Supporting Information

Stepwise Organization of Nanoparticle toward Pickering Emulsion

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Calculation of degree of polymerization (DP).

Molecular weight of VSt is 158, while St is 104. DP of $PVSt_{4.4k}$ is calculated 28. DPs of PS in the samples of $PVSt_{4.4k}$-*b*-$PS_{29.7k}$, $PVSt_{4.4k}$-*b*-$PS_{7.7k}$ and $PVSt_{4.4k}$-*b*-$PS_{5.6k}$ are calculated 286, 74 and 54, respectively.

Calculation of grafting number of the polymer chain on PVSt-*b*-PS@Fe_3O_4 composite NPs.

The weight ratio of polymer to the amine-capped Fe_3O_4 NP in one composite NP is given as: $$\frac{V_0 - V}{V\bar{M}\mathrm{n}} = kN$$

where V_0: the saturation magnetization of the amine-capped Fe_3O_4 NP; V: the saturation magnetization of the composite NP; $\bar{M}_n$: the number average molecular weight of the grafting polymer chain; k: a constant; N: grafting number.

Based on the number average molecular weight of the grafting polymer (**Figure 1a**) and VSM results (**Figure 2d and Figure S2**), the grafting number ratio is calculated as

N_1:N_2:N_3=1:4:10 by using $PVSt_{4.4k}$-*b*-$PS_{29.7k}$, $PVSt_{4.4k}$-*b*-$PS_{7.7k}$ and $PVSt_{4.4k}$-*b*-$PS_{5.6k}$.

