

Supporting Information:

From Unimolecular Template of Water-Soluble Multi-Arm Star Brush Copolymers to One-Dimensional (1D) Colloidal Nanocrystal Clusters: Facile Synthesis via a Combination of Magnetic Assembly with Photo-Induced Cross-Linking

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Synthesis of Double-Hydrophilic Star Brush Copolymer PEO-*g*-PAA Template.

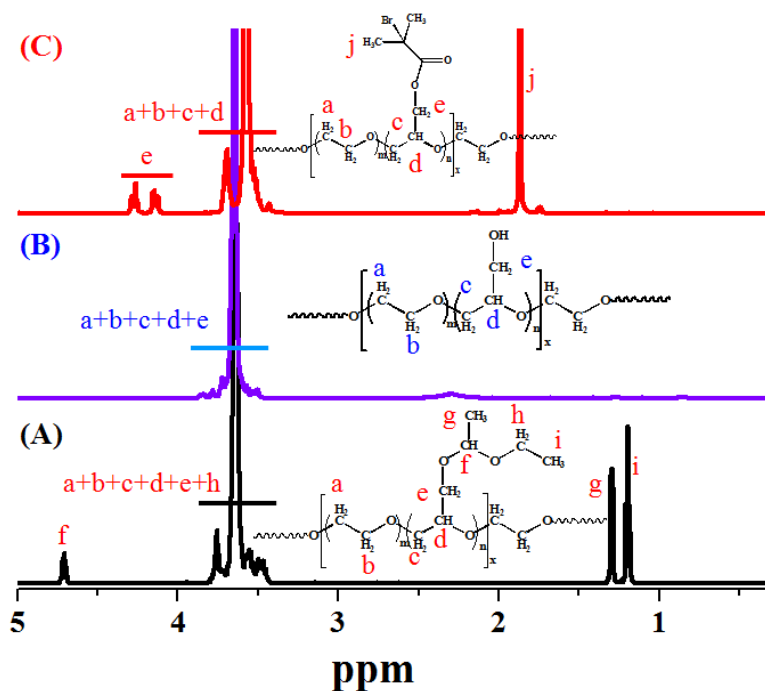


Figure S1. ^1H NMR spectra of the star brush macroinitiator and its precursor in CDCl_3 : (A) star copolymer poly(EO-co-EEGE) (Sample A in **Table 1**); (B) the corresponding hydrolyzed star copolymer poly(EO-co-Gly); (C) the corresponding star brush ATRP macroinitiator.

Figure S1(A) is a typical ^1H NMR spectrum of star copolymer poly(EO-co-EEGE), the chemical shift at $\delta = 4.70-4.73$ are assigned to the methyl protons (H_f) of EEGE moiety, the doublets at $\delta = 1.30, 1.29$ and the triplet at $\delta = 1.21, 1.19, 1.18$ are assigned to methyl protons of EEGE moiety (H_g, H_i), in addition, the chemical shift at $\delta = 3.53-3.80$ are assigned to protons of main chain ($\text{H}_a, \text{H}_b, \text{H}_c, \text{H}_d$) and protons of lateral chains (H_h, H_e). The composition of two monomers in star

copolymer poly(EO-*co*-EEGE) can be calculated by using following equation based on the ^1H NMR spectrum:

$$R_T = \frac{4A_f}{A_{\text{sum}} - 7A_f} \quad (\text{S1})$$

Where R_T is the molar ratio of EEGE to EO in star copolymers; A_{sum} and A_f represent the sum of peak integral area of the protons a, b, c, d, e and h and the peak areas of the methine protons of the EEGE moiety, respectively. The R_T values of copolymers A and B are 1/6.1 and 1/6.5, respectively, which is nearly equivalent to the monomer feed ratio of EEGE to EO (1/5). GPC traces of the two samples with monomodal traces were shown in **Figure S2**. The molecular weight of star copolymer poly(EO-*co*-EEGE) can be tuned by changing the molar ratio of monomers to initiators, and polydispersity index (PDI) values of all polymers were low (PDI < 1.20). Comparing the number-average molecular weights of two samples based on the theoretical values to those obtained from GPC, the remarkable difference is due to the different hydrodynamic volume of star architectures comparing with the linear PS standard used in GPC characterization.

