Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Controlling the Orientations of Gold Nanorods Inside Highly Packed 2D Arrays

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Synthesis of gold nanorods

Seed-mediated growth technique was used to prepare gold nanorods (AuNRs). The seeds were prepared as fellow, in a 30 mL vial, 2.5 mL of a 1.0 mM aqueous solution of $HAuCl_4$ was mixed with 5 mL of a 0.2 M aqueous solution of cetyltrimethylammonium bromide (CTAB). Then, under stirring, 0.6 mL of a 10 mM ice-cold sodium borohydride solution was added. The gold seed particles were formed after 5 minutes stirring. The growth solution was prepared by mixing 200 mL of a 1.0 mM $HAuCl_4$ aqueous solution with 200 mL of 0.2 M CTAB in a 500 mL flask, then 9 mL of a 4.0 mM $AgNO_3$ solution was added followed by 2.8 mL of 78.8 mM ascorbic acid. AuNRs were obtained by adding 320 μL seed solution to the growth solution and left to react overnight.

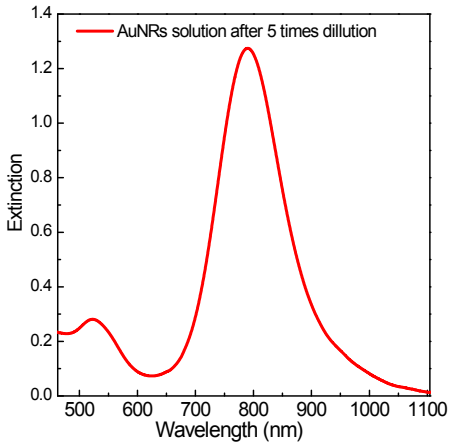

Figure S1 LSPR spectrum of gold nanorods solution dispersed in chloroform after 5 times dilution. The concentration of AuNRs is 3.24 nM (Extinction coefficient of the AuNRs is taken to be ~$3x10^{11}$ nanorod/mL).

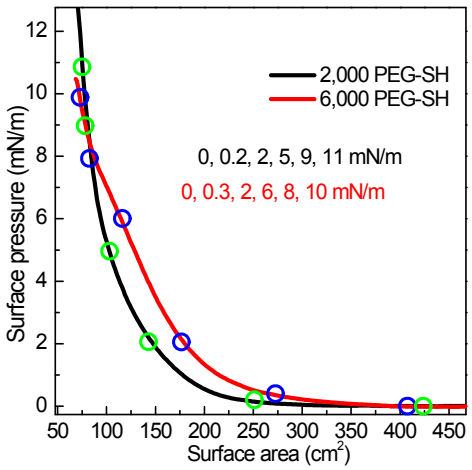

Figure S2. LB isotherm for gold nanorods assembled into monolayer on the top of water sub layer of the Langmuir-Blodgett trough: Black curve is for the nanorods functionalized with short chain 2K PEG. Red curve is for the gold nanorods functionalized with the long chain 6K PEG. Three different phases (gaseous, liquid condensed, and solid) was observed in case of the gold nanorods assembly when functionalized with either the long or short chain PEG. The phase transitions in case of the 6K PEG is steeper than in case of 2k PEG. Red and blue circles in the curves are the surface pressures measured during the transfer of the 2D arrays to the surface of the substrate.

