## **Electronic Supporting Information (ESI)**

## A Novel Approach to the Construction of 3-D Ordered Macrostructure with Polyhedral Particles<sup>†</sup>

Yonghui Deng, Chong Liu, Jia Liu, Fang Zhang, Ting Yu, Fuqiang Zhang, Dong Gu,

Dongyuan Zhao\*



**Figure S1.** FT-IR spectrum of the as-synthesized monodispersed poly(St-co-TMSPT) microspheres.



**Figure S2** The DSC thermogram of the poly(St-*co*-TMSPT) microspheres with TMSPM content of 20% at a heating rate of  $10^{\circ}$ C/min under a nitrogen atmosphere.



**Figure S3** SEM images of the packed polymer microspheres obtained by the centrifugation of the poly(St-*co*-TMSPT) microspheres dispersed in ethanol solution containing (a) phenolic resols, (b) triblock copolymer F127.



**Figure S4.** SEM images of (a) the packed poly(St-*co*-TMSPM) microspheres after impregnated with resols, followed by thermosetting at 90°C and (b) the ordered macroporous carbons obtained from (a) after pyrolyzed at 800°C in  $N_2$ . The inserts are the images with large magnification.