

Supporting Information

Self-Assembly of Gold Nanoparticles Grafted with Amphiphilic Supramolecular Block Copolymers

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1. Calculation of Grafting density

The polymer grafting density of PGNPs was determined by following equation:

$$\frac{\text{Polymer Chain}}{\text{NPs}} = \frac{\text{Numbers of polymer}}{\text{Surface area of an AuNP} \times \text{Number of AuNPs}} = \frac{\frac{m_{poly}}{M_{poly}} \times N_A}{S_{NP} \times \frac{m_{Au}/M_{Au}}{\rho_{Au} \times \frac{V_{NP}}{M_{Au}}}}$$

where m_{poly} and m_{Au} represent the mass of polymers on the AuNPs and AuNPs, respectively. M_{poly} and M_{Au} are the molecular weight of polymer and AuNPs; ρ_{Au} is the density of Au; S_{NP} is the surface area of AuNPs; V_{NP} is the volume of the single nanoparticles.

The mass of polymers on the surface of the AuNPs was determined by thermogravimetric analysis. As shown Figure S12b, the mass loss for PS₁₈₂-DPA-Cu²⁺ is 99.2 wt% after thermal decomposition at 700 °C.

To calculate the grafting density of PS₁₈₂-DPA-Cu²⁺ modified 14 nm AuNPs, 2.61 mg of PS₁₈₂-DPA-Cu²⁺-AuNPs and unmodified AuNPs were carried out for TGA. The weight loss of P4-Cu²⁺-AuNPs and unmodified AuNPs is 17.3 wt% and 0 wt%, at 700 °C respectively. Thus, it gives the weight ratio of PS₁₈₂-DPA-Cu²⁺ is (17.3 wt%-0 wt%)/99.16 wt.% = 17.4 wt%. The m_{poly} of PS₁₈₂-DPA-Cu²⁺ is 0.46 mg and the m_{Au} of AuNPs is 2.15 mg. The S_{NP} is 615 nm²; The M_{Au} is 196 g mol⁻¹; The ρ_{Au} is 19.3 g cm⁻³ and V_{NP} is 1.436 × 10⁻²⁴ m³.

$$\text{Based on the equation of the grafting density} = \frac{\frac{0.46 \text{ mg}}{19452.3 \text{ g mol}^{-1}} \times 6.02 \times 10^{23} \text{ mol}^{-1}}{615 \text{ nm}^2 \times \frac{2.15 \text{ mg}/196 \text{ g mol}^{-1}}{19.3 \text{ g cm}^{-3} \times \frac{1.436 \times 10^{-24} \text{ m}^3}{196 \text{ g mol}^{-1}}}} = 0.31 \text{ chains/nm}^2$$

Similarly, the grafting density of linear BCP of PDMA₅₂-*b*-PS₁₅₈-Cu²⁺ modified AuNPs is 0.79 chains/nm².

For DLS, the grafting density is determined by the differences of hydrodynamic radius of AuNPs before and after polymer modification. For example, the hydrodynamic radius of unmodified AuNPs and PS₁₈₂-DPA -Cu²⁺ modified AuNPs are $R = 7.0$ nm and $R+L = 12.82$ nm, respectively. Therefore, the thickness of polymer is $L = 5.82$ nm. The volume of grafted polymers (V_{poly}) is calculated to be ~ 7.4 K nm³ using the equation of

$$V_{poly} = \frac{4\pi}{3} ((R + L)^3 - R^3)$$

The average number of polymer chains on each AuNP is calculated to be ~ 197 chains/AuNP from the equation of

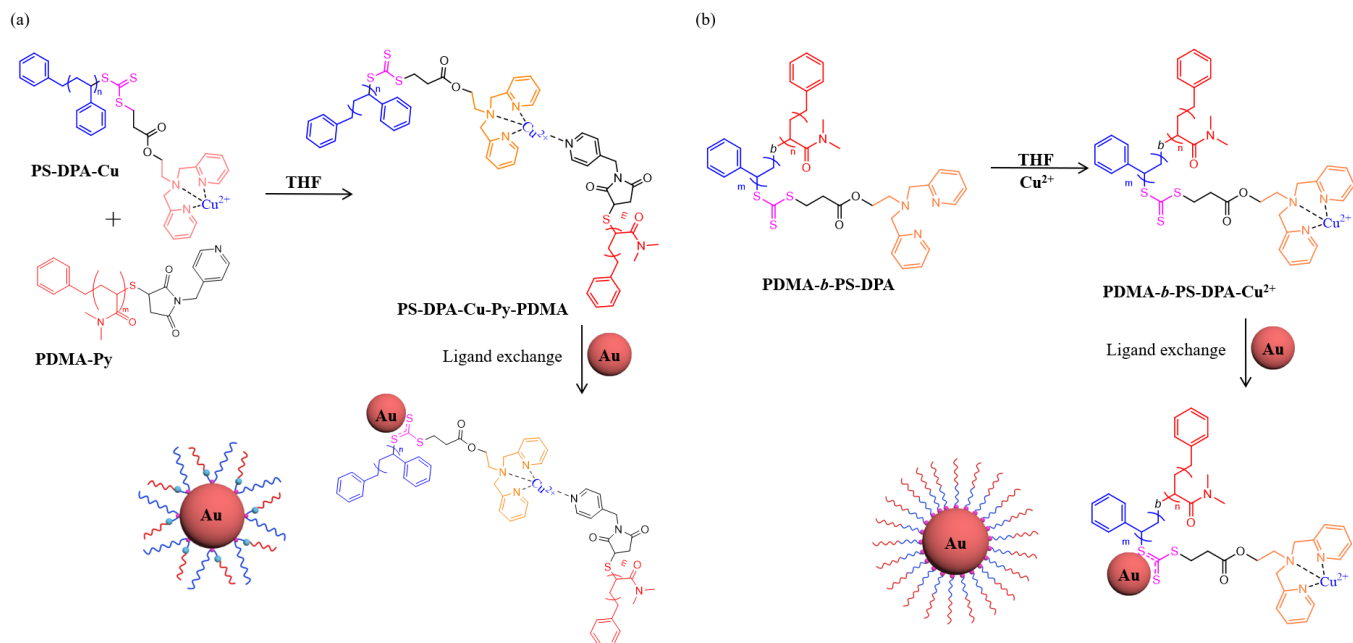
$$N_{poly} = \frac{\rho_{ps} V_{poly} N_A}{M_n}$$

where ρ_{ps} is the density of PS, we assume that is close to bulk density of PS of 1.05 g cm⁻³. N_A is Avogadro number.

The grafting density is calculated to be ~ 0.32 chains·nm⁻² by the equation of

$$\sigma = \frac{N_{poly}}{4\pi R^2}$$

For the grafting density to other PGNPs were summarized in Table S1.



Scheme S1. Scheme of surface modification with (a) “V-shape” block copolymers and (b) linear BCPs on AuNPs.

