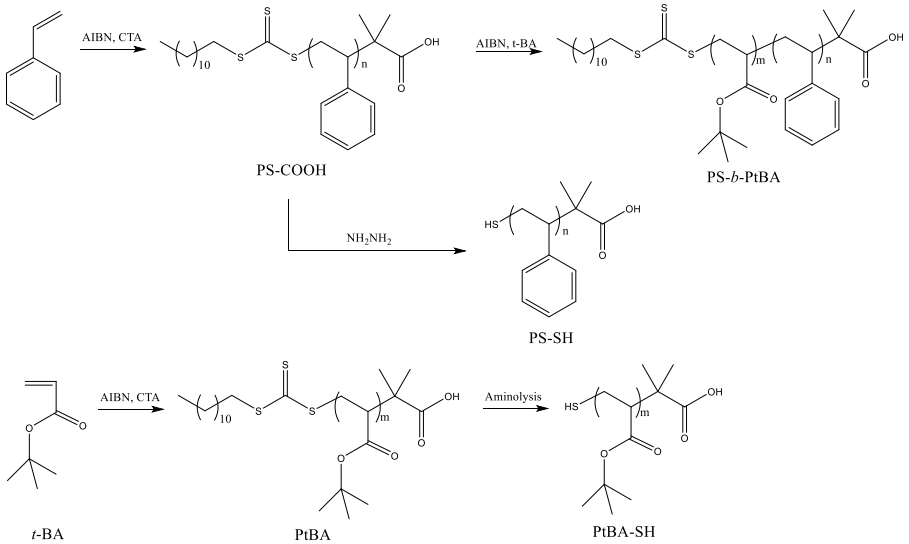
Electronic Supplementary Information (ESI) for

Circular assembly of colloidal nanoparticles at the liquid-air interface mediated by block copolymers

Lei Wang,[a] Yuchi Yang,[a] Xiudi Shen,[a] Tongtao Li,[b] Jianhua Hu,[a] Dong Yang,*[a] and Angang Dong*[b]

[a]*State Key Laboratory of Molecular Engineering of Polymer and Department of Macromolecular Science, Fudan University, Shanghai 200433, China.*

[b]*Collaborative Innovation Center of Chemistry for Energy Materials, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, and Department of Chemistry, Fudan University, Shanghai 200433, China.*



Scheme S1. Synthesis of COOH- or SH-terminated polymeric ligands and PS-*b*-PtBA.

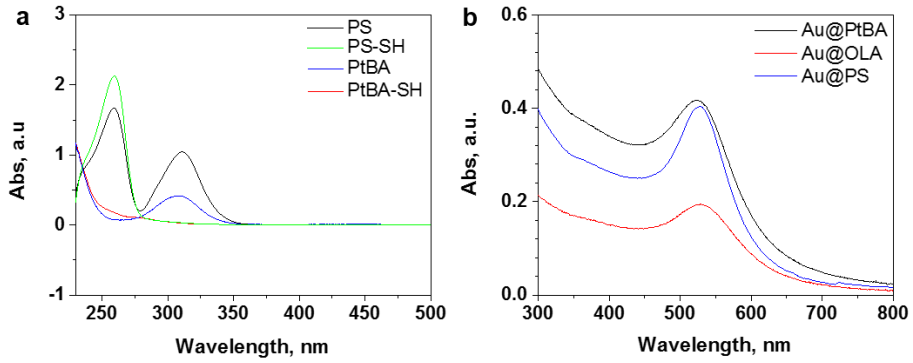


Fig. S1. (a) UV-visible absorption spectra of PtBA-SH and PS-SH after aminolysis and hydrazinolysis, respectively. The disappearance of the absorption peak of trithiocarbonate at about 308 nm suggested the successful formation of SH-terminated polymeric ligands. (b) UV-visible Absorbance spectra of Au NPs after ligand exchange. The unshifted peaks upon ligand exchange suggested that the polymer-tethered Au NPs were highly dispersible without aggregation.