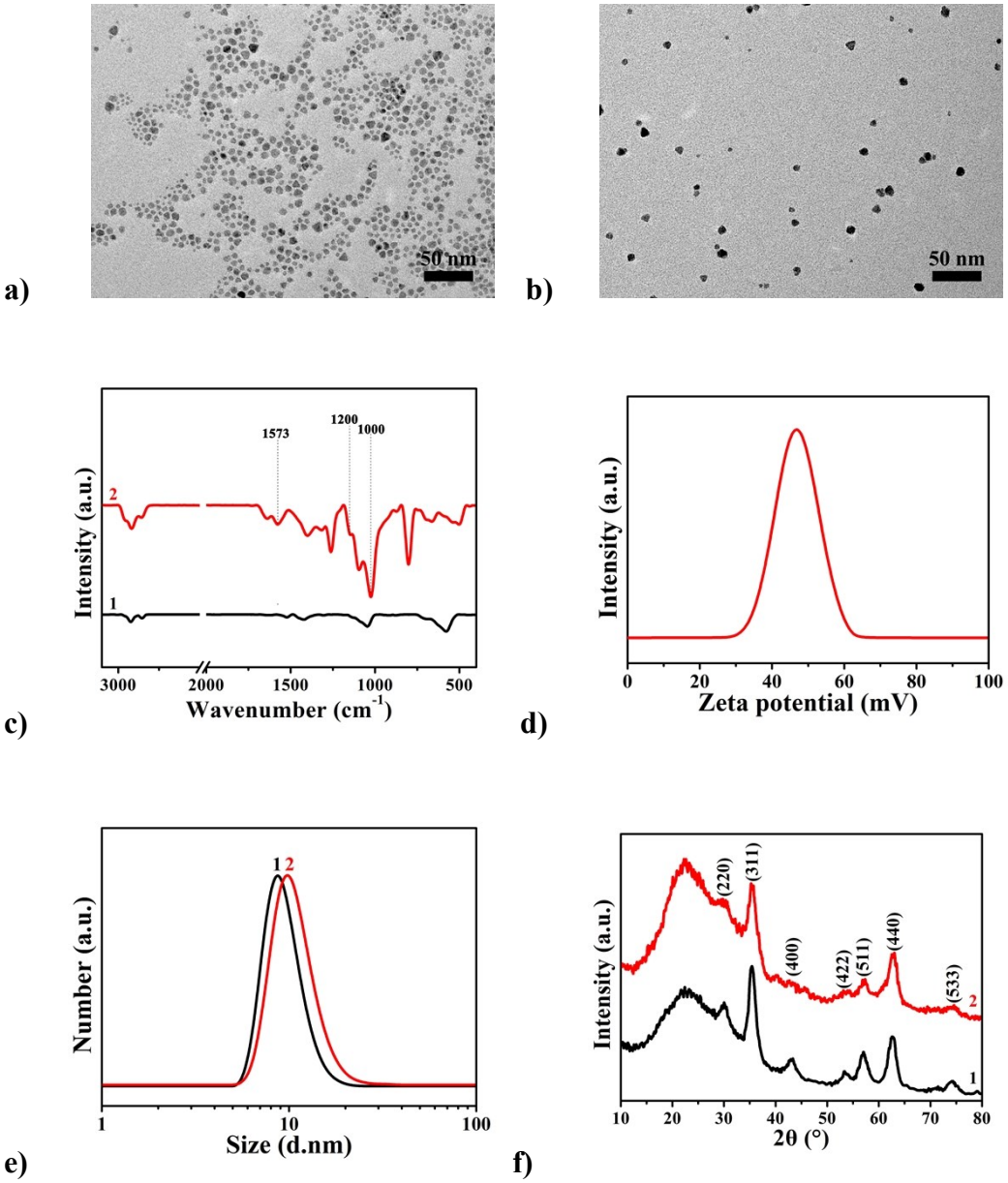

Figure S1. TEM images of (a) the oleic acid capped Fe_3O_4 NP and (b) the amine-capped Fe_3O_4 NP; (c) FT-IR spectra of (1) the oleic acid capped Fe_3O_4 NP and (2) the amine-capped Fe_3O_4 NP; (d) Zeta potential of the amine-capped Fe_3O_4 NP in water; (e) DLS traces of (1) the oleic acid capped Fe_3O_4 NP in toluene and (2) the amine-capped Fe_3O_4 NP in water; (f) XRD patterns of (1) the oleic acid capped Fe_3O_4 NP and (2) the amine-capped Fe_3O_4 NP.

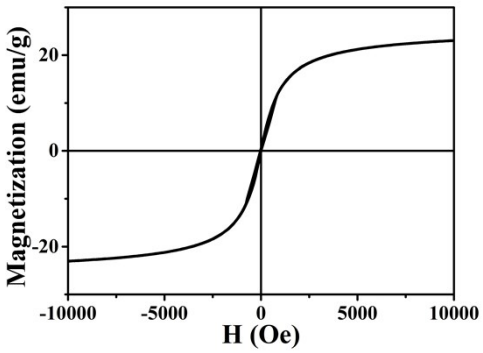

Figure S2. VSM curve of the amine-capped Fe_3O_4 NP.

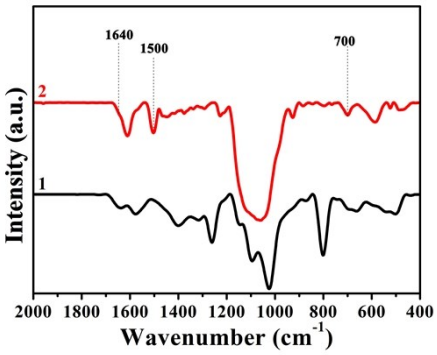

Figure S3. FT-IR spectra of (1) the amine-capped Fe_3O_4 NP and (2) the PVSt-*b*-PS@Fe_3O_4 composite NP.

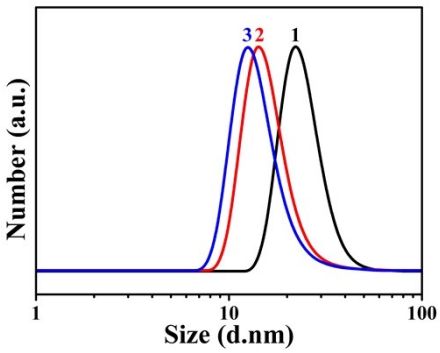

Figure S4. DLS traces of the three composite NPs after grafting varied polymers: (1) $PVSt_{4.4k}$-*b*-$PS_{29.7k}$, (2) $PVSt_{4.4k}$-*b*-$PS_{7.7k}$ and (3) $PVSt_{4.4k}$-*b*-$PS_{5.6k}$. The measurement was performed in dimethyl sulfoxide (DMSO).

