Electronic Supplementary Material (ESI) for Nanoscale.

SUPPORTING INFORMATION

A Detour Strategy for Colloidal-Stable Block-Copolymer Grafted $MAPbBr_3$ Quantum Dots in Water with Long Photoluminescence Lifetime

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EXPERIMENTAL SECTION

Materials. All reagents were used as received without further purification: lead(ll) bromide (≥99%, Aladdin), hydrobromic acid (48 wt % in H_2O, ≥99.99%, Aladdin), oleic acid (≥85%, Aladdin), N,N-dimethylformamide (≥99.8%, anhydrous grade, Aladdin), N,N′-dicyclohexylcarbodiimide (≥99.0%, Aladdin), 4-dimethylaminopyridine (≥99%, Aladdin), 2,2′- bipyridyl (≥99%, Aladdin), copper(I) bromide (≥99%, Aladdin), cyclohexane (≥99%, Aladdin), methanol (≥99%, Aladdin), sodium borohydride (powder, ≥98%, Sigma Aldrich) and poly(ethyl oxide) methyl ether (M_n = 2,000, Sigma Aldrich), styrene (99.0%, Xilong Chemical Co., Ltd., China), sodium azide (98%, Shanghai Chemical Reagent, Co., Ltd., China), methylamine (CH_3NH_2, 33 wt% in absolute ethanol, Xiya Reagent, Co., Ltd., China), 2-brama-2-methylprapianic acid (98%, Energy Chemical, Co., Ltd., China). Toluene, hexane, dichloromethane, and tetrahydrofuran (analytical grade) were purchased from Beijing Chemical Reagent Co., Ltd., China, and used as received without further purification except dichloromethane that was distilled under N_2 before use.

Synthesis of MeO-PEO-Br Macro-Initiator. N,N′-Dicyclohexylcarbodiimide (618.9 mg, 3 mmol) was dissolved in dichloromethane (21 mL) in an Erlenmeyer flask. The solution was cooled to 0 °C in an ice-bath under N_2, and stirred for 5 mins, before 2-brama-2-methylprapianic acid (501 mg, 3 mmol) and 4-dimethylaminopyridine (73.2 mg, 0.6 mmol) were added. Finally, poly(ethyl-oxide) methyl ether (MeO-PEO-OH, 3.6 g, 1.8 mmol) was added into the reaction solution, and then the flask was removed from ice-bath and stirred for 48 hrs at room temperature. The reaction solution was evaporated to half of its original volume, and precipitated in cold diethyl ether. The precipitate was dissolved in THF. The solution was purified by filtration and evaporated at 40 °C, at 10 mbar. The PEO-macroinitiator was dried under vacuum (45 °C, 24 hrs).

Synthesis of PEO-b-PS-NH_2. The block copolymer was synthesized by ATRP polymerization according to a method reported previously. Firstly, CuBr (72 mg, 0.50 mmol) was added in a flask at 90 °C under N_2 flow. 2,2′- bipyridyl (234 mg, 1.50 mmol) and styrene (5 mL, polymerization inhibitor removed) were added into an Erlenmeyer flask by injection. A 1 mL DMF solution of PEO-macroinitiator (500 mg, 0.25 mmol) was dropwise injected into the flask. The reaction mixture was degassed under vacuum for 10 mins and refilled with nitrogen for three times. The flask was then placed in a pre-heated oil bath at 110 °C for 7 hrs. After polymerization, the crude polymer product was dissolved in dichloromethane, filtered, and precipitated in a large excess of n-hexane before dried under vacuum at 45 °C for 24 hrs. From gel permeation chromatography (GPC) measurements using polystyrene (PS) standards, the polymer sample has a M_n of 13.1 kg mol^{-1} and a polydispersity index (M_w/M_n) PDI= 1.09. From the ^{1}H NMR spectrum (in $CDCl_3$, see Figure. S1), the NMR-based M_n (NMR) is 8.1 kg mol^{-1}, by comparing the integrals of the resonance peaks of aromatic ring of PS block (6.4-7.3 ppm) and the methylene groups of PEO block (3.65 ppm). By varying the polymerization time, we synthesized block copolymers with different PS block lengths, including M_n of 8.1, 9.2, and 13.1 kg mol^{-1} (listed in Table 1).

PEO_{45}-*b*-PS_{106}-Br (500 mg, 0.05 mmol) and NaN_3 (32.5 mg, 0.5 mmol) were dissolved in DMF (10 mL) at 55 °C and held for 5 hrs. After the reaction, the solution was evaporated at 57 °C under 10 mbar. The crude products were redissolved in THF, filtered, and dried under vacuum. FTIR spectrum of the product (Figure S4) confirmed the present of $-N_3$ group, of which vibration was assigned to the peak at 2098 wavenumber (cm^{-1}). To reduce $–N_3$ end group to $–NH_2$, a large excess of $NaBH_4$ (111 mg, 3mmol) was added in 10 mL THF solution of PEO_{45}-*b*-PS_{106}- N_3 (500 mg, 0.038 mM), and 3 mL methanol was injected into the solution to dissolve $NaBH_4$. The reaction solution was heated to 50 °C and held for 12 hrs. After the reaction, the solution was evaporated at 45 °C under 10 mbar. The crude products were redissolved in toluene, filtered, and dried under vacuum. The product was extracted with 10 mL cyclohexane at room temperature for 24 hrs to remove PS homopolymer and repeated for three times. FTIR spectrum of the final product showed the significant decrease of the peak intensity for $-N_3$ group at 2097 cm^{-1} and the appearance of $–NH_2$ peak attributed by 3200, 3360 cm^{-1} probably caused by hydrogen bond, and bending vibration absorption at 1660 and 1631 cm^{-1}.

Preparation of MABr. Methylamine (7.85 g, 0.25 mol) in absolute ethanol (10 mL) was cooled at 0 °C before HBr (6 mL) was added. The reaction solution was stirred for 2 hrs before the solvent was evaporated under 10 mbar at 40 °C. The precipitate was washed three times with diethyl ether and dried under vacuum (45 °C, 12 hrs) for future use.

Preparation of PEO-b-PS grafted $MAPbBr_3$ QDs in toluene.

