# Supporting Information:

## Water-soluble Star-Shaped Brush-Like Block Copolymers: Synthesis and Application as Multicompartment Nanoreactors for Fabrication of Quantum Dot Colloidal Nanocrystal Clusters

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**Synthesis of Star-Shaped Brush-Like Block Copolymer (PEO-*g*-PAA)-*b*-PEO Template.**

**Synthesis of the Star-shaped Copolymers Poly (EO-*co*-EEGE) Based on α-CD**.

GPC traces of the samples with monomodal traces were shown in **Figure S1**. The molecular weight of multi-arm star-shaped copolymers 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 < 1.15). Owing to the different hydrodynamic volume of multi-arm star-shaped copolymers poly(EO-*co*-EEGE)

comparing with the linear PS standard used in GPC measurements, notably, the number-average molecular weights of all the samples based on the theoretical values are remarkably different from those obtained from GPC.

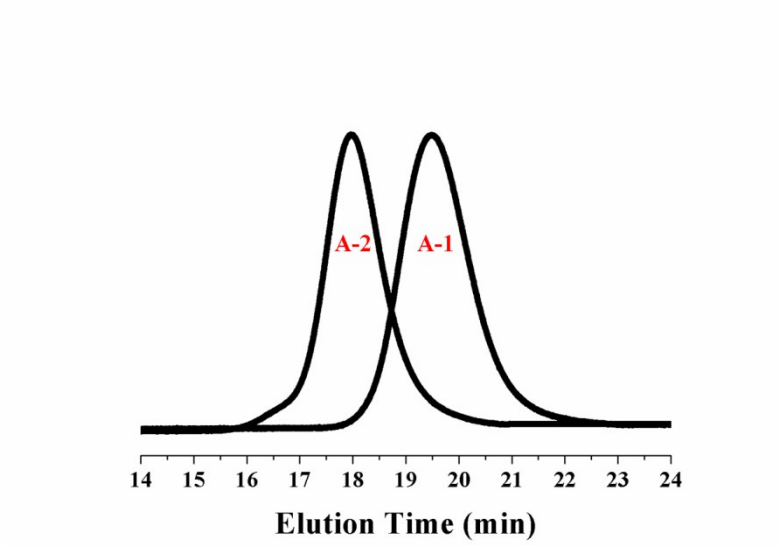



**Figure S1**. GPC traces of multi-arm star-shaped copolymers poly(EO-*co*-EEGE) (A-1 and A-2 samples were shown in **Table 1**).

**Synthesis of Star-shaped Block Copolymers Poly (EO-*co*-EEGE)-*b*-PEO**.

According to GPC traces (**Figure S2**), the major elution peak of star-shaped block copolymer poly(EO-*co*-EEGE)-*b*-PEO was shifted to the smaller elution time owing to the larger molecular weight.

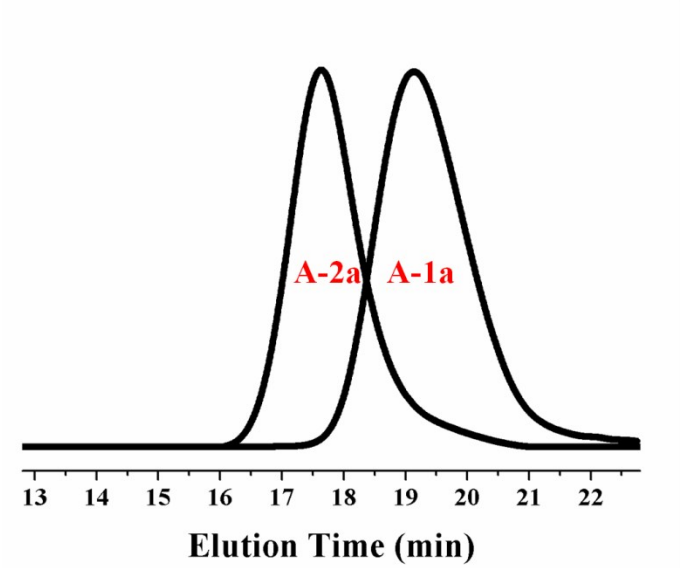



**Figure S2**. GPC traces of multi-arm star-shaped block copolymers of poly(EO-*co*-EEGE)-*b*-PEO (A-1a and A-2a samples were shown in **Table 3**).

