Supporting Information for:

Ordered Gold Nanoparticle Arrays Obtained with Supramolecular Block Copolymers

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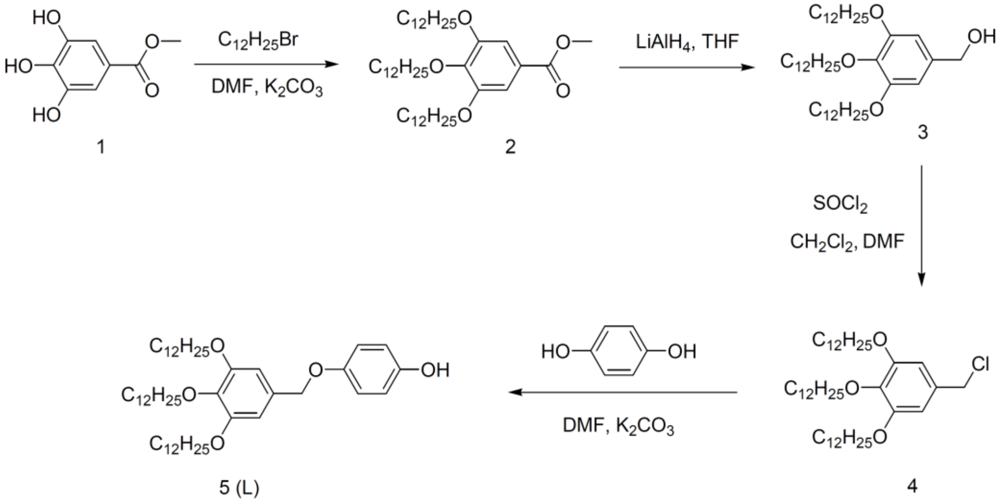
Contents

Synthesis of Small Molecule L

The small molecule L was prepared following the synthetic route shown in Scheme S1.

Scheme S1. Synthetic Route for the Preparation of L



Preparation of 2. Compound 1 (6.00 g, 32.58 mmol), potassium carbonate (15.00 g, 108.53 mmol), 1-bromododecane (30.00 g, 120.37 mmol), and 150 mL of *N*,*N*-dimethylformamide (DMF) were mixed together. The resulting suspension was stirred and heated to 70 ^{o}C under a nitrogen atmosphere for 24 h. The mixture was then cooled down to ambient temperature and filtered. The solvent was removed under vacuum. The crude product was purified by silica gel column chromatography with ethyl acetate/petroleum ether (1:30, v:v) as eluent to yield 17.59 g (78.34%) of 2 as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.96 (t, 9H, $\mathit{CH_3}CH_2$), 1.27-1.31 (m, 54H, $CH_2\mathit{CH_2}CH_2$), 1.71 (m, 6H, $OCH_2\mathit{CH_2}$), 3.88 (s, 3H, CH_3O), 3.94 (t, 6H, $CH_2\mathit{CH_2}O$), 6.93 (d, 2H, Ar-H). MS (LR-ESI): m/z 688.6 $[M]^+$.

Preparation of 3. Compound 2 (17.00 g, 24.69 mmol) was dissolved in 150 mL of tetrahydrofuran (THF), to which $LiAlH_4$ (1.41 g, 37.03 mmol) in 5 mL of THF was added drop-wise with vigorous stirring at ambient temperature under a nitrogen atmosphere. The mixture was stirred at ambient temperature for 1 h and filtered, and the solution was washed with deionized water. The solvent was removed under vacuum. Finally, the crude product was purified by silica gel column chromatography with dichloromethane as eluent to yield 3 (14.09 g, 86.41%) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.96 (t, 9H, $\mathit{CH_3}CH_2$), 1.27-1.31 (m, 54H, $CH_2\mathit{CH_2}CH_2$), 1.71 (m, 6H, $OCH_2\mathit{CH_2}$), 2.05 (s, 1H, $CH_2\mathit{OH}$), 3.94 (t, 6H, $CH_2\mathit{CH_2}O$), 4.79 (d, 2H, $\mathit{CH_2}OH$), 6.15 (d, 2H, Ar-H). MS (LR-ESI): m/z 660.6 $[M]^+$.