The colloidal PEO-*b*-PS grafted $MAPbBr_3$ QDs were synthesized in toluene following the ligand-assisted reprecipitation method reported previously. In a typical synthesis of PEO-*b*-PS grafted $MAPbBr_3$ QDs, MABr (0.04 mmol), $PbBr_2$ (0.04 mmol), and oleic acid (200 µL) were dissolved in 6 ml of DMF to form a precursor solution. 200 µL of the precursor solution was dropwise added into a 10 mL toluene of PEO-*b*-PS-NH_2 (M_n = 13.1 kg mol^{-1} , 0.15 mg mL^{-1}). Along with the mixing, strong green photoluminescent emission was observed, indicating the formation of the colloidal PQDs. The solution was then centrifuged at 7000 rpm for 10 mins to remove impurities. The toluene supernatant containing the PQDs was precipitated in n-hexane to form a thin film at the bottom of a container. The volume ratio of n-hexane to toluene was 5:1 to facilitate the microphase separation between PS and PEO blocks. The thin film was then steadily kept for 24 hours to finish the microphase separation between the PS and PEO blocks. The thin film was washed multiple times with hexane to remove remaining toluene.

Transfer of PEO-b-PS grafted $MAPbBr_3$ QDs to water:

The thin film of PEO-*b*-PS grafted $MAPbBr_3$ QDs was dried under N_2 flow, and then dissolved in 15.0 mL water under sonication for 1 hr.

Characterization. ^1H NMR spectra were recorded at 500 MHz on a Bruker Avance 500 spectrometer. IR spectra were recorded with a Bruker VERTEX 80V spectrometer on a KBr plate using a liquid sample (dissolved in CH_2Cl_2). Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) was performed on carbon-coated TEM grids using a JEOL JEM-2100F transmission electron microscope operated at 200 kV. PL emission spectra were collected with a Shimadzu RF-5301PC spectrophotometer using a quartz cuvette with a 10 mm path length. UV-vis absorption spectra were recorded in the same 10 mm quartz cell using a PerkinElmer LAMBDA 950 UV-vis-NIR spectrometer, with a data interval of 1 nm. Gel permeation chromatography (GPC) measurements were performed using a Agilent 1260 Infinity chromatograph at 35 °C. THF was used as the eluent at an elution rate of 1 mL min^{-1}, and polystyrene standards were used for calibration. Dynamic light scattering (DLS) experiments were performed using a Malvern Instruments Nano ZS Zetasizer at 25 °C. PLQY and time-resolved PL lifetime were measured with an Edinburgh Instruments FLS920 fluorescence spectrometer equipped with a Xenon lamp; a monochromator was used for steady-state PL, and a time-correlated single photon counting unit coupled with a pulsed laser diode (λ = 405 nm, pulse width = 50 ps) was used for time-resolved PL. PLQY values were obtained from toluene solutions of PQDs in a quartz cuvette at the excitation wavelength (λ = 450 nm) using a calibrated integrating sphere. PXRD was performed with a PANalytical Empyrean X-ray diffractometer using a Cu Kα radiation source. The samples were scanned from $5° < 2\theta < 50°$ with an increment of 2° min^{-1}. Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis for the lead toxicity of PQDs@PS_{106}-*b*-PEO_{45} aqueous solutions supernatant was measured by Agilent 725 ICP-OES system.

Photo-stability of PQDs in aqueous solutions. The samples of PQD@PS-*b*-PEO were measured with a 365 nm Ocean Optics LLS-LED as the excitation source. The excitation light with intensity of 7.0, 5.3, and

3.5 mW cm^{-2} was introduced into an optical integration sphere through a optical fiber. The PQD@PS-b-PEO aqueous solution was irradiated continuously, and the PL intensity was collected every 3 minutes.

Thermo-stability of PQDs in aqueous solutions. The thermos-stability of PQD@PS-*b*-PEO was studied from 20 to 90 °C in 5 °C intervals. For each sample, 600 µL of an aqueous solution of PQDs was heated to a corresponding temperature and held for 30 minutes before heating to a higher target temperature.

pH-stability of PQDs in aqueous solutions. 3 mL aqueous solutions of PQDs@PS_{106}-*b*-PEO_{45} vesicles were adjusted pH value from 1 to 13. The samples were heated at 37°C for 70 hours.

ICP-OES for PQDs aqueous solutions supernatant. The PQDs@PS_{106}-*b*-PEO_{45} aqueous solution that was prepared 7 months ago was concentrated at 17000 rpm for 20 mins three times. The supernatant has no green emission. This supernatant was diluted 10 times for ICP-OES measurement.

Cell culture. HeLa cells were cultured in minimum essential medium containing 10% fetal bovine serum and antibiotics (100 units mL^{-1} penicillin and 100 mg mL^{-1} streptomycin) in a 5% carbon dioxide humidity incubator at 37 °C.

Cell imaging. HeLa cells were grown overnight at 37 °C in a 20 mm Petri dish. The living cells were stained with PQDs at a final concentration of 15 µg mL^{-1} and incubated for 3 hours. Cell nuclei were subsequently stained with 1 mg mL^{-1} of 4',6-Diamidino-2-phenylindole (DAPI). The adherent cells were washed three times with PBS and imaged with an Olympus FV1000 confocal laser scanning microscope in inverted mode (λ_{ex} = 405 nm for DAPI, λ_{ex} = 458 nm for PQDs, fluorescent signals were collected at 430 – 475 nm for DAPI and 515 – 615 nm for PQDs, respectively). The images of the cells were captured using a photomultiplier.

Cytotoxicity assay. The standard MTT assay was used to test the cytotoxicity of polymeric micelles to HeLa cells. HeLa cells were cultured in a 96-well microplate (200 µL per well, density of 1 × 104 cells mL^{-1}) at 37 °C in a 5% CO_2 atmosphere overnight. On the second day, various concentrations of polymeric micelles in fresh DMEM were incubated with the HeLa cells for 24 hours. Then, the DMEM was discarded and 100 µL of MTT solution (5 mg mL^{-1} in DMEM) was added to each well, followed by incubation at 37 °C for 4 hours. The supernatant was removed, and 150 µL of DMSO was added to each well to dissolve the formed formazan. After shaking the plates for 5 minutes, absorbance values of the wells were measured with a microplate reader at 490 nm. The cell viability rate (VR) was calculated according to the equation:

$VR = A/A_0 \times 100\%$

where A is the absorbance of the experimental group (*i.e.,* cells treated with PQDs) and A_0 is the absorbance of the control group (*i.e.,* cells not treated with PQDs).

Table S1. Table of PL decay fitting data for PQD@PS$_{106}$-*b*-PEO$_{45}$ in toluene and H_2O.

$$\text{Fit: } A+B1\exp(-t/\tau_1)+B2\exp(-t/\tau_2)$$

Solution	τ_1	τ_2	$\chi2$	$<\tau>$
Toluene	52.41 ns (0.6078)	207.8 ns (0.3922)	0.956	113 ns
H_2O	80.98 ns (0.5461)	264.7 ns (0.4539)	1.416	164 ns

Table S2. Table of photoluminescence properties of PQDs reported in the literature.