**Preparation of Multi-Arm Star-Shaped Block Copolymers Poly(EO-*co*-Gly)-*b*-PEO by Hydrolysis of the Ethoxyethyl Groups of Poly(EO-*co*-EEGE) Arms.**

To deprotect the reactive hydroxyl groups of multi-arm star-shaped block copolymers poly(EO-*co*-Gly)-*b*-PEO, ethoxyethyl groups of EEGE units were hydrolyzed by the cleavage of the ethoxyethyl group. After hydroxyl groups were recovered, multi-arm star-shaped block copolymers poly(EO-*co*-EEGE)-*b*-PEO was transformed into multi-arm star-shaped block copolymers poly(EO-*co*-Gly)-*b*-PEO with multi-pending hydroxyl groups along the first block. The success hydrolysis of the ethoxyethyl groups was confirmed by $^{1}$H NMR characterization. All the peaks were assigned to the ethoxyethyl group of EEGE units in poly(EO-*co*-EEGE) block in **Figure 1** disappeared completely after hydrolysis, as shown in **Figure S3**. In order to confirm that the star-shaped structures survives after hydrolysis of the ethoxyethyl groups of poly(EO-*co*-EEGE)-*b*-PEO arms, the aqueous phase GPC characterization of multi-arm star-shaped block copolymers poly(EO-*co*-Gly)-*b*-PEO was performed

(0.1 M aqueous $NaNO_3$ as eluent) (**Figure S4**). Comparing with GPC trace of corresponding multi-arm star-shaped block copolymers of poly(EO-*co*-EEGE)-*b*-PEO (Sample A-1a in **Table 3**, $M_n$=154kg/mol, PDI=1.13), the molecular weight of star-shaped block copolymer poly(EO-*co*-Gly)-*b*-PEO slightly decreased ($M_n$=131kg/mol, PDI=1.16) owing to removal of ethoxyethyl groups of EEGE units. Except GPC confirmation, $^1$H-NMR characterization of multi-arm star-shaped block copolymers poly(EO-*co*-Gly)-*b*-PEO after deprotecting the EEGE monomeric units in concentrated HCl was also used to confirm phenyl groups as end group of arm chains (endstoppers) (in **Figure S3**), and the appearance of chemical shift at δ =6.89-7.24 ppm is assigned to the protons of phenyl groups as end group of arm chains.

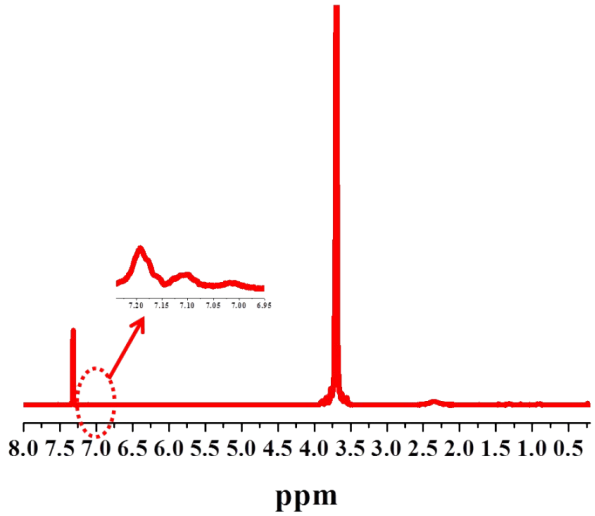



**Figure S3**. $^1$H-NMR spectrum of multi-arm star-shaped block copolymers poly(EO-*co*-Gly)-*b*-PEO after the cleavage of the ethoxyethyl group (A-1a sample was used as the precursor in **Table 3**, solvent: $CDCl_3$).

