Supplementary Materials for

Carbon dots with high fluorescent quantum yield: the fluorescence originates from organic fluorophores

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Experimental

Materials

Citric acid monohydrate (99.9%), L-cysteine (97%) and L-cystamine (97%) were obtained from Aladdin.1-Ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDC), N-hydroxy succinimide (NHS), sodium alginate (>350 mpas), acrylic acid (AA) and sodium periodate ($NaIO_4$) were purchased from Alfa Aesar. Chitosan (degree of deacetylation 86%, Mw = 200 000 Da) was obtained from Tokyo Kasei. Dialysis bag (Mwco.1000, HT0534) was purchased from Yobios.

Synthesis of TPDCA and TPCA

TPDCA was synthesized by heating the powder mixture of citric acidand L-cysteine. In a typical procedure, 0.1 mol powders of citric acid monohydrate (21.01g) and L-cysteine (12.11g) were mixed into a beaker and heated to 150 ºC in an oven. In the reaction process, the white powders melted to transparent thick syrup and then gradually turned from yellow color to deep brown with reaction time. After 3 h, 100 ml deionized water was added into the beaker to purify the products. The resulting precipitate was collected by suction filtration and rinsed many times with cold deionized water. The TPDCA crystal was obtained by dissolving the precipitate into 200 mL of deionized water under 90 ºC, and further recrystallizing for 24 h at room temperature. Typical yield of the product was 47%±3. As for TPCA, it can be prepared by heating TPDCA powder to decarboxylate under 240 ºC. TPCA also can be produced in the same manner of TPDCA but substituted L-cysteine by cysteamine. The TPCA crystal was prepared via the same method of obtaining TPDCA crystal. Typical yield of the product was 51%±2 when molar ratio of citric acid and cysteamine is 1:1.

Synthesis of N,S-CDs

N,S-CDs were prepared by hydrothermal reaction of citric acid and L-cysteine according to the literature(*16*). The optical behaviors of the as-prepared N,S-CDs are nearly the same to that of the literature.

Cell line and animal

The NIH/3T3 fibroblasts were purchased from Peking Union Medical College (Beijing, China). The rabbits were purchased from the Experiment Animal Center, Medical School of Xi'an Jiaotong University(Xi’an,China). The zebrafishes were supplied by Hunter Biotech Co., Ltd (Hangzhou, China). The animals were housed and handled in strict accordance with the Guidelines of the Institutional and National Committees of Animal Use and Protection. The protocolswere approved by the Committee on the Ethics of Animal Experiments of Xi’an Jiaotong University(Certificate No. 22–9601018). All efforts were made to minimize animals’ suffering and the numbers of animals used.

Characterizations of TPDCA and TPCA

Single-crystal diffraction analysis was carried out on APEXIJ DVO4096*4096 resolution of Bruker Instruments. CCDC number is 1424269 for TPDCA and 1424268 for TPCA.

For analyzing the empirical formula of TPDCA and TPCA, high resolution mass spectra (HRMS) were acquired using the MALDISynapt G2-S HDMS (Waters Corporation, Milford, MA, USA), coupled to a Waters TQD mass spectrometer (electrospray ionization mode ESI-tandem quadrupole). According to the spectra of HRMS, the empirical formula is $C_9H_7NO_5S$ (241 g mol^{-1}) for TPDCA (**fig. S1a**), $C_8H_7NO_3S$ (197 g mol^{-1}) for TPCA (**fig. S1b**).

The chemical structures of TPDCA and TPCA were confirmed by ^{1}H NMR and ^{13}C NMR analysis carried out in (methyl sulfoxide)-d6 (DMSO-d6) solution using a nuclear magnetic resonance (NMR) spectrometer (Bruker Advance III 400MHz). ^{1}H-NMR (400 MHz, DMSO, δ) of TPDCA (**fig.S2a**): 13.63 (s, 2H, COOH), 6.56-6.61 (d, 2H, CH), 5.49- 5.47 (d, H, CHCOOH), 3.60-3.94 (m, 2H, CH_2). ^{1}H-NMR (400 MHz, DMSO, δ) of TPCA (**fig S2c**): 13.60 (s, H, COOH), 6.52-6.56 (d, 2H, CH), 4.34-4.37 (t, 2H, NCH_2), 3.49- 3.53 (t, 2H, SCH_2). **Fig S2b** and **fig S2d** is the ^{13}C-NMR spectrum of TPDCA and TPCA, respectively.

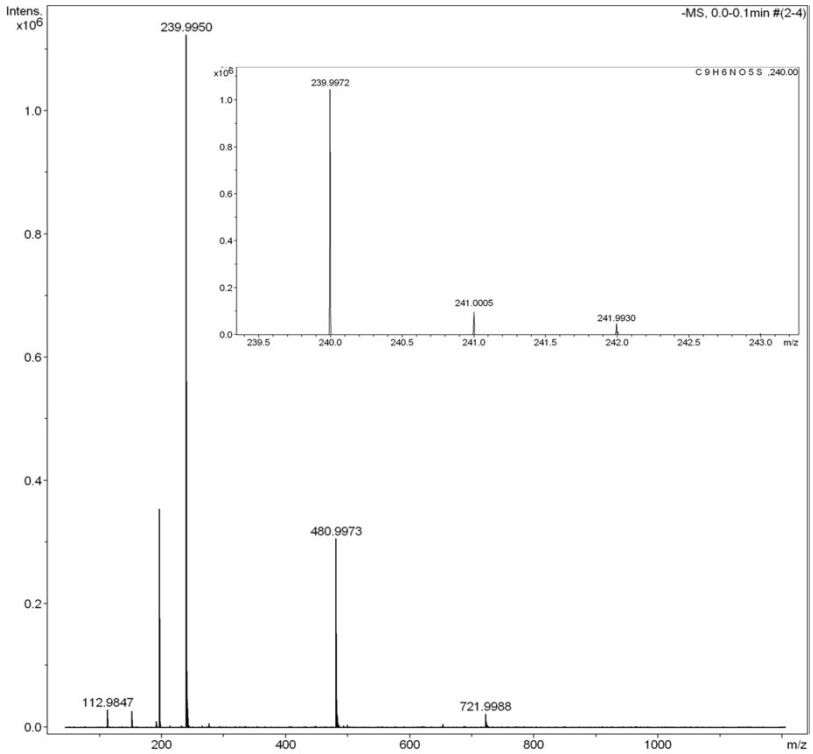

Fig. S1a. The HRMSspectra of TPDCA. Insert: the amplified part of low m/z.