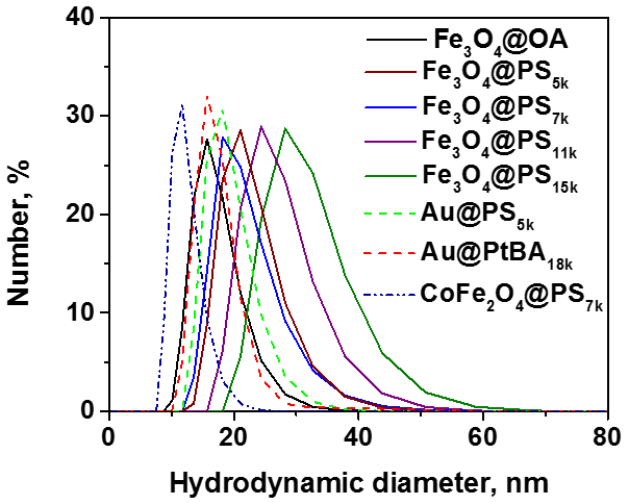


Fig. S2. Hydrodynamic radius of various polymer-tethered NPs.

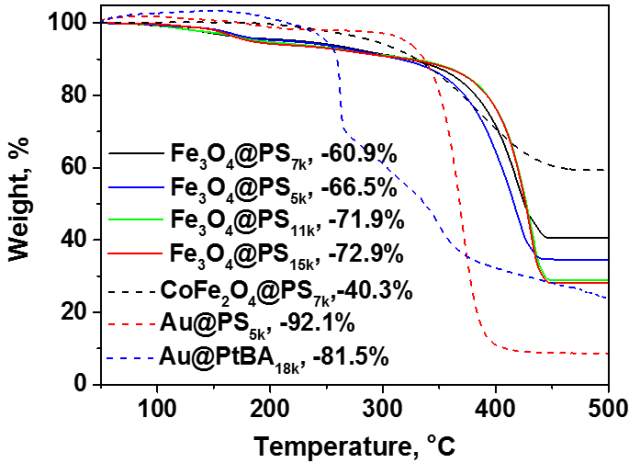


Fig. S3. TGA scans of various polymer-tethered NPs.

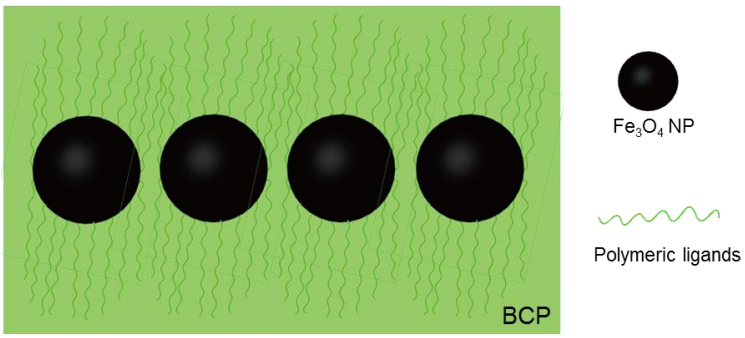


Fig. S4. Illustration of the possible conformation of polymeric ligands tethered to NPs upon co-assembly with BCPs. The strong interaction between polymeric ligands with the surrounding BCPs likely lowers the ligand grafted density between neighboring NPs, thereby leading to the observed small interparticle spacing.