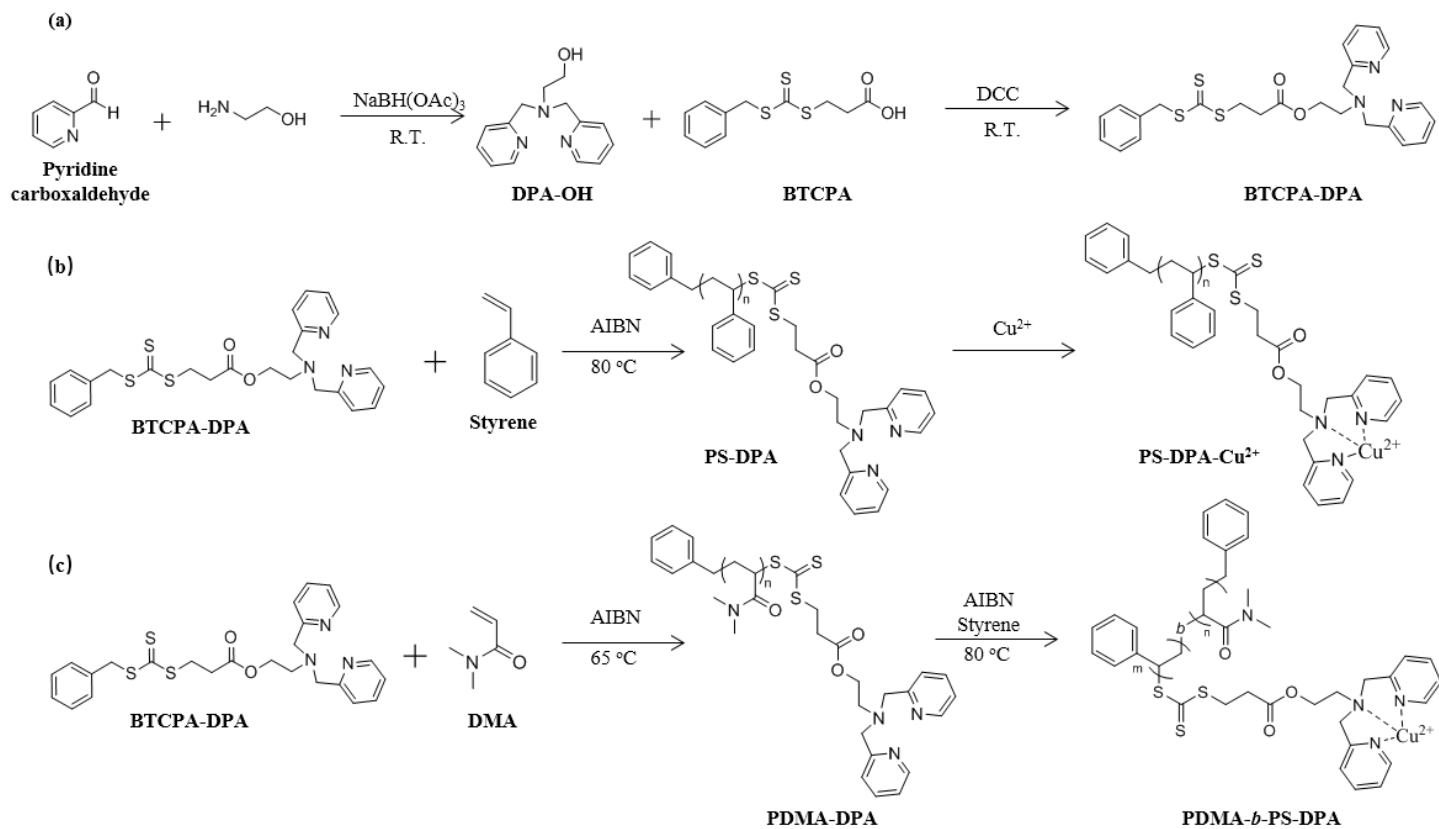


Figure S1. Synthetic routes of (a) BTCPA-DPA; (b) PS-DPA, PS-DPA-Cu²⁺; (c) linear BCP of PDMA-*b*-PS-DPA and PDMA-*b*-PS-Cu²⁺.

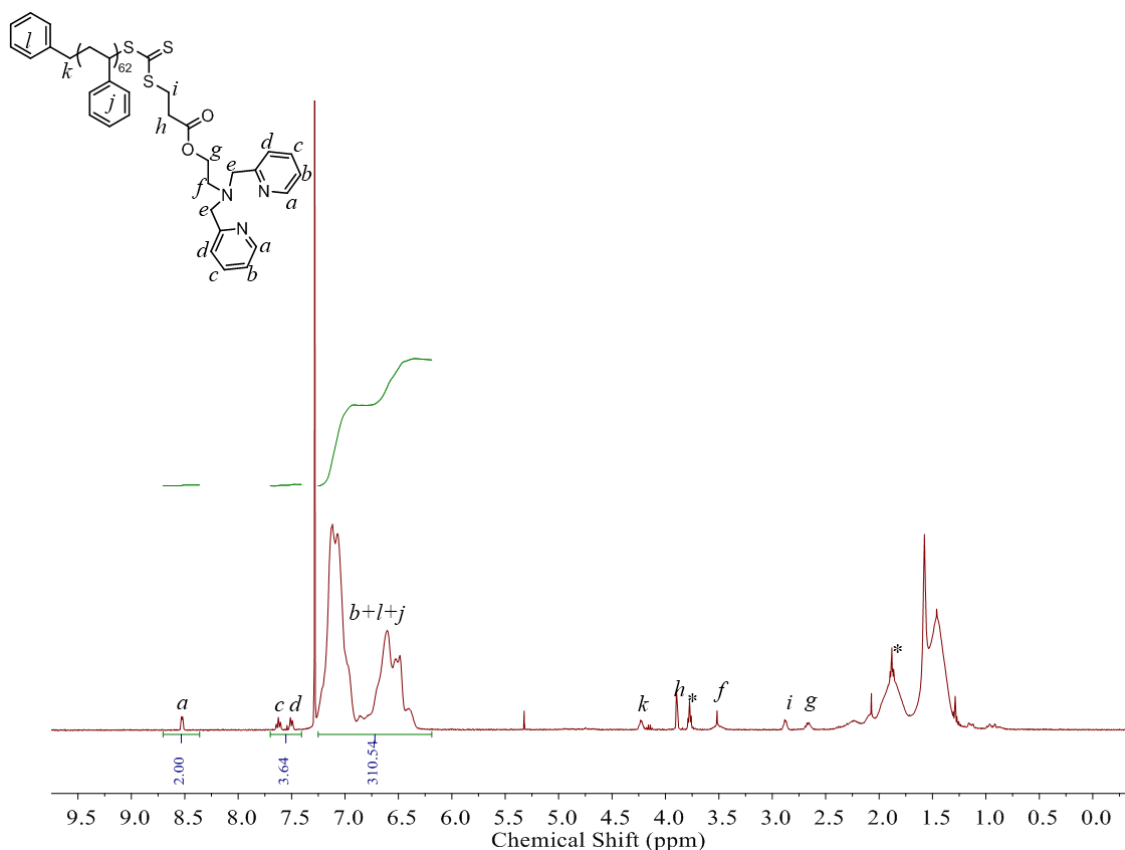


Figure S2. The Chemical structure and ¹H NMR spectrum of PS₆₂-DPA in CDCl₃.