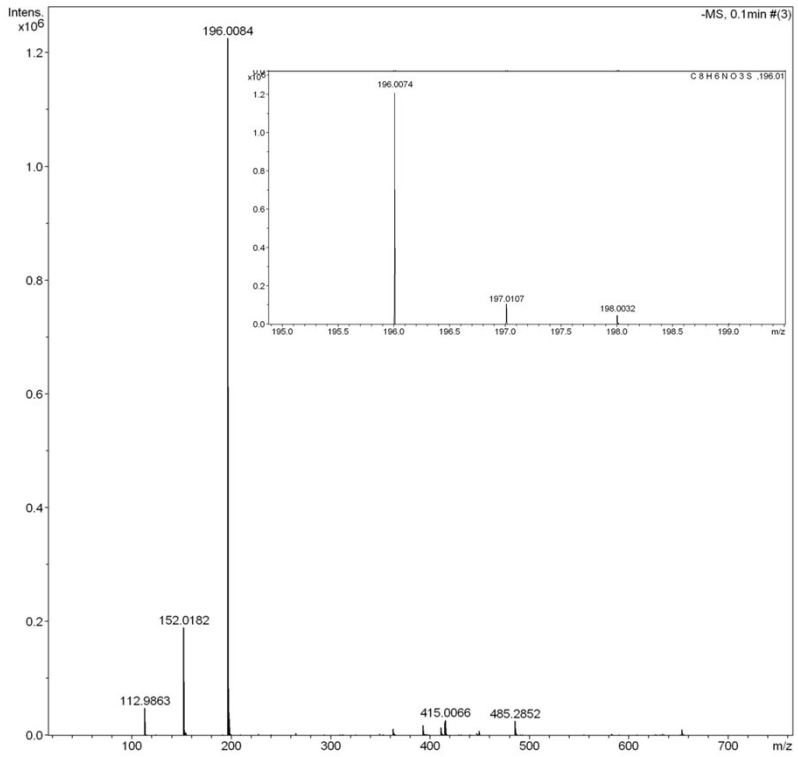

Fig.S1b. The HRMS spectra of TPCA. Insert: the amplified part of low m/z.

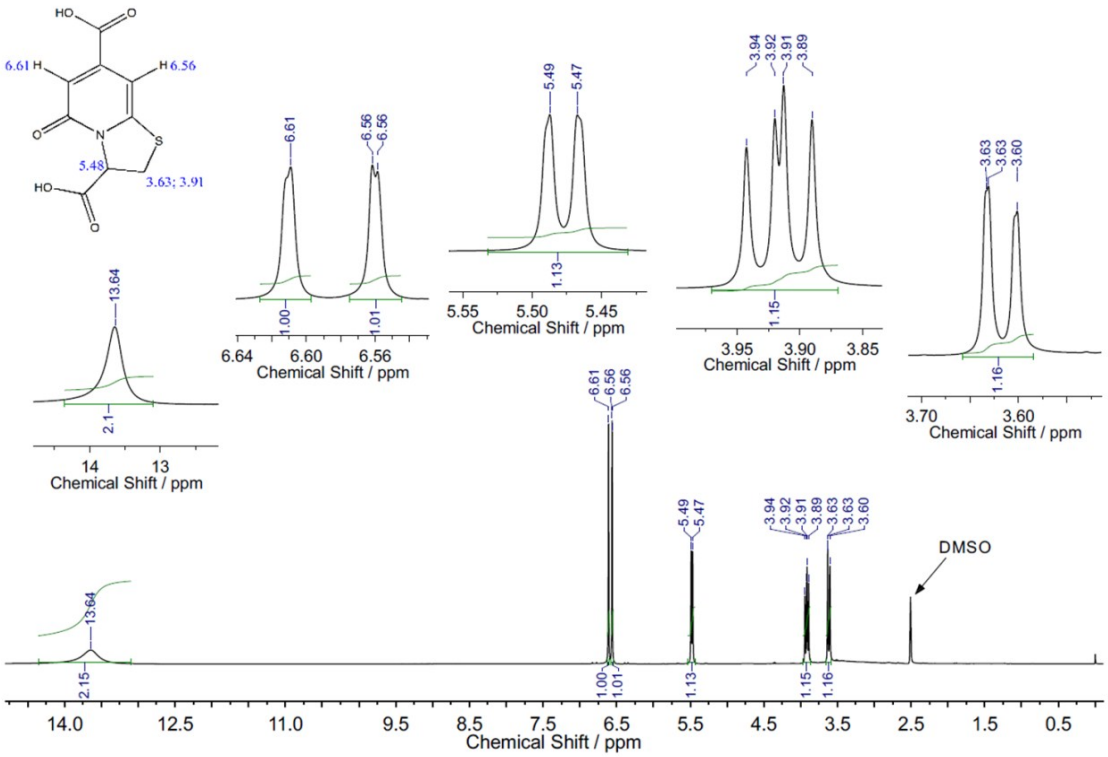

Fig.S2a. The ^{1}H-NMR spectra of TPDCA.