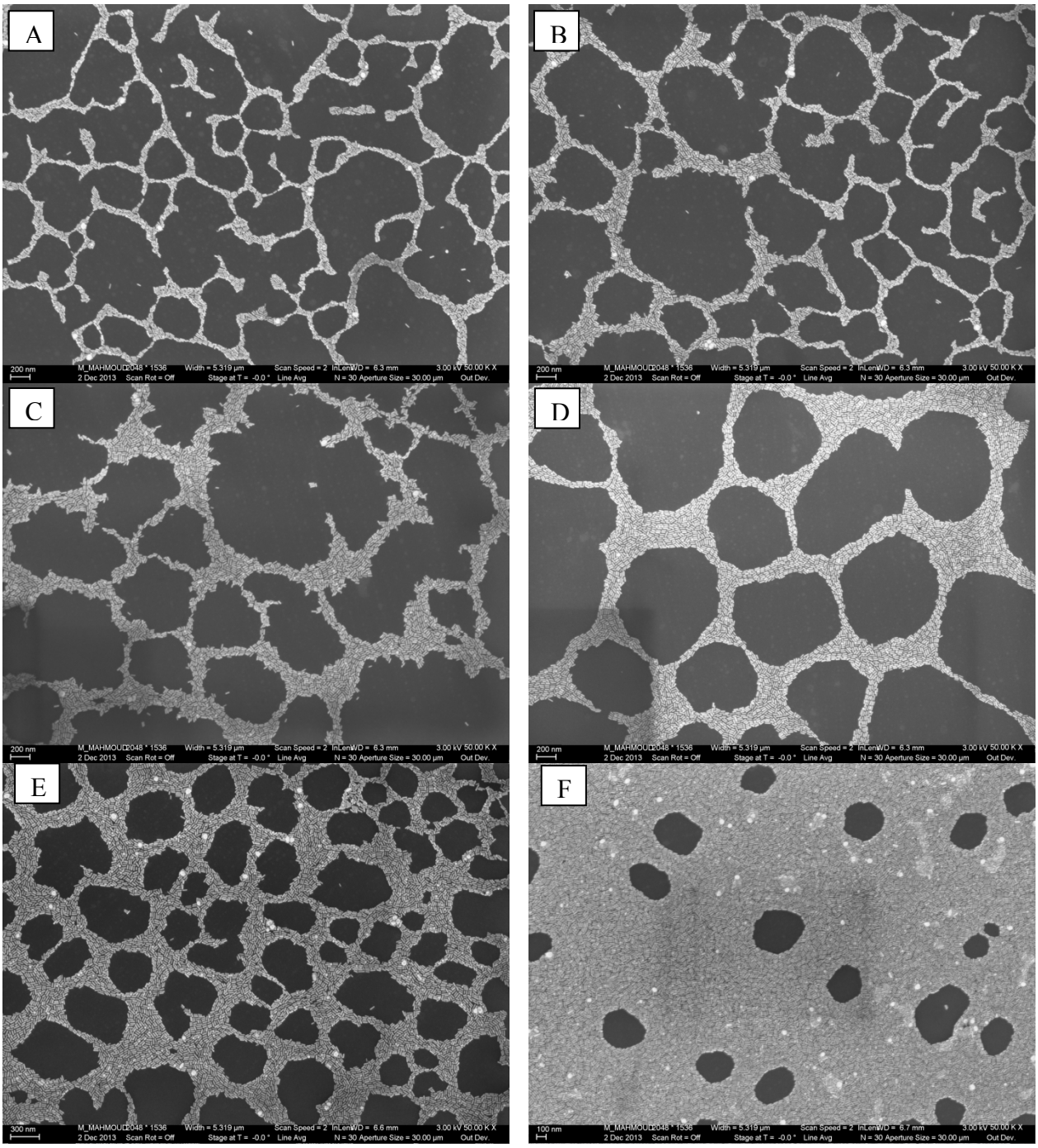

Figure S3. Low magnification SEM images of 2D arrays of gold nanorods fabricated by Langmuir-Blodgett technique on the surface of silicon substrate when nanorods are functionalized with 6K thiolated polyethylene glycol. The nanorods were transferred to the surface of silicon substrate at surface pressure of: A) 0 mN/m, B) 0.3 mN/m, C) 2 mN/m, D) 6 mN/m, E) 8 mN/m, and F) 10 mN/m.

