

Electronic Supplementary Material (ESI) for Materials Chemistry Frontier.

This journal is © The Royal Society of Chemistry 2019

## **Supporting Information for** **Chain-Length Effect on Binary Superlattices of Polymer-** **Tethered Nanoparticles**

Ke Wang,<sup>a,c</sup> Fan Li,<sup>a</sup> Seon-Mi Jin,<sup>b</sup> Kui Wang,<sup>a</sup> Di Tian,<sup>a</sup> Mubashir Hussain,<sup>a</sup> Jiangping Xu,<sup>a</sup>

Lianbin Zhang,<sup>a,\*</sup> Yonggui Liao,<sup>a</sup> Eunji Lee,<sup>b</sup> Gi-Ra Yi,<sup>\*c</sup> Xiaolin Xie<sup>a</sup> and Jintao Zhu<sup>\*a</sup>

<sup>a</sup>. Key Laboratory of Materials Chemistry for Energy Conversion and Storage (HUST), Ministry of Education, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology (HUST), Wuhan 430074, China.

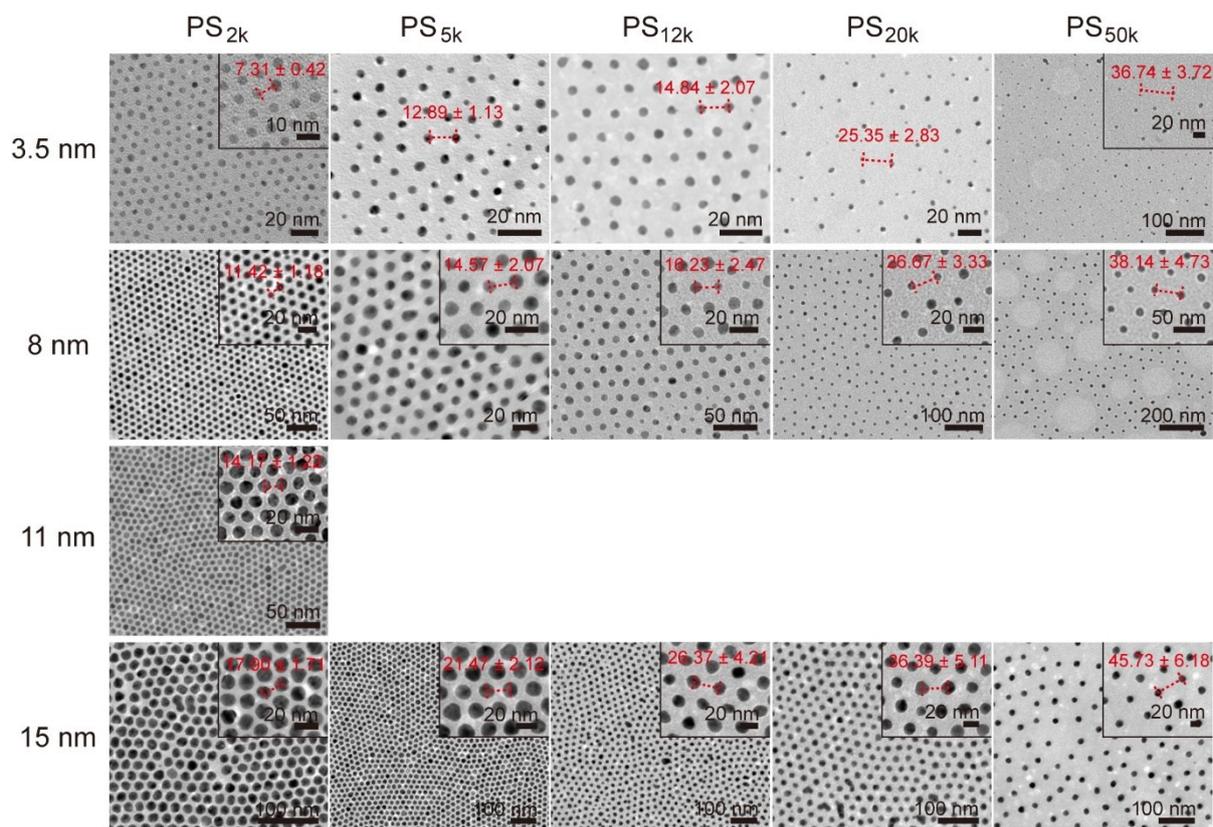
<sup>b</sup>. School of Materials Science and Engineering, Gwangju Institute of Science and Technology