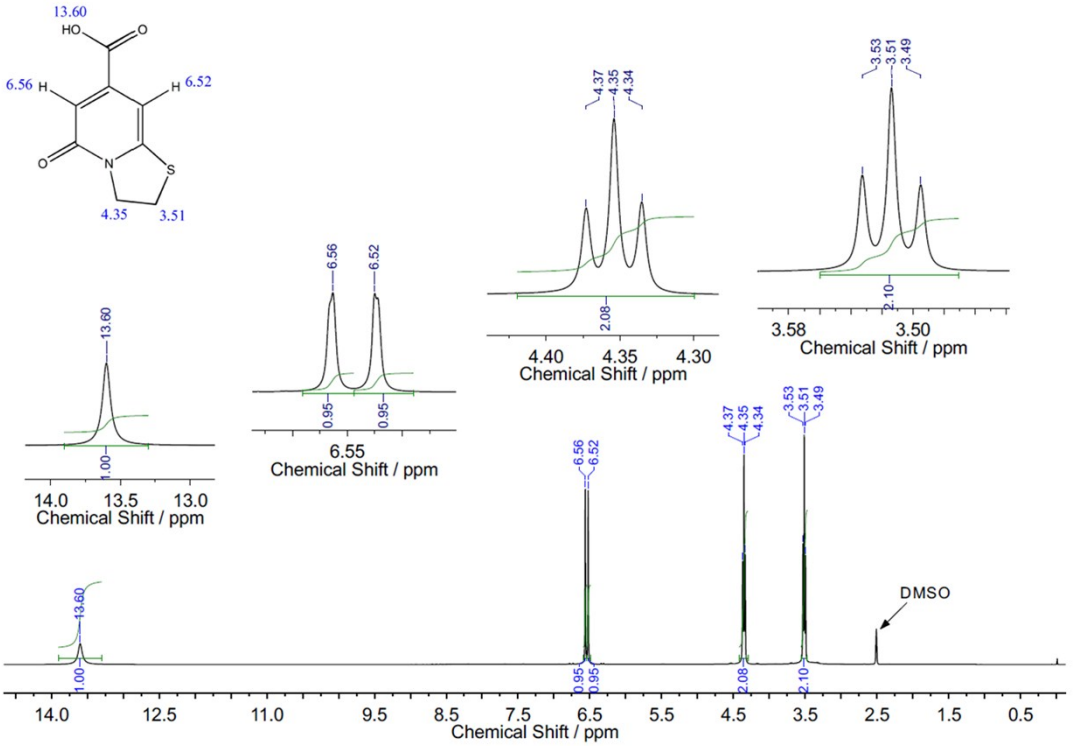

Fig. S2b. The ^{1}H-NMR spectra of TPCA.

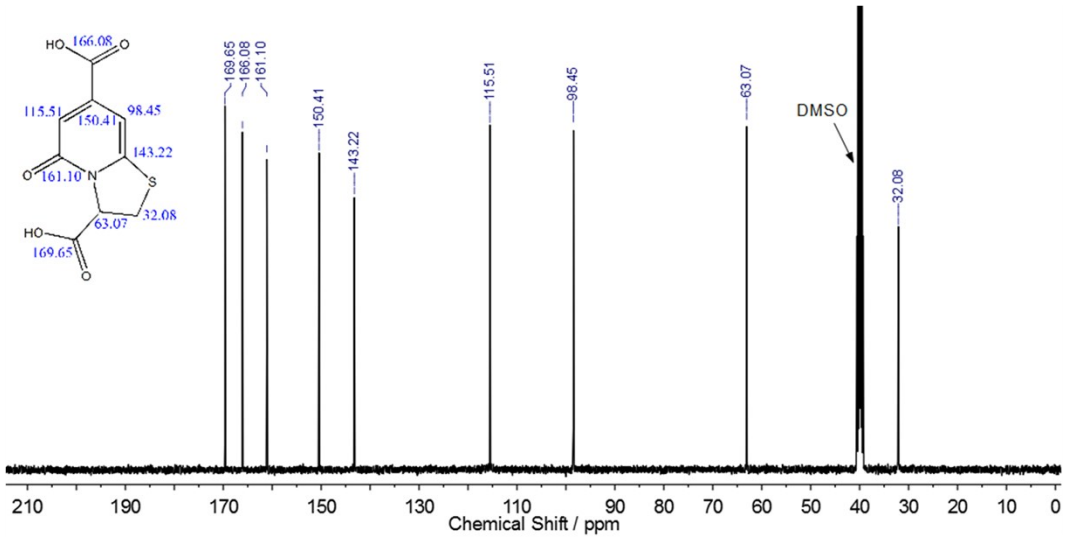

Fig. S2c. The ^{13}C-NMR spectra of TPDCA.

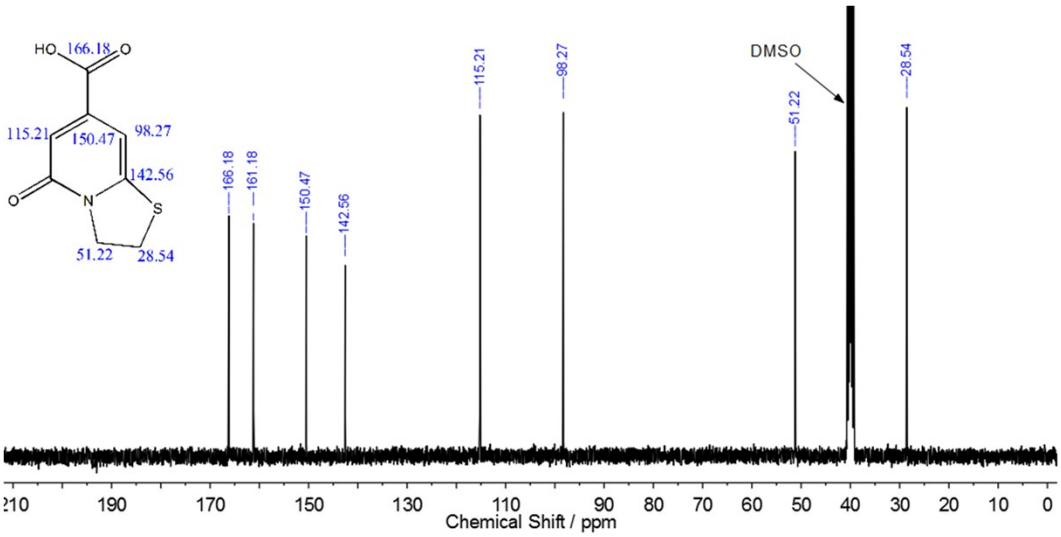

Fig.S2d. The ^{13}C-NMR spectra of TPCA

Characterization of optical properties of TPDCA, TPCA and N,S-CDs

UV-vis absorption spectra were obtained using a Shimadzu 3100 UV-vis spectrophotometer. The excitation and emission spectra were acquired using Edinburgh-FSP920 steady state and phosphorescence lifetime spectrometer, Hamammatsu R928P photomultiplier detector with cooling system (-20ºC).

The quantum yield (QYs) of TPDCA and TPCA in aqueous solution were calculated according to slope method quinine sulfate in 0.1M H_2SO_4 (QY=0.54) was employed as standards. The equation $\varphi_x=\varphi_{st}(K_x/K_{st})(\eta_x/\eta_{st})^2$ was used to calculate the QY, Where φ is the QY, K is the slope and η is the refractive index. The subscript "st" refers to the standards and "x" refers to the unknown samples. For these aqueous solutions, $\eta_x/\eta_{st}=1$.

The emission peaks of TPDCA and TPCA does not change when excitation wavelength is changed from 280 nm to 400 nm. The emission peak of N,S-CDs does not change when excitation wavelength changes from 305 nm to 395 nm.

