Supplementary Material (ESI) for Chemical Communications

Supporting Information

Core-crosslinked block copolymer nanorods as templates for grafting $[SiMo_{12}O_{40}]^{4-}$ keggin ions

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Experimental section:

Synthesis of polymer and crosslinking reactions: The synthesis of the polybutadiene-*block*-poly(2-vinylpyridine) diblock copolymers (PB-P2VP) was accomplished via sequential living anionic polymerization. Butadiene polymerization was initiated with sec-BuLi at -70°C, and butadiene was allowed to polymerize at -10°C for 8 h. After subsequent cooling to -70°C, 2-vinylpyridine was added to the reaction mixture. After 1h reaction time the polymerization was terminated with degassed methanol, and the product precipitated in a water/methanol mixture. According to NMR and GPC, coupled to a multi-angle laser light scattering detector, the polymer synthesized is $PB_{30}P2VP_{70}^{200}$. The subscript numbers denote the mass fraction in percent, and the superscripts give the number-average molecular weight in kg/mol. For crosslinking of the block copolymer in the bulk state, a 10 wt% solution of PB-P2VP in THF was allowed to evaporate slowly in the presence of 40 wt% of Lucirin TPO, corresponding to the amount of polymer. After complete evaporation of the solvent and film annealing, the films were crosslinked on a UV lamp (cut-off < 350 nm) for 2 – 6 hours. Subsequently, soxhlet extraction was performed in THF and the insoluble product underwent ultrasonication in a THF dispersion in order to obtain soluble PB-P2VP core-crosslinked cylinders.

Synthesis of $[SiMo_{12}O_{40}]^{4-}$ keggin-type POM nanostructures: The template directed synthesis of the polyoxometalate nanostructures was carried out at room temperature. The core-crosslinked PB-P2VP polymer solution in THF (0.5 wt%) (colour less) was added to 10 mL of 10^{-2} M $H_4[SiMo_{12}O_{40}]$ in THF (yellow solution due to yellow colour of the $H_4[SiMo_{12}O_{40}]$) with continuous stirring for 6h. With the addition of polymer solution, a coloured precipitate was produced while the yellow colour of the POM solution starts fading. The yellow precipitate was formed by grafting coloured $[SiMo_{12}O_{40}]^{4-}$ on the polymer template. When the solution reached the neutralization point the yellow colour

of the solution had disappeared completely due to complete grafting of the coloured $H_4[SiMo_{12}O_{40}]$ on the polymer template. The resultant precipitate was allowed to age in the reaction mixture for 12 h. Finally, the precipitate was washed 3 times with deionized water and kept at 100°C for 12h to dry.

$[PMo_{12}O_{40}]^{3-}$ keggin-type POM nanostructures were synthesized following the same procedure while using $H_3[PMo_{12}O_{40}]$ .xH_2O as keggin source.

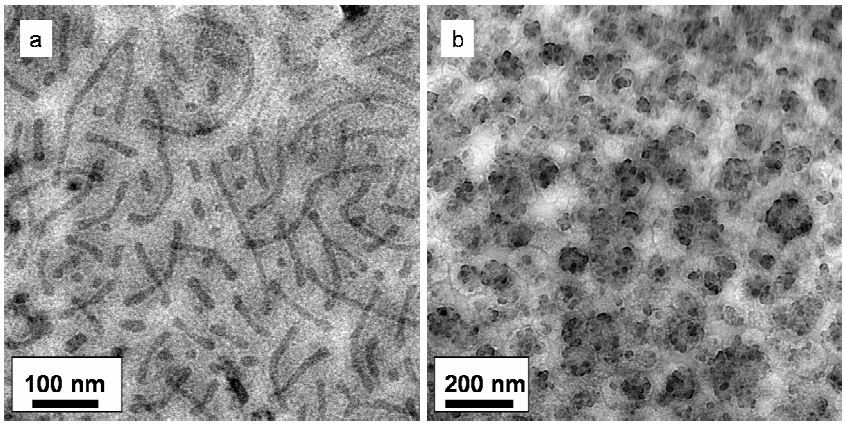

Fig. S1. Cryo-TEM images of the (a) 1 wt% of PB_{80}-$P2VP_{20}$ (64,900 g/mol) in THF wormlike micelles without core crosslinking, (b) 1 wt% of PB_{80}-$P2VP_{20}$ (64,900 g/mol) in THF acidified with 2M HCl.