Preparation of 4. Compound 3 (14.00 g, 21.19 mmol), a few drops of DMF, and 300 mL of dichloromethane were mixed together, and then 0.2 mL of thionyl chloride was added dropwise with vigorous stirring at 0 ^{o}C for 1 h. Potassium carbonate (10.00 g, 72.46 mmol) was added to the reaction solution, and the resultant suspension was stirred at ambient temperature for 2 h. The system was filtered, and the solvent was removed under vacuum. The crude product was dried in vacuum to yield 13.25 g (92.07%) of 4 as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.96 (t, 9H, $\mathit{CH_3}CH_2$), 1.27-1.31 (m, 54H, $CH_2\mathit{CH_2}CH_2$), 1.71 (m, 6H, $OCH_2\mathit{CH_2}$), 3.94 (t, 6H, $CH_2\mathit{CH_2}O$), 4.64 (s, 2H, $\mathit{CH_2}Cl$), 6.22 (s, 2H, Ar-H). MS (LR-ESI): m/z 678.6 $[M]^+$.

Preparation of 5. Compound 4 (13.00 g, 19.16 mmol), 1,4-dihydroxybenzene (3.79 g, 34.49 mmol), potassium carbonate (10.00 g, 72.46 mmol), and 200 mL of acetone were mixed together. The resulting suspension was gently stirred and refluxed under a nitrogen atmosphere for 24 h. The mixture was then cooled to ambient temperature and filtered. The solvent was removed under vacuum. The crude product was purified by silica gel column chromatography with dichloromethane as eluent to yield 8.38 g (58.09%) of 5 as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.96 (t, 9H, $\mathit{CH_3}CH_2$), 1.27-1.31 (m, 54H, $CH_2\mathit{CH_2}CH_2$), 1.71 (m, 6H, $OCH_2\mathit{CH_2}$), 3.94 (t, 6H, $CH_2\mathit{CH_2}O$), 5.20 (s, 1H, Ar-OH), 5.20 (s, 2H, Ar-$\mathit{CH_2}O$), 6.15 (s, 2H, Ar-H) , 6.59-6.63 (d, 4H, Ar-H). MS (LR-ESI): m/z 753.64 $[M]^+$. Anal. Calcd. For $C_{49}H_{84}O_5$: C 78.14, H 11.24. Found: C 77.84, H 11.42.

Syntheses of *n*-Alkyl-Protected Gold Nanoparticles

A hydrogen tetrachloroaurate aqueous solution (50 mL, 145 mM) was mixed with a solution of methyltrioctylammonium bromide in toluene (50 mL, 125 mM). The mixture was vigorously stirred until discoloration of the aqueous layer. Dodecanethiol (l.20 g, 5.97 mmol) was then added, and the mixture was stirred for 20 min. The toluene solution obtained was reduced with a freshly prepared aqueous solution of sodium borohydride (50 mL, 400 mM). After the mixture was further stirred for 3 h, the organic phase was separated, concentrated to 5 mL in a rotary evaporator, and mixed with 200 mL of ethanol. The mixture was kept at −4 °C for 12 h. The dark brown precipitate was sonicated for 1 min and centrifuged (5 min, 13 000 rpm). Then the precipitate was dissolved in a small amount of toluene (5 mL), precipitated with ethanol (200 mL), and centrifuged. Such a procedure was repeated until no trace of excess thiol was detected in the system, as determined by ^{1}H NMR and thin layer chromatography.

Calculation of Volume Fractions

Weight fractions of gold and the alkyl thoil ligand were measured by thermal gravimetric analysis (TGA). The weight fractions of the NPs were converted into volume fractions using the densities of PS (1.05 g/cm^3), P4VP (1.15 g/cm^3), gold (19.30 g/cm^3), 1-dodecanethiol (0.85 g/cm^3), and L (1.00 g/cm^3). The volume fraction of the nanoparticle in the hybrid is defined as □$\phi_{\mathrm{NP}} = V_{\mathrm{NP}}/(V_{\mathrm{NP}} + V_{\mathrm{PS}\text{-}b\text{-}\mathrm{P4VP(L)}n})$, where V_{NP} and $V_{\mathrm{PS}\text{-}b\text{-}\mathrm{P4VP(L)}n}$ are the volumes of the nanoparticle and the supramolecular block copolymer, respectively.