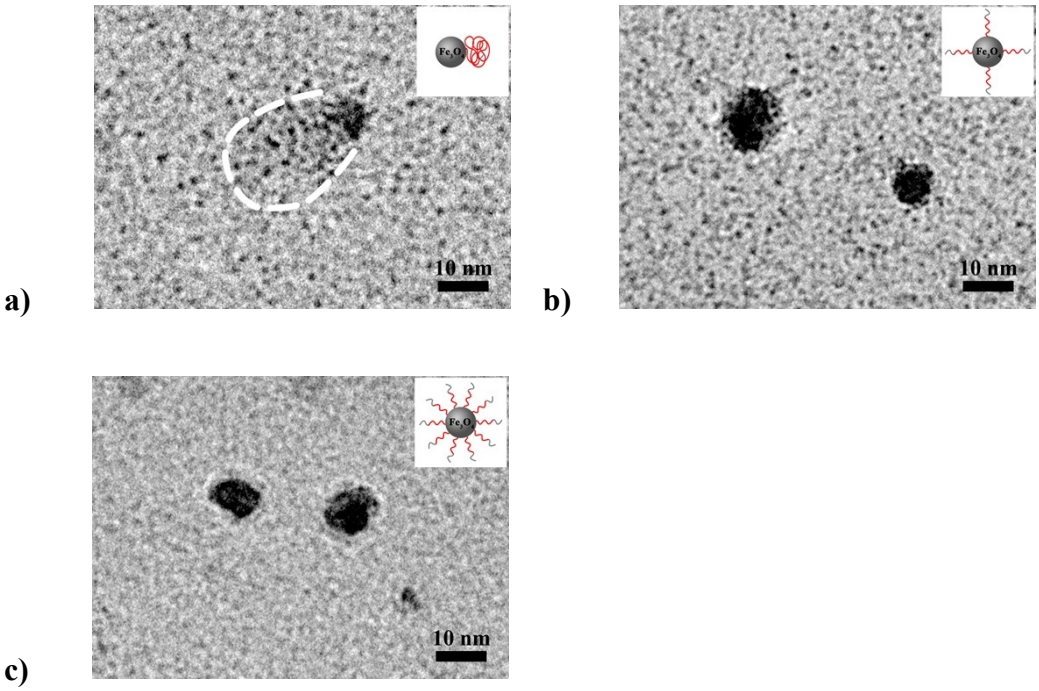

Figure S5. Magnified TEM images of the three representative PVSt-*b*-PS@Fe_3O_4 composite NPs after conjugating with different polymers: (a) $PVSt_{4.4k}$-*b*-$PS_{29.7k}$, (b) $PVSt_{4.4k}$-*b*-$PS_{7.7k}$, and (c) $PVSt_{4.4k}$-*b*-$PS_{5.6k}$, the samples were stained with RuO_4.