Gwangju 361005, Republic of Korea

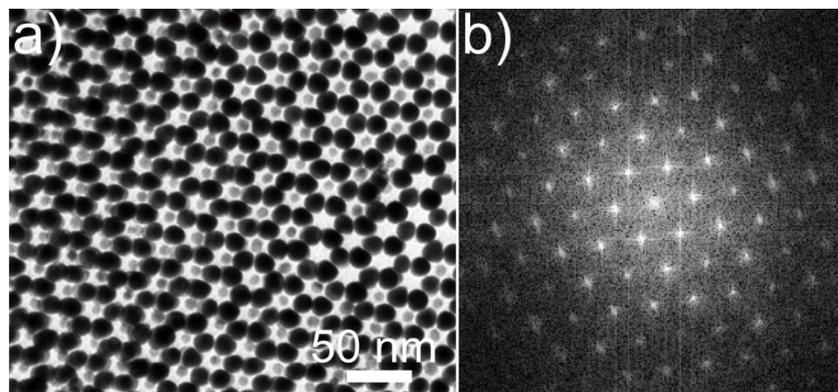
<sup>c</sup>. School of Chemical Engineering, Sungkyunkwan University

Suwon 16419, Republic of Korea

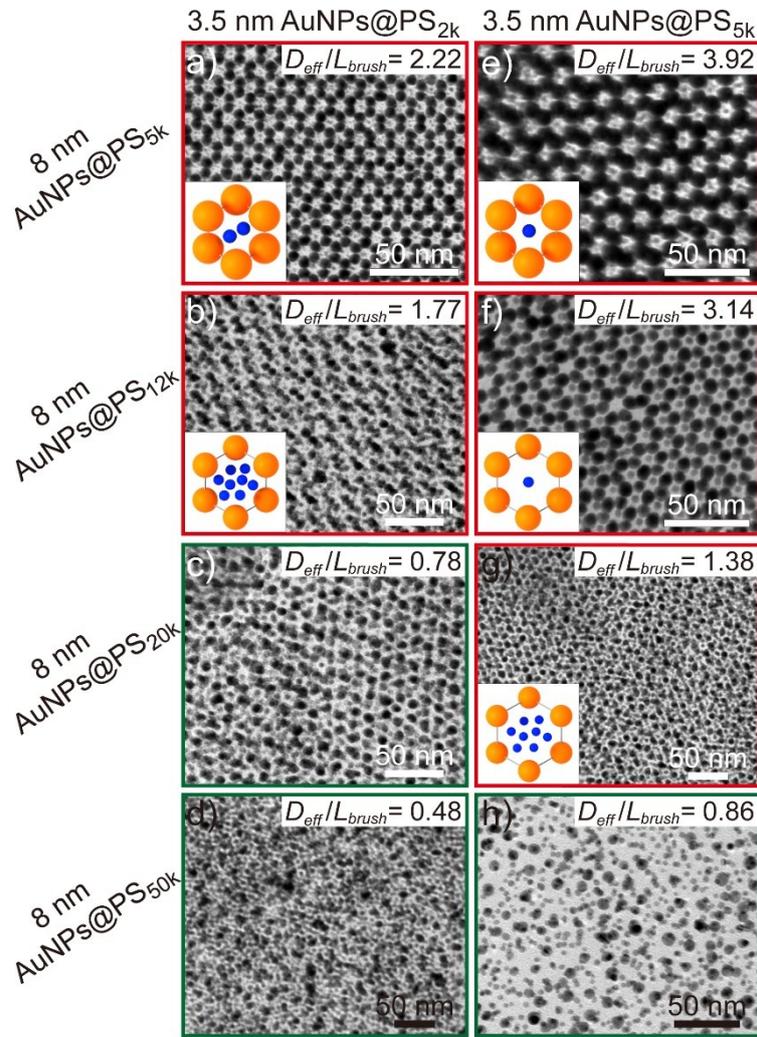
E-mail: zhanglianbin@hust.edu.cn (L. Zhang); yigira@g.skku.edu (G. Yi); jtzhu@mail.hust.edu.cn (J. Zhu);