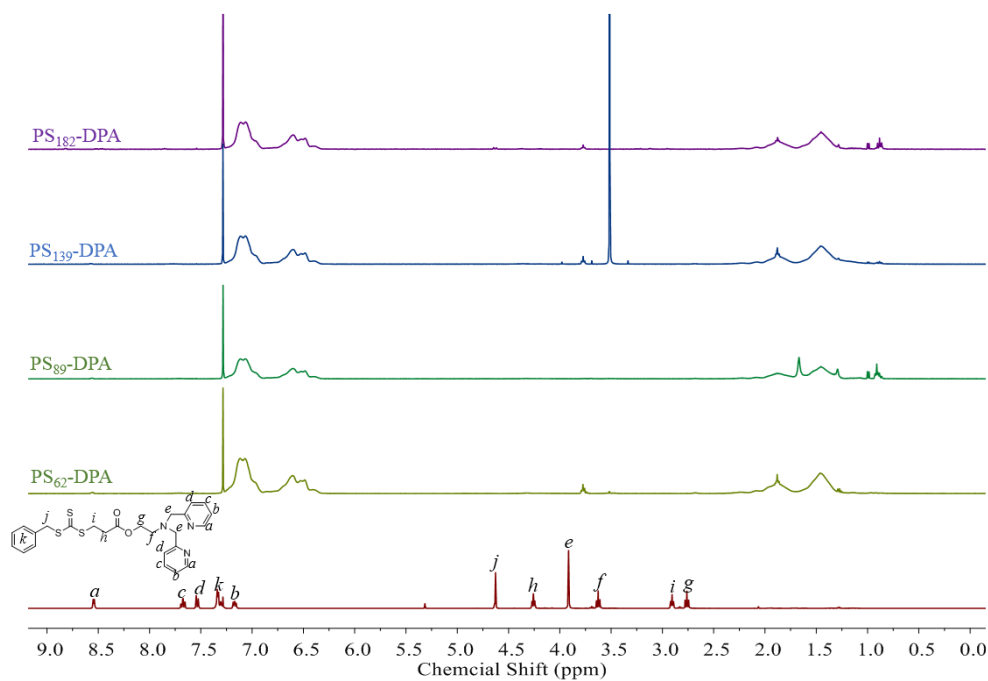


Figure S3. Chemical structure and ¹H NMR spectra of BCTPA-DPA, PS-DPA with different molecular weight in CDCl₃.

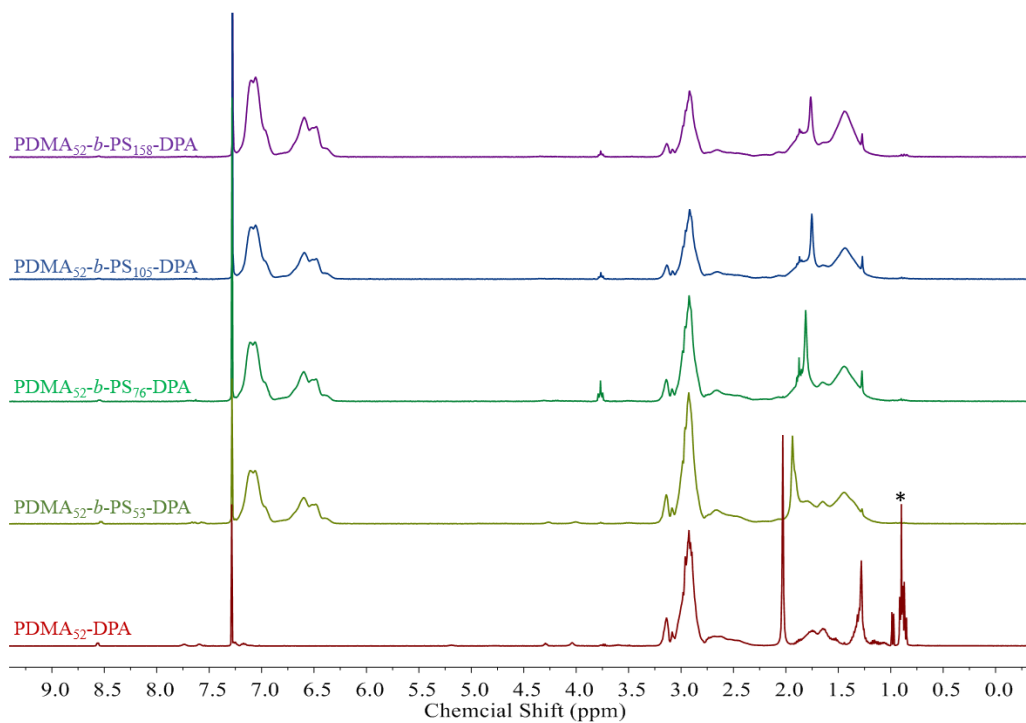


Figure S4. ^1H NMR spectra of $\text{PDMA}_{52}\text{-DPA}$ and linear BCPs of $\text{PDMA-}b\text{-PS}$ with different molecular weight in CDCl_3 . * is the solvent residual of hexane.

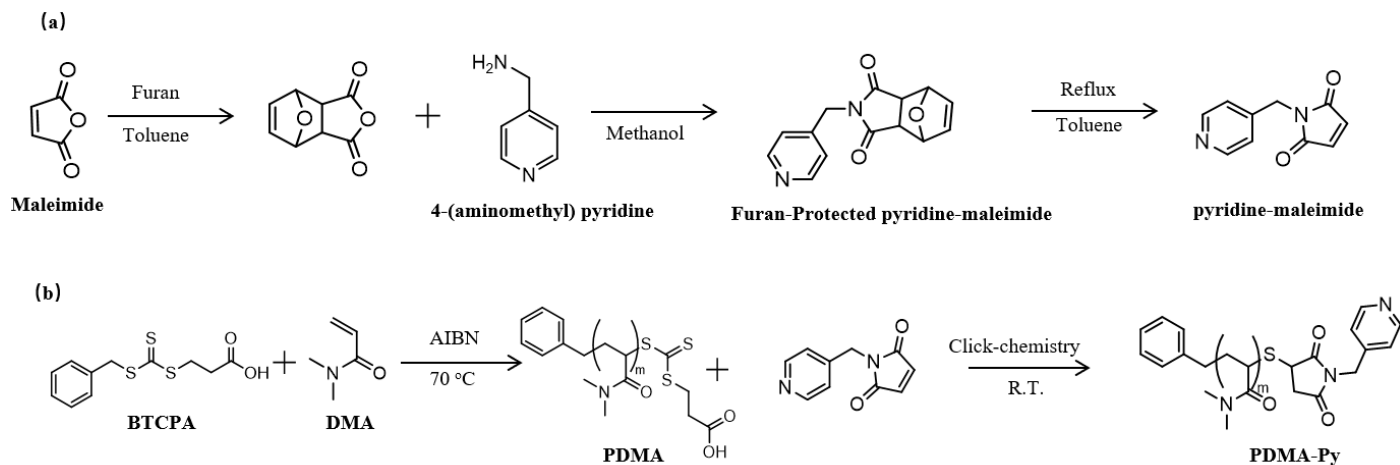


Figure S5. Synthetic routes of (a) pyridine-maleimide and (b) PDMA-Py.