In aqueous solutions

Reference	Matrix/ ligands	hydrodynamic radius	PQD size (nm)	PL Lifetime (ns)	FWHM (nm)	PLQY %
Chem. Sci., 2016, **7**, 5699	POSS	N/A (powder)	12-15	N/A	N/A	61% (solid state)
Adv. Funct. Mater., 2017, **27**, 1604382	PVP/PS	3-5 μm	25-35	N/A	16 nm	27 %
Adv. Mater., 2016, **28**, 10710	PS	N/A (Film)	5-60	131 ns	18	34%
	ABS	N/A (Film)	N/A	502 ns	20	48%
	PMMA	N/A (Film)	N/A	15 ns	30	N/A
Adv. Mater., 2016, **28**, 9163	PVDF	N/A (Film)	3-5	N/A	23.2	94.6%
J. Mater. Chem. C, 2017, DOI: 10.1039/C7TC01562C	PDMS	N/A (Film)	5.6	3.73	20	2%
The present work	**PEO-*b*-PS-NH$_2$**	**25.8-104 nm**	**3.5**	**164**	**18**	**43%**

In toluene solutions

Reference	Matrix/	PQD size	PL Lifetime	FWHM	PLQY

	Ligand	(nm)	(ns)	(nm)	%
ACS Nano, 2015, **9**, 4533	n-octylamine, oleic acid	3.3	10.75	22	70%
ACS Nano, 2017, **11**, 2689	n-octylamine, oleic acid	3.0	12.6±0.6	20	92%
Adv. Mater., 2017, **29**, 1700047	n-octylamine, oleic acid	6.4	13.2	N/A	92%
Scientific Reports, 2016, **6**, 35931	Oleate	3.3	13.5	N/A	N/A
Adv. Mater., 2016, **28**, 10088	Silica	5.9	13.6	25	78%
J. Am. Chem. Soc., 2016, **138**, 5749	SiO_2	2.4	16.3	32	87%
Nano Lett., 2015, **15**, 3692	Oleylamine, oleic acid	4-15	1-29	6-21	50-90%
Nano Lett., 2017, **17**, 2765	Oleylamine, oleic acid	15-25	5-166[a]	20-44	26-84 %
J. Mater. Chem. C, 2016, **4**, 11387	$NaNO_3$	30-50	155.5	N/A	42%
The present work	**PEO-*b*-PS-NH_2**	**3.5**	**113**	**18**	**56%**

N/A: Not available in the reference.

[a] The longer PL lifetimes of PQDs in literature are caused by lager size relatively;

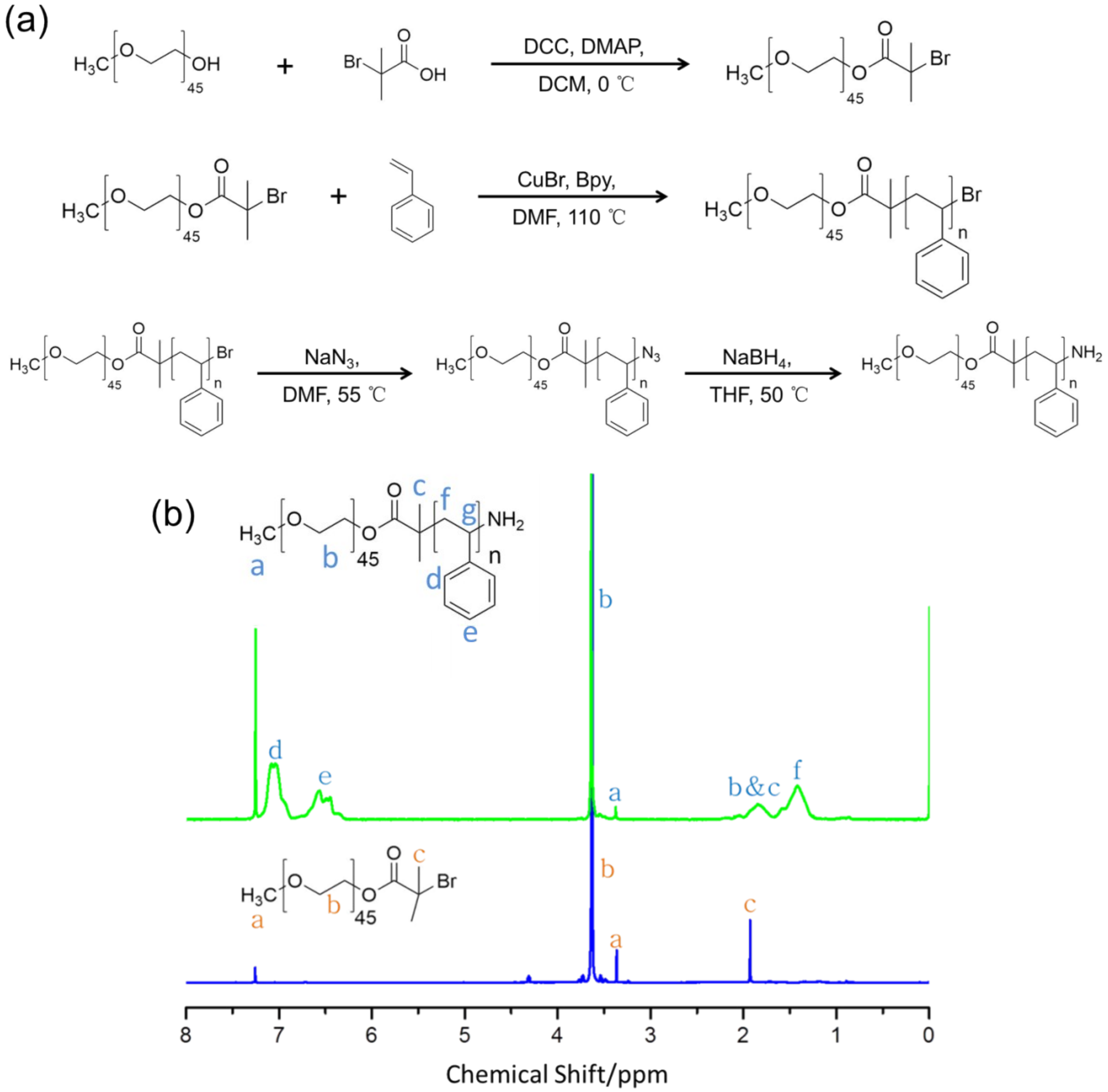

Figure S1. (a) The synthetic route of PEO-*b*-PS-NH_2.[1] (b) ^{1}H NMR spectra of MeO-PEO-Br Macro-Initiator (bottom) and PEO_{45}-*b*-PS_{106}-NH_2 (top) in $CDCl_3$.

