

Electronic Supplementary Information (ESI)

## Multipod-like silica/polystyrene clusters

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### Supplementary figures and tables (in the order in which they are called from the main text)

**Table S1.** Experimental conditions of the silica synthesis and regrowth stages and size measurement results of the silica seeds obtained (as extracted from statistical analysis of TEM images). Final silica batches used as seeds in styrene emulsion polymerization are mentioned in bold type.

Silica “pre-seeds” synthesis <sup>(1)</sup>			1 <sup>st</sup> regrowth stage <sup>(2)</sup>			2 <sup>nd</sup> regrowth stage (optional) <sup>(2)</sup>		
introduced V <sub>TEOS</sub> (mL)	D <sub>silica</sub> (nm)	PDI <sup>(3)</sup>	TEOS/silica (wt. ratio)	D <sub>silica</sub> (nm)	PDI <sup>(3)</sup>	TEOS/silica (wt. ratio)	D <sub>silica</sub> (nm)	PDI <sup>(3)</sup>
1	17	1.04	80	<b>54</b>	1.003	-	-	-
2	19	1.04	81	65.5	1.004	0.8	<b>69</b>	1.003
						13	<b>110</b>	1.002
						38	<b>146</b>	1.002
3	19.5	1.02	284	82	1.002	0.7	<b>85</b>	1.002
10	28.5	1.02	10	<b>44</b>	1.004	-	-	-
			28	<b>55</b>	1.003	-	-	-
			115	<b>96</b>	1.002	-	-	-
20	36	1.01	142	<b>123</b>	1.003	-	-	-

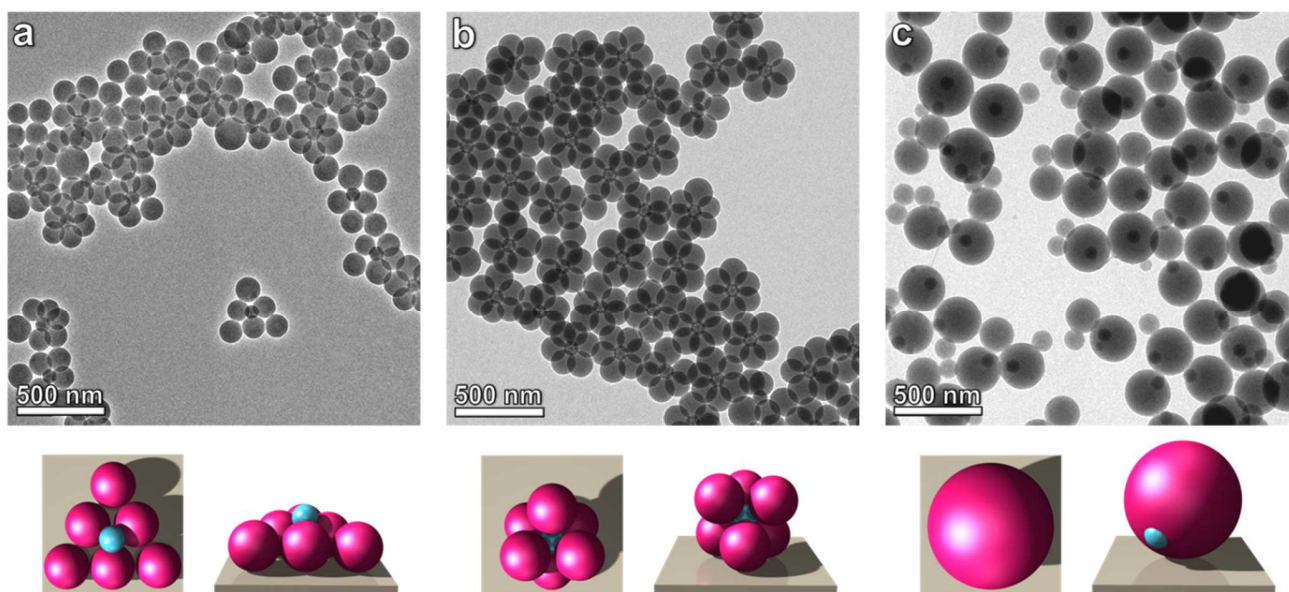
<sup>(1)</sup> Reacting medium: 100 mL of L-arginine aqueous solution (6 mM) at 60°C

<sup>(2)</sup> Reacting medium: 250 mL of ethanol, 35 mL of ammonia and 10 mL of the aqueous dispersion of silica and completed to 500 mL with ethanol, at room temperature