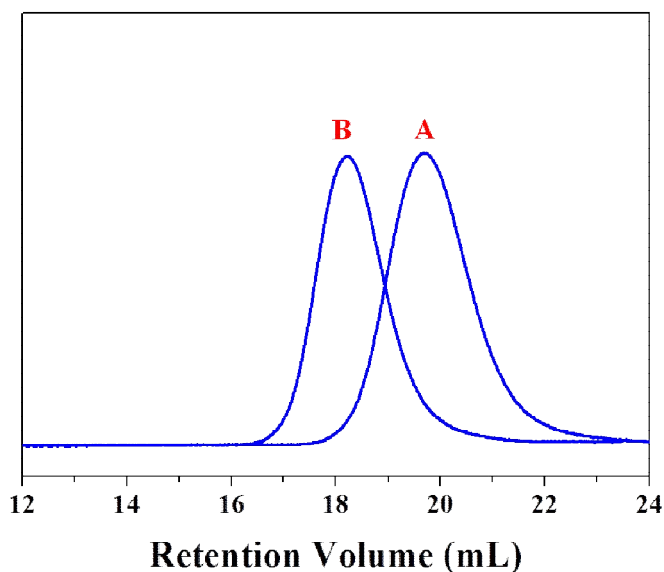


Figure S2. GPC traces of star copolymers poly(EO-*co*-EEGE) (Sample-A and Sample-B were shown in **Table 1**).

In order to prepare star brush macroinitiator poly(EO-*co*-BiBGE), the hydroxyl groups of star copolymer poly(EO-*co*-Gly) were esterified with 2-bromoisobutryl bromide, and the complete esterification of the hydroxyl groups was also confirmed by ^1H NMR spectrum (**Figure S1(C)**). The hydroxyl group conversion can be calculated by the following formula:

$$E_T = \frac{(3 + \frac{4}{R_T}) \times A_e}{2A_{\text{sum}}} \times 100\% \quad (\text{S2})$$

where E_T is the conversion efficiency of hydroxyl groups of star copolymer poly(EO-*co*-Gly); A_{sum} and A_e represent the integral area of the protons of PEO main ring (the peaks at $\delta=3.35\text{-}3.90$) and the integral area of the protons (H_e) linked to the ester (the peaks at $\delta=4.13\text{-}4.42$); and R_T is the molar ratio of EEGE to EO in original star copolymer poly(EO-*co*-EEGE) measured by ^1H NMR (shown in **Figure S1(A)**).

The E_T value is nearly 100%, and this suggests that hydroxyl groups are completely converted to bromoisobutyryl units.

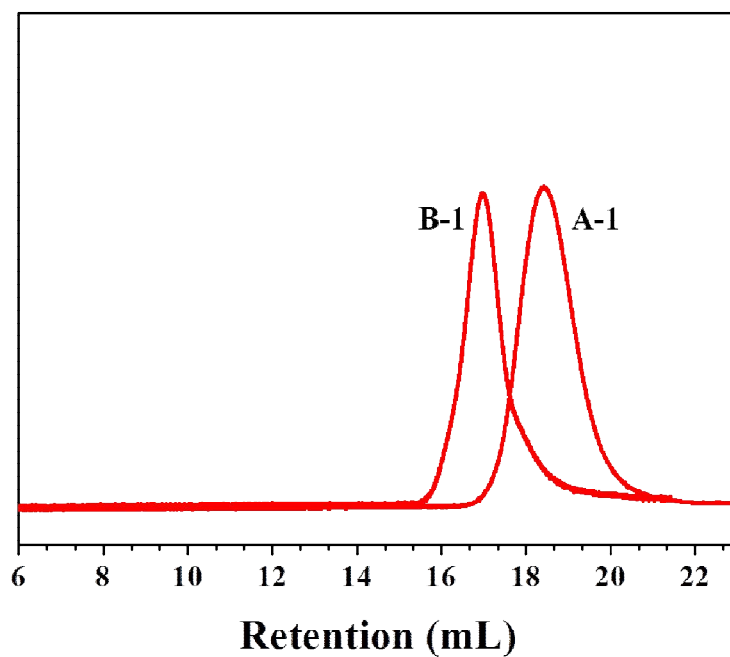


Figure S3. GPC traces of amphiphilic multi-arm star brush copolymer PEO-g-PtBA (A-1 and B-1 samples were shown in **Table 2**).