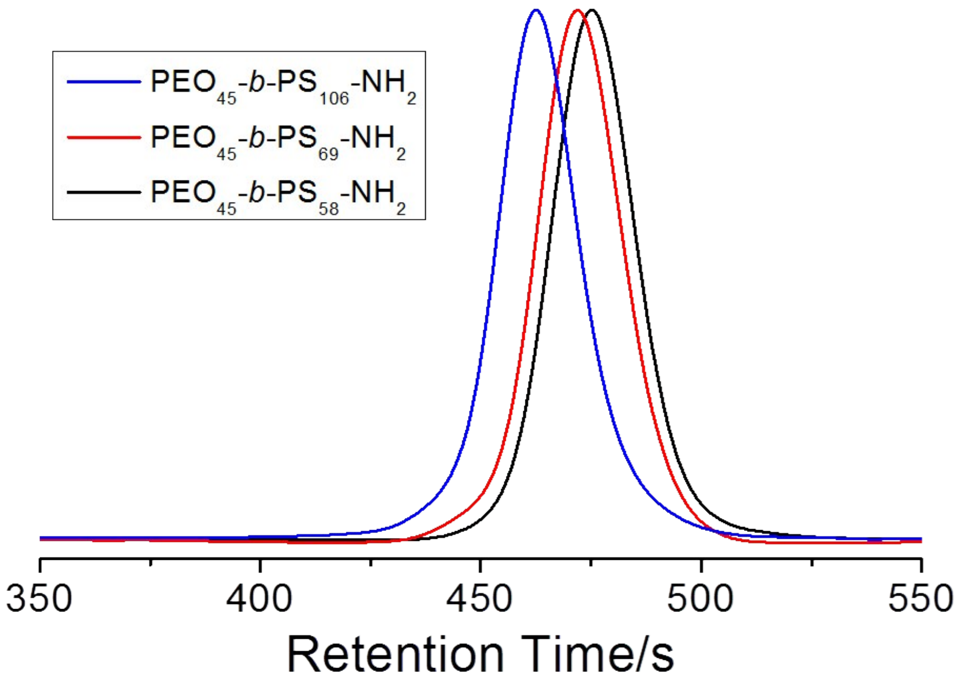

Figure S2. The GPC elution curves of PEO$_{45}$-*b*-PS$_{58}$-NH$_2$, PEO$_{45}$-*b*-PS$_{69}$-NH$_2$, and PEO$_{45}$-*b*-PS$_{106}$-NH$_2$, from right to left, respectively.

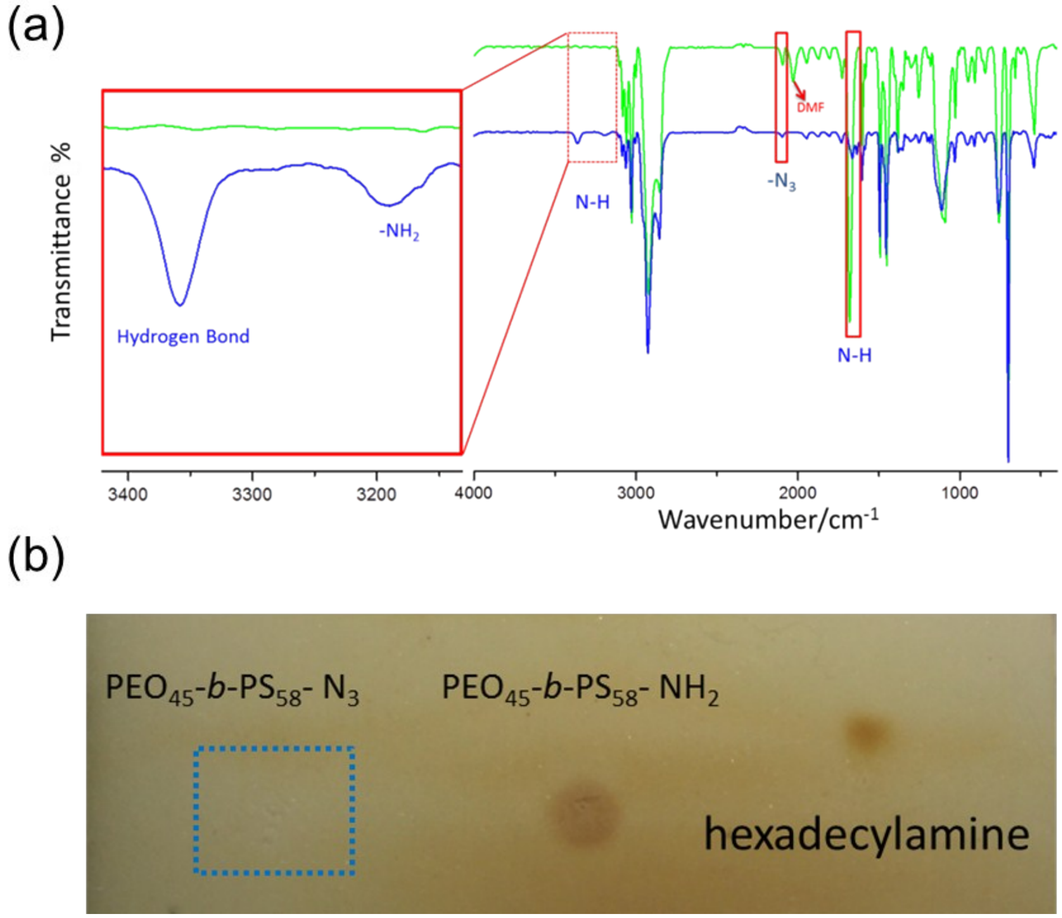

Figure S3. (a) FTIR of PEO$_{45}$-*b*-PS$_{106}$-N$_3$ (green), PEO$_{45}$-*b*-PS$_{106}$-NH$_2$ (blue). (b) Ninhydrin coloration study of PEO$_{45}$-*b*-PS$_{58}$-N$_3$ (left), PEO$_{45}$-*b*-PS$_{58}$-NH$_2$ (middle), and hexadecylamine (right).