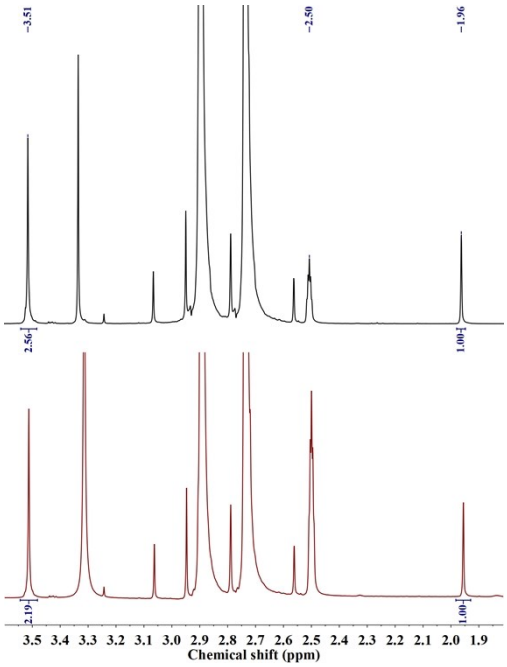

Figure S6. ^{1}H-NMR (DMSO-d6, 400MHz) spectra of the serum after removal of the $PVSt_{4.4k}$-*b*-$PS_{5.6k}$@Fe_3O_4 composite NP from the dispersion in DMF (a) before and (b) after click reaction with mPEG-SH (10 mg). N, N-dimethylacetamide (DMA) was

added as the internal standard to monitor the conversion of mPEG-SH.

The intense characteristic peak at δ=1.96 ppm is assigned to the methyl proton of DMA as the internal standard.

The intense characteristic peak at δ= 3.51 ppm is assigned to the methylene proton of mPEG-SH.

For one composite NP of $PVSt_{4.4k}$-*b*-$PS_{5.6k}$@Fe_3O_4, the masses of Fe_3O_4 NP and PVSt segment are estimated as:

$m_{Fe_3O_4}=\rho V=\rho 4/3\pi r^3=5.18\times 4/3\times 3.14\times (5\times 10^{-7})^3 = 2.71\times 10^{-18}$ g.

$m_{PS\text{-}b\text{-}PVSt} = NM_n/N_A = 10\times 10\times 10^3/ (6.02 * 10^{23}) = 1.66 \times 10^{-19}$ g.

$m_{PVSt}=NM_{nPVSt}/N_A = 10\times 4.4\times 10^3/ (6.02 * 10^{23}) = 7.31 \times 10^{-20}$ g

The PVSt mass fraction in respect to the composite NP is calculated: $7.31\times 10^{-20}/ (2.71\times 10^{-18}+1.66 \times 10^{-19}) = 2.54\%$.

Molar amount of VSt in 30 mg of the $PVSt_{4.4k}$-*b*-$PS_{5.6k}$-Fe_3O_4 composite NP is calculated: $30\times 2.54\%/158 = 4.82 \times 10^{-3}$ mmol.

NMR peak at 3.51ppm is decreased by 14.5% after the click reaction, equal to the conversion of mPEG-SH. Molar amount of the reacted mPEG-SH is calculated: $10\times 14.5\%/1000 = 1.45\times 10^{-3}$ mmol.

The grafting ratio of mPEG-SH is measured $1.45\times 10^{-3}/4.82 \times 10^{-3} = 30.1\%$.

Number of the grafted mPEG-SH side chain onto one $PVSt_{4.4k}$-*b*-$PS_{5.6k}$ chain is calculated: $4400/158\times 30.1\% \approx 8$.

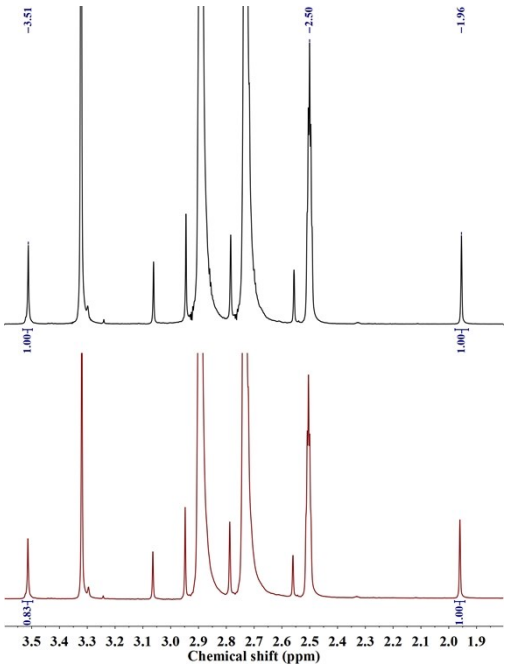

Figure S7. ^{1}H-NMR (DMSO-d6, 400MHz) spectra of the serum after removal of the $PVSt_{4.4k}$-*b*-$PS_{5.6k}$@Fe_3O_4 composite NP from the dispersion in DMF (a) before and (b) after click reaction with mPEG-SH (4 mg). N, N-dimethylacetamide (DMA) was added as the internal standard to monitor the conversion of mPEG-SH.