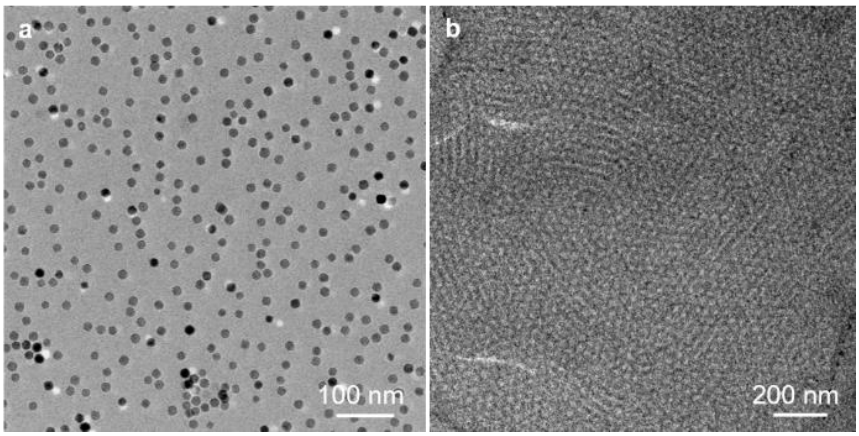


Fig. S5. (a) TEM image of the product resulting from the assembly of Fe_3O_4@PS_{7k} NPs and PS_{110}-*b*-$PtBA_{170}$ on carbon-coated TEM grids at 60 ºC. (b) TEM image of the product resulting from the assembly of PS_{110}-*b*-$PtBA_{170}$ alone on carbon-coated TEM grids at 60 ºC after PTA staining.

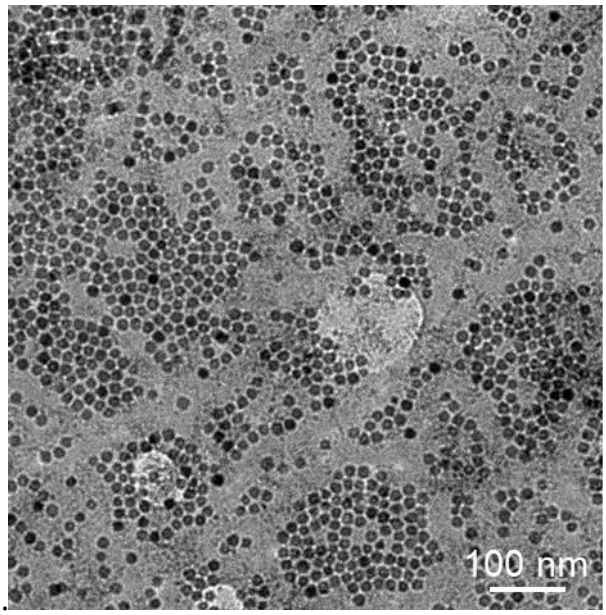


Fig. S6. TEM image of the product resulting from the assembly of Fe_3O_4@OA NPs and PS_{110}-*b*-$PtBA_{170}$ at the DEG-air interface at 60 ºC.

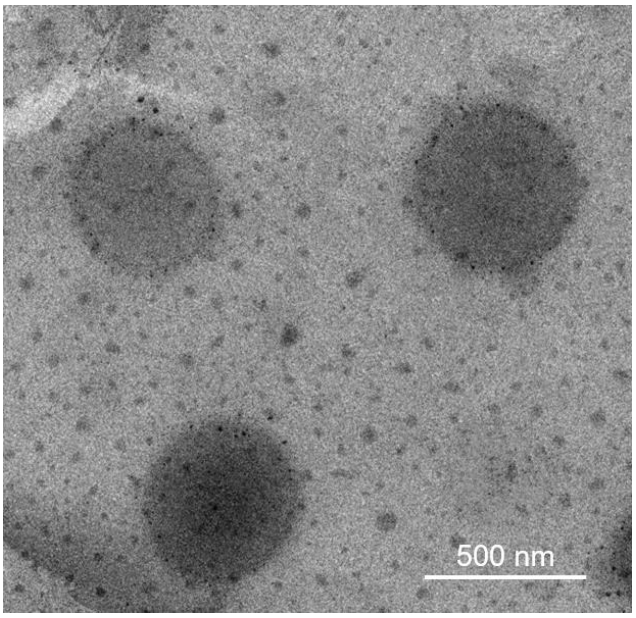


Fig. S7. TEM image of the product resulting from the self-assembly of pure PS_{110}-*b*-$PtBA_{170}$ at the DEG-air interface at 60 ºC after PTA staining.