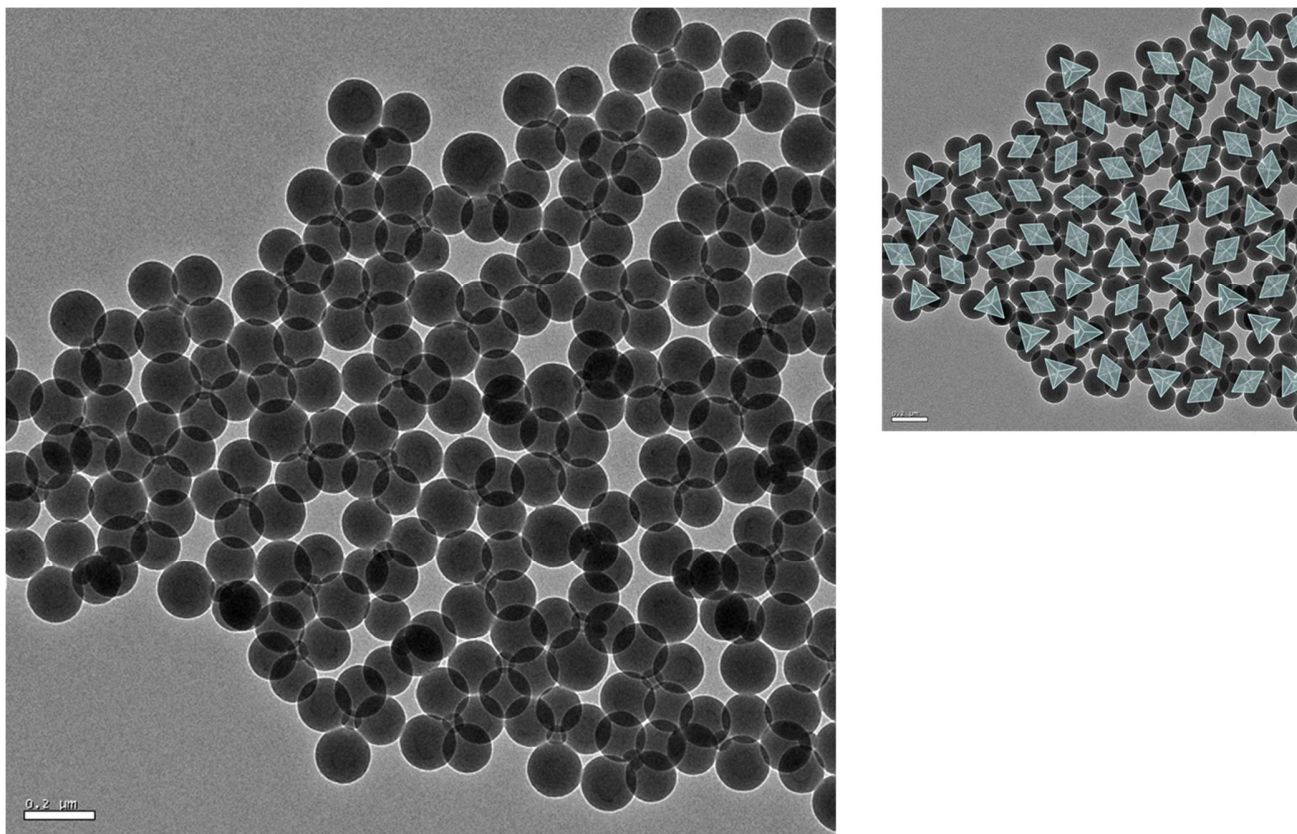
<sup>(3)</sup> Based on a minimum of 1000 nanoparticles per batch, the polydispersity index PDI was calculated using the following equation:

$$PDI = \frac{\overline{D_w}}{\overline{D_n}} \quad \text{where} \quad \overline{D_n} = \frac{\sum_i n_i D_i}{\sum_i n_i} \quad \text{and} \quad \overline{D_w} = \frac{\sum_i n_i D_i^4}{\sum_i n_i D_i^3}$$

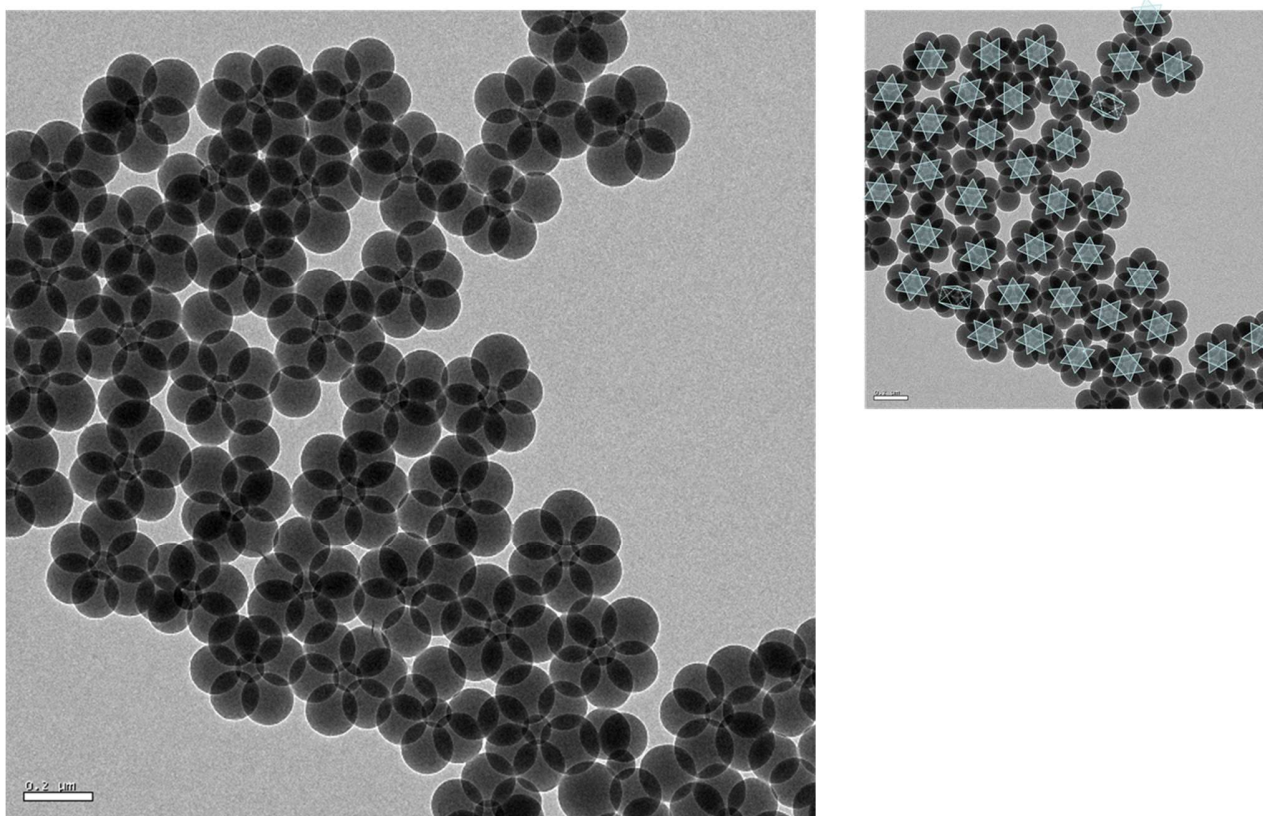
are the number-average and the weight-average diameter, respectively, and  $n_i$  the number of particles of diameter  $D_i$ .