NMR peak at 3.51ppm is decreased by 17% after the click reaction, equal to the conversion of mPEG-SH. Molar amount of the reacted mPEG-SH is calculated: $4\times17\%/1000 = 0.68\times10^{-3}$ mmol.

The grafting ratio of mPEG-SH is measured $0.68\times10^{-3}/4.82\times10^{-3} = 14.1\%$.

Number of the grafted mPEG-SH side chain onto one $PVSt_{4.4k}$-*b*-$PS_{5.6k}$ chain is calculated: $4400/158\times14.1\% \approx 4$.

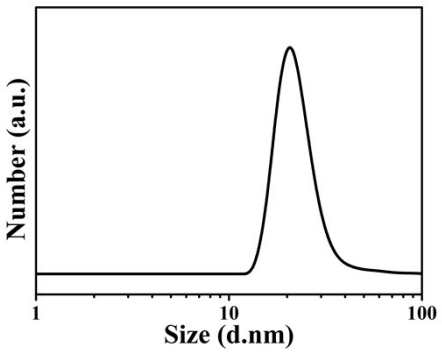

Figure S8. DLS trace of the dispersion as shown in Figure 3a1.

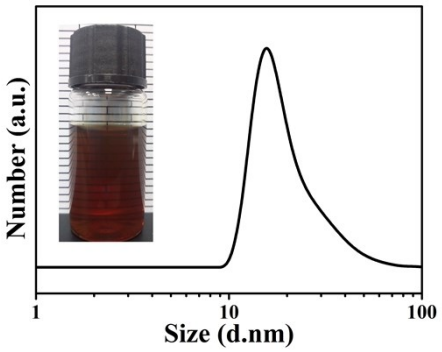

Figure S9. DLS trace of the oil/water mixture containing 1.5 μL of cyclohexane.

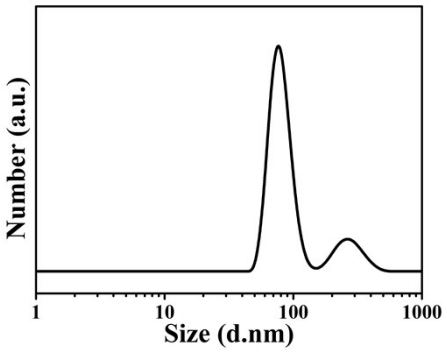

Figure S10. DLS trace of the dispersion as shown in Figure 3a2.

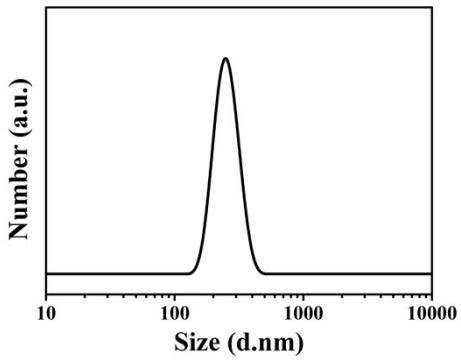

Figure S11. DLS trace of the oil/water mixture containing 12.0 μL of cyclohexane.

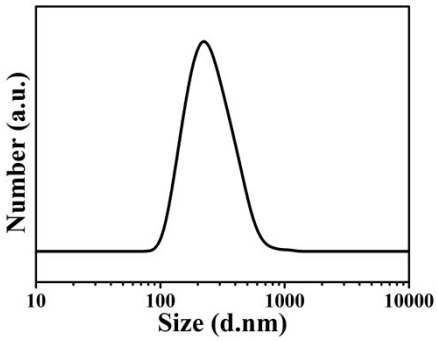

Figure S12. DLS trace of the bottom dispersion as shown in Figure 3a3.