Results and Discussion

Table 1. Volume Fractions of Materials Used

L/4VP	0.2	0.5	1.0	2.0	2.5	3.0
$f_{\mathrm{P4VP(L)}n}$ (vol%)	25	40	54	69	73	77
$f_{\mathrm{Au/P4VP(L)}n}$ (vol%)	29	42	56	71	75	78

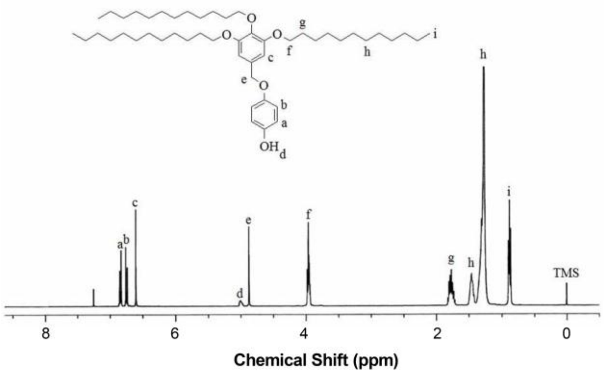


Figure S1. ^{1}H NMR spectrum of small molecule L.

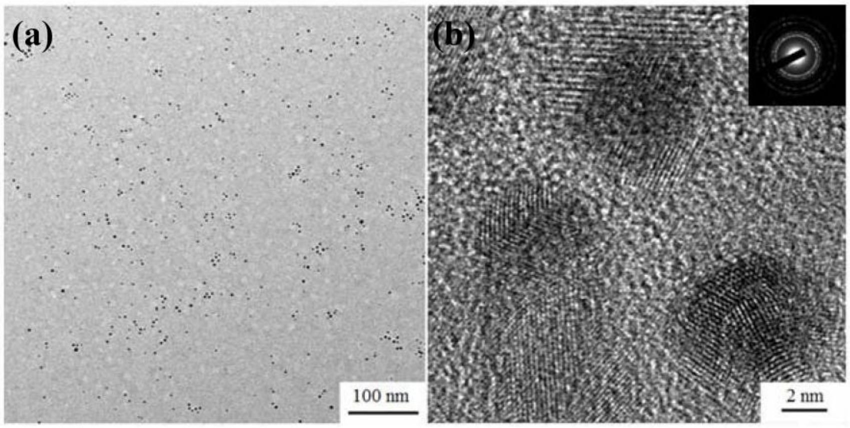


Figure S2. TEM micrographs of *n*-alkyl-protected Au NPs (scale bars: a, 100 nm; b, 2 nm).

FT-IR spectroscopy provides evidence for the formation of hydrogen bonds between L and pyridine fragments of P4VP. As shown in Figure S3, pure P4VP has absorption bands at 1597, 1415, and 993 cm^{-1}. As n increases (from 0.2 to 2.0), these bands shift to higher frequencies, indicating the formation of hydrogen bonds. However, it is difficult to calculate the actual degree of complexation based on the FT-IR data because of the nearby absorption bands of pure L, which is similar to those reported in literature for hydrogen-bonded P4VP(PDP).[1, 2] When $n > 2.0$, the spectra are different, which can be attributed to the overlapping of the hydrogen-bonding bands with those of the L molecule due to the largely excessive amount of L.

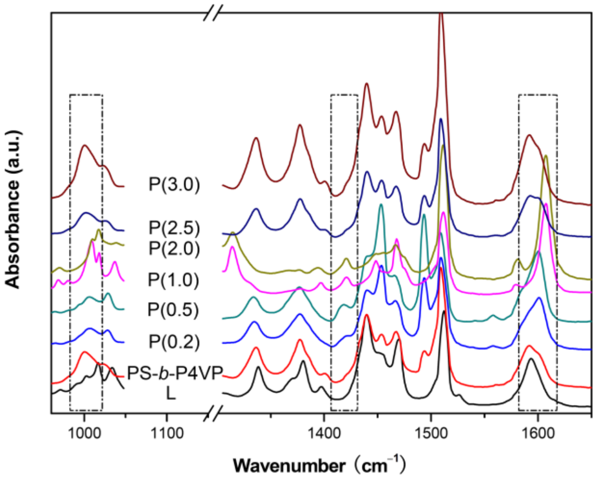


Figure S3. FT-IR spectra of PS-*b*-P4VP, L, and PS-*b*-P4VP(L)$_n$.