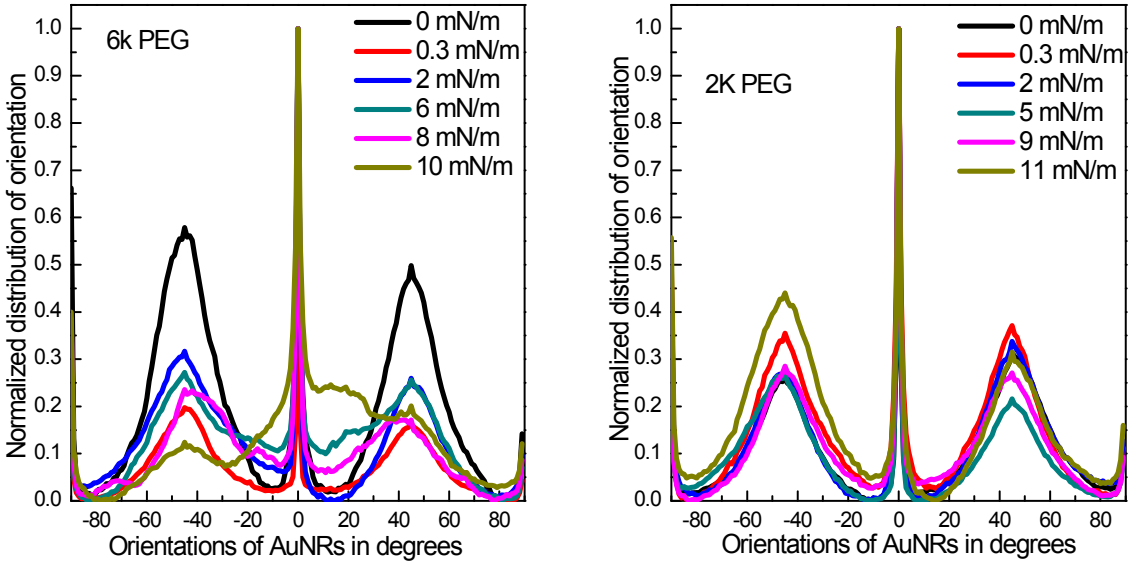

Figure S4 analysis of the distribution of the angles of orientation of AuNRs forming the 2D arrays fabricated at different LB surface pressures: A) the AuNRs are functionalized with 6k PEG, B) The AuNRs are functionalized with 2K PEG. The calculation carried out on the SEM images in Figure 2 and 3 using the image J.