**Figure S1.** TEM images of PS/silica clusters prepared from 85-nm silica seeds demonstrating the influence of the MMS surface density on their stability/morphology: a) super-triangles after falling-in of unstable hexapods on the TEM grid (MMS:  $0.2 \text{ fct.nm}^{-2}$ ), b) robust hexapods (MMS:  $0.5 \text{ fct.nm}^{-2}$ ) and c) snowman-like particles resulting of the partial encapsulation of the silica seed in a single and large PS latex particle (MMS:  $1.5 \text{ fct.nm}^{-2}$ ). On this last image, the silica seeds observed within the latex particles shall not be got mixed up with particles of intermediary size which results here from a secondary nucleation of polystyrene.

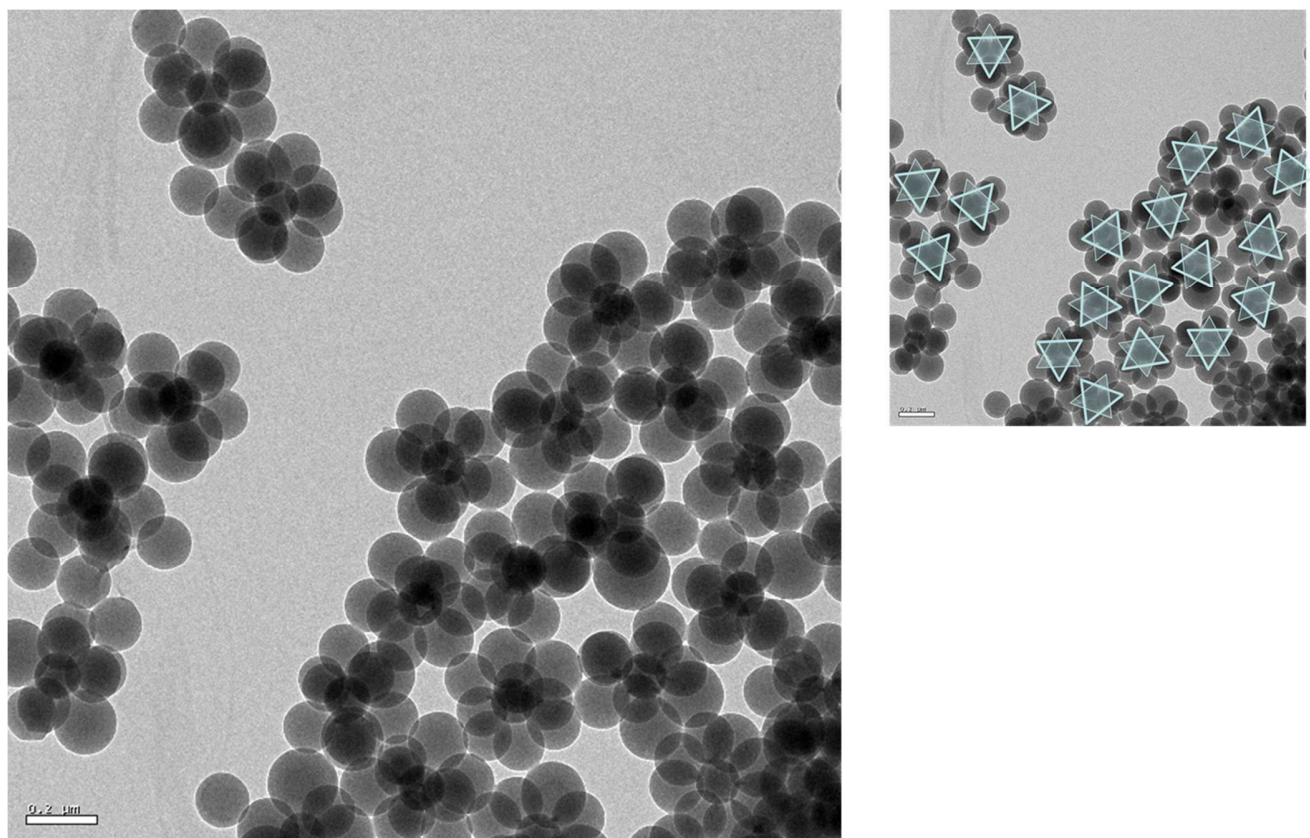


**Figure S2.** TEM image of tetrapods obtained by styrene emulsion polymerization from 55-nm silica seeds (Entry #2.2, Table 2). On the right image, the undoubtedly-identified tetrapods were labelled for appreciating the yield of tetrapod morphology: from this single image, it was estimated to 100 % with respect to silica seeds (59 tetrapods for 59 silica seeds). Scale bar: 200 nm.