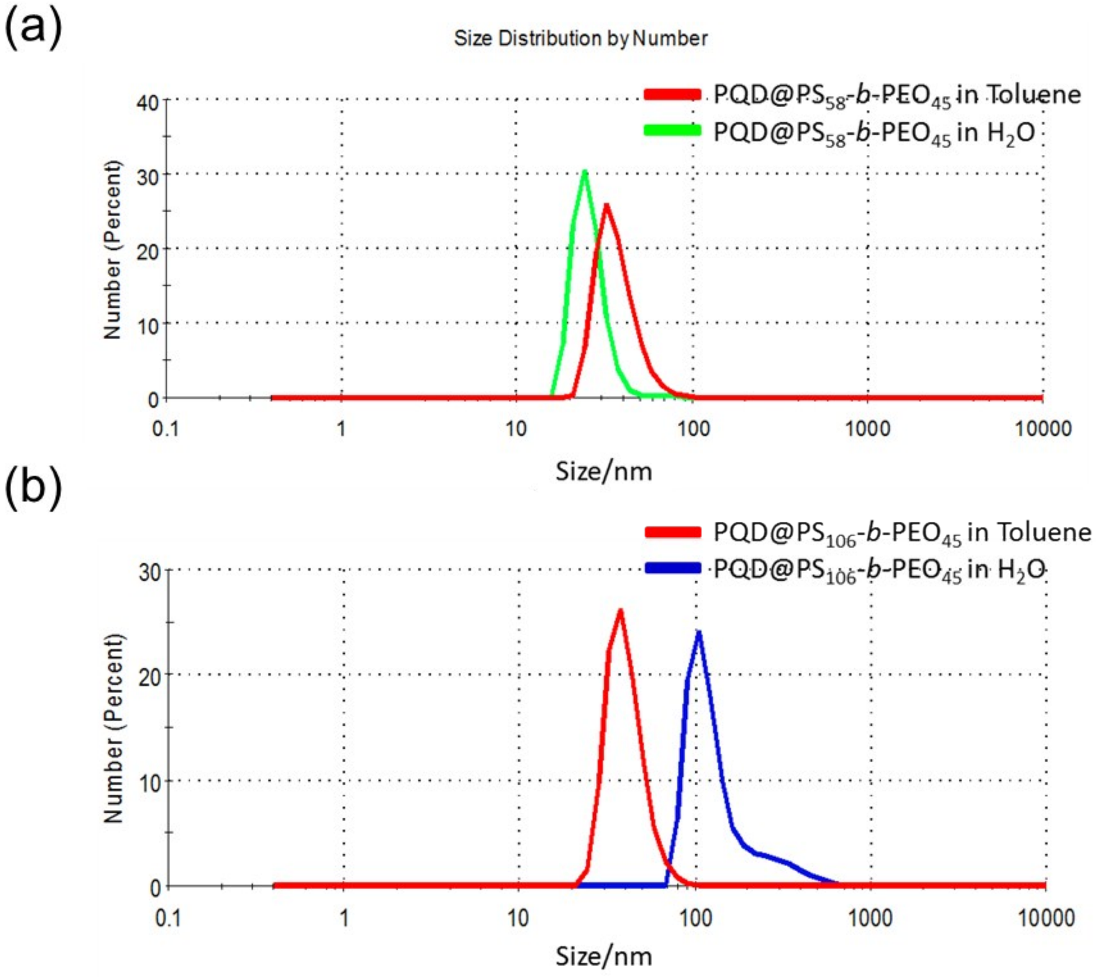

Figure S4. DLS of (a) PQD@PS_{58}-*b*-PEO_{45} and (b) PQD@PS_{106}-*b*-PEO_{45} in H_2O and in toluene, respectively. The PQD@PS_{58}-b-PEO_{45} remained as single particles after transferred in water. Hence the reduce of their average hydrodynamic diameter was mainly attributed to the shrinkage of PS block. On the other side, PQD@PS_{106}-b-PEO_{45} formed large vesicles which contained multiple PQDs. Therefore, although the PS block was also shrunk upon transferred into water, the average hydrodynamic diameter of the vesicles was still larger than that of individual PQD@PS_{106}-b-PEO_{45} in toluene.

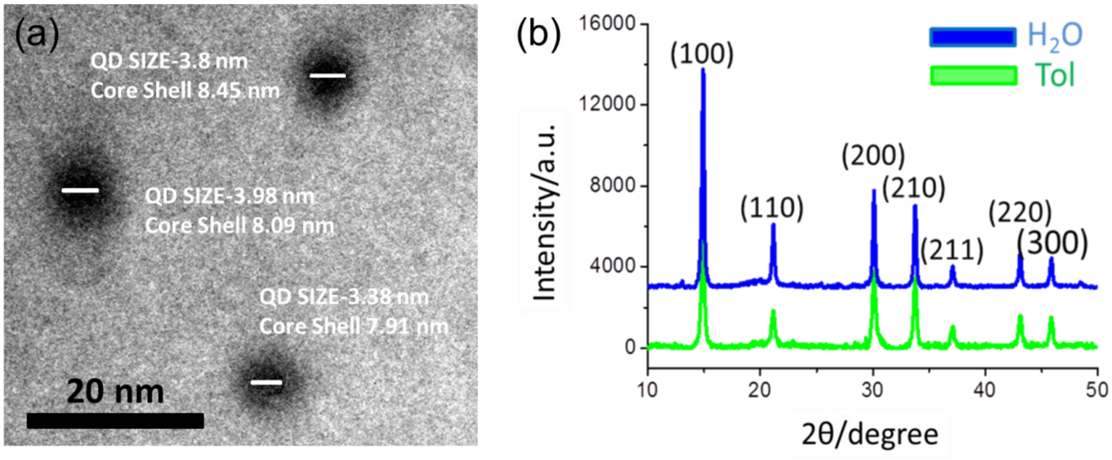

Figure S5. (a) TEM image of PQD@PS_{58}-*b*-PEO_{45} vesicles in H_2O. (b) PXRD of PQD@PS_{106}-*b*-PEO_{45} in toluene (bottom) and H_2O (top).