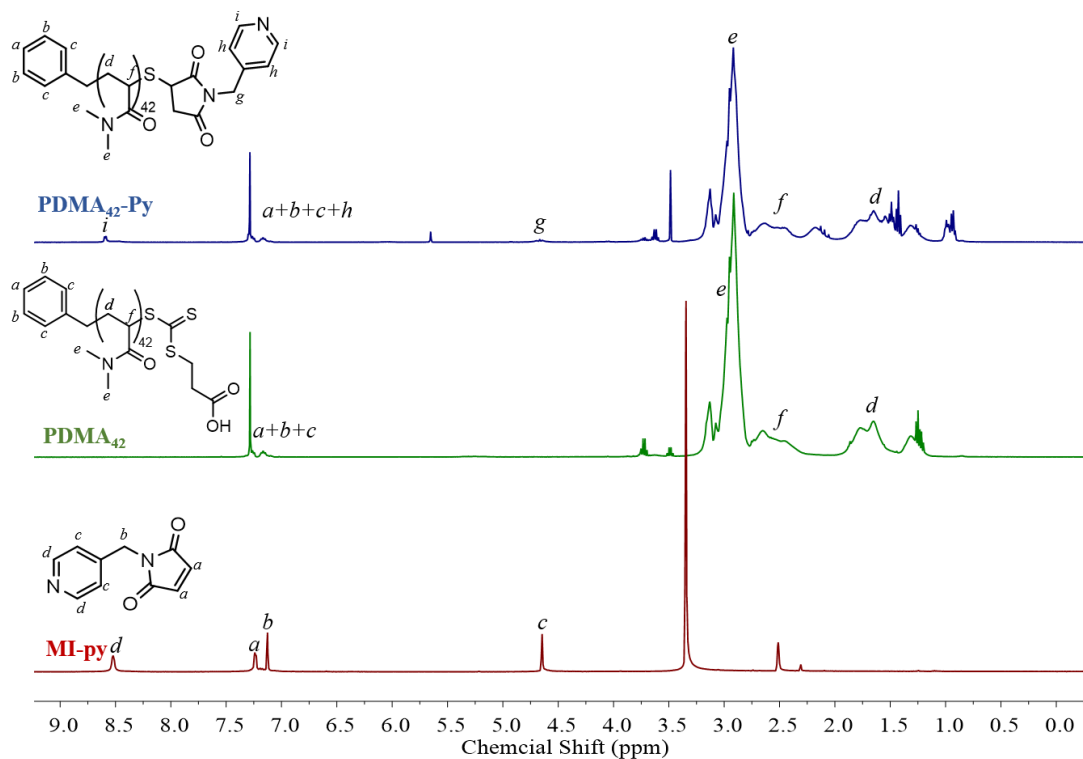


Figure S6. ^1H NMR spectra of MI-Py, PDMA and PDMA-Py in CDCl_3 .

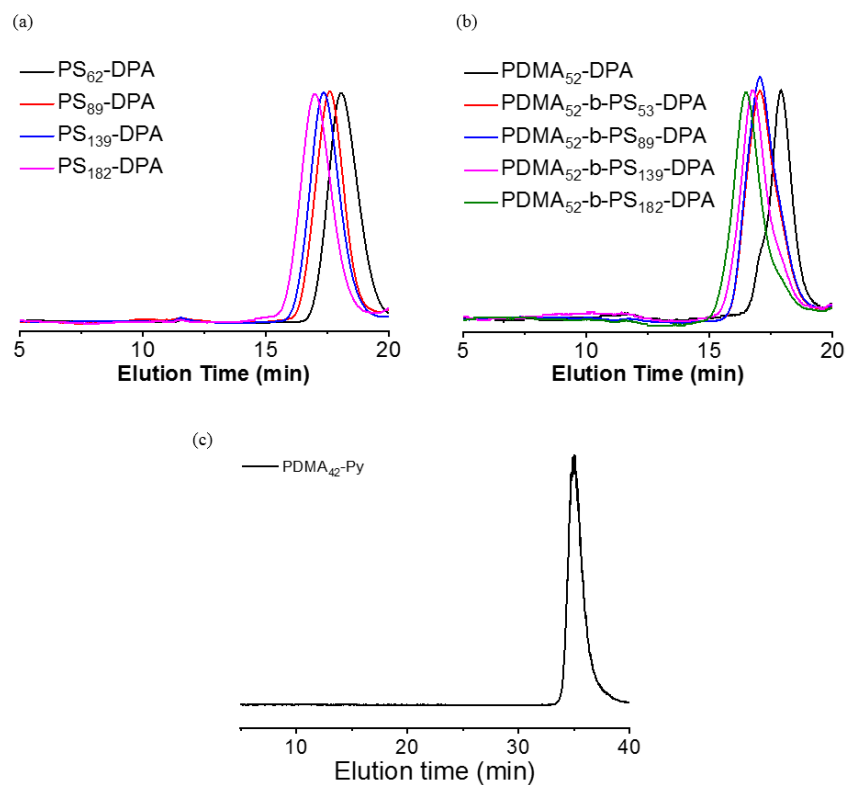


Figure S7. GPC elution curve of (a) homopolymers of PS-DPA, (b) linear BCPs of PDMA-*b*-PS-DPA and (c) PDMA-Py in DMAc.