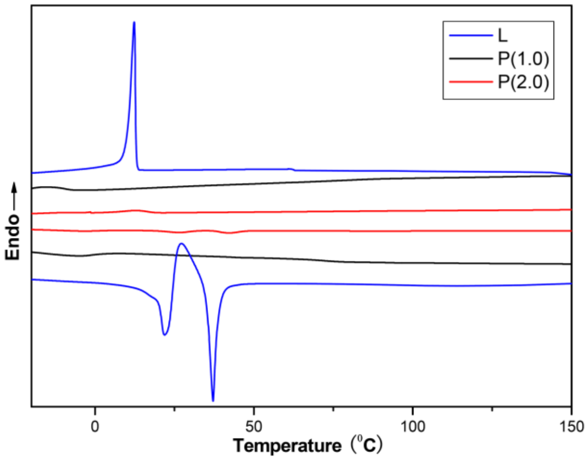


Figure S4. DSC thermograms of L and PS-*b*-P4VP(L)$_n$ (n = 1.0 and 2.0) during the first cooling and the second heating processes at a rate of 5 °C/min under a N_2 atmosphere.

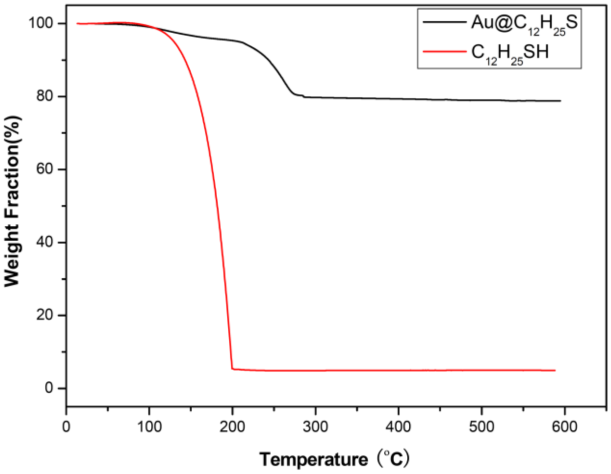


Figure S5. TGA profiles of n-alkyl-protected Au NPs and alkyl thiol at a rate of 10 ℃/min under a N_2 atmosphere.

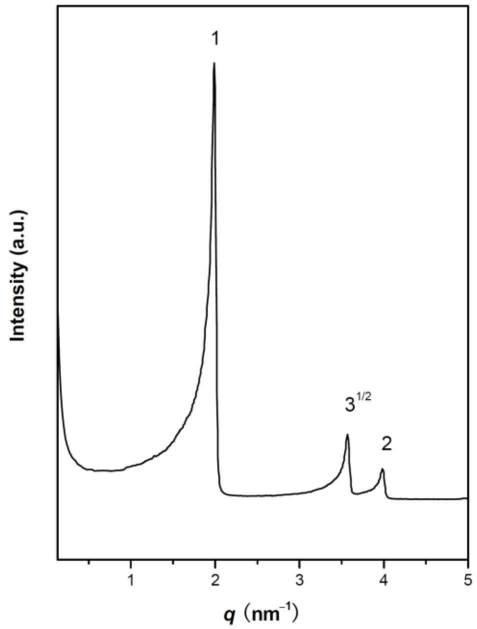


Figure S6. SAXS profile of L.