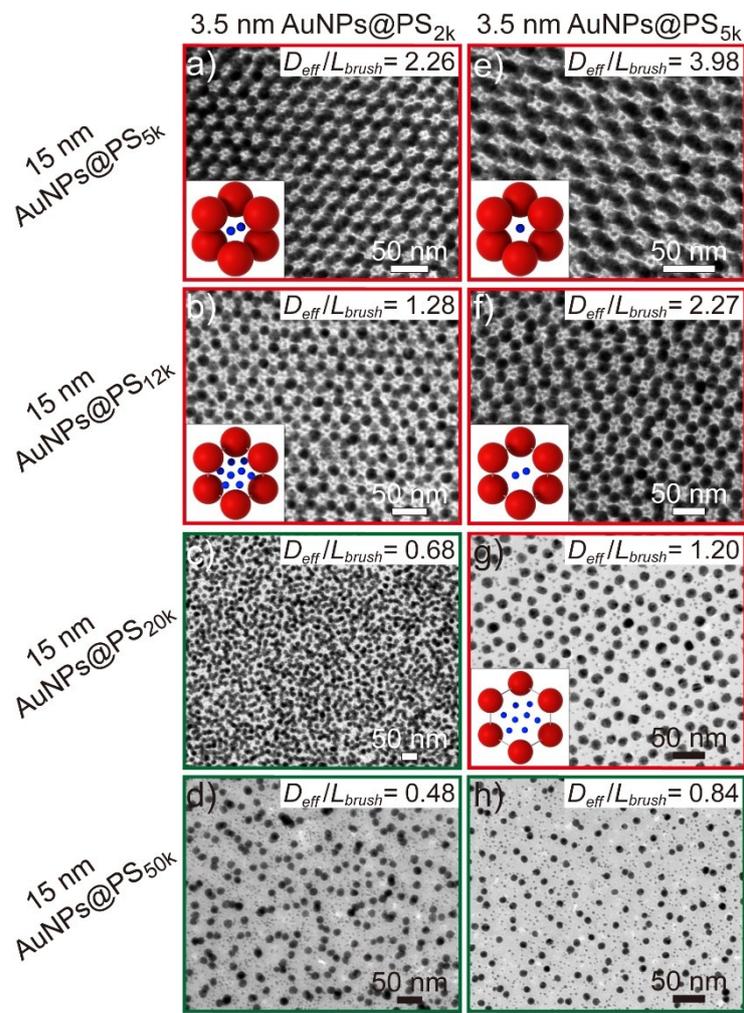
**Fig. S1** TEM images of the monolayer fabricated from AuNPs@PS with different core and various molecular weight of PS ligand. The effective diameter ( $D_{eff}$ ) was measured from the core to core between two adjacent AuNPs@PS.