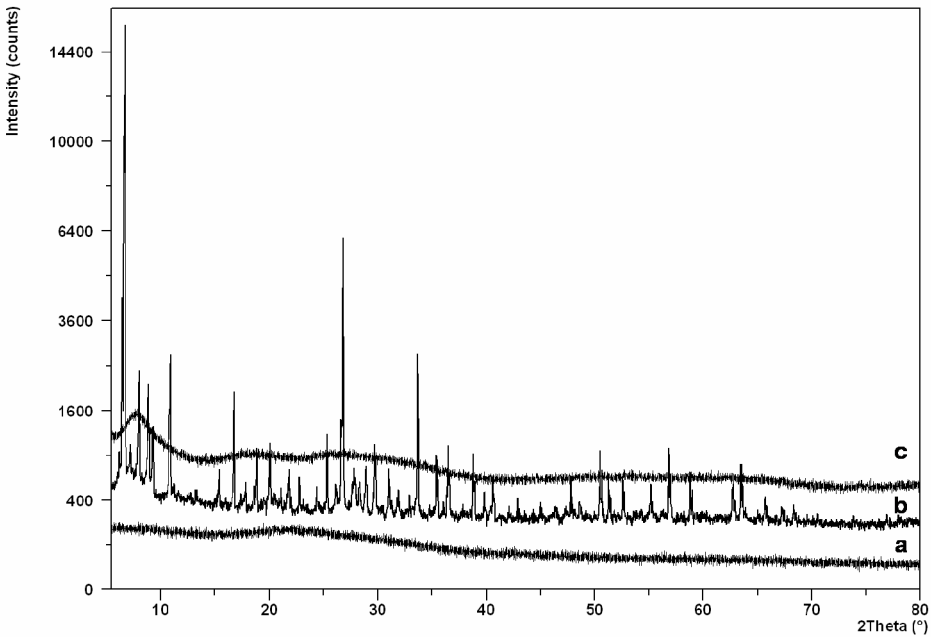

Fig. S2. Powder X-ray diffraction patterns of (a) core-crosslinked PB-P2VP polymeric nanorod template (b) pure $H_4[SiMo_{12}O_{40}]$ and (c) POM-1

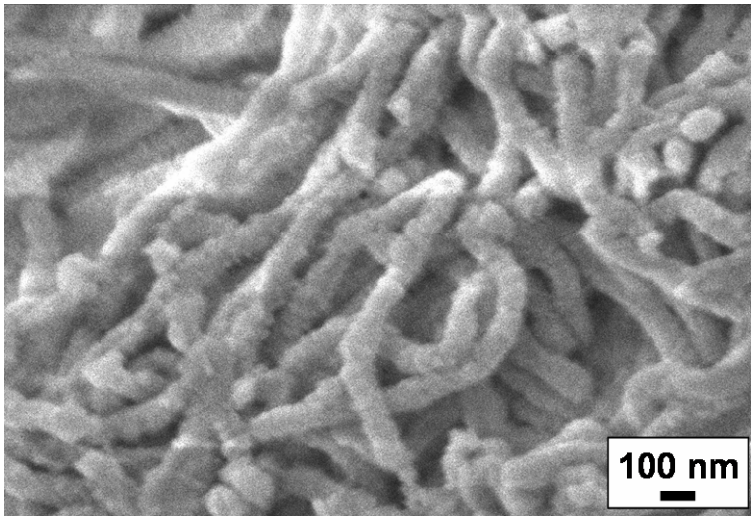

Fig. S3 SEM image of the $[PMo_{12}O_{40}]^{3-}$ keggin POM grafted over core-crosslinked PB-P2VP worm-like polymer template

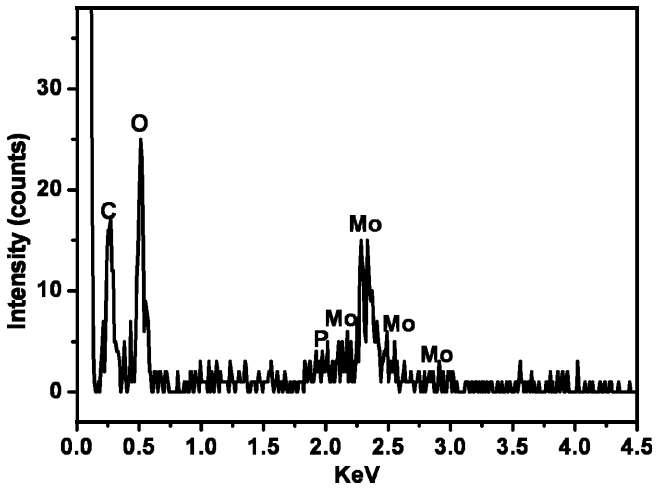

Fig. S4 EDX spectrun of the $[PMo_{12}O_{40}]^{3-}$ keggin POM grafted over core-crosslinked PB-P2VP worm-like polymer template