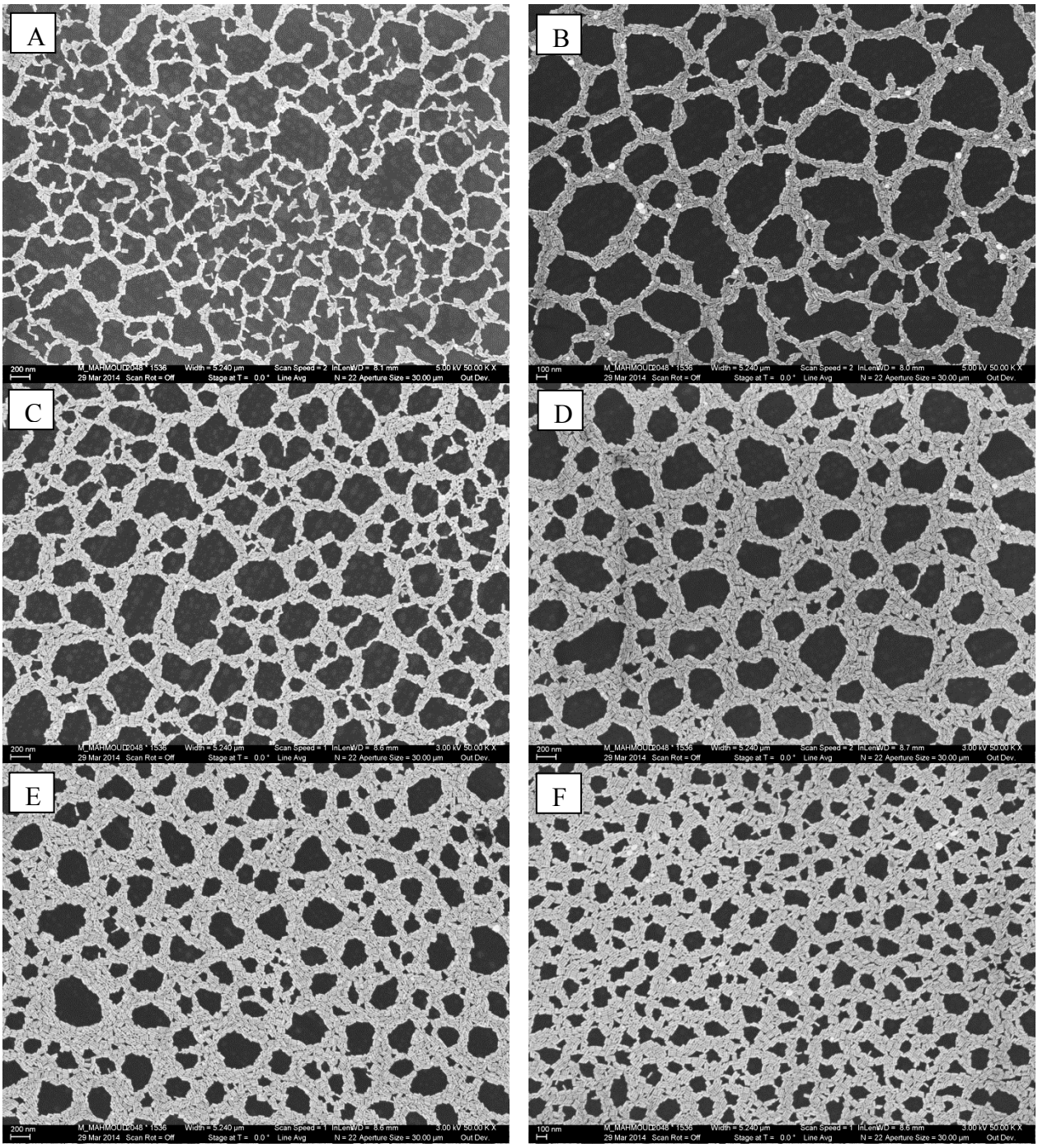

Figure S5. Low magnification SEM images of Langmuir-Blodgett 2D arrays of gold nanorods functionalized with short chain thiolated polyethylene glycol (M_n=2,000) polymers and assembled on the surface of silicon substrate at surface pressure of: A) 0 mN/m, B) 0.3 mN/m, C) 2 mN/m, D) 5 mN/m, E) 9 mN/m, and F) 11 mN/m.

Calculation of the potential energy of a pair of gold nanorods

I- van der Waals potential energy

Due to the presence of charges within the gold nanorods and the PEG bound to their surfaces, a van der Waals (vdW) attractive force is formed between the rods; this attractive force generates vdW potential. For any neighboring pair gold nanorods, aligned either end-to-end (EE) or side-by-side (SS), the following vdW forces is expected to form: 1) between the gold surfaces, 2) between the PEG bound to one AuNR and the surface of the other AuNR, 3) between the PEG chains, and finally 4) between the surface of water and both the surface of gold surface and polymer (solvation force). The vdW potentials were calculated for the AuNRs pair when aligned SS and EE as follow.

I.A.1. End-to-end assembly

The end-to-end assembly was assumed to be as the interaction between two nanospheres of diameter equal to the width of AuNR.[1] Figure S4 shows the schematic diagram for a pair of gold nanorods (red color) aligned EE and coated with PEG polymer (blue color).