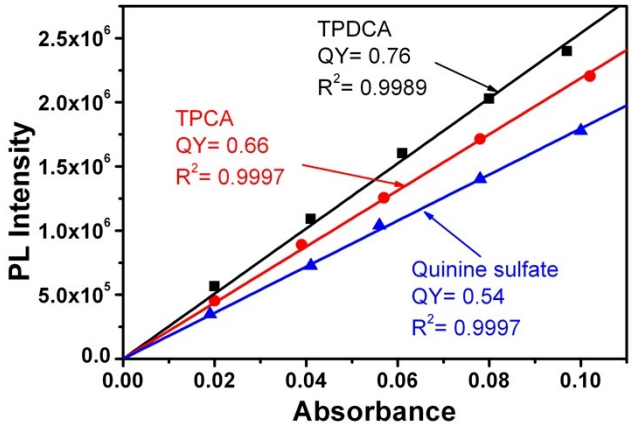

Fig.S3.The quantum yield measurements of TPDCA and TPCA in aqueous solution.

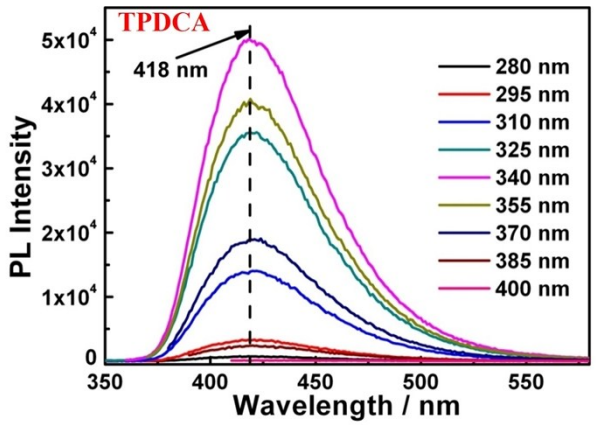

Fig.S4a.Excitation-independent-emission spectra of TPDCA.

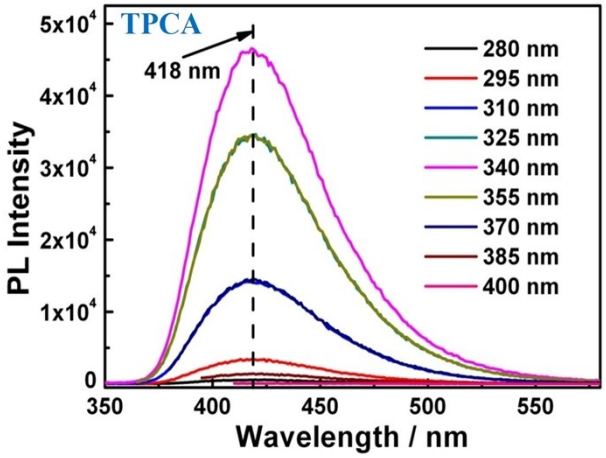

Fig.S4b. Excitation-independent-emission spectra of TPCA.

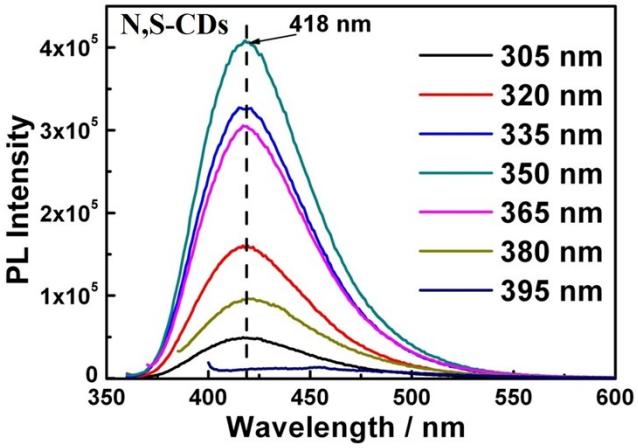

Fig.S4c. Excitation-independent-emission spectra of N,S-CDs.

Identification of the compositions and the chemical structures of N,S-CDs

Thermogravimetric analysis (TGA) measurements were performed on a TGA Q 5000 via scanning a temperature range from room temperature up to 800 °C (10 ^{o}C min^{-1}) under flowing N_2. The curve shows a sharp weight loss (~70 wt%) of the N,S-CDs sample when temperature was increased to the range of 250-350°C, which is similar with that of TPDCA and TPCA, indicating organic nature of N,S-CDs.

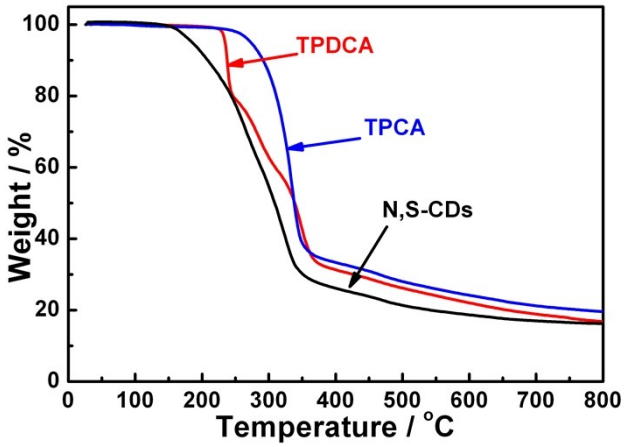

Fig. S5. Thermogravimetric curve of TPDCA, TPCA and N,S-CDs.

Dialysis of N,S-CDs and analysis the optical behaviors of products

In order to evaluate the contribution of organic fluorophores to the optical behaviors of N,S-CDs, we design the dialysis experiments. Briefly, 1 g N,S-CDs powder was dissolved into 20ml aqueous solution, and then the solution was poured into a 30 cm long dialysis bag (1000 D) in a container with 10000 ml deionized water. The water was changed every 4-6 h.The solution outside the dialysis bag (denoted as outside)was collected.The outside with orange-yellow color show bright blue fluorescence under UV light (365 nm). After 6 times changing water, the outside solution was colorless and appeared no fluorescence. The outside and inside product was collected after rotary evaporation and freeze-dried, respectively. The weight percentage of the inside product is 97.85±1.4wt% averaged from 3times parallel experiments. The deep brown solution inside the dialysis bag was collected (denoted as inside) and freeze-dried. The weight percentage of the inside product is 2.15±1.38wt%.The results indicate small organics are major ingredients of N,S-CDs.

The UV-Vis absorption spectraof N,S-CDs is overlap with that of the outside solution, which is quite different with that of the inside solution.The QY of outside is high (0.64), which is identical to that of N,S-CDs. Whereas, the QY of inside is very low (0.038).