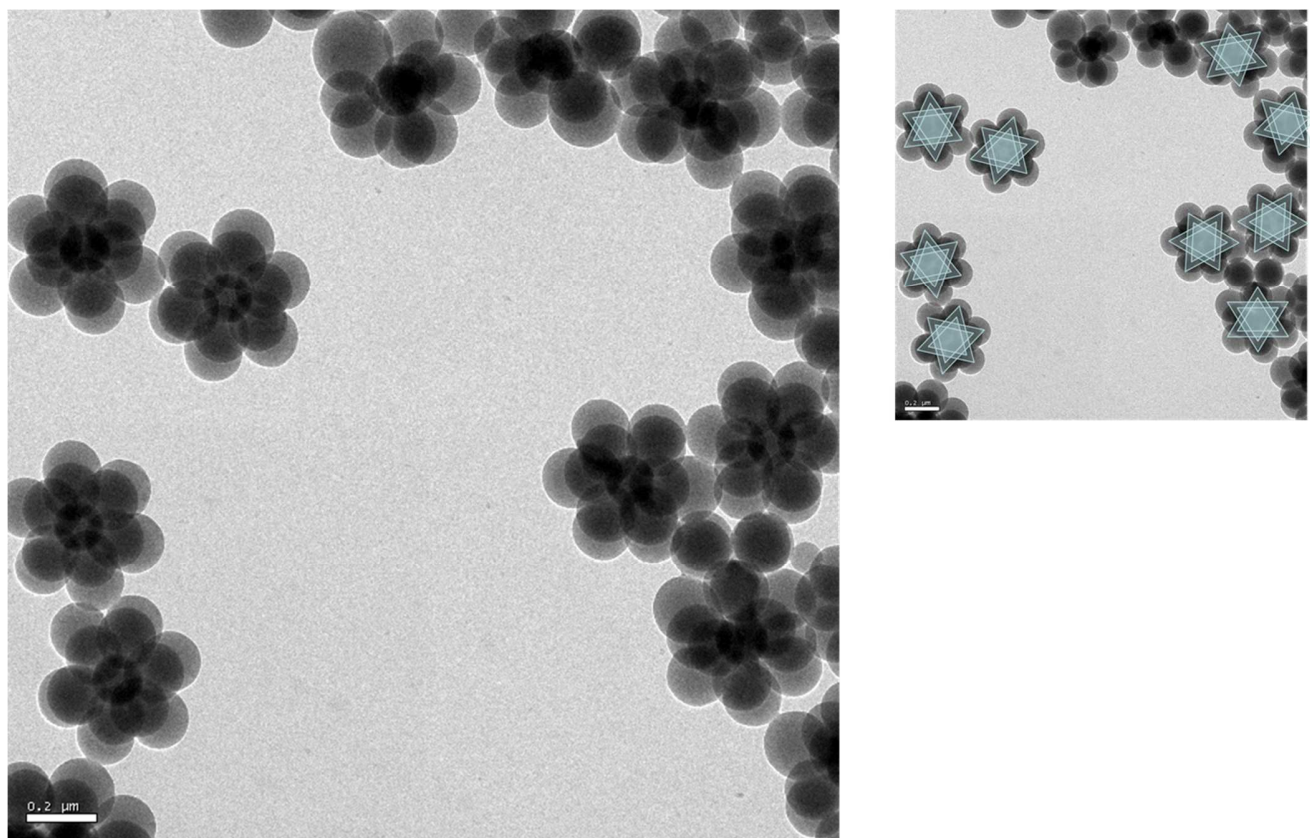


**Figure S3.** TEM image of hexapods obtained by styrene emulsion polymerization from 85-nm silica seeds (Table 2, Entry #2.4). On the right image, the undoubtedly-identified hexapods were labelled for appreciating the yield of hexapod morphology: from this single image, it was estimated to 97 % with respect to silica seeds (38 hexapods against 1 silica seed bearing only four PS nodules). Scale bar: 200 nm.

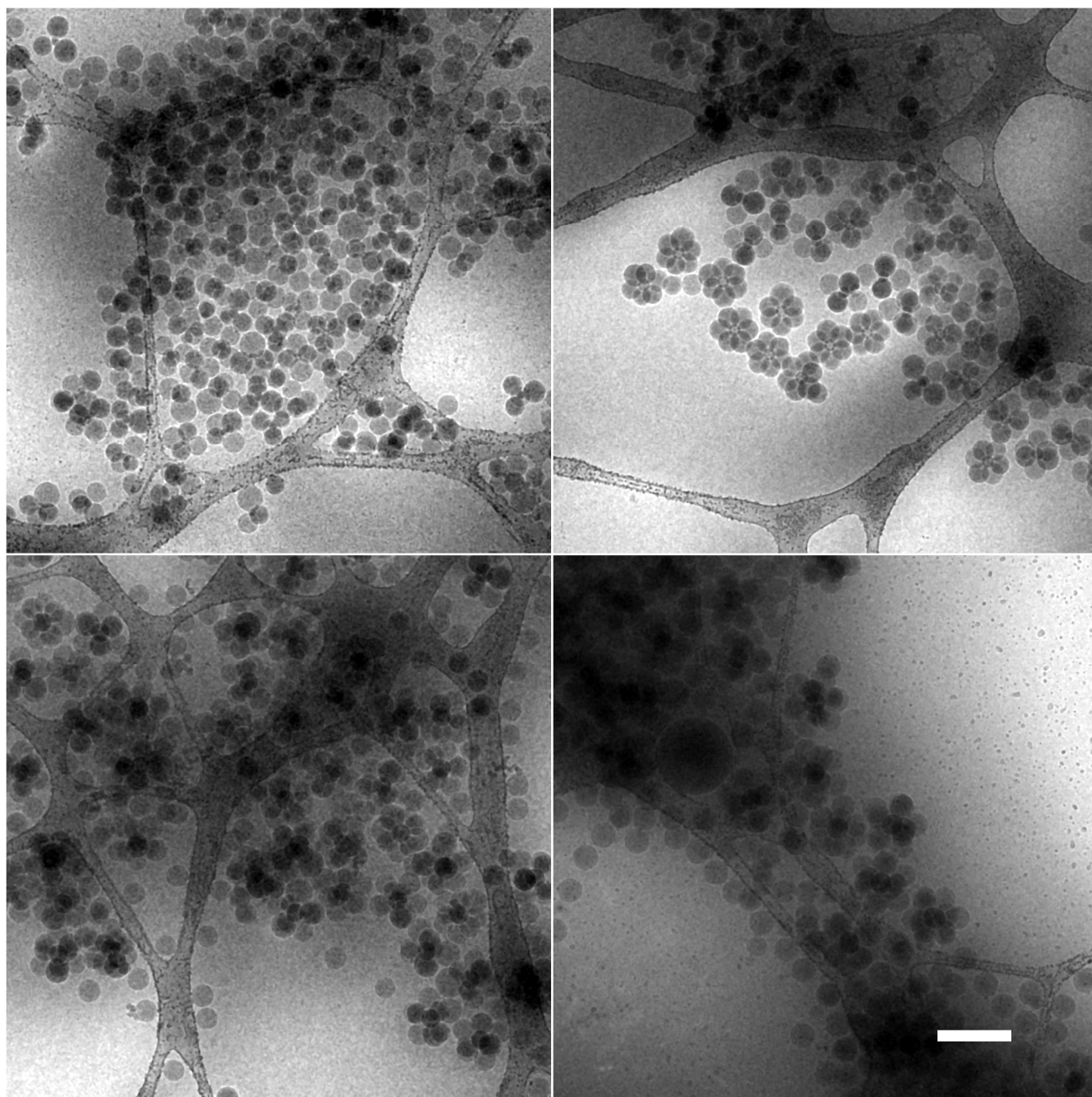




**Figure S4.** TEM image of nonapods obtained by styrene emulsion polymerization from 123-nm silica seeds (Table 2, Entry #2.7). On the right image, the undoubtedly-identified nonapods were labelled for appreciating the yield of nonapod morphology: from this single image, it was estimated to 86 % with respect to silica seeds (19 nonapods against 3 silica seeds bearing only eight PS nodules). Scale bar: 200 nm.