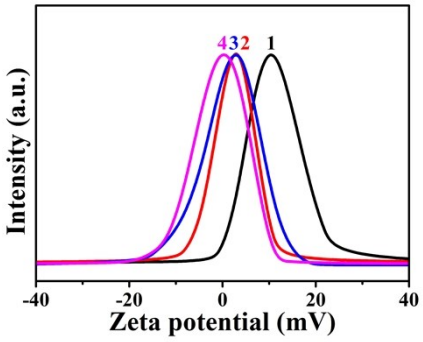

Figure S13. Zeta potential values of (1) the ($PVSt_{4.4k}$-*g*-PEG_8)-*b*-$PS_{5.6k}$@Fe_3O_4 composite NP dispersion in water; (2-4) the dispersions as shown in Figures 3a1, 3a2 and 3a4, respectively.

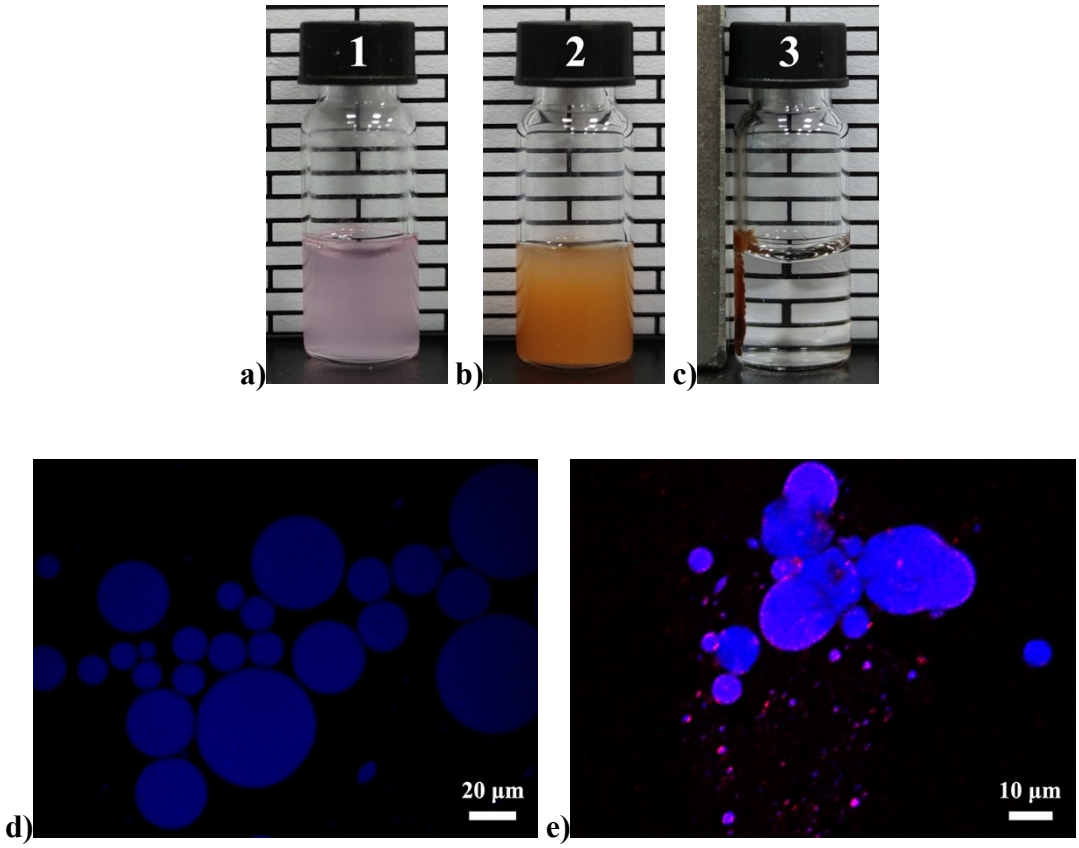

Figure S14. Magnetic collection of the emulsion stabilized with SDS: (a) the emulsion and (b) after feeding the composite NP; (c) magnetic collection of the emulsion; (d) CLSM image of the emulsion (a); (e) CLSM image of the emulsion (b).