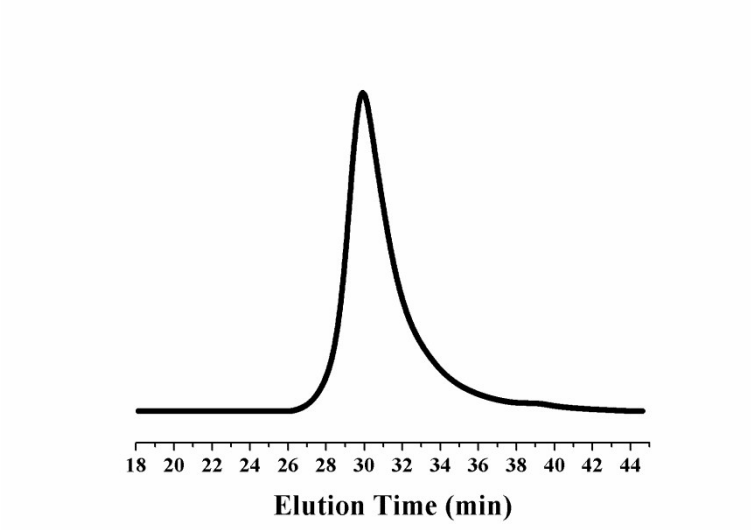



**Figure S4**. GPC trace of multi-arm star-shaped block copolymers poly(EO-*co*-Gly)-*b*-PEO after the cleavage of the ethoxyethyl group (A-1a sample was used as the precursor in **Table 3**, 0.1 M aqueous $NaNO_3$ as eluent).

**Synthesis of Macroinitiator Multi-Arm Star-Shaped Block Copolymer Poly(EO-*co*-BiBGE)-*b*-PEO.**

After hydroxyl groups were recovered, multi-arm star-shaped block copolymers of poly(EO-*co*-EEGE)-*b*-PEO were transformed into multi-arm star-shaped block copolymers poly(EO-*co*-Gly)-*b*-PEO with multi-pending hydroxyl groups along the first block. In order to prepare star-shaped brush-like macroinitator, multi-arm star-shaped block copolymers poly(EO-*co*-BiBGE)-*b*-PEO, the hydroxyl groups of multi-arm star-shaped block copolymers poly(EO-*co*-Gly)-*b*-PEO were modified by the esterification with 2-bromoisobutyryl bromide. The successful esterification of the hydroxyl groups was also confirmed by $^1$H NMR shown in **Figure S5**, in which the appearance of new peaks at δ=1.8-2.2 and δ=4.13-4.42 can be assigned to the methyl protons of ATRP initiating sites and the protons ($H_e$) linked to the ester, respectively.

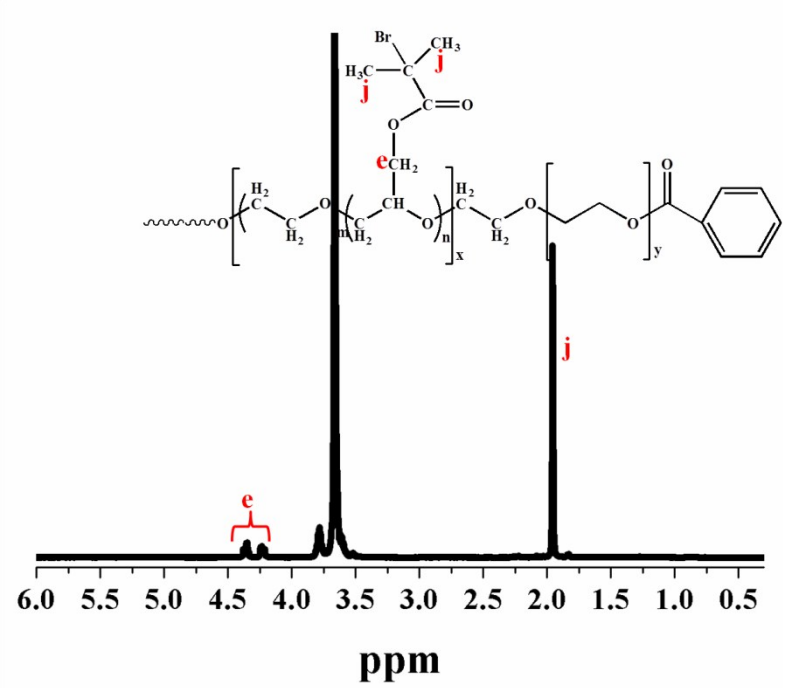



**Figure S5**. $^{1}$H-NMR spectrum of multi-arm star-shaped block copolymers poly(EO-*co*- BiBGE)-*b*-PEO after the esterification with 2-bromoisobutyryl bromide of star-shaped block copolymers poly(EO-*co*-Gly)-*b*-PEO (A-1a sample was used as the precursor in **Table 3**, solvent: $CDCl_3$).