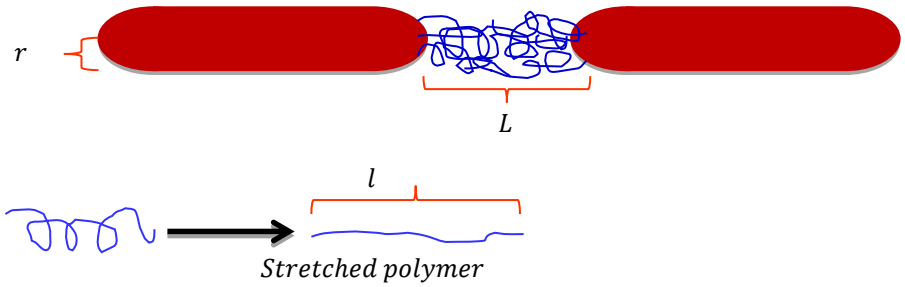

Figure S6. Schematic diagram of pair of AuNRs functionalized with PEG polymer aligned end-to-end and undergoing vdW interaction.

I.A.1.1. van der Waals force between the gold surfaces (EE alignment):

Hamaker integral approximation[2] was used to calculate the van der Walls potential energy between two AuNRs from equation 1:

$$U_g = \frac{-A_g r}{24L} \qquad (1)$$

where A_g is the Hamaker coefficient which is $4x10^{-19}$ for gold in air medium[3], L is the separation distance between the two gold nanorods, *r* is radius of the nanorod.

I.A.1.2. van der Waals potential energy between polymer chains (EE alignment):

The Hamaker integral approximation is also used to calculate the potential energy of the vdW force between the polymer chains as in equation 2:

$$U_P = \frac{-A_P l}{24L} \qquad (2)$$

where A_p is the Hamaker coefficient of polyethylene glycol which is $6x10^{-20}$ in air[4], *l* is half of the length of the stretched polymer chain. The length of the stretched polymer is calculated from equation 3:

$$Length\ of\ the\ stretched\ polymer = (\frac{MWt\ of\ the\ polymer}{MWt\ of\ each\ repearing\ unit})X\ length\ of each\ unit \qquad (3)$$

The molecular weight of each repeated (-CH_2-CH_2-O-) unit is 44 g/mole, the bond lengths of the C-O and C-C bonds are 0.145 and 0.15 nm, respectively. The length of the repeating monomer will be 0.44 nm. The length of the polymer is calculated from the following equation:

The length of the stretched PEG (6,000) is 60 nm, while for the 2,000 is 20 nm.

I.A.1.3. van der Waals force between polymer and gold surface (EE alignment):

The potential energy of the van der Waals force is calculated from equation 4:

$$U_{gp} = \frac{-A_{gp} r}{24L} \qquad (4)$$

where A_{gp} is the Hamaker constants of PEG-gold interface. For different materials, Hamaker constants can be estimated from equation 5

$$A_{gp} = \sqrt{A_g . A_p} \quad (5)$$

A_{gp} is the average of Hamaker of PEG and gold ($1.55x10^{-19}$ J).

I.A.1.4. van der Waals potential energy of the interaction of water surface and both the polymer and gold surfaces (EE alignment):

For each individual AuNR, vdW potential energy for the interaction of the gold surface and the PEG organized around the AuNR in brush structure; with the surface water sub layer of the LB trough is the summation of the vdW potential energy of the interaction of the polymer with the water surface and the vdW potential energy of AuNR-water surface interaction as shown in equation 6:

$$U_w = \frac{-A_g r}{24L} + \frac{-A_p l}{24L} \qquad (6)$$

A_g in this case will be $(3\times10^{-19}J)^3$ and A_p will be $(7.2\times10^{-20}J)^5$

I.B.1. Side-by-side assembly

Similar calculations which carried out for the end-to-end were repeated for the side-by-side alignment of the nanorods pair after modifying the equations to fit the change in the geometry. The schematic diagram of the side-by-side assembly of a pair of AuNRs is shown in Figure S5