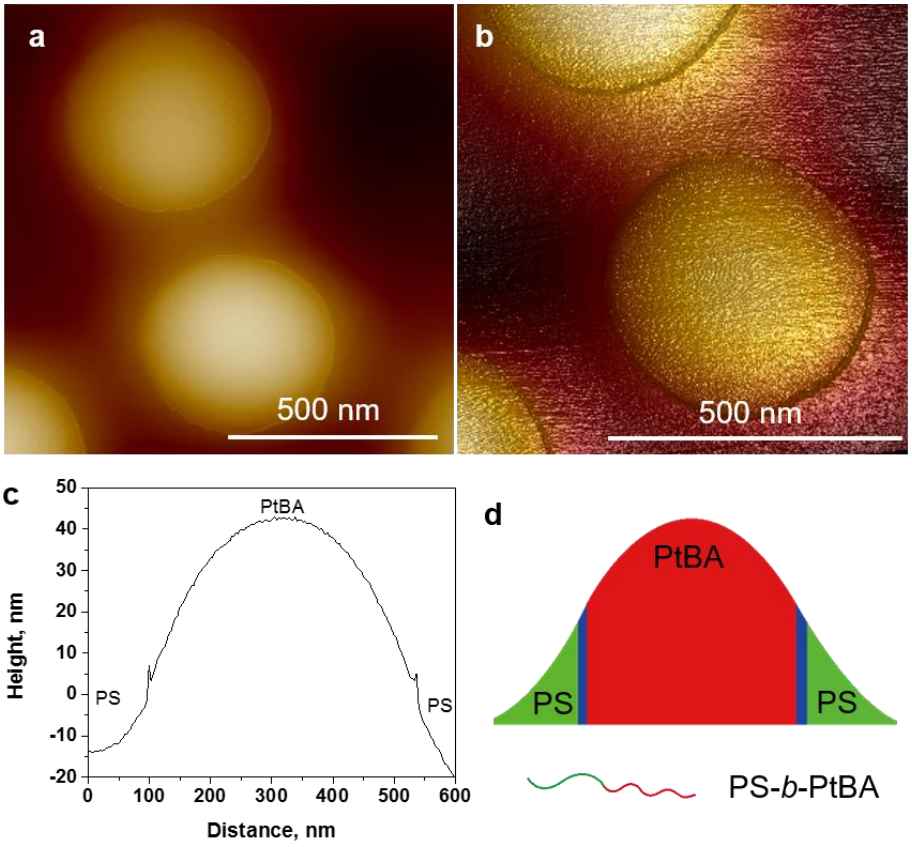


Fig. S8. AFM characterization of the product resulting from the self-assembly of pure PS_{110}-*b*-$PtBA_{170}$ at the DEG-air interface at 60 °C: (a) AFM height image; (b) 3D AFM image; (c) height profile; (d) cross-sectional illustration. The blue areas refer to the interfacial region between PtBA (red) and PS (green) phases.