In order to further confirm that the star-shaped structures survives after hydrolysis of the ethoxyethyl groups of poly(EO-*co*-EEGE)-*b*-PEO arms, macroinitiator multi-arm star-shaped block copolymer poly(EO-*co*-BiBGE)-*b*-PEO for ATRP was also characterized by THF phase GPC. Comparing with GPC trace of corresponding multi-arm star-shaped block copolymers of poly(EO-*co*-EEGE)-*b*-PEO (Sample A-1a in Table 3, $M_n$=154kg/mol, PDI=1.13), the major elution peak of macroinitiator multi-arm star-shaped block copolymer poly(EO-*co*-BiBGE)-*b*-PEO for ATRP ($M_n$=173kg/mol, PDI=1.09) was shifted to the slightly smaller elution time

owing to the modification of hydroxyl groups by 2-bromoisobutyryl bromide (larger molecular weight than ethoxyethyl groups).

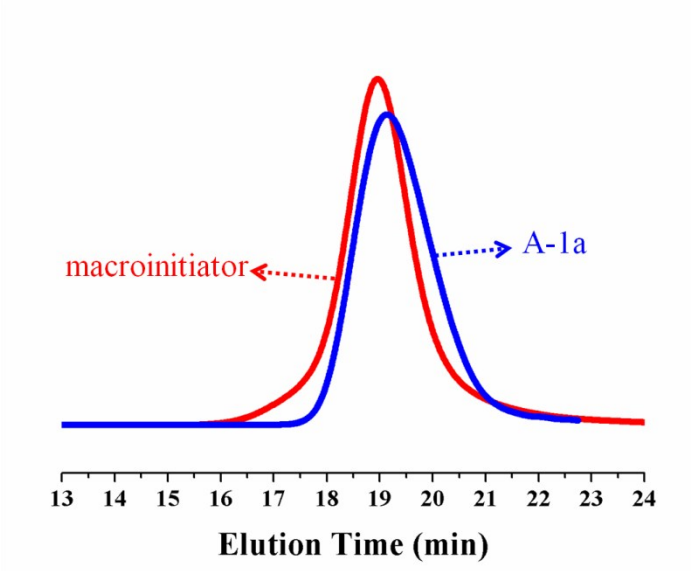



**Figure S6**. GPC traces of macroinitiator multi-arm star-shaped block copolymer poly(EO-*co*-BiBGE)-*b*-PEO (A-1a sample was used as the precursor in **Table 3**, THF as eluent).

**Preparation of Star-Shaped Brush-Like Block Copolymer (PEO-*g*-P*t*BA)-*b*-PEO by ATRP.**

**Figure S7** shows GPC traces of two multi-arm star-shaped brush-like block copolymers (PEO-g-P*t*BA)-*b*-PEO samples. All the star-shaped brush-like copolymers with symmetric GPC peaks were obtained no matter what star-shaped brush-like ATRP macroinitators were used. In addition, and the narrow molecular weight distribution of the star-shaped polymeric brushes as low as 1.15 demonstrates that all the samples have uniform molecular weights.

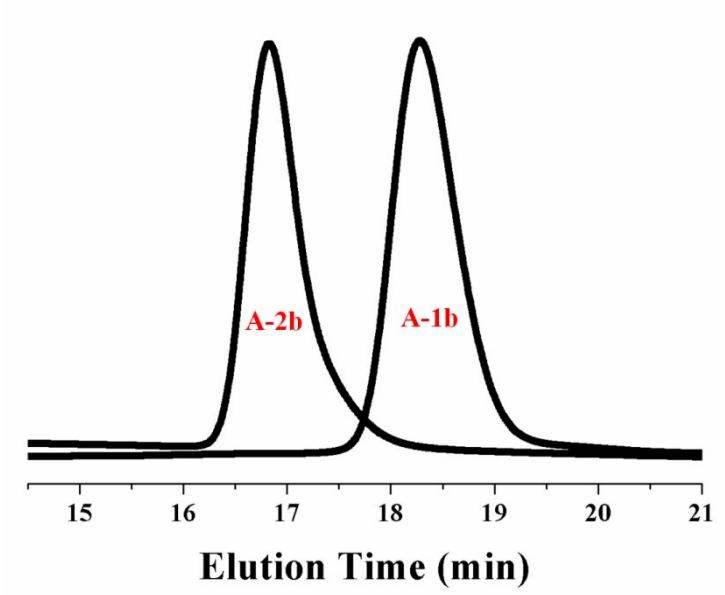



**Figure S7**. GPC traces of multi-arm star-shaped brush-like block copolymers of (PEO-g-P*t*BA)-*b*-PEO (A-1b and A-2b samples were shown in **Table 4**).