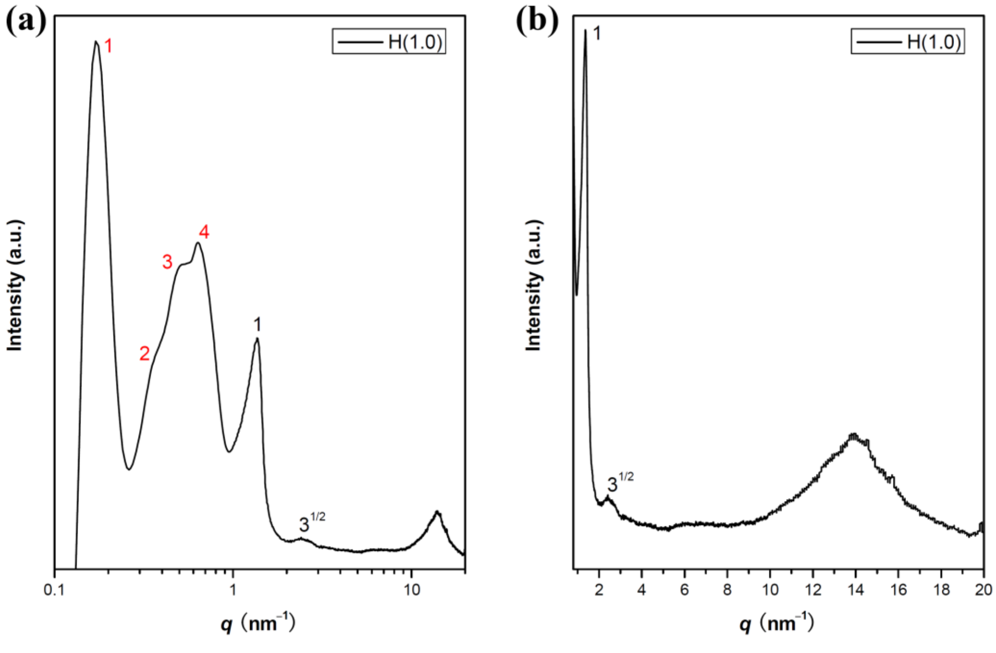


Figure S7. SAXS (log-log plot) profile in a large range (a) and SAXS profile in the wide-angle range (b) of the as-cast film of Au/PS-*b*-P4VP(L)$_{1.0}$.

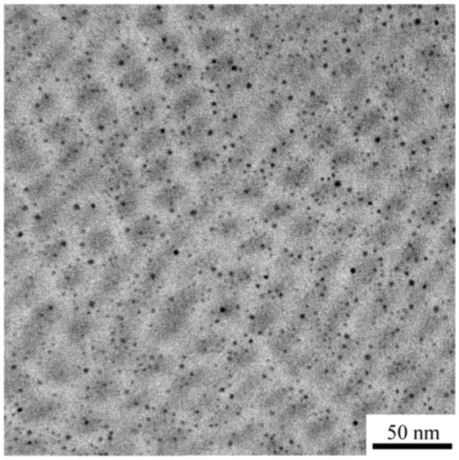


Figure S8. TEM micrograph of a thin film of the Au/PS-*b*-P4VP blend stained with I_2.