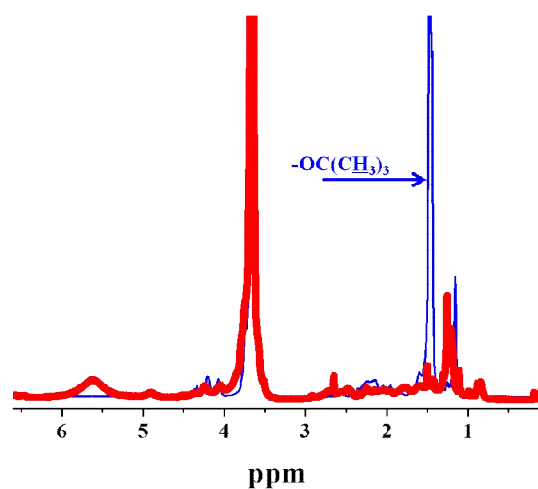


Figure S4. ^1H NMR spectra of multi-arm star brush copolymer PEO-*g*-PtBA (Sample A-1 in **Table 2**) in CDCl_3 (blue curve) and the resulting double-hydrophilic star brush copolymer PEO-*g*-PAA in CD_3OD (red curve).

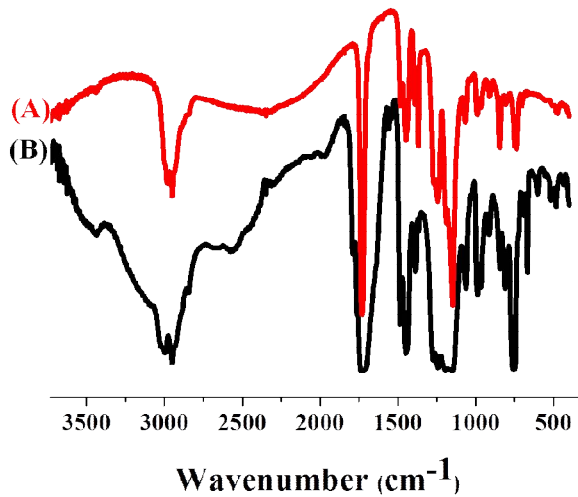


Figure S5. FT-IR spectra of multi-arm star brush copolymers (A) PEO-*g*-PtBA (Sample A-1 in **Table 2**) and (B) the corresponding double-hydrophilic star brush copolymer PEO-*g*-PAA.

Preparation of the spherical Superparamagnetic Fe_3O_4 Colloidal Nanocrystal Clusters by Using Unimolecular Templates of Multi-Arm Star Brush Copolymer PEO-g-PAA as Templates.

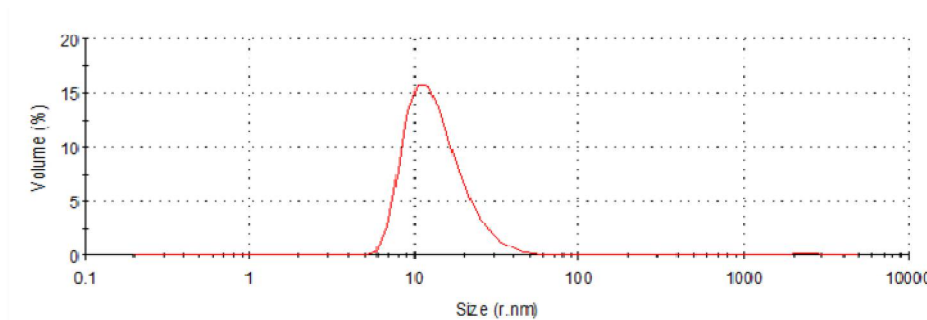


Figure S6. Dynamic light scattering (DLS) measurement on unimolecular template of water-soluble star brush copolymer PEO-g-PAA in DMF (Sample A-1 as precursor in **Table 2**).