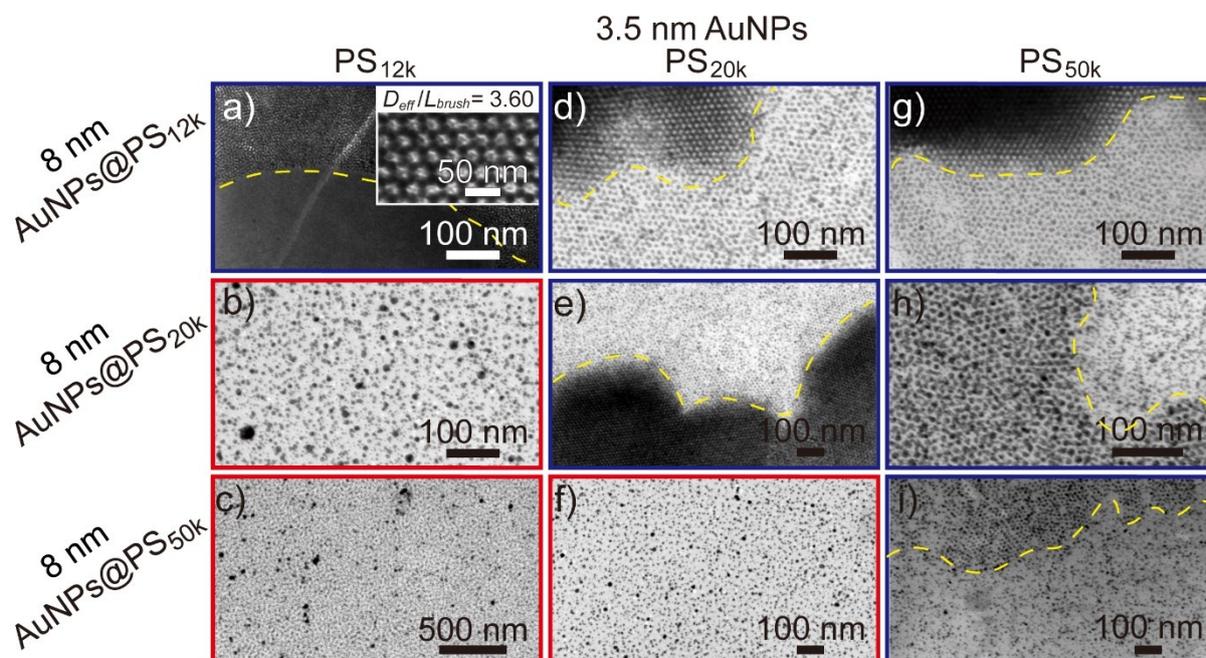
**Fig. S2** a) TEM image of BNSLs formed from 8 nm AuNPs@PS<sub>5k</sub> and 15 nm AuNPs@PS<sub>12k</sub>, and b) its FFT pattern.



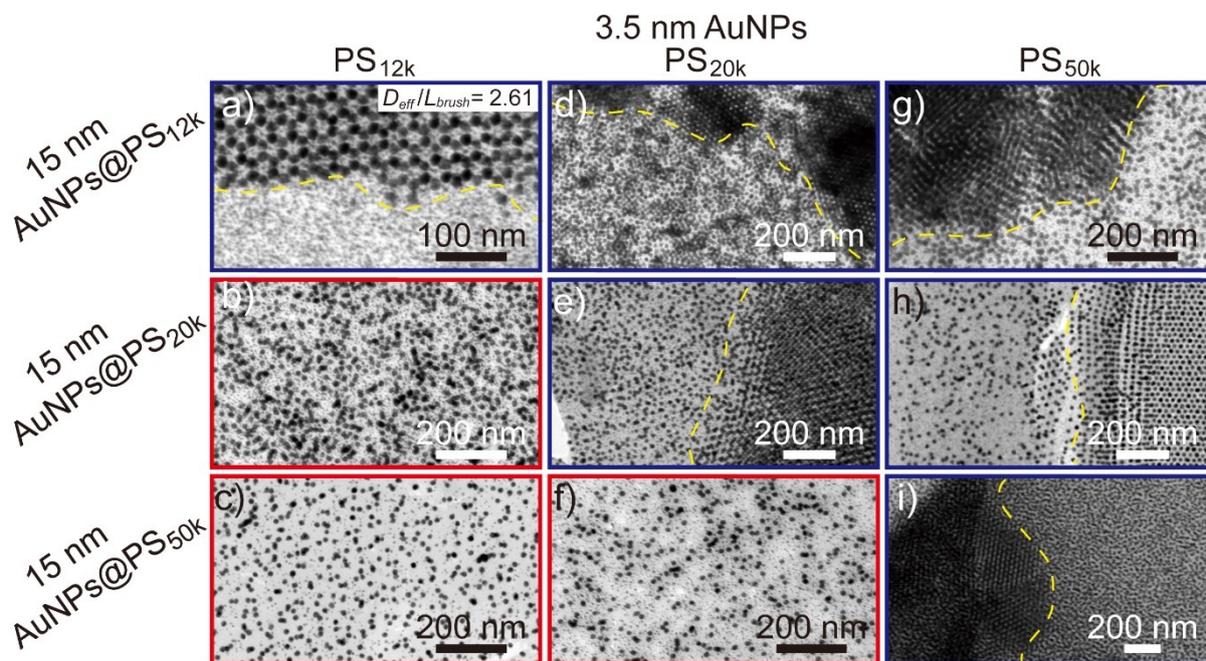
**Fig. S3** Low-magnification TEM images of BNSLs formed in *S-L* model. a-d) 3.5 nm AuNPs@PS<sub>2k</sub> and 8 nm AuNPs@PS with various  $M_{w-PS}$ : a) PS<sub>5k</sub>, b) PS<sub>12k</sub>, c) PS<sub>20k</sub>, and d) PS<sub>50k</sub>. e-h) 3.5 nm AuNPs@PS<sub>5k</sub> and 8 nm AuNPs@PS with various  $M_{w-PS}$ : e) PS<sub>5k</sub>, f) PS<sub>12k</sub>, g) PS<sub>20k</sub>, and h) PS<sub>50k</sub>. The TEM images with red and green frame showed the OVF-HCP structure and the disordered structure, respectively. Insets in a), b), e), f) and g) are the cartoons showing the crystal models of the BNSLs.