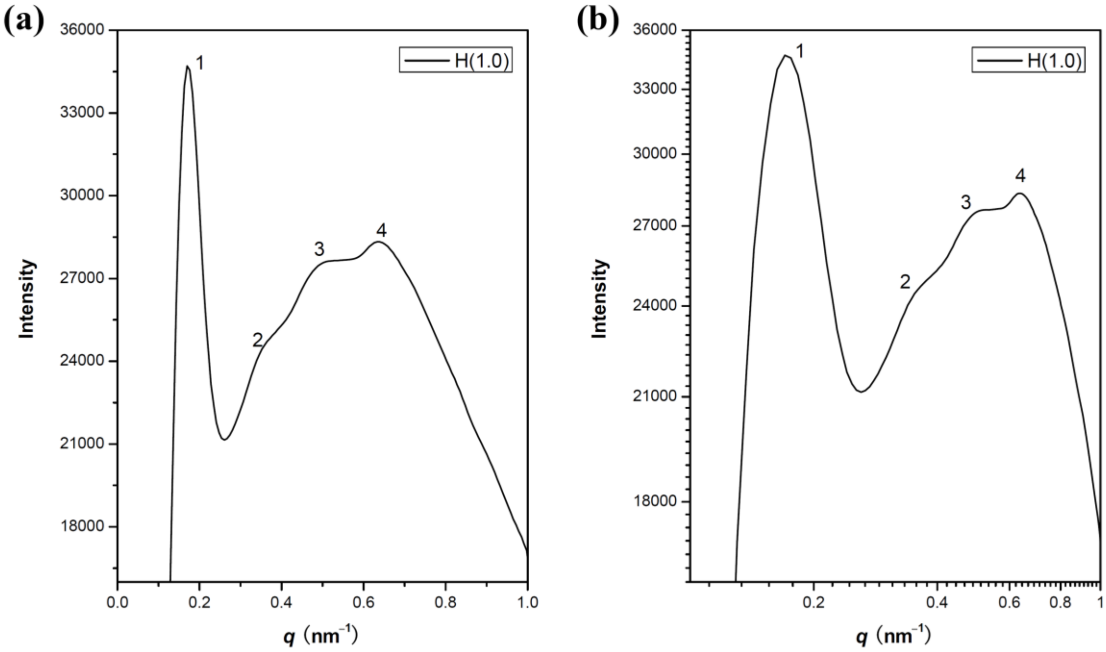


Figure S9. SAXS profiles (a: regular plot; b: log-log plot) of the as-cast film of Au/PS-*b*-P4VP(L)$_{1.0}$.

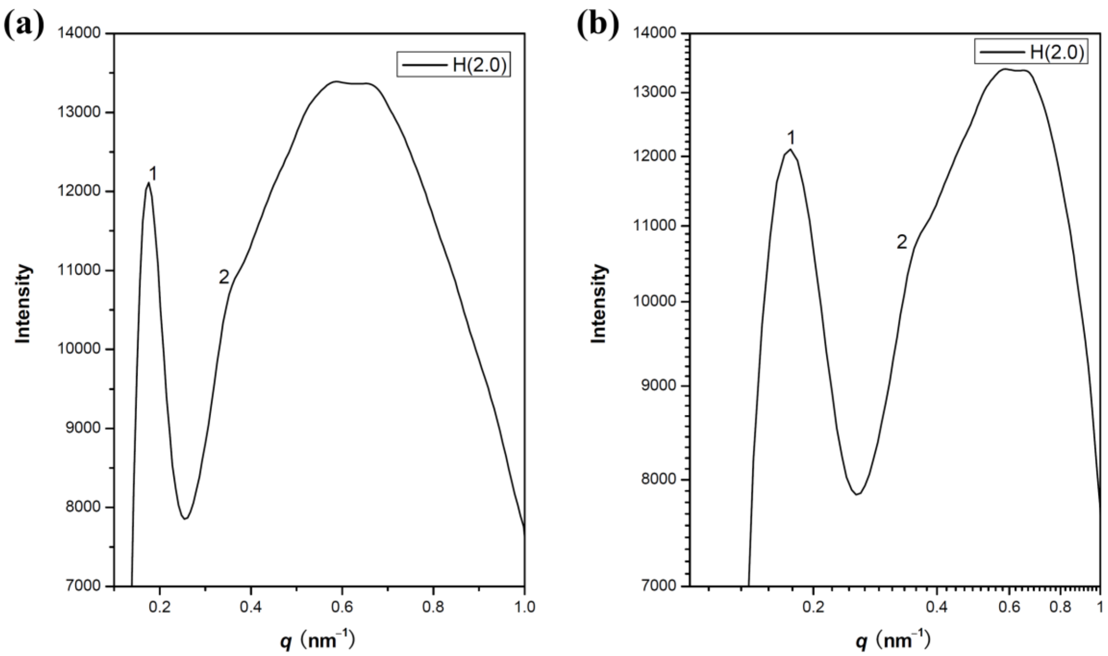


Figure S10. SAXS profiles (a: regular plot; b: log-log plot) of the as-cast film of Au/PS-*b*-P4VP(L)$_{2.0}$.

References:

1. J. Y. Lee, P. C. Painter and M. M. Coleman, *Macromolecules*, 1988, **21**, 954-960.
2. J. Ruokolainen, G. Ten Brinke, O. Ikkala, M. Torkkeli and R. Serimaa, *Macromolecules*, 1996, **29**, 3409-3415.