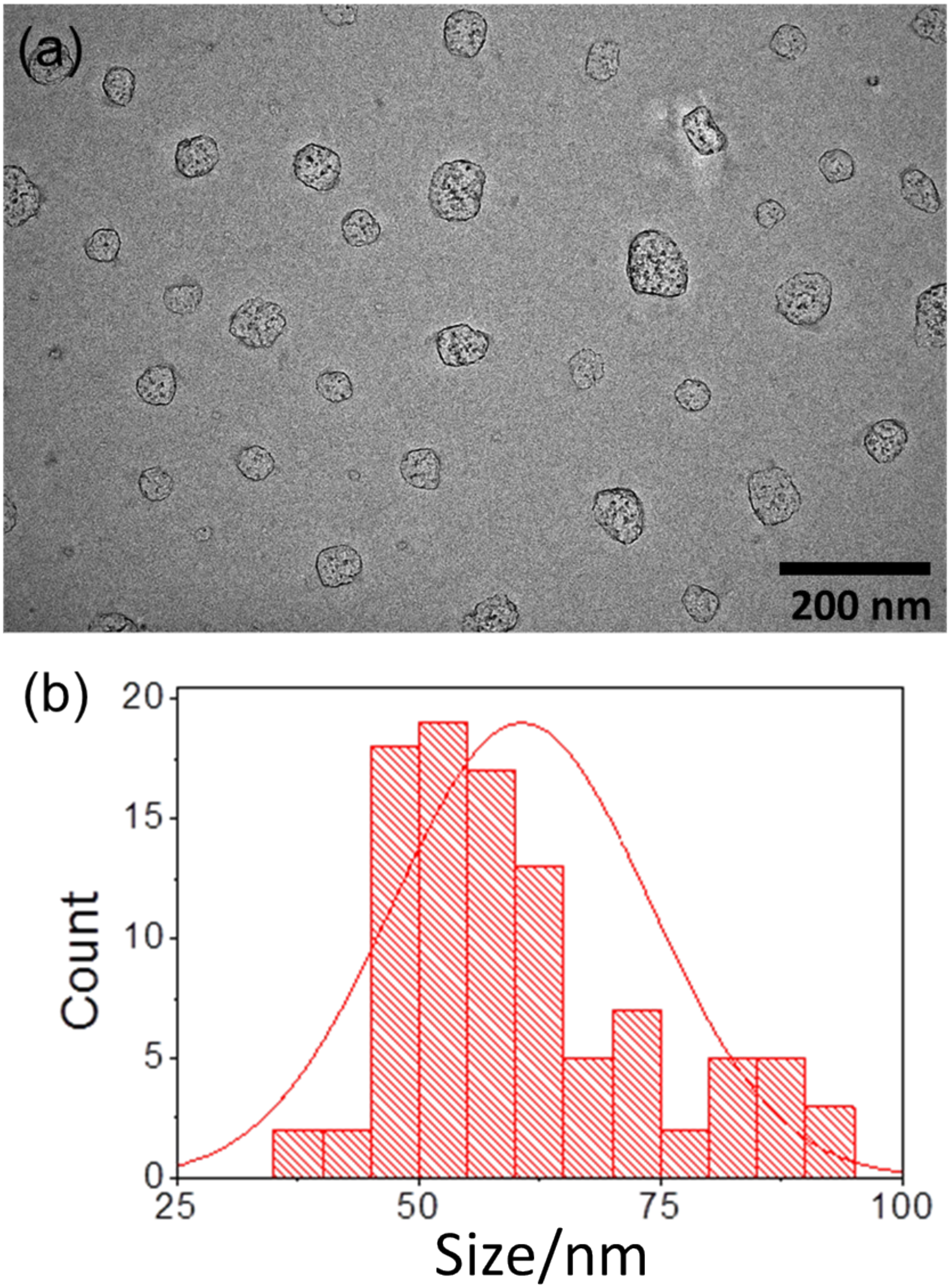

Figure S6. (a) Low magnification TEM image of PQD@PS_{106}-*b*-PEO_{45} vesicles in H_2O, and (b) the correspond size distribution of the vesicles

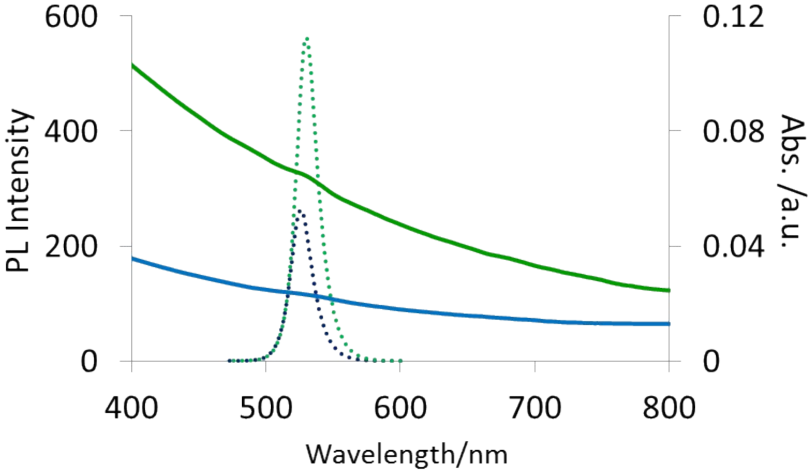

Figure S7. UV-Vis absorbance (solid lines) and PL emission spectra (dash lines) of the aqueous solutions of PQD@PS$_{69}$-*b*-PEO$_{45}$ (green) and PQD@PS$_{58}$-*b*-PEO$_{45}$ (blue) in water, respectively.