**Fig. S4** Low-magnification TEM images of BNSLs formed in *S-L* model. a-d) 3.5 nm AuNPs@PS<sub>2k</sub> and 15 nm AuNPs@PS with various  $M_{w-PS}$ : a) PS<sub>5k</sub>, b) PS<sub>12k</sub>, c) PS<sub>20k</sub>, and d) PS<sub>50k</sub>. e-h) 3.5 nm AuNPs@PS<sub>5k</sub> and 15 nm AuNPs@PS with various  $M_{w-PS}$ : e) PS<sub>5k</sub>, f) PS<sub>12k</sub>, g) PS<sub>20k</sub>, and h) PS<sub>50k</sub>. The TEM images with red and green frame showed the OVF-HCP structure and the disordered structure, respectively. Insets in a), b), e), f) and g) are the cartoon showing the crystal models of the BNSLs.



**Fig. S5** High-magnification TEM images of the assemblies formed by: a-c) 3.5 nm AuNPs@PS<sub>12k</sub> and 8 nm AuNPs@PS with various  $M_{w-PS}$ : a) PS<sub>12k</sub>, b) PS<sub>20k</sub>, and c) PS<sub>50k</sub>. d-f) 3.5 nm AuNPs@PS<sub>20k</sub> and 8 nm AuNPs@PS with various  $M_{w-PS}$ : d) PS<sub>12k</sub>, e) PS<sub>20k</sub>, and f) PS<sub>50k</sub>. g-i) 3.5 nm AuNPs@PS<sub>50k</sub> and 8 nm AuNPs@PS with various  $M_{w-PS}$ : g) PS<sub>12k</sub>, h) PS<sub>20k</sub>, and i) PS<sub>50k</sub>. Inset in a) is the TEM image of OVf-HCP structure. The TEM images with red and blue frame showed the binary phase-coexistence regions, and the macrophase separated structures, respectively. The dashed yellow lines indicate the phase boundary.



**Fig. S6** High-magnification TEM images of the assemblies formed by: a-c) 3.5 nm AuNPs@PS<sub>12k</sub> and 15 nm AuNPs@PS with various  $M_{w-PS}$ : a) PS<sub>12k</sub>, b) PS<sub>20k</sub>, and c) PS<sub>50k</sub>. d-f) 3.5 nm AuNPs@PS<sub>20k</sub> and 15 nm AuNPs@PS with various  $M_{w-PS}$ : d) PS<sub>12k</sub>, e) PS<sub>20k</sub>, and f) PS<sub>50k</sub>. g-i) 3.5 nm AuNPs@PS<sub>50k</sub> and 15 nm AuNPs@PS with various  $M_{w-PS}$ : g) PS<sub>12k</sub>, h) PS<sub>20k</sub>, and i) PS<sub>50k</sub>. The TEM images with red and blue frame showed the binary phase-coexistence regions, and the macrophase separated structures, respectively. The dashed yellow lines indicate the phase boundary.