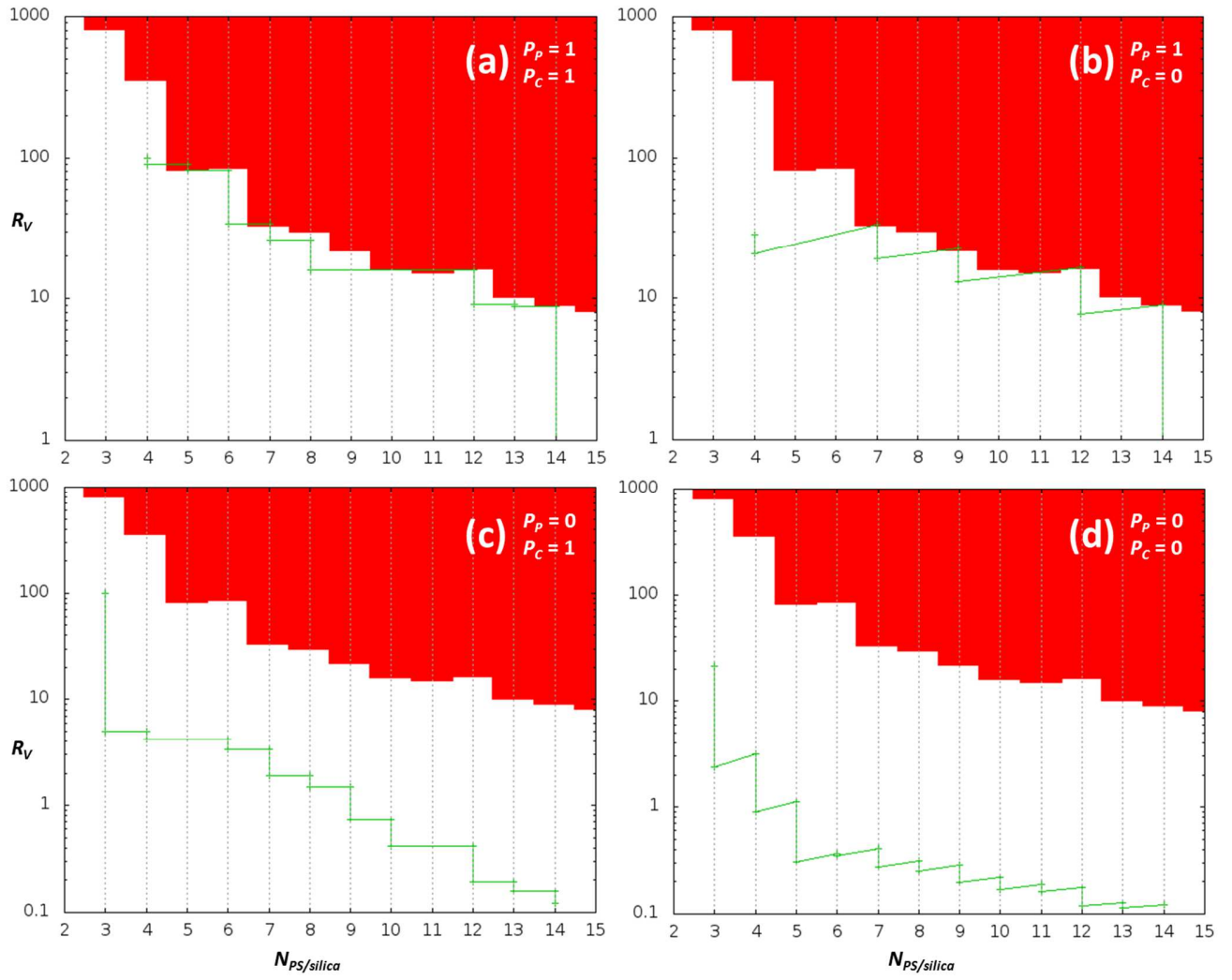


**Figure S5.** TEM image of dodecapods obtained by styrene emulsion polymerization from 146-nm silica seeds (Table 2, Entry #2.8). On the right image, the undoubtedly-identified dodecapods were labelled for appreciating the yield of dodecapod morphology: from this single image, it was estimated to 82 % with respect to silica seeds (9 dodecapods against 2 silica seeds bearing only ten or eleven PS nodules). Scale bar: 200 nm.