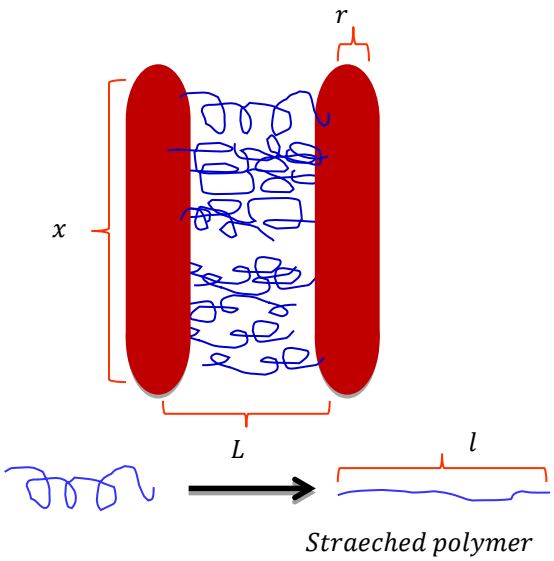

Figure S7. Schematic diagram of a pair of AuNRs functionalized with PEG polymer aligned side-by-side and undergoing vdW interaction.

I.B.1.1. van der Waals force between the gold surfaces (SS alignment):

The vdW potential energy was calculated for the side-by-side alignment of a pair of AuNRs by the Hamaker integral approximation[2], equation 7 was used to calculate the potential energy between the gold surfaces of AuNR pairs when aligned side-by-side:

$$U_g = \frac{-A_g x.r^{1/2}}{24L^{3/2}} \qquad (7)$$

where *x* is the length of nanorod, which is 54 nm.

I.B.1.2. van der Waals potential energy between polymer chains (SS alignment):

Equation 8 was used to calculate the vdW potential energy between the polymer chains bound to the surface of the nanorods:

$$U_g = \frac{-A_g x.l^{1/2}}{24L^{3/2}} \qquad (8)$$

I.B.1.3. van der Waals force between polymer and gold (SS alignment):

For calculation of the potential energy of the vdW force between the polymer chains functionalized with each AuNR and the surface of gold of the other rod was determined from equation 9:

$$U_{gp} = \frac{-A_{gp} x.r^{1/2}}{24L^{3/2}} \qquad (9)$$

I.B.1.4. van der Waals potential energy of the interaction of water surface with both the polymer and gold surfaces (SS alignment):

The potential energy resulting from the vdW force between the gold surface and polymer brush with surface of water surface was calculated using equation 10:

$$U_w = \frac{-A_g x.r^{1/2}}{24L^{3/2}} + \frac{-A_p x.rl^{1/2}}{24L^{3/2}} \qquad (10)$$

Total van der Waals force

The overall vdW potential energy is the summation of the individual vdW potentials (equation 11) calculated from equations (1-10), the vdW potential energy diagrams for a pair of AuNRs aligned either the SS or EE are shown in Figure 3

$$U_{vdW} = U_g + U_p + U_{gp} + U_w \quad (11)$$

II. Steric repulsion

Strong steric repulsion force is generated between the nanorods due to the interaction of the PEG polymers bound to their surface. Equation 12 was used to calculate the potential energy of the steric repulsion between a pair of AuNRs aligned end-to-end.[6] For the side-by-side assembly the steric potential in equation 12 was multiplied by twice of aspect ratio of the AuNRs.[1]

$$U_{steric} = \frac{\pi^3 rkT\Gamma h^3}{6Nb^2}\left[-ln\mu - \frac{9}{5}(1-\mu) + \frac{1}{3}(1-\mu^3) - \frac{1}{30}(1-\mu^6)\right] \quad (12)$$

where $h \sim N(\Gamma b^5)^{1/3}$ $\mu = \frac{L}{2h}$

where Kuhn length of PEG (b) is 1.1 nm[7]; Γ is the grafting density (number of polymer chain per nm^2) which is 0.1 PEG chain/nm^2 , N is number of Kuhn segments which is the ratio of the

length of the stretched polymer and the Kuhn length,[8] the value of N is 54 and 18 for 6K and 2K PEG respectively. h is Flory radius (an estimated size of the polymer coil), the value of h is 29 and 10 nm for 6K and 2K PEG respectively. T is the absolute temperature (300 k); *K* is Boltzmann constant (1.38×10^{-23} $J.K^{-1}$). Figure S6 clarifies meaning of these constants.