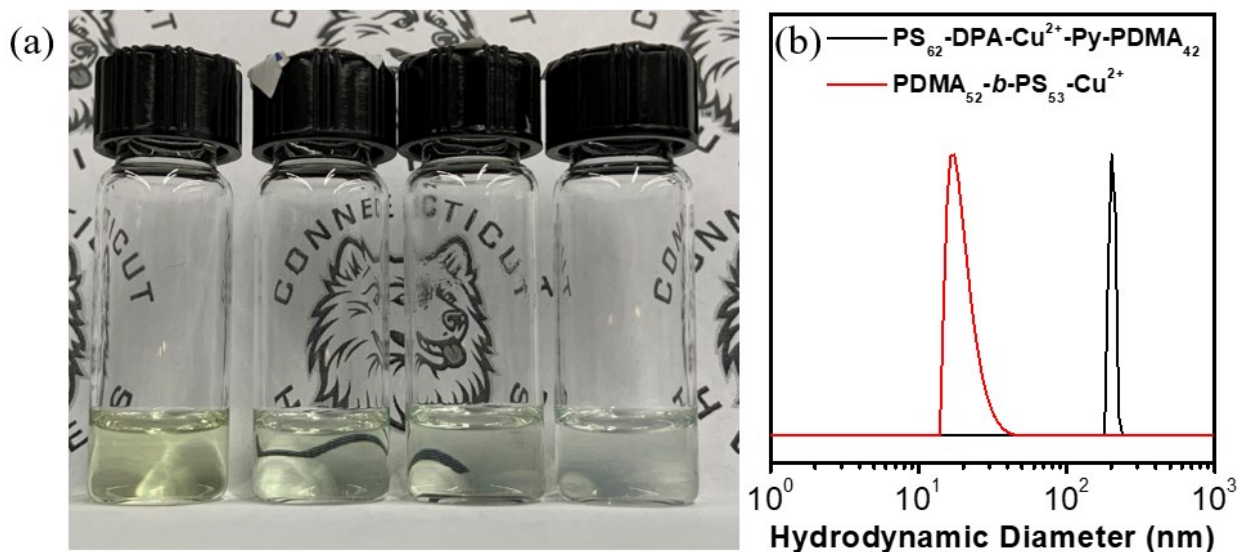


Figure S8. (a) Optical image to show micellar solution in selective solvent (volume ratio of DMF/H₂O = 7:3) formed by linear BCPs of PDMA₅₂-*b*-PS₅₃-Cu²⁺, PDMA₅₂-*b*-PS₇₆-Cu²⁺, PDMA₅₂-*b*-PS₁₀₅-Cu²⁺ and PDMA₅₂-*b*-PS₁₅₈-Cu²⁺ (left to right); (b) Hydrodynamic diameter of PS₆₂-DPA-Cu²⁺-Py-PDMA₄₂ (black) and PDMA₅₂-*b*-PS₅₃-Cu²⁺ (red) measured in DMF/H₂O = 7:3 by dynamic light scattering;

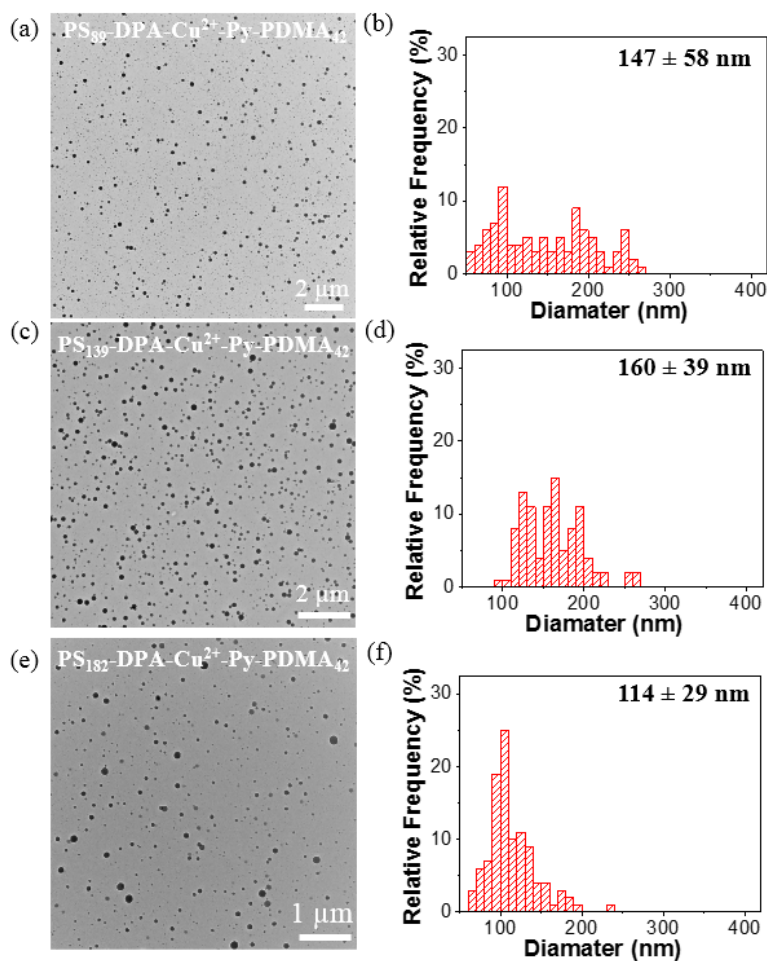
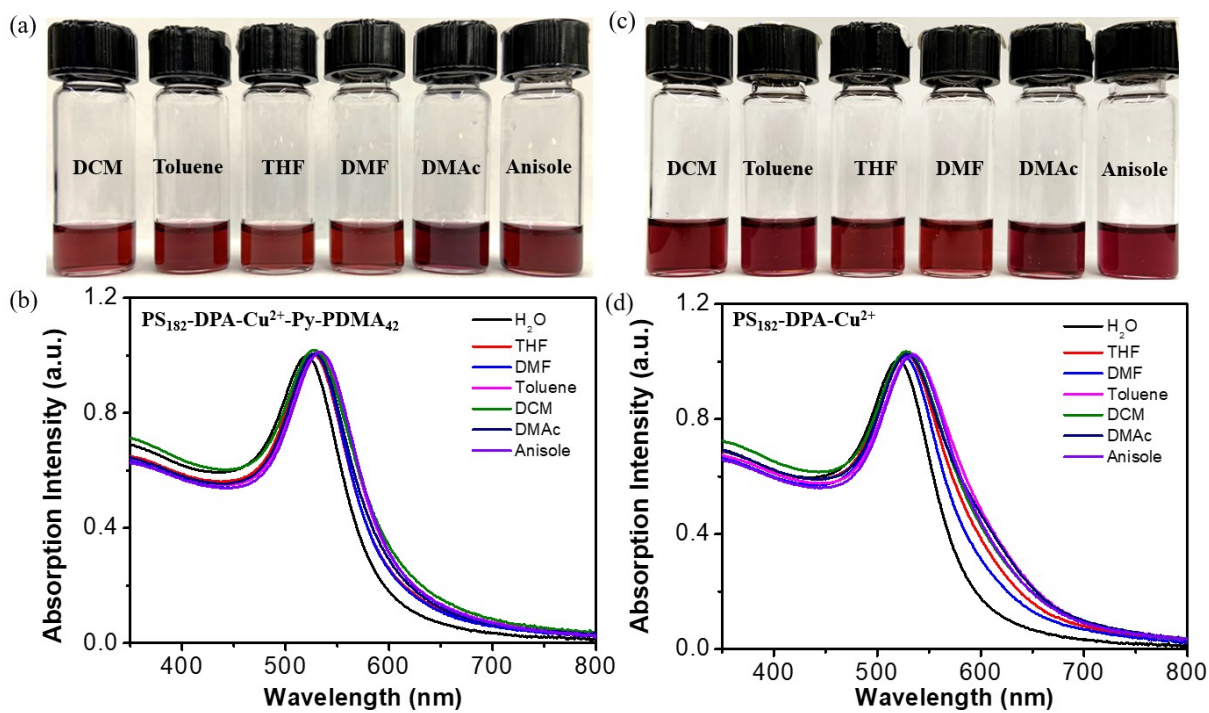
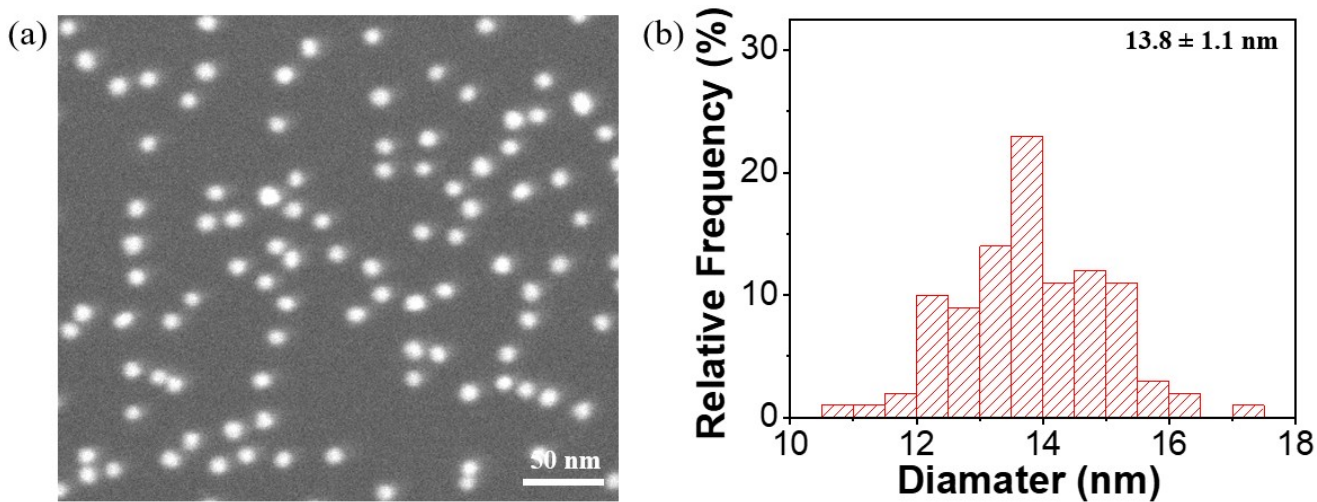