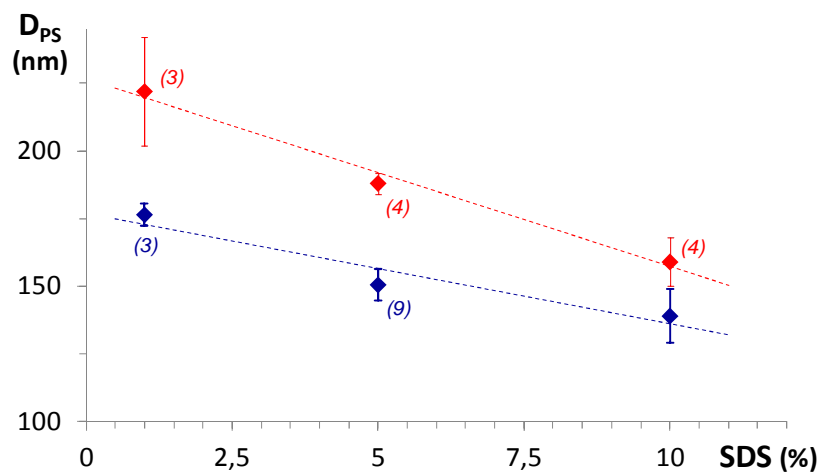
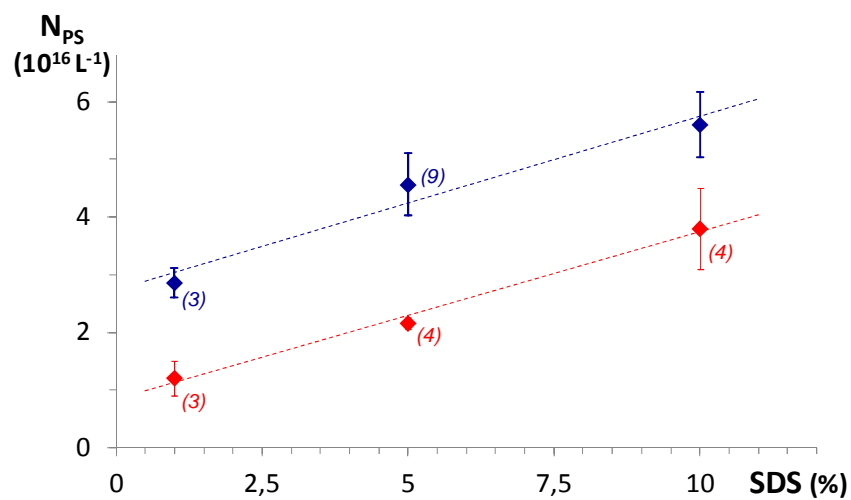
**Figure S6.** 0° tilt projections of cryo-TEM images used for the computation of the tomograms of Fig. 1 obtained from silica seeds of respective diameters: a) 55 nm (Entry #2.2), b) 85 nm (Entry #2.4), c) 123 nm (Entry #2.7), and d) 146 nm (Entry #2.8). Scale bar: 500 nm.



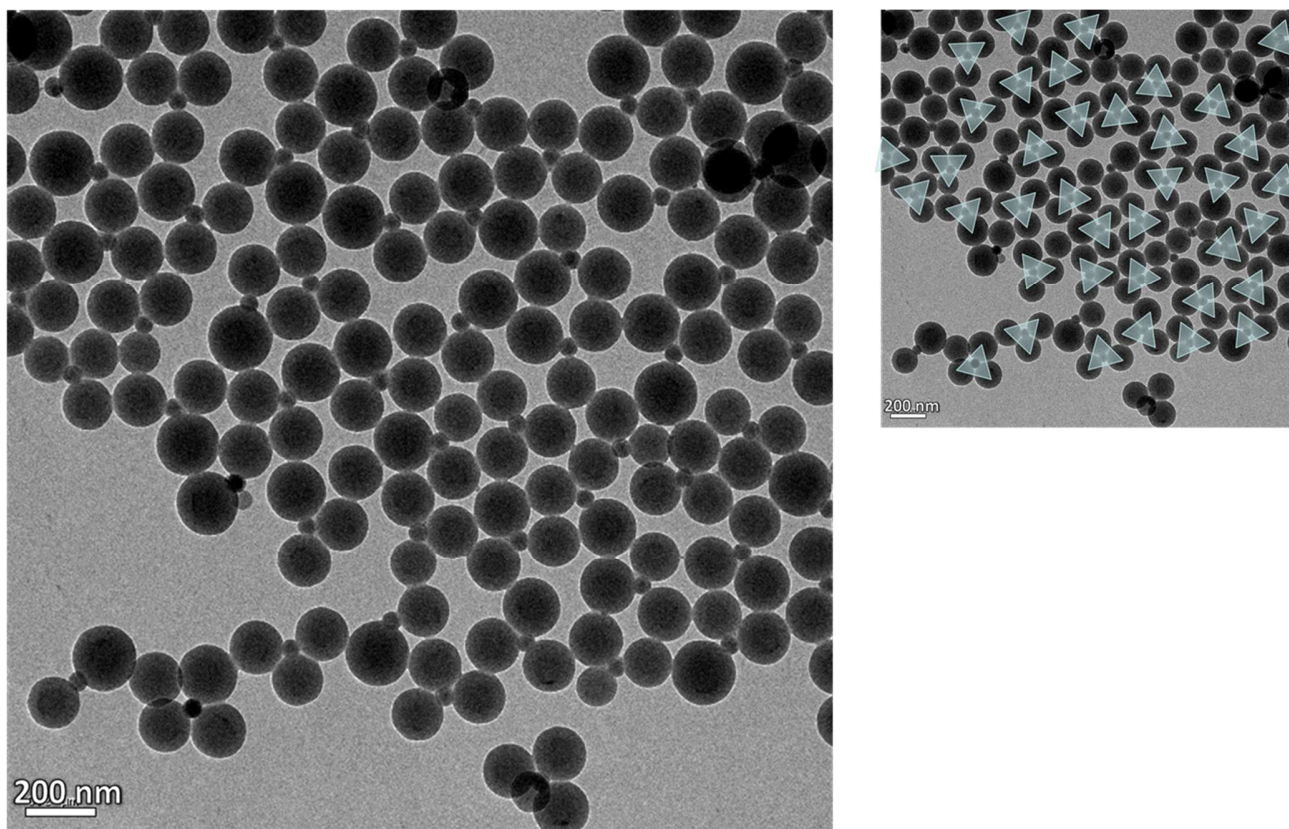


**Figure S7.** Simulated fate of a multipod initially made of a silica seed and 14 nuclei of PS growing according to extreme scenarios ( $P_p$  and  $P_c$  are set to 0 or 1): a) mutual repulsion and coalescence, b) mutual repulsion and expulsion, c) fixed position and coalescence, and d) fixed position and expulsion.

