## **Supporting Information:**

## Unimolecular Micelles Composed of Inner Coil-Like Blocks and Outer Rod-Like Blocks Crafted by Combination of Living Polymerization with Click Chemistry

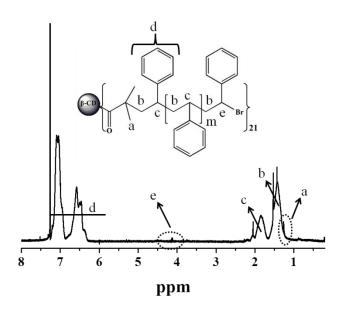
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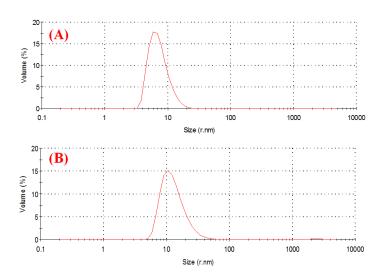
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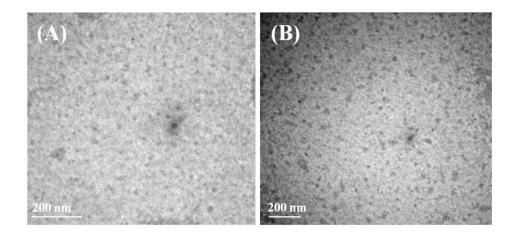
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**Figure S1**. <sup>1</sup>H-NMR spectrum of 21-arm, star-shaped PS (i.e., sample-2 in Table 1; solvent: CDCl<sub>3</sub>).



**Figure S2**. Dynamic light scattering (DLS) measurements of unimolecular micelles of (A) 21-arm star-shaped  $PS-N_3$  (derived from sample-2 in Table-1) and (B) the corresponding star-shaped PS-b-P3HT in chloroform (i.e., sample-b in Table-2).



**Figure S3.** TEM images of star-shaped  $PS-N_3$  (from sample-2 in Table-1) and the corresponding star-shaped PS-b-P3HT (sample-b in Table-2). All the samples were stained with ruthenium tetroxide (RuO<sub>4</sub>).

**Table S1.**  $D_h$  of star-shaped PS-N<sub>3</sub> and the corresponding star-shaped PS-*b*-P3HT in chloroform measured by DLS.

Entry	Star-shaped PS-N <sub>3</sub> (nm)	Star-shaped	PS- <i>b</i> -P3HT
		(nm)	
Sample-a	~10	~18	
Sample-b	~15	~26	
Sample-c	~22	~31	