Figure S9. (a)(c)(e) TEM images to show the spherical micelles prepared from VBCPs and (b)(d)(f) their size distributions were measured from TEM images by averaging more than 100 particles.



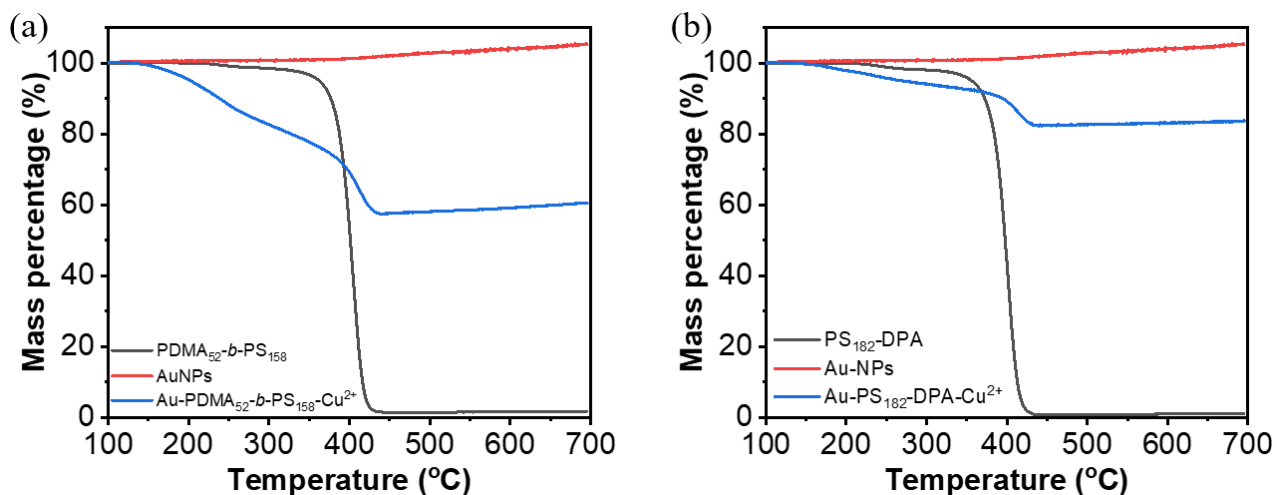


Figure S12. TGA thermograms of (a) PDMA₅₂-*b*-PS₁₅₈, AuNPs and PGNPs of PDMA₅₂-*b*-PS₁₅₈-Cu²⁺; (b) PS₁₈₂-DPA, AuNPs and PGNPs of PS₁₈₂-DPA-Cu²⁺.

Table S1. The grafting density of polymer grafted AuNPs

Sample name	Radius from DLS (nm)	σ (Chains/nm ²) (DLS)	σ (Chains/nm ²) (TGA)
AuNPs	7.0	-	-
Au-PS ₆₂ -DPA-Cu ²⁺	11.7	0.46	-
Au-PS ₈₉ -DPA-Cu ²⁺	11.8	0.38	-
Au-PS ₁₃₉ -DPA-Cu ²⁺	12.3	0.32	-
Au-PS ₁₈₂ -DPA-Cu ²⁺	12.8	0.32	0.31
Au-PDMA ₅₂ - <i>b</i> -PS ₅₃ -Cu ²⁺	12.6	0.62	-
Au-PDMA ₅₂ - <i>b</i> -PS ₇₆ -Cu ²⁺	12.9	0.55	-
Au-PDMA ₅₂ - <i>b</i> -PS ₁₀₅ -Cu ²⁺	13.2	0.49	-
Au-PDMA ₅₂ - <i>b</i> -PS ₁₅₈ -Cu ²⁺	14.5	0.51	0.79

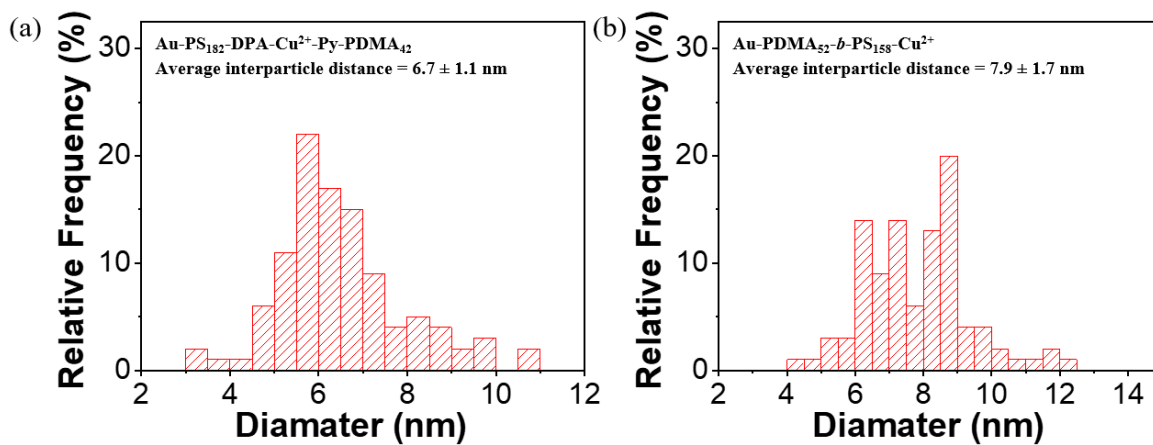


Figure S13. Histogram of interparticle distance for (a) layered assemblies from PGNPs of PS₁₈₂-DPA-Cu²⁺-Py-PDMA₄₂; (b) fractal particles from PGNPs of PDMA₅₂-*b*-PS₁₅₈-Cu²⁺.