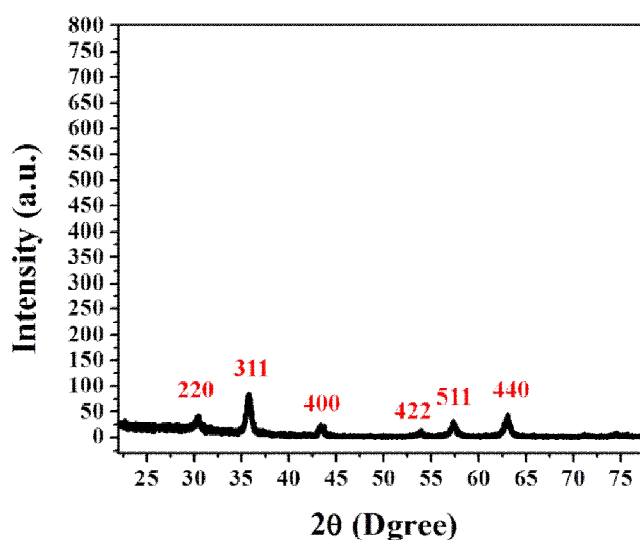


Figure S7. XRD pattern of spherical Fe_3O_4 colloidal nanocrystal clusters by using the water-soluble star brush copolymer PEO-g-PAA (Sample A-1 as precursor in **Table 2**) as unimolecular template.

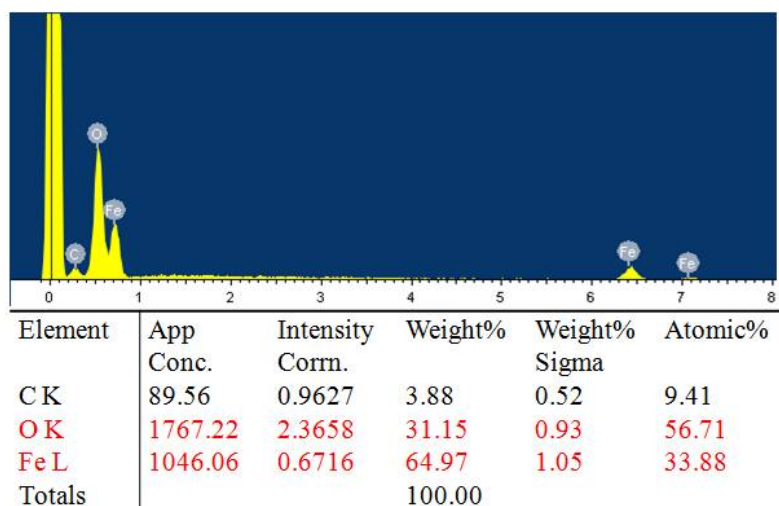


Figure S8. EDS spectrum of spherical Fe_3O_4 colloidal nanocrystal clusters by using the water-soluble star brush copolymer PEO-g-PAA (Sample A-1 as precursor in **Table 2**) as unimolecular template.

Fabrication of 1D Colloidal Superparamagnetic Fe₃O₄ Nanocrystal Clusters by a Combination of Magnetic Assembly and Photo-Cross-Linking.

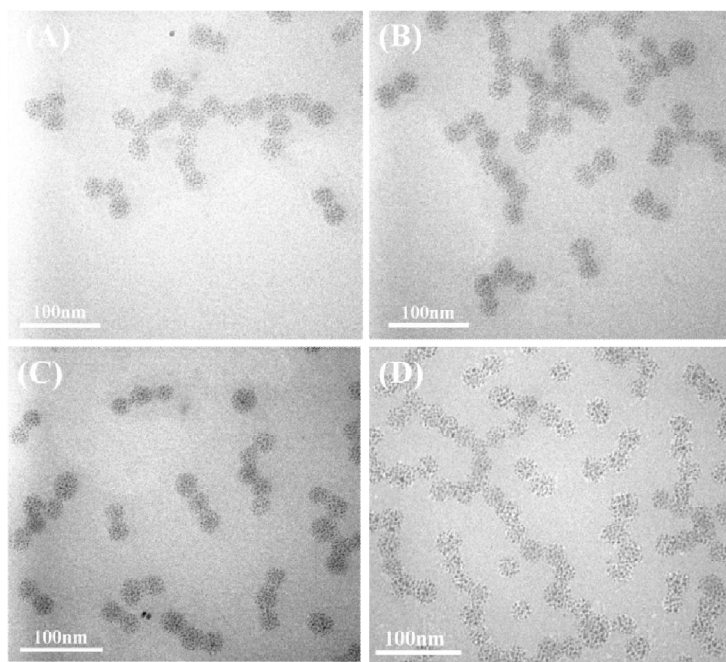


Figure S9. Representative TEM images of 1D Fe₃O₄ colloidal nanocrystal clusters at different region on the TEM grid, using the water-soluble multi-arm star brush copolymer PEO-g-PAA (Sample A-1 as precursor in **Table 2**) as unimolecular template. The magnetic field strength of 500 G was used.