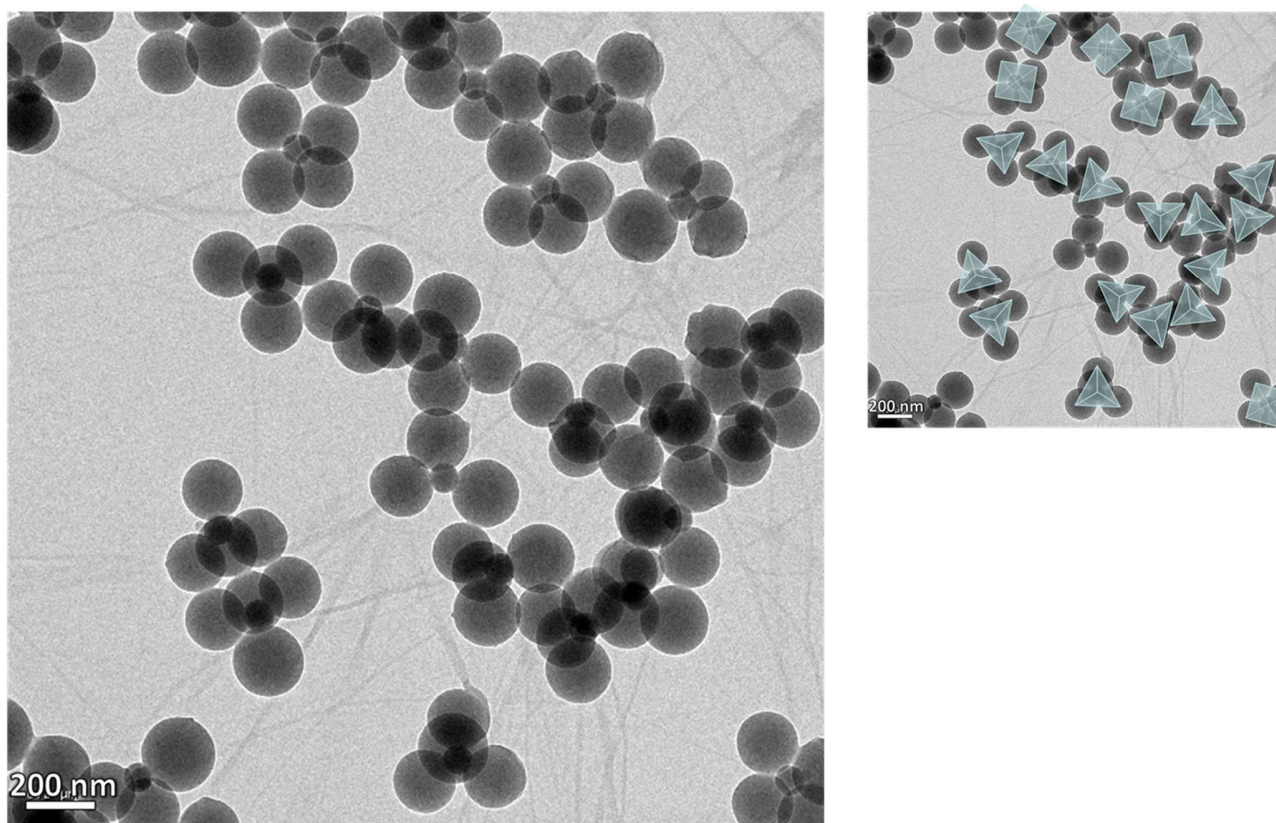




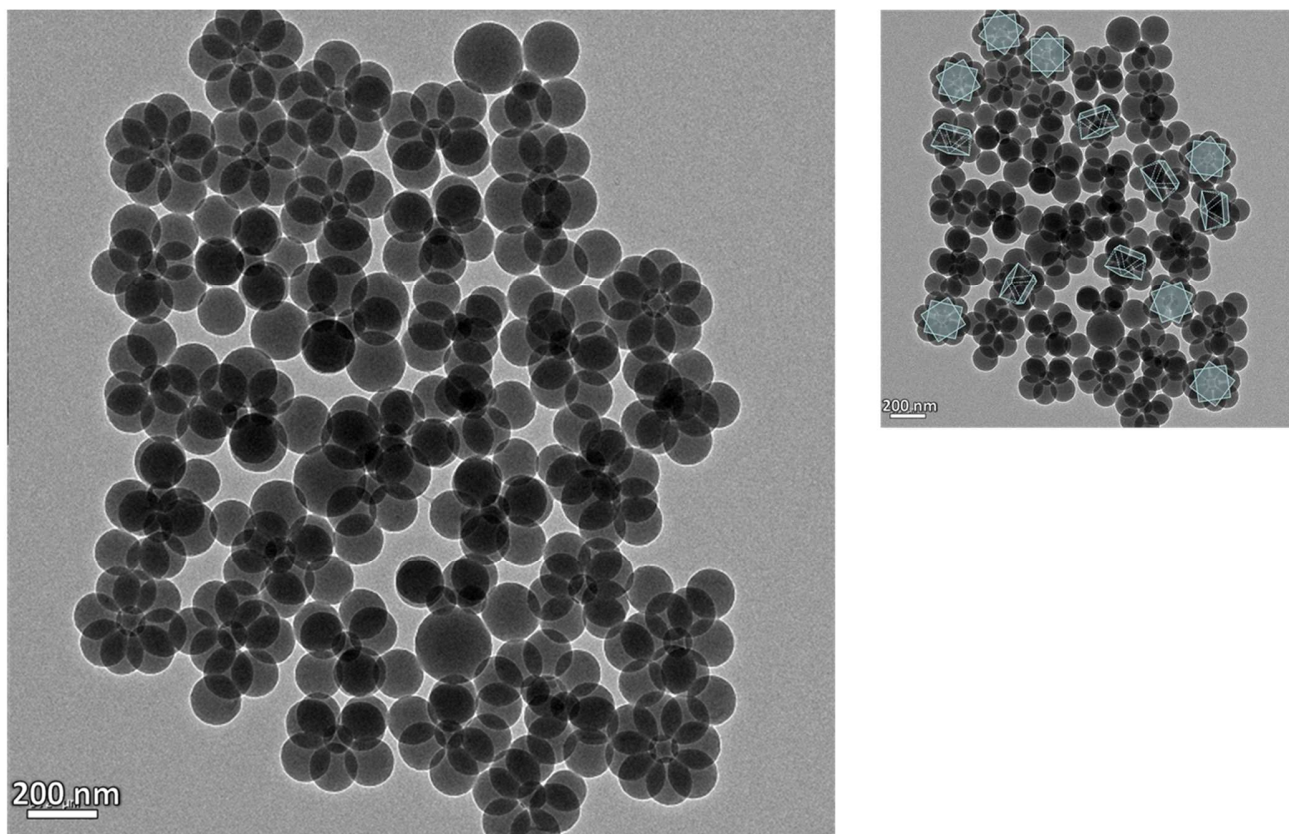
**Figure S8.** Influence of the substitution for several wt.% of Synperonic® NP30 by SDS on the final diameter and concentration of the latex particles obtained by emulsion polymerization of styrene ( $[styrene]_0 = 100 \text{ g.L}^{-1}$ ;  $[Na_2S_2O_8]_0 = 0.5 \text{ g.L}^{-1}$ ;  $[surfactant] = 3 \text{ g.L}^{-1}$ ;  $T = 70^\circ\text{C}$ ) in the absence (red dots) and in the presence (blue dots) of ~85-nm silica seeds at the concentration of  $7.3 \cdot 10^{15} \text{ L}^{-1}$ . Some data were averaged from several similar experiments whose number is mentioned in brackets.