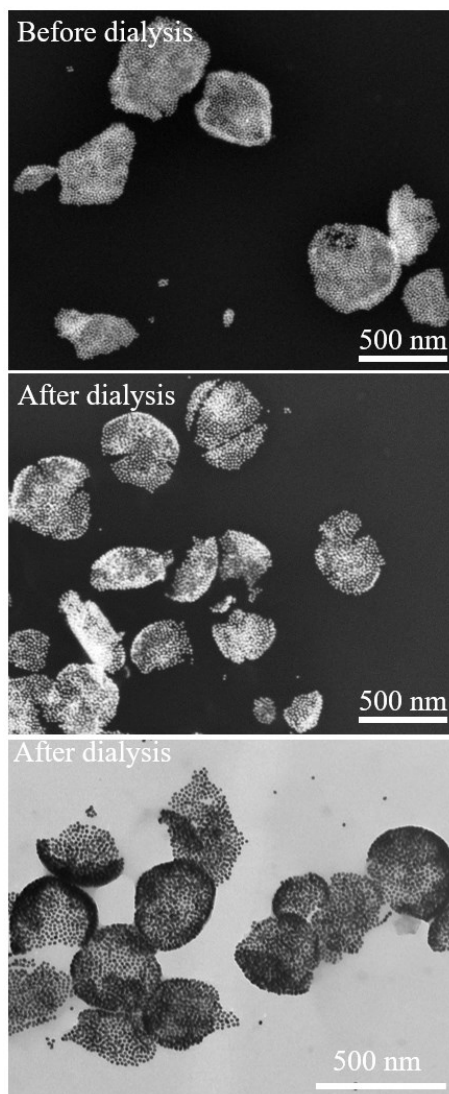


Figure S14. SEM images to show layer assemblies from PS₁₈₂-DPA-Cu²⁺-Py-PDMA₄₂ (a) before and (b) after doing the dialysis against to water, respectively and the (c) TEM images after the dialysis.

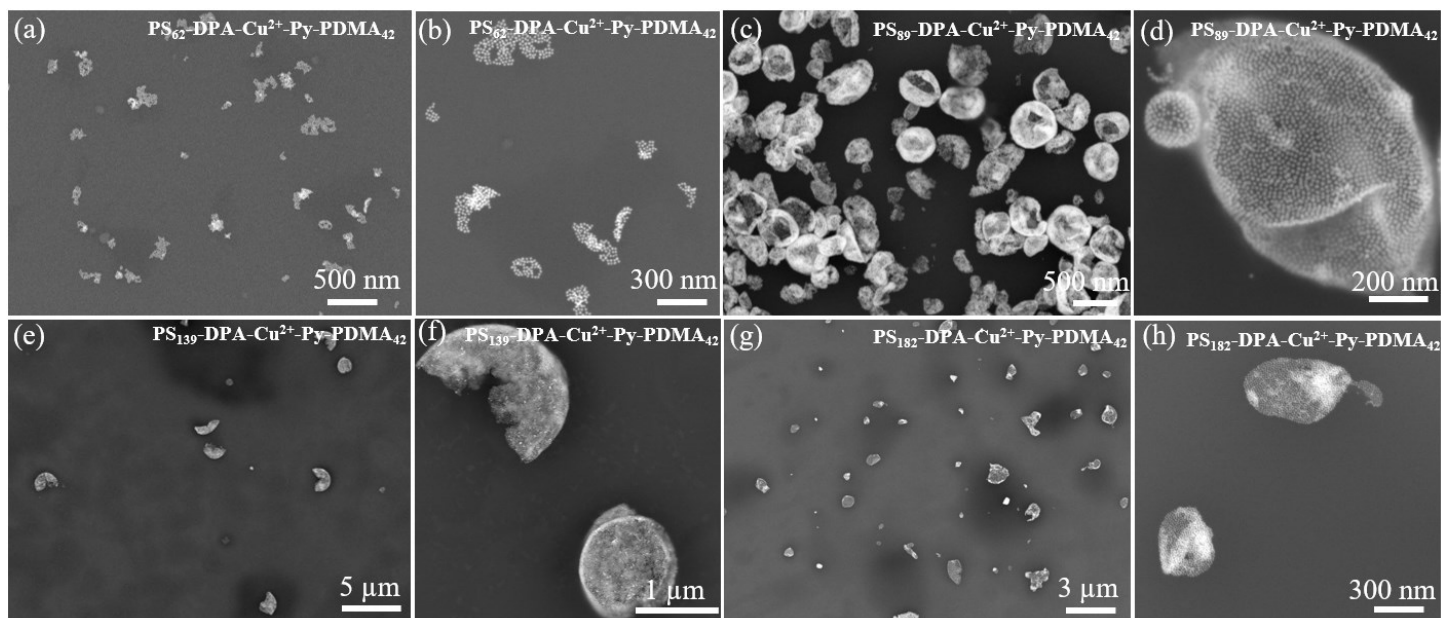


Figure S15. Represent SEM images to show the (a) (b) fractal particle assemblies were assembled from PGNPs with PS₆₂-DPA-Cu²⁺-Py-PDMA₄₂, (c) (d) vesicles were assembled from PGNPs with PS₈₉-DPA-Cu²⁺-Py-PDMA₄₂, (e) (f) PS₁₃₉-DPA-Cu²⁺-Py-PDMA₄₂, and (g) (h) layer assemblies from PGNPs with PS₁₈₂-DPA-Cu²⁺-Py-PDMA₄₂.