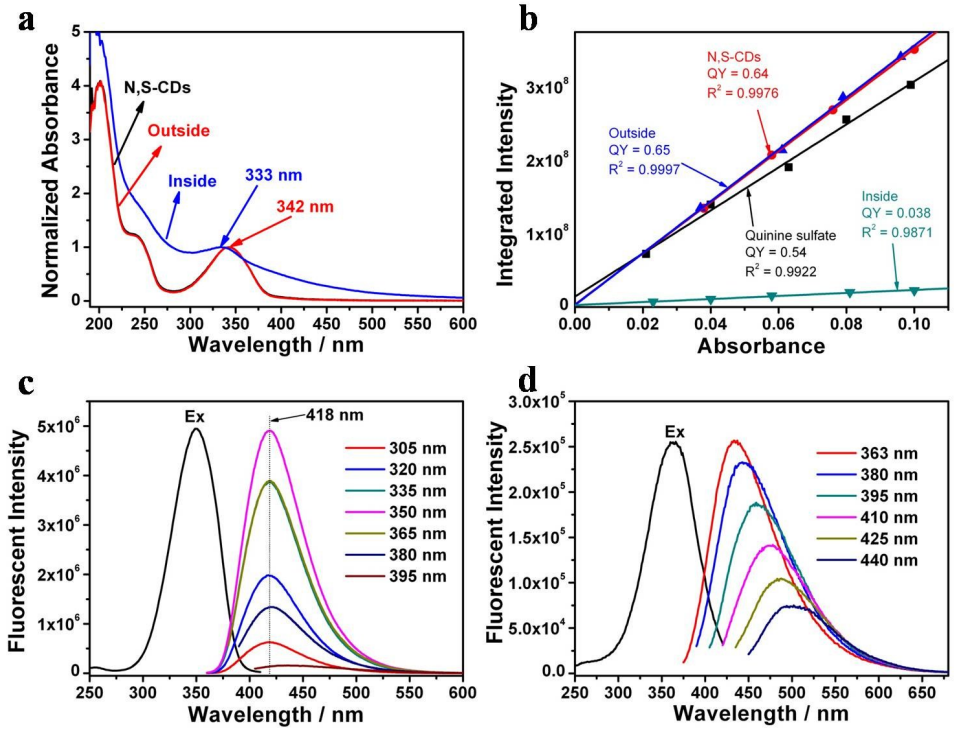

Fig.S6.Opticalbehaviors of dialysis products and N,S-CDs.(**a**)The UV-Vis absorption spectra.(**b**)Quantum yield measurements.(**c**)Excitation-independent-emission spectra of the solution outside dialysis bag.(**d**)Excitation-dependent-emission spectra of the solution inside dialysis bag.

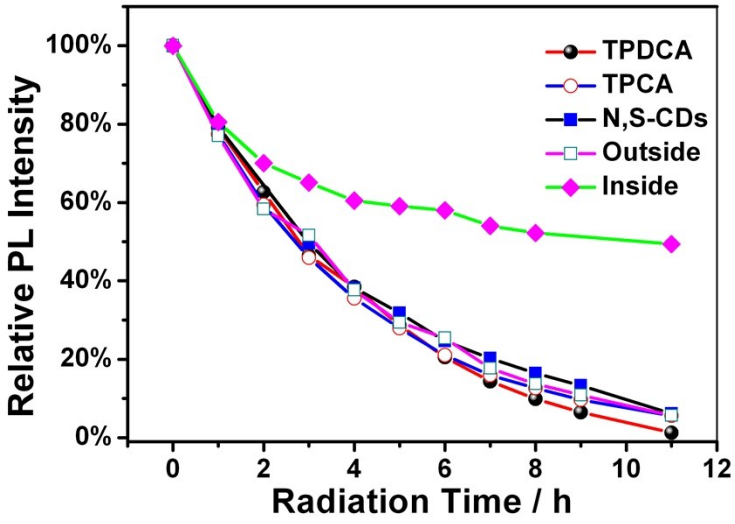

Fig. S7. Photobleaching test of TPDCA, TPCA, N,S-CDs, outside and inside solution.

Table S1 Typical examples of carbon dots synthesized from bottom up method.

Preparation method	Precursors[a]	Reaction conditions	Carbon content (wt%)	X/C[b]	QY (%)	Ref.[c]
Hydrothermal	citric acid, EDA	150°C, 5 h	48.01	2.02	75	(*15*)
		200°C, 5 h	51.13	2.03	60	
		250°C, 5 h	56.60	1.95	25	
		300 °C, 5 h	70.25	1.48	17	
	citric acid, EDA	140°C, 4 h	--	--	79	(*19*)
		160°C, 4 h	--	--	94	
		180°C, 4 h	--	--	82	
		200°C, 4 h	--	--	76	
	citric acid, urea	140°C, 24 h	--	--	75	
		160°C, 24 h	--	--	82	
		180°C, 24 h	--	--	77	
		200°C, 24 h	37.10	3.18	73	
	citric acid, urea	130°C, 6 h	--	--	35	(*32*)
		160°C, 6 h	--	--	45	
		200°C, 6 h	--	--	28	
		240°C, 6 h	--	--	20	
	sodium citrate, NH_4HCO_3	180°C, 4 h	--	--	68	(*33*)
	ammonium citrate, EDA	200°C, 5 h	47.80	2.75	66.8	(*34*)
	sodium citrate, sodium thiosulfate	200°C, 6 h	--	--	67	(*35*)
	pomelo peel	200°C, 3 h	--	--	6.9	(*36*)
	chitosan	180°C, 12 h	59.02	1.79	43	(*37*)
	soy milk	180°C, 3 h	--	--	2.6	(*38*)
Microwave	glucose, PEG-200	500W, 5 min	--	--	6.3	(*39*)
		500W, 10 min	--	--	3.1	
	glycerol, PEI	700W, 5 min	47.53	3.21	9.4	(*40*)
		700W, 10 min	54.13	2.66	15.3	
		700W, 15 min	57.60	2.30	7.0	
	citric acid, urea	750W, 4-5 min	41.54	2.30	40	(*17*)
	citric acid, EDA	700W, 2 min	53.39	1.96	30	(*18*)
Thermal	citric acid, ODE, HDA	300°C, 3 h	80.79	1.97	53	(*10*)
	citric acid, AEAPMS	240°C, 1 min	--	--	47	(*14*)
	citric acid, BPEI	200°C, 3 h	--	--	42.5	(*21*)
	citric acid, EA	180°C, 30 min	41	3.24	50	(*13*)
		230°C, 30 min	44.85	2.39	15	
		300°C, 1 h	50.5	1.59	4	
	citric acid, DETA	170°C, 30 min	--	--	88.6	(*41*)
	ascorbic acid, $Cu(Ac)_2$	90°C, 5 h	--	--	3.22	(*42*)
	ascorbic acid, KH791	92°C, 12 h	--	--	8.6	(*43*)

[a] EDA = ethylenediamine, PEG = poly(ethylene glycol), TTDDA = 4,7,10-trioxa-1,13-tridecanediamine, PEI = Polyethylenimine,ODE = octadecene, HDA = 1-hexadecylamine, AEAPMS = N -(β-aminoethyl)-γ-aminopropyl methyl-dimethoxy silane, DETA = diethylenetriamine, BPEI = branched polyethylenimine, EA = ethanolamine KH791 = (N-(2-aminoethyl)-3-aminopropyl)tris-(2-ethoxy) silane.[b] X/C = the molar ratios of heteroatom (X=H, O, N, S and others) versus carbon.[c]The reference numbers are according to the main text.