**Fabrication of Hybrid Inorganic-Organic Core-Shell CdSe QD Colloidal Nanocrystal Clusters Capped with Hydrophilic PEO as Shell.**

Besides TEM images of the water-soluble multi-arm star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO macromolecular structures (**Figure 7**), the macromolecular structures of multi-arm star-shaped brush-like block copolymer (PEO-g-P*t*BA)-*b*-PEO before the hydrolysis of the *t*-butyl groups of P*t*BA were also characterized by TEM (**Figure S8**). For TEM characterization of star-shaped brush-like block copolymer (PEO-*g*-P*t*BA)-*b*-PEO, TEM samples were prepared by using a drop of star-shaped copolymers dichloromethane ($CH_2Cl_2$, good solvent for both P*t*BA and PEO segments) solution (c=1mg/mL) onto a carbon-coated copper TEM grid (300 mesh) and leaving $CH_2Cl_2$ to completely evaporate at room temperature, and then the TEM grid was exposed to vapors of ruthenium tetraoxide ($RuO_4$) with

which the PEO and P*t*BA blocks were stained.[1-3] The dark spherical structures in the TEM micrographs corresponded to macromolecular structures, the average diameter was 39±4.1 nm, and the size was slightly larger than that of hydrophilic PAA brush core (34±3.8 nm, in **Figure 7(c, d)**) of star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO owing to the second PEO as shell. In addition, the size is similar with the AFM results of star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO (in **Figure 7(a, b)**).

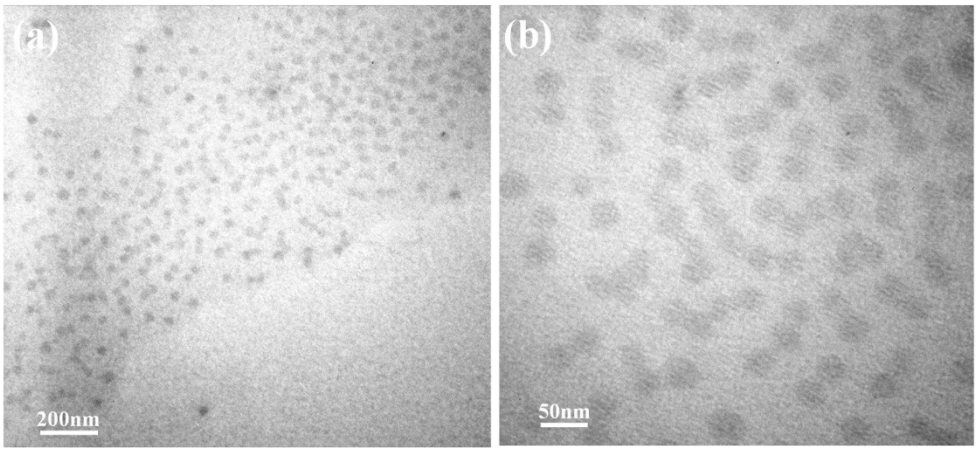



**Figure S8.** TEM images of star-shaped brush-like block copolymer (PEO-*g*-P*t*BA)-*b*-PEO (Sample A-1b in **Table 4**) with different scale bars. The samples were treated with uranyl acetate before imaging to selectively stain the hydrophilic core PAA segments.

Except TEM characterization of the macromolecular structures of multi-arm star-shaped brush-like block copolymer (PEO-g-P*t*BA)-*b*-PEO before the hydrolysis of the *t*-butyl groups of P*t*BA (**Figure S8**), the hydrodynamic diameter of multi-arm star-shaped brush-like block copolymer (PEO-g-P*t*BA)-*b*-PEO in $CH_2Cl_2$ (good solvent for both P*t*BA and PEO segments), $D_h$~41 nm (**Figure S9**), was also measured by

dynamic light scattering (DLS). We note that $D_h$ obtained from DLS was similar with that from TEM (**Figure S9**), and moreover the $D_h$ obtained from DLS was also similar with the AFM results of star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO (in **Figure 7(a, b)**).