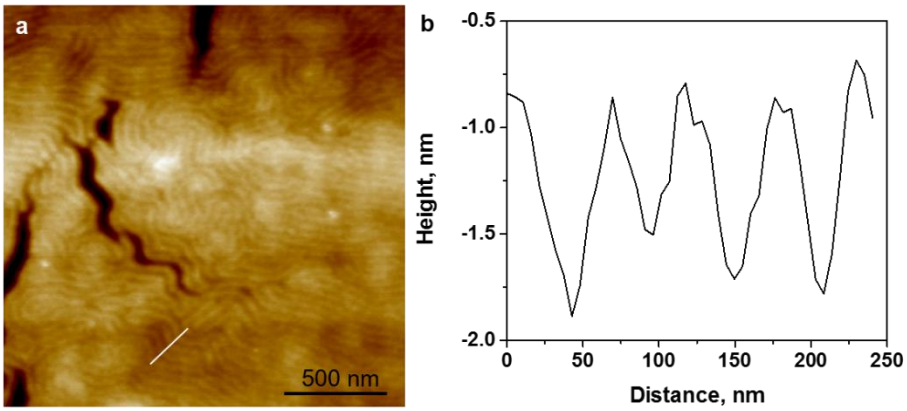


Fig. S9. AFM characterization of the bottom surface (in contact with DEG) of the film assembled from PS_{110}-*b*-$PtBA_{170}$ alone on DEG at 60 ^{o}C: (a) Height image and (b) height profile as indicated in (a).

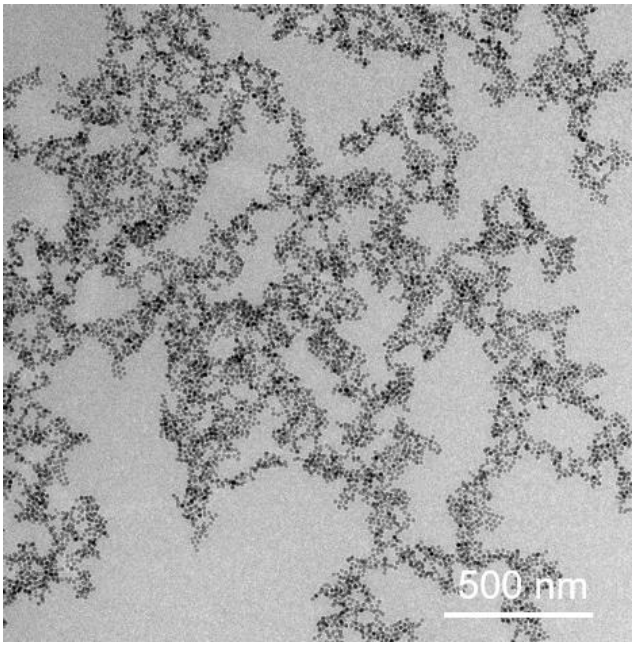


Fig. S10. TEM image of the product resulting from the interfacial assembly of Fe_3O_4@PS_{7k} NPs and PS_{110}-*b*-$PtBA_{170}$ at 30 ºC.