Cell viability assay

In order to evaluate the cytotoxicity of sodium salt of TPDCA and TPCA, i.e., TPDCNa and TPCNa, we measured the relative cell viability by 3-(4,5)-dimethylthiahiazo(-z-y1)-3,5-di-phenytetrazoliumromide (MTT) assay. The procedures of preparing TPDCNa and TPCNa as follows. 2 g TPDCA or TPCA was dissolved into 10 ml aqueous solution containing 5 wt% NaOH, respectively.After crystallization of precipitate in deionized water, TPDCNa and TPCNa were obtained. NIH/3T3 fibroblasts (ATCC, Manassas, US) cultured in α-MEM (Sigma-aldrich, China) containing 10% (v/v) fetal bovine serum (Invitrogen, Carlsbad, CA, USA), 100 U/mL penicillin, 100 U/mL streptomycin (Invitrogen, Carlsbad, CA, USA) was used for evaluating the cytotoxicity. Briefly, 200 μL NIH/3T3 fibroblasts (2×10^4 cells/ml) suspension was seeded into 96-well tissue culture polystyrene (TCPS) and incubated for 24 h. After discarding the culture medium, the culture medium containing 100, 200, 400, 800, 1000, 2000 μg/mL TPDCNa or TPCNa was added into each well. After treatment by TPDCNa or TPCNa for 24 h, the medium was discarded and 200 μl fresh complete medium containing 20 μl MTT (5 mg/mL in PBS) were added to each well and further incubated for 4 h. Then, all media were removed and 150 μl dimethyl sulfoxide (DMSO) was added to each well, followed by shaking for 10 min. The absorbance of each well was measured at 570 nm using Multi-Mode Microplate Reader (BioTek, USA) with pure DMSO as a blank. Non-treated cell (cultivation in α-MEM) was used as a positive control and the relative cell viability (mean±SD, n=3) was expressed as $OD_{sample}/OD_{control}\times$ 100%. Cell viability is calculated by the absorbance ratio of TPDCNa or TPCNa treated sample to that of positive control sample. The results demonstrate that both TPDCNa and TPCNa exhibit high cytocompatibility, even under the concentration as high as 2000 μg/mL, the cell viability is higher than 90%(**fig.S8a**).

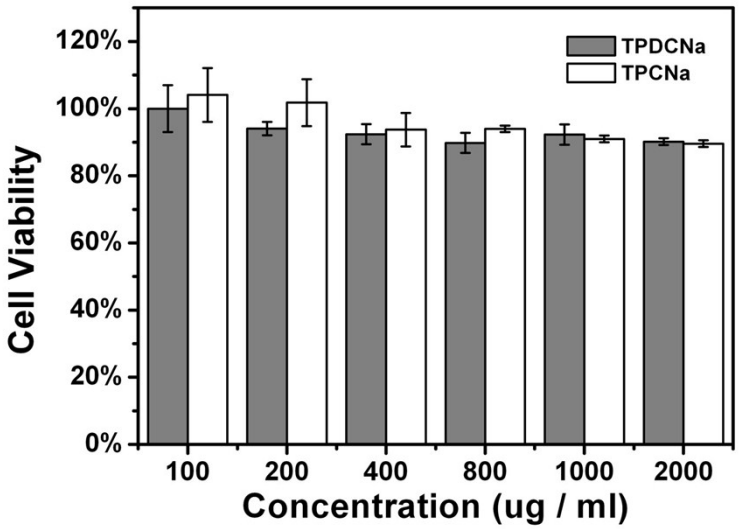

Fig. S8a.Cytotoxicity of NIH/3T3cells treated by TPDCNa and TPCNa under various concentration. Data represent mean ±SD (n=3).

In vivo toxicity of TPDCNa and TPCNa in zebrafish

The *in vivo* toxicity of TPDCNa and TPCNa was evaluated by a vertebrate model, zebrafish. For all experiments, zebrafishes (AB strain) were maintained at 28ºC in E3 medium under a 14 h/10 h light/dark cycle. For in vivo toxicity test, the 30 of 3 dpf larvae were raised in E3 medium containing TPDCNa and TPCNa with various concentration, respectively. After incubation for 3 days, the number of surviving fish was counted. The acute toxicity on the internal organs was observed though phase contrast microscope (IX81, Olymps, Japan).

Both TPDCNa and TPCNa does not affect the survival of zebrafish larvae after the continuous treatment for 3 days in the medium containing 1, 10, 1000μM TPDCNa or TPCNa. All the zebrafish larvae were alive after the treatment. Moreover, 100% zebrafish larvae were alive and no absorption of yolk sac when they were treated under the concentration of TPCNa as high as 10000μM. The main organ involved in the acute poisoning by TPDCNa is absorption of yolk sac when concentration is 1000μM. On the other hand, the size of liver is not changed when be treated by 1000μM TPDCNa or 10000μM TPCNa. The results demonstrate that both TPDCNa and TPCNa exhibit low toxicity for zebrafish even under high concentration.