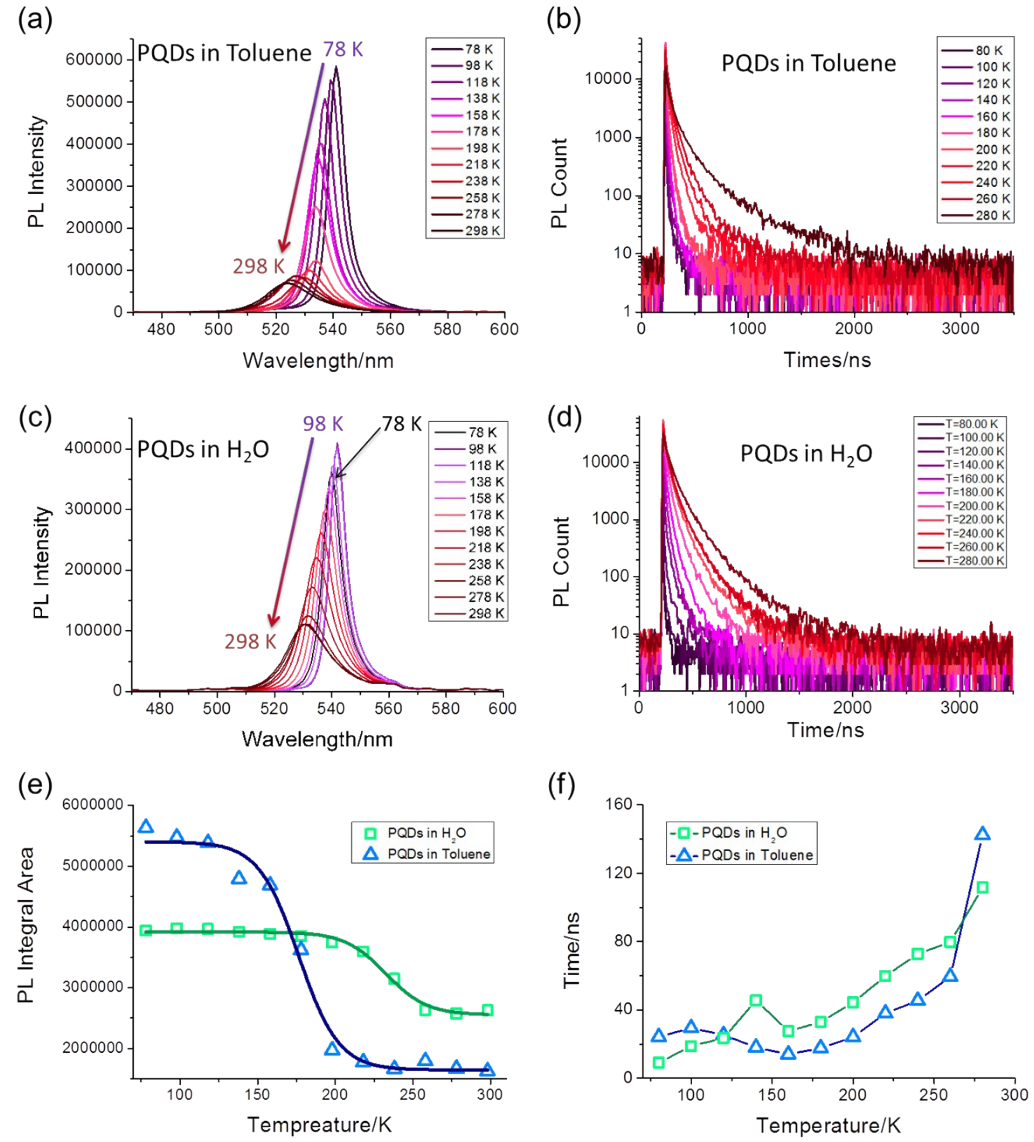

Figure S8. Temperature dependent PL spectra and lifetime of PQD@PS$_{106}$-*b*-PEO$_{45}$. (a), (c) PL spectra of PQD@PS$_{106}$-*b*-PEO$_{45}$ in toluene and H_2O from 78K to 298K. (b), (d) PL lifetime of PQD@PS$_{106}$-*b*-PEO$_{45}$ in toluene and H_2O from 80K to 280K. (e) The plot of temperature versus PL integral area of PQD@PS$_{106}$-*b*-PEO$_{45}$ in toluene (blue) and H_2O (green) from 78K to 298K. (f) The plot of temperature versus the PL lifetime of PQD@PS$_{106}$-*b*-PEO$_{45}$ in toluene (blue) and H_2O (green) from 80K to 280K.

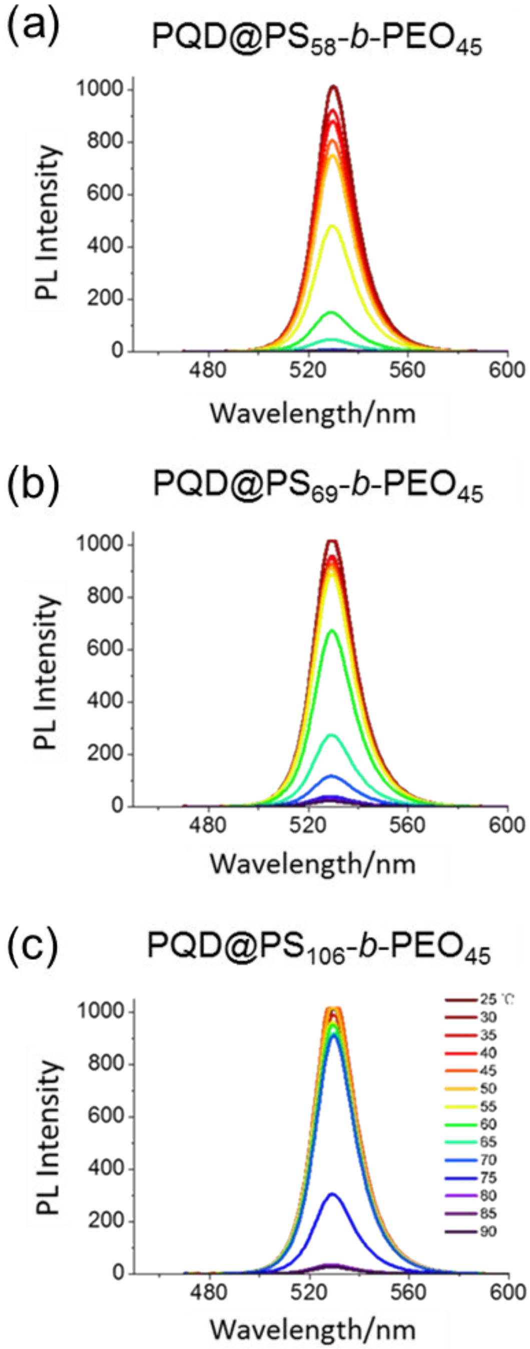

Figure S9. Thermal-stabilities of PQD@PS-*b*-PEO in water. The evolution of PL spectra of (a) PQD@PS$_{58}$-*b*-PEO$_{45}$, (b) PQD@PS$_{69}$-*b*-PEO$_{45}$, and (c) PQD@PS$_{106}$-*b*-PEO$_{45}$ aqueous solutions heated up from 25 to 90 °C (corresponding colors listed in (c)) and held for 30 mins at each temperature before increased to higher temperatures.

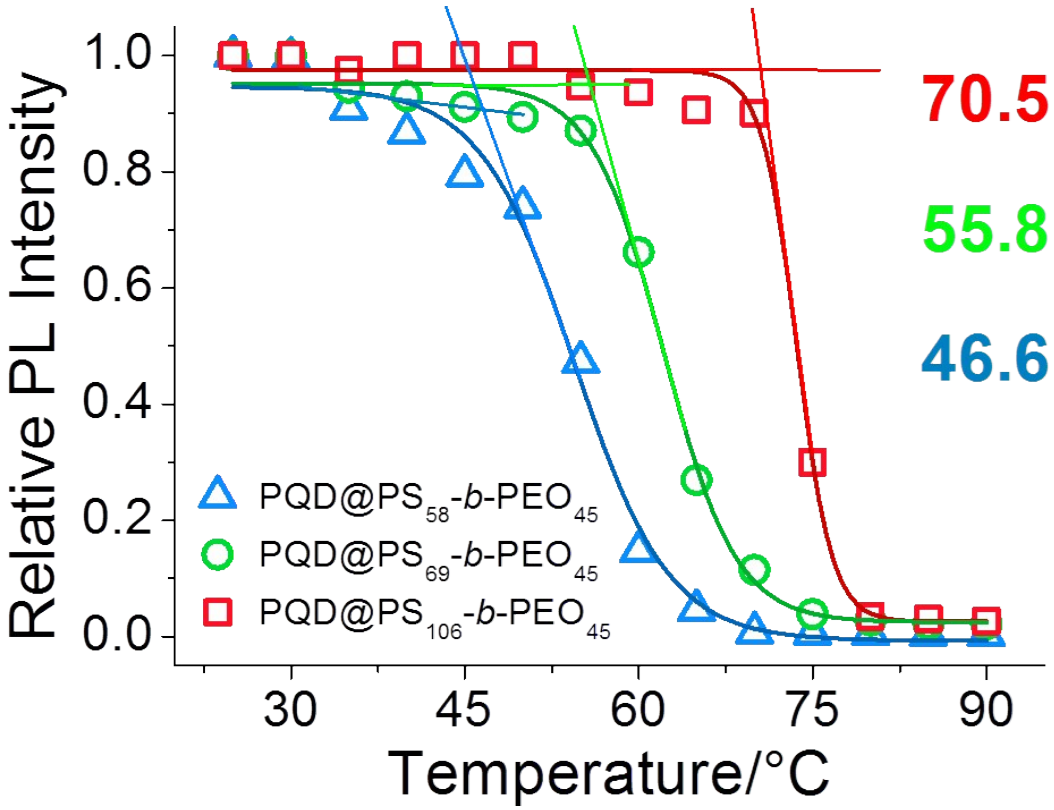

Figure S10. The extrapolated onset temperatures (listed on the right side) for thermal-stabilities of PQD@PS-*b*-PEO in water.