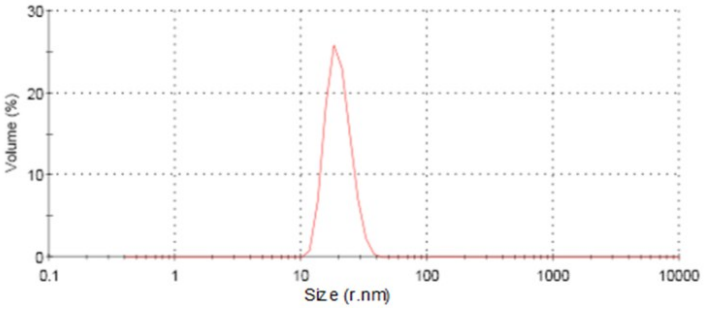



**Figure S9.** Dynamic light scattering (DLS) measurement on macromolecular architectures of multi-arm star-shaped brush-like block copolymer (PEO-g-P*t*BA)-*b*-PEO in $CH_2Cl_2$ (Sample A-1b in **Table 4**).

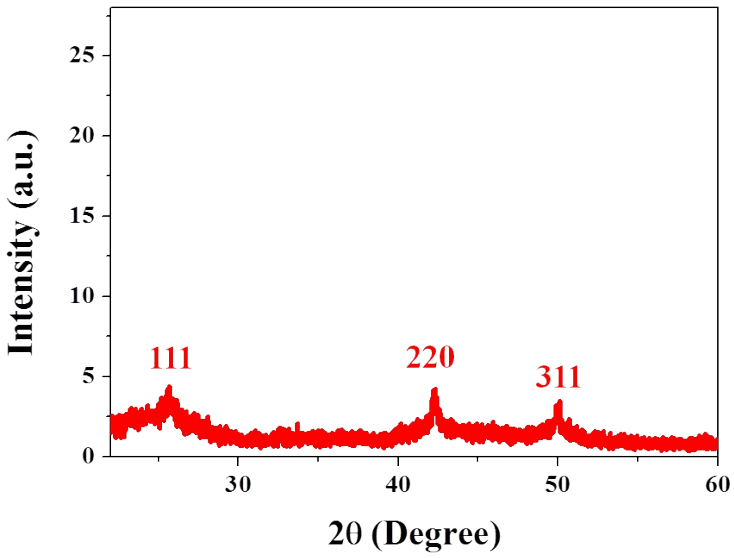
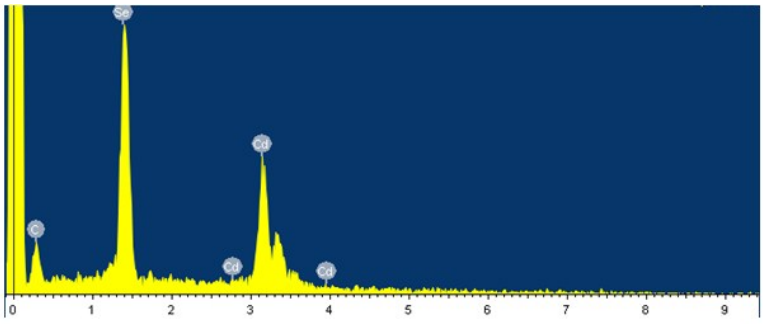



**Figure S10.** XRD pattern of CdSe colloidal nanocrystal clusters by using the water-soluble multi-arm star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO

(Sample A-1b as precursor in **Table 4**) as polymeric template. Wurtzite CdSe (JCPDS 77-2307).




| Element | App Conc. | Intensity Corrn. | Weight% | Weight% Sigma | Atomic% |
|---|---|---|---|---|---|
| C K | 309.53 | 0.9068 | 9.46 | 1.11 | 45.51 |
| **Se L** | **1052.35** | **0.8024** | **36.33** | **1.25** | **26.60** |
| **Cd L** | **1759.40** | **0.8990** | **54.22** | **1.46** | **27.89** |
| Totals | | | 100.00 | | |

**Figure S11.** EDS spectrum of CdSe colloidal nanocrystal clusters by using the water-soluble multi-arm star-shaped brush-like block copolymer (PEO-*g*-PAA)-*b*-PEO (Sample A-1b as precursor in **Table 4**) as polymeric template.

Notes and references:


1. Wu, J., Thio, Y.S. & Bates, F.S. Structure and properties of PBO–PEO diblock copolymer modified epoxy. *J. Polym. Sci., Part B: Polym. Phys.* **43**, 1950-1965 (2005).
2. Dean, J.M., Lipic, P.M., Grubbs, R.B., Cook, R.F. & Bates, F.S. Micellar structure and mechanical properties of block copolymer-modified epoxies. *J. Polym. Sci., Part B: Polym. Phys.* **39**, 2996-3010 (2001).
3. Sawyer, L.C., Grubb, D.T. & Meyers, G.F. Polymer Microscopy. (Springer Science & Business Media, 2008).