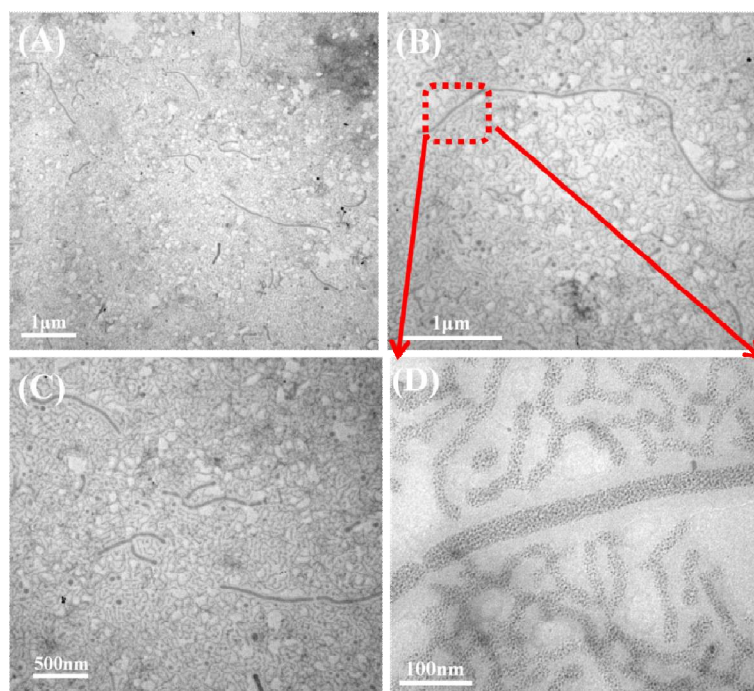


Figure S10. Representative TEM images of 1D Fe₃O₄ colloidal nanocrystal clusters with different scale bars, using the water-soluble multi-arm star brush copolymer PEO-g-PAA (Sample A-1 as precursor in **Table 2**) as unimolecular template. The magnetic field strength of 900 G was used.

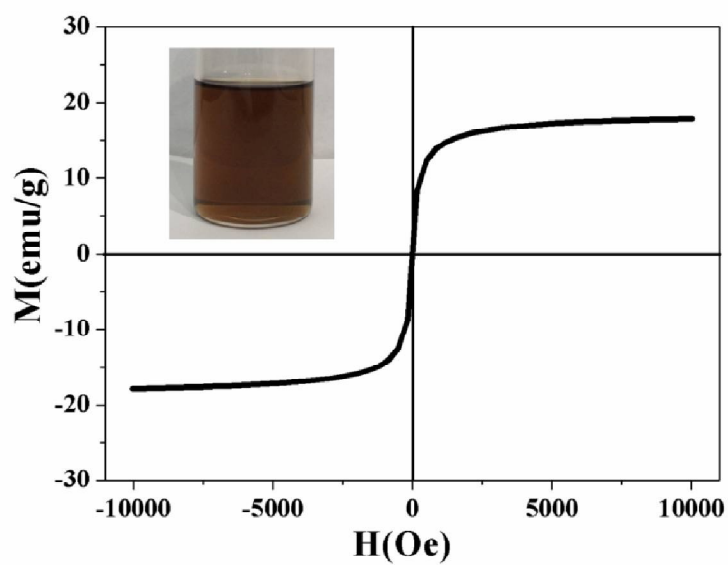


Figure S11. Mass magnetization M as a function of applied external field H at 300K. Inset: Digital image of an aqueous 1D Fe_3O_4 colloidal nanocrystal clusters as shown in **Figure 8** (2mg/mL). The magnetic field strength of 700 G was used for magnetic assembly.