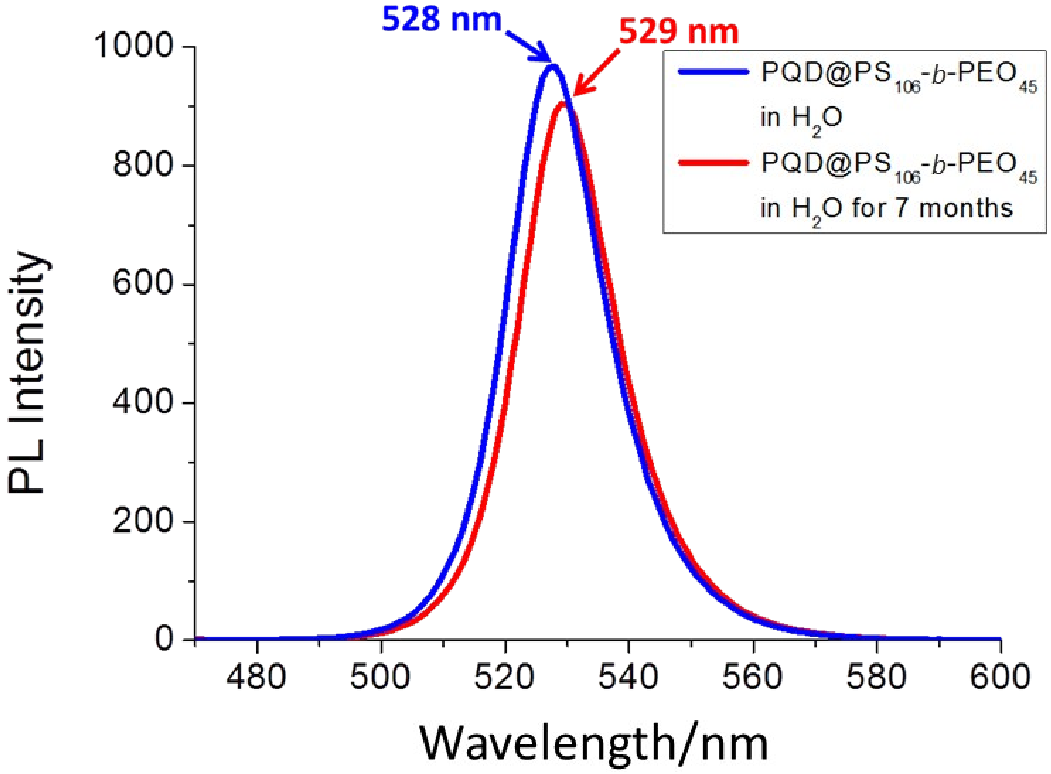

Figure S11. The long-term stability of PQD@PS$_{106}$-*b*-PEO$_{45}$ in water. PL spectra of PQD@PS$_{106}$-*b*-PEO$_{45}$ aqueous solution as-prepared (blue line) and after stored for over 7 months (red line).

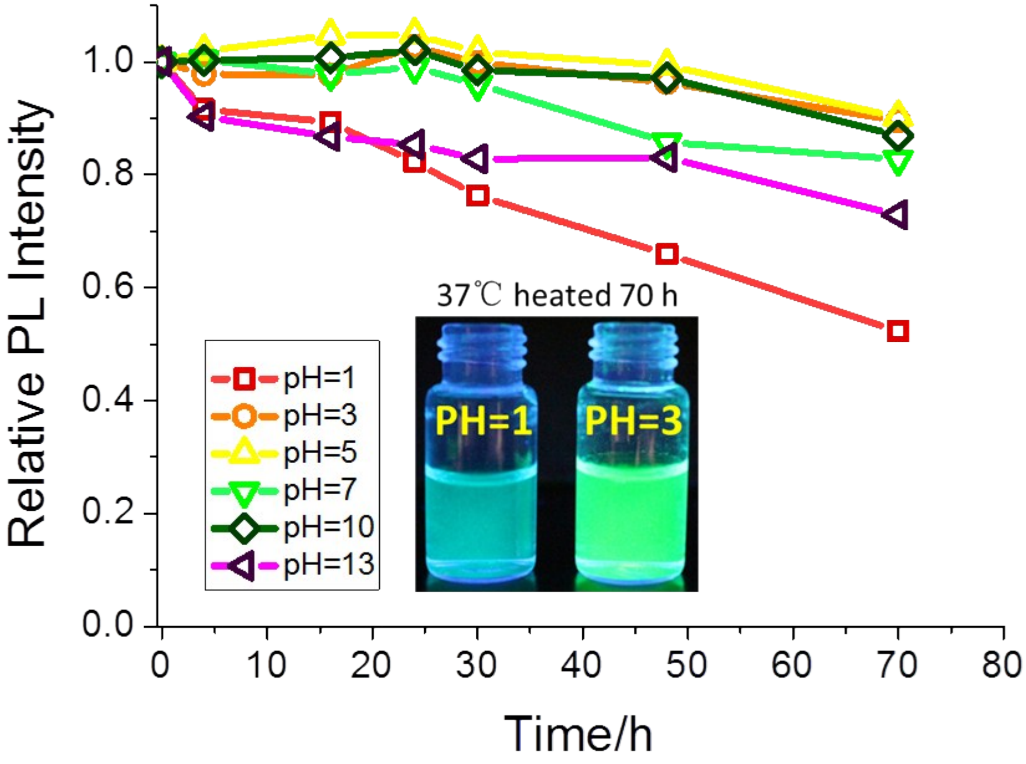

Figure S12. The relative PL intensity of PQD@PS_{106}-*b*-PEO_{45} aqueous solutions with various pH values from 1 to 13 at 37 °C for 70 hours.

REFERENCE

1. K. Jankova, X. Chen, J. Kops, W. Batsberg, *Macromolecules*, 1998, **31**, 538-541