**Figure S9.** TEM image of tripods obtained by styrene emulsion polymerization from 54-nm silica seeds (Entry #5.1, Table 5). On the right image, the undoubtedly-identified tripods were labelled for appreciating the yield of tripod morphology: from this single image, it was estimated to 70 % with respect to silica seeds (38 tripods for 54 silica seeds).

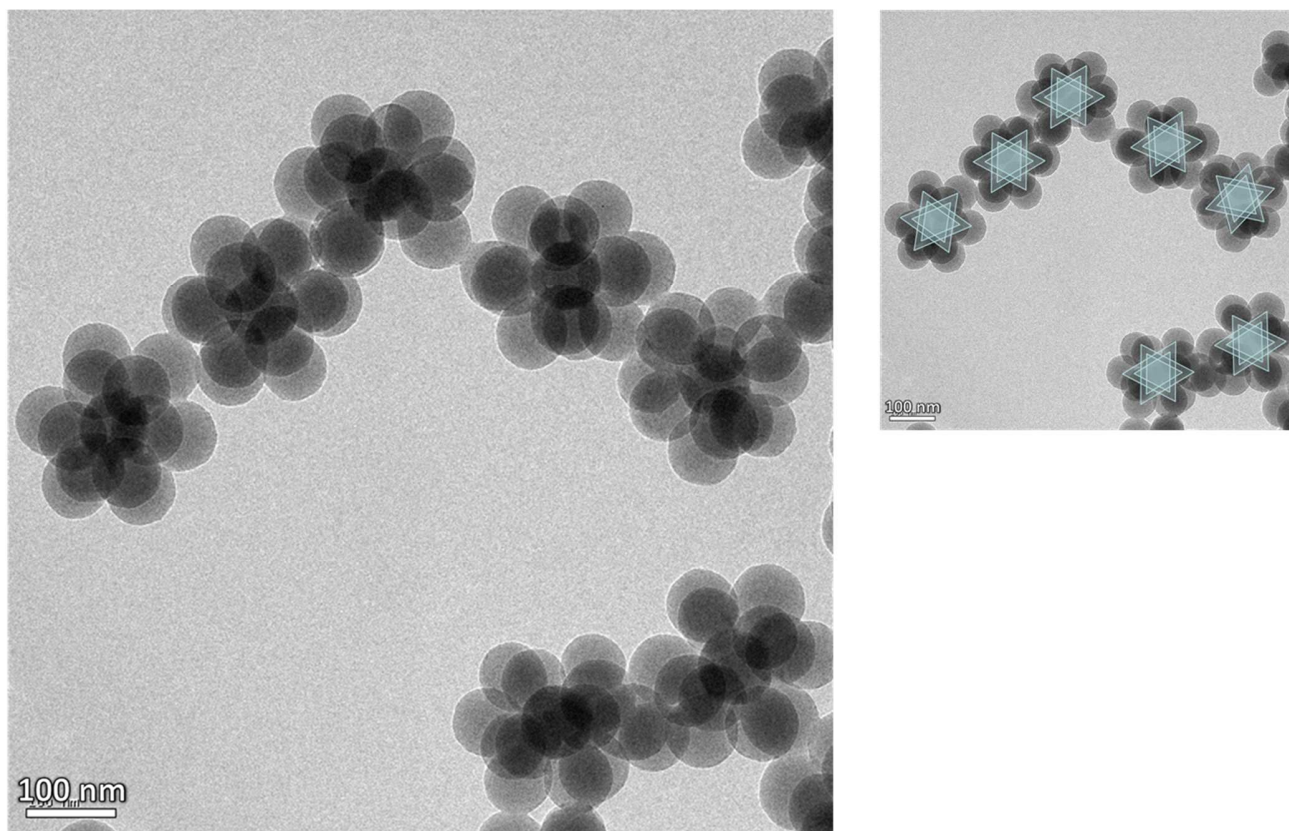


**Figure S10.** TEM image of tetrapods obtained by styrene emulsion polymerization from 85-nm silica seeds (Entry #5.2, Table 5). On the right image, the undoubtedly-identified tetrapods were labelled for appreciating the yield of tetrapod morphology: from this single image, it was estimated to 91 % with respect to silica seeds (21 tetrapods for 23 silica seeds).



**Figure S11.** TEM image of octopods obtained by styrene emulsion polymerization from 85-nm silica seeds (Entry #5.3, Table 5). On the right image, the undoubtedly-identified octopods were labelled for appreciating the yield of octopod morphology: from this single image, it was estimated to 29 % with respect to silica seeds (13 octopods for 45 silica seeds).





**Figure S12.** TEM image of dodecapods obtained by styrene emulsion polymerization from 85-nm silica seeds (Entry #5.4, Table 5). On the right image, the undoubtedly-identified dodecapods were labelled for appreciating the yield of dodecapod morphology: from this single image, it was estimated to 100 % with respect to silica seeds (7 dodecapods for 7 silica seeds).