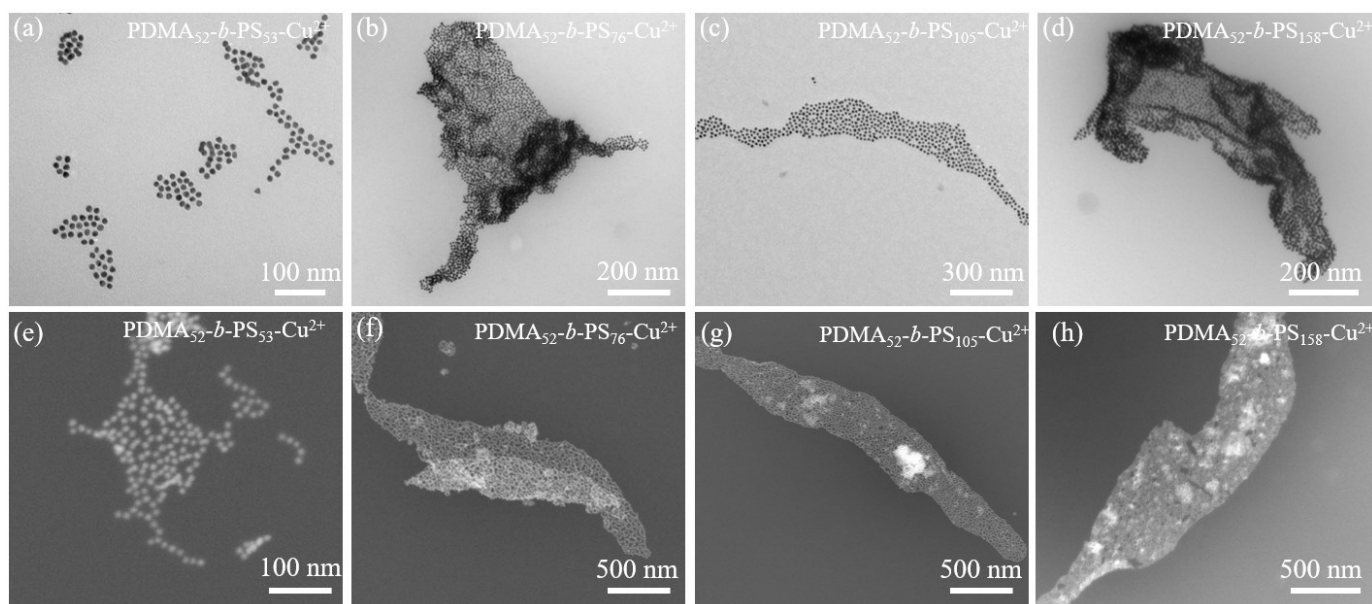


Figure S16. Represent TEM and SEM images to show fractal particle assemblies were assembled from PGNPs with (a) and (e) PDMA₅₂-*b*-PS₅₃-Cu²⁺; (b) and (f) PDMA₅₂-*b*-PS₇₆-Cu²⁺; (c) and (g) PDMA₅₂-*b*-PS₁₀₅-Cu²⁺; (d) and (h) PDMA₅₂-*b*-PS₁₅₈-Cu²⁺.

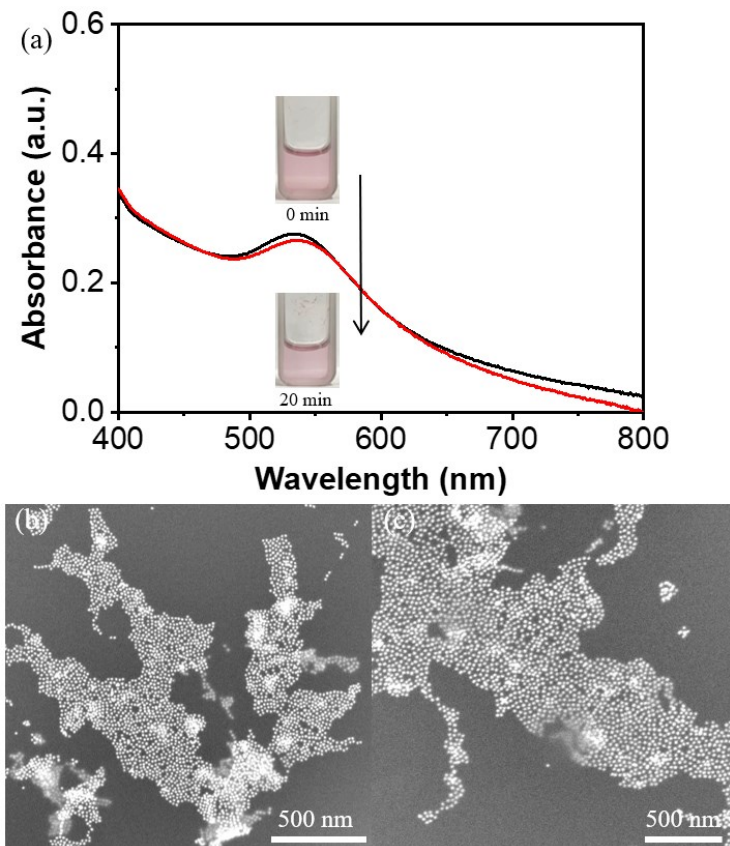


Figure S17. (a) UV-vis spectra to show the plasmonic peak changes of the assemblies from PGNPs with PDMA₅₂-*b*-PS₁₅₈-Cu²⁺ before (black) and after (red) in addition of 10 μ L of 1 mM HCl aqueous solution to 1 mL of solution after 20 mins. And the representative SEM images to show the morphology changes (b) before and (c) after the addition of HCl.

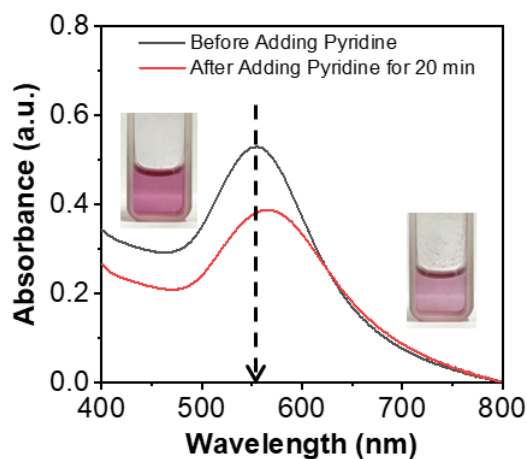


Figure S18. UV-vis spectra to show the plasmonic peak changes of the assemblies from PS₁₈₂-DPA-Cu²⁺-Py-PDMA₄₂ before (black) and after (red) when adding 5 μ L of pyridine to 1 mL of solution after 20 min.

Fitting Model for scattering results

Scattering intensity, $I(q)$, of a particulate system can be expressed by the multiplication of volumetric concentration, c_{lp} , a contrast factor, $\Delta\rho^2$, form factor $P(q)$ and a structure factor $S(q)$ as

$$I(q) \propto c_{lp} \cdot \Delta\rho^2 \cdot P(q) \cdot S(q)$$

For SAXS data, spherical model and Hardsphere (HS) model were used as the form factor and structure factor, respectively.[1] In addition, the power law was also used to describe the slope at the low q region. The best fitting procedure was performed using SasView.

Spherical model (Form factor).

The intensity of spherical model can be expressed

$$I(q) = \frac{scale}{V} \left[3V(\rho - \rho_s) \cdot \frac{\sin(QR) - QR\cos(QR)}{(QR)^3} \right]^2 + background$$

where V is the volume of a particle, r is the radius of sphere. ρ and ρ_s are the scattering length density (SLD) of particles and solvent, respectively.

Hard-sphere model (structure factor)

This model is to describe the interparticle structure factor for spherical particles interacting through hard sphere interactions. The hard-sphere model uses the Percus-Yevick closure where the interparticle potential is

$$U(r) = \begin{cases} \infty & r < 2R \\ 0 & r \geq 2R \end{cases}$$

where r is the distance from the center of the sphere of a radius R

Power Law

We utilized this model to describe the slope in the low q region. The scattering intensity, $I(q)$, can be expressed as

$$I(q) = scale \cdot q^{-n} + background$$

where n is the power law exponent.

References

[1] A. Guinier, G. Fournet, K.L. Yudowitch, Small-angle scattering of X-rays, 1955.