

Supporting Information

A universal polymer precursor strategy for precise synthesis of uniform hairy carbon dots and polymer dots

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1. