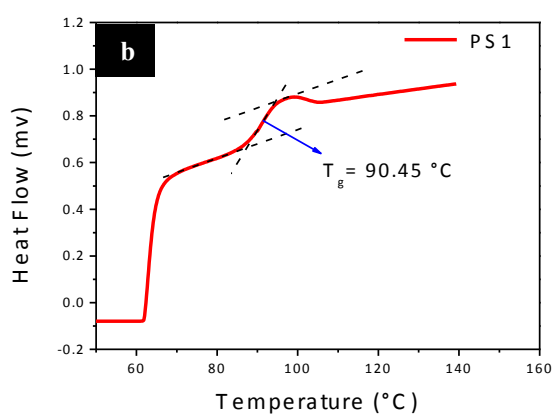
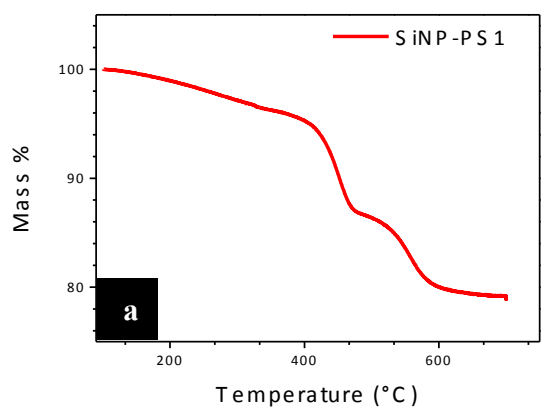
**b**



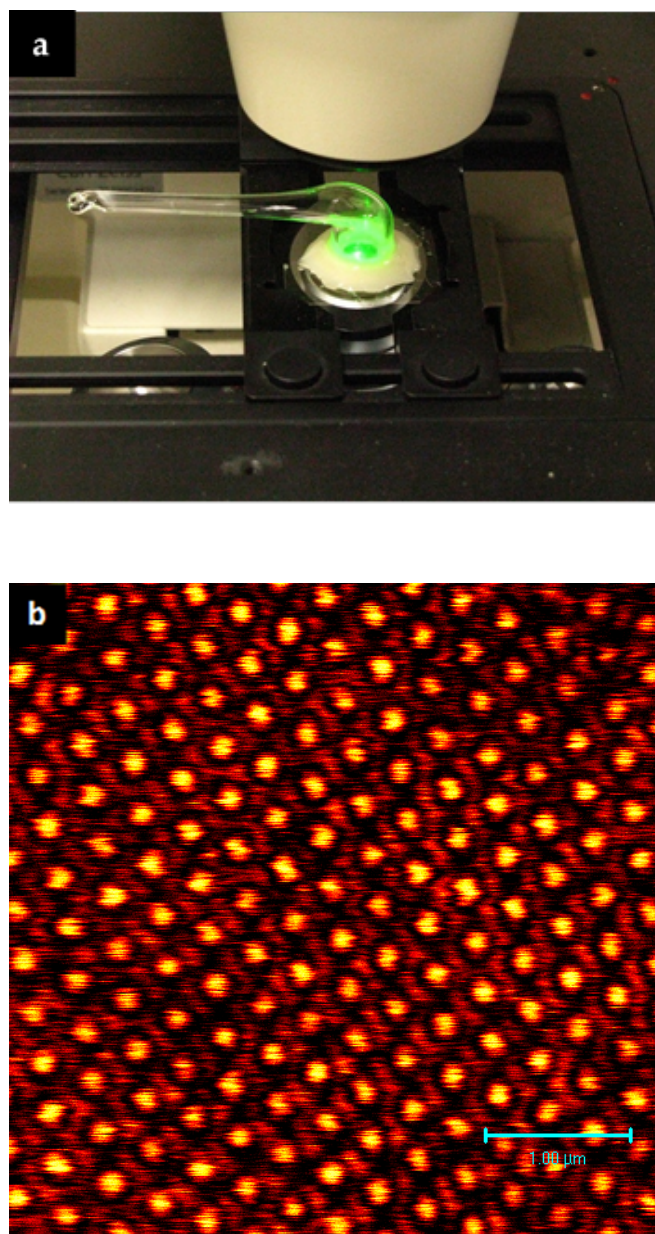
**c**



**Figure S4.  $^1\text{H}$  NMR spectra of 5 grafted polystyrene. Monomer conversions for (a) SiNP-PS2, (b) SiNP-PS3, (c) SiNP-PS4, (d) SiNP-PS5 and (e) SiNP-PS6 are 80 %, 83 %, 80 %, 57 % and 91 %, respectively. \* represents solvent peaks.**



**Figure S5. (a) TGA analysis of SiNP-PS1, there is a mass loss of ~21 % for organic moieties corresponds to PS. (b) DSC graph of PS1 free polymer,  $T_g$  of this polystyrene was measured at around 90 °C which was the midpoint value between the onset and the end of a step transition.**



**Figure S6. (a) A hand-made glass cell in confocal laser microscope with a glass cover slip glued at the bottom as a holder for colloidal suspension. After transferring the colloidal crystals into the cell, the tip of the cell was flamed sealed to stop solvent evaporation, (b) a close-up image of microcrystals formed throughout the suspension of SiNP-PS6 in mixed solvent acquired by confocal laser microscope. Observation was performed using an Ar laser of wavelength 488 nm and x63 objective in reflection mode. Yellow dots represent silica core particles surrounded by pale polystyrene shells. The scale bar is 1  $\mu\text{m}$ .**