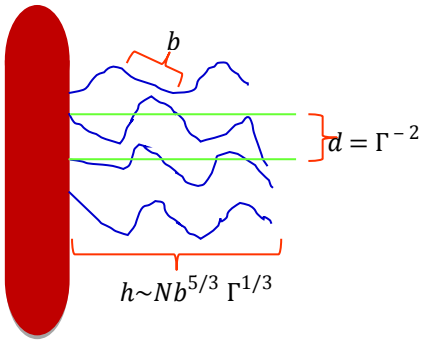

Figure S8. Schematic diagram of the PEG (blue color) functionalized with the surface of gold nanorod (red color).

III. Depletion force of the interparticle micelles [9]

The diffusion of the nanomicelles from the area between a pair of AuNRs applies osmotic pressure on the nanoparticles pair and generates depletion potential. This depletion force balances the strong steric repulsion between the polymer brushes.

III.A. Depletion force of the interparticle micelles for the end-to-end aligned AuNRs:

The depletion potential of AuNR pair assembled end-to-end was calculated from the equation (13):[10,11]

$$U_{depletion} = -\frac{\pi P}{4}\left[\frac{1}{3}(d-L)^2.(6r+2d+L)\right] \quad (13)$$

Where *d* is the diameter of the polymer micelles and is found to be respectively 31 and 88.9 nm for the 2K PEG and 6K PEG as calculated from the Stokes-Einstein equation. P is the osmotic pressure generated by the micelles, which can be calculated from (P=n.RT), R is the universal

gas constant (8.31 J.K-1.mole^{-1}), n is the number of micelles, where n is the ratio between the concentration of PEG and the aggregations number. The concentration of PEG is 0.5 mM, and the aggregation number is ~ 50. Schematic diagram showing the depletion force applied of a pair of AuNR assembled end-to-end is in Figure S7

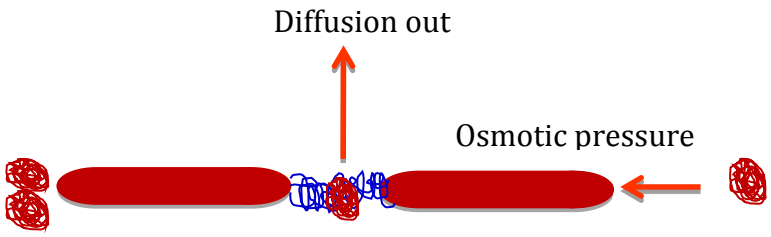

Figure S9. Schematic diagram showing the depletion force applied of a pair of AuNR assembled end-to-end

III.B. Depletion force of the interparticle micelles for side-by-side aligned AuNRs:

The depletion potential for the side-by-side alignment of the AuNRs (see the schematic diagram in Figure S8) was calculated from equation (14).[10,11]

$$U_{depletion} = -\frac{x.P}{2}\left[L\sqrt{(2r+d)^2 - L^2} + (2r+d)^2.arccos(\frac{L}{(2r+d)}\right] \quad (14)$$

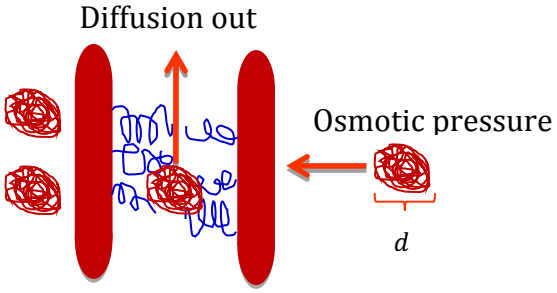

Figure S10. Schematic diagram showing the depletion force applied of a pair of AuNR assembled side-by-side.

Overall potential energy at zero surface pressure:

The overall potential energy generated between a pair of AuNRs was calculated from equation 15 for either side-by-side or end-to-end alignment. In fact this calculation is valid when no external surface pressure is applied by the Langmuir-Blodgett (LB) barrier.

$$U_{Total} = U_{vdW} + U_{depletion} + U_{steric} (15)$$

References

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