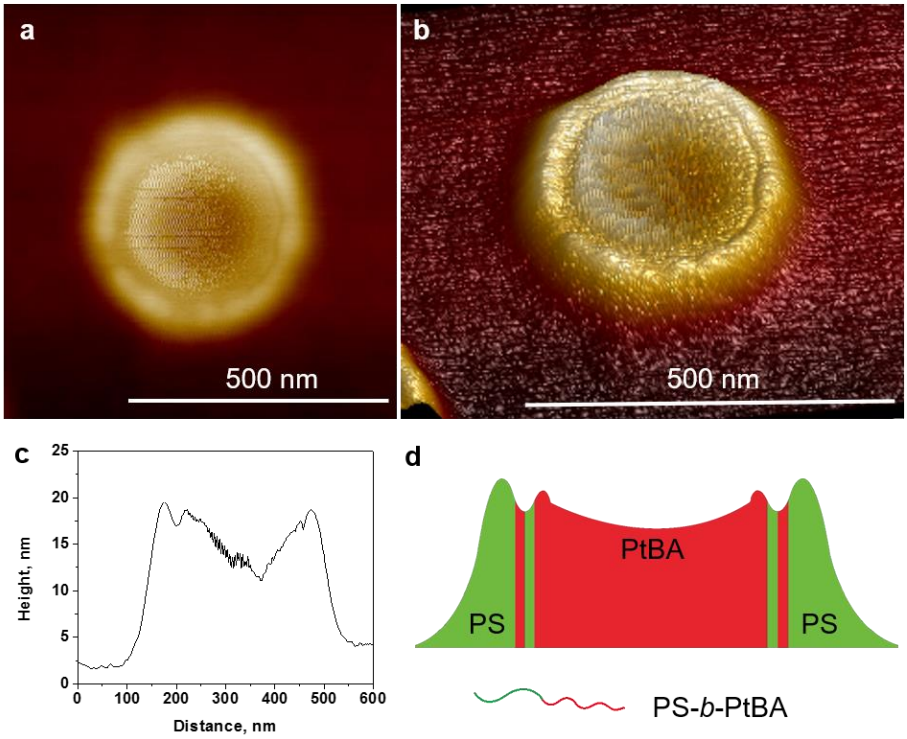


Fig. S11. AFM characterization of the product resulting from the self-assembly of PS_{110}-*b*-$PtBA_{170}$ at the DEG-air interface at 50 °C: (a) AFM height image; (b) 3D AFM image; (c) height profile; (d) cross-sectional illustration. The interfacial regions between neighboring PtBA (red) and PS (green) phases are omitted for clarity.

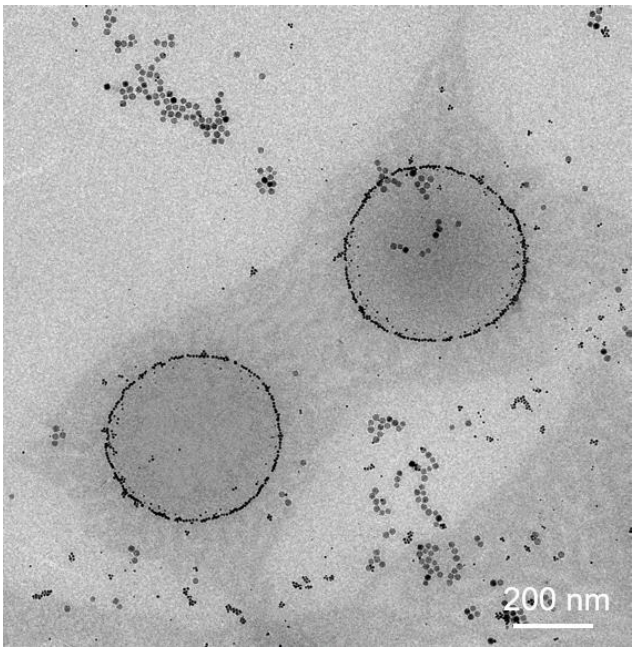


Fig. S12. TEM image of the product resulting from the interfacial assembly of Fe_3O_4@PS_{7k} NPs, Au@$PtBA_{18k}$ NPs, and PS_{110}-*b*-$PtBA_{170}$ at 60 ^oC. The rings are mainly composed of Au@$PtBA_{18k}$ NPs, while Fe_3O_4@PS_{7k} NPs remained largely unassembled.

Table S1. BCPs, polymeric ligands, and NPs used in the experiment.

Polymers	Mn*	Functions	NPs	Abbreviations
PS_{110}-*b*-$PtBA_{170}$	3.16×10^4	Template	/	BCP
PS_{5k}	4.99×10^3	Ligands	Fe_3O_4 (15 nm)	$Fe_3O_4@PS_{5k}$
PS_{7k}	6.99×10^3	Ligands	Fe_3O_4 (15 nm)	$Fe_3O_4@PS_{7k}$
PS_{11k}	1.13×10^4	Ligands	Fe_3O_4 (15 nm)	$Fe_3O_4@PS_{11k}$
PS_{15k}	1.54×10^4	Ligands	Fe_3O_4 (15 nm)	$Fe_3O_4@PS_{15k}$
PS_{7k}	6.99×10^3	Ligands	$CoFe_2O_4$ (6 nm)	$CoFe_2O_4@PS_{7k}$
PS_{5k}	4.99×10^3	Ligands	Au (6 nm)	$Au@PS_{5k}$
$PtBA_{18k}$	1.87×10^4	Ligands	Au (6 nm)	$Au@PtBA_{18k}$

*Mn denotes the molecular weight.