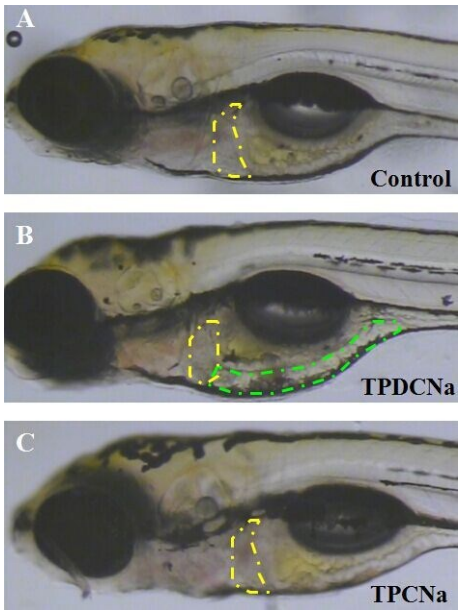

Fig. S8b.Detection of yolk sac absorption and liver size in zebrafish larvae incubated at TPDCNa and TPCNa solution for 3 days. (**A**)Control group, (**B**)1000μM TPDCNa, (**C**)10000μM TPCNa. Yellow dotted lines denoted notchange of the size of liver, and green dotted lines denoted the absorption of yolk sac.

Hemolytic activity assay

The in vitro hemolytic activity of TPDCNa and TPCNa was measured based on a reported universal method,(*44*). Briefly, 200 μL diluted rabbit blood was added to 2000 μg/mL TPDCNa or TPCNa, and the volume was adjusted to 1 mL with sterile normal saline. 200 μL rabbit blood mixed with 800 μl normal saline served as positive control, and 200 μL rabbit blood mixed with 800 μL NH_4Cl solution (10 wt%) to cause complete

hemolysis was used as the negative control. After incubation for 3 h at 37 ºC, the solutions were centrifuged at 2000 rpm for 10 min. Then,200 μl supernatant was collected and seeded in each well of 96-well plate. The absorbance at a wavelength of 543 nm was recorded by a Synergy HT Multi-Mode Microplate Reader (BioTek, USA). The percentage of hemolysis is calculated using the negative control with 100% hemolysis.

Whereas, the presence of obvious red hemoglobin in the supernatant for the sample containing negative control (NH_4Cl) demonstrates the membrane damage of red blood cells. Both TPDCNa and TPCNa exhibited a very low hemolysis due to not induction of red hemoglobin even under the concentration as high as 4000 μg/mL (**Fig. S8c)**. The corresponding percentage of hemolysis (the hemolysis ratio of test sample tonegative control) of TPDCNa and TPCNa isas low as 5.72% and 2.35%, respectively. The results demonstrate low hemolytic activity of TPDCNa and TPCNa.

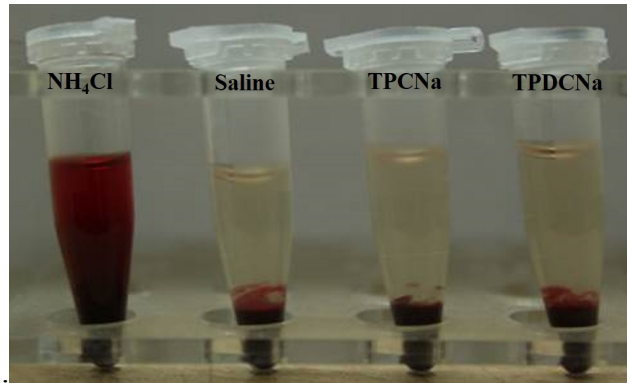

Fig. S8c.Photographs of hemolytic activity test after exposuring blood to 2000 μg/mL TPCNa and TPDCNa for 3 h. (**A**) NH_4Cl, negative control, (**B**) normal saline, positive control, (**C**) TPCNa, (**D**) TPDCNa.

Preparation of TPCA-based fluorescent hydrogel

PCA-based CEC-l-OSA fluorescent hydrogel can be synthesized via the reaction between TPCA modified N-carboxyethyl chitosan (CEC) (TPCA-CEC) and oxidized sodium alginate (OSA). CEC and OSA was synthesized as previously reported method(*45*).TPCA-CECwas preparedvia a carbodiimide coupling reaction.TPCNa (21.9 mg, 0.1 mmol) was dissolved in 10 mL 2-morpholinoethanesulfonic acid (MES) buffer solution (pH=5.5) containing 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC·HCl) (19.17mg, 0.1mmol) and N-hydroxysuccinimide(NHS) (11.5 mg, 0.1 mmol). The solution of TPCNa and 50ml MES buffer solution of CEC (200 mg, 0.324mmol) was stirred vigorously.After 24 h of stirring at the room temperature, the reaction products was dialyzed in distilled water for 3 days with repeated change of water.The powder of TPCA-CEC polymer was collected by lyophilization.Typical yield of the TPCA-CEC was 69.2%. The chemical structure of TPCA-CEC was confirmed by ^{1}H-NMR according the characteristic peaks of TPCNa occurred at δ=6.45 and δ=6.63 (**Fig. S9a)**.

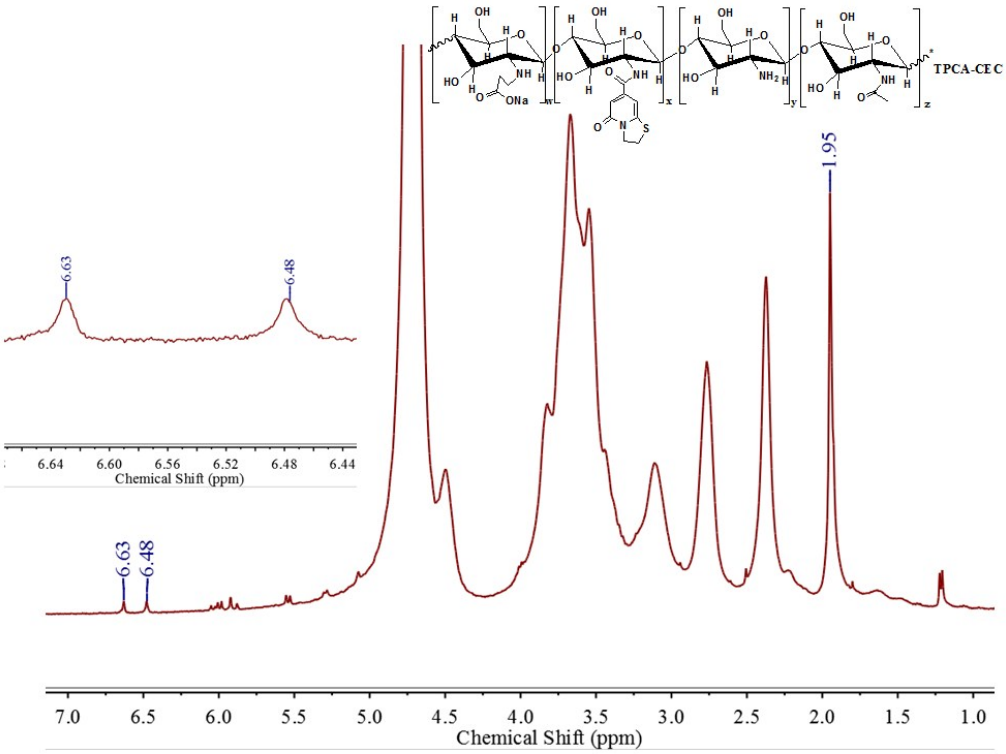

Fig. S9a.The ^{1}H NMR spectra of TPCA-CEC

The TPCA-based fluorescent hydrogel was prepared by mixing phosphate buffer saline (PBS) solution of 1 ml TPCA-CEC and 0.1 mol OSA (10wt%) under ambient temperature. The total concentration of TPCA-CEC and OSA is 3.78 wt%, the molar ratios of amino groups from CEC to aldehyde groups from OSA is 1:1. The fluidic mixture transformed into hydrogel after homogeneously stirring the mixed solution for c.a. 30s. The imine bonds (derived from the reaction of amino groups and aldehyde groups) contribute to form the crossslinks of polymer networks. The gelation was confirmed through vial tilting method. After equilibrating in PBS for 24 h, photoluminescent behaviors of the TPCA-based hydrogel was tested. When be excited at 365 nm with ultraviolet lamp, the TPCA-based hydrogel exhibited broad symmetrical emission with the maximal emission wavelength at 418 nm(**fig.S9b**). The characteristics of the emission spectra for TPCA-based hydrogel is similar to that of TPCA aqueous solution.The results demonstrate that TPCA can be modified on the natural polymerand further used for fabricating novel photoluminescent hydrogels. Moreover, TPCA-based hydrogels can retain photoluminescent characteristics of TPCA molecule.

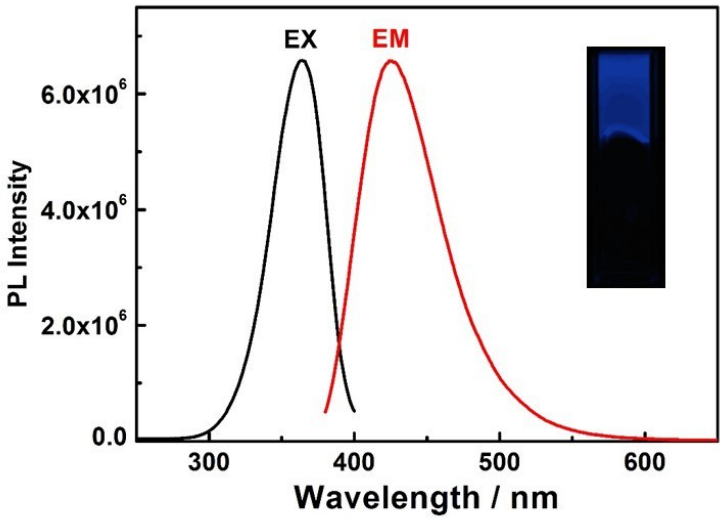

Fig. S9b. The photoluminescent spectra of TPCA-based hydrogel, insert photo is the hydrogel excited under 365 nm UV light.

Preparation of fluorescent TPCA-based silk fibers

Silk is natural fiber with good biocompatibility and satisfying mechanical properties, the additive fluorescent substances for dying of silk fibroin should be at least non-toxic. TPDCA and TPCA with strong fluorescence and good biocompatibility are suitable fluorescent dyes for silk fibroin. As an example, herein, we fabricated fluorescent TPCA-based silk fibers. In order to eliminate the effect of other additive or whitening agents of silk to the maximum extent,we using home-grown raw silk produced by rearing silkworm in our laboratory. The silkworms were bought from farming house, and were reared in a container with air flow. Fresh mulberry leaves were feed and updated on a daily basis. During this period, the worms molt four times, change their color from gray to a translucent color, and increase in size to ~ 9 cm. After 5 main phases (24-28 days), silkworms grew mature and began cocooning. The produced cocoons were collected and sorted according to their color, and those cleaned cocoons were stored for TPDCA dying.

The fluorescent TPDCA-based silk fibers were prepared as follows. Firstly, sericin was degummed from fibroin by stirring the cocoons in 5.0g/L Na_2CO_3 solution for 45 min under 85°C, and washing by deionzed water for three times. The degummed silk fibers were reeled by hand to make those fiber masses less compact and loose.

Then the TPCA was dyed onto the silk fibers. 5g silk fiber was immersed into the flask containing 500ml TPCA solution (2g/L) for 20 min under room temperature. The temperature was gradually increased to 85 ºC with raising 2 ºC per minute. At the same time, the pH of the solution is adjusted to 3.5-4.5 by using acetic acid (CH_3COOH). After keeping for 40 min. under 85 ºC, the flask was cooled down to ambient temperature. In fixing process, 1.5g fixation agent, dodecyl trimethyl ammonium chloride (DTAC), was soluble into the flask, and stirring for 20min. Harvesting the dyed silk fibers from solution and drying them at room temperature, we can obtained the fluorescent TPCA-based silk fibers. The fluorescent silk fibers can maintain their high fluorescence after washing by soap water for many times (**fig.S10**). It is confirmed that TPCA can be firmly

fixed onto silk fibers, which sustain repeated washes. The positive charged DTAC can serve as a "bridge" to connect negative charged TPCA molecules and the proteins of silk fibroin via electricstatic interactions.

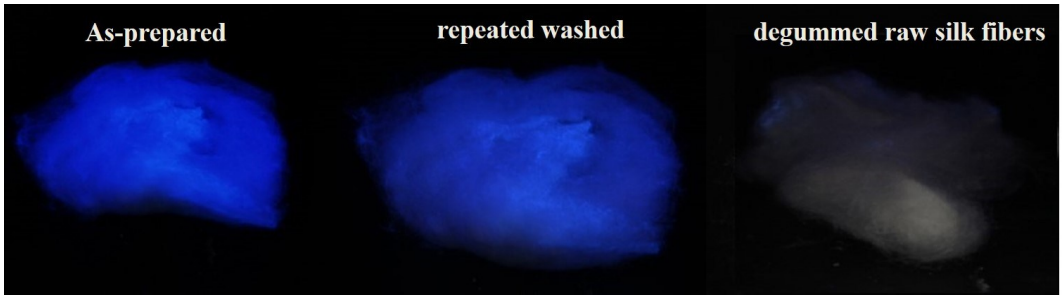

Fig. S10.The photos of silk fibers under 365 nm UV light. As-prepared fluorescent silk fibers (left), repeated washed fluorescent silk fibers (middle), and degummed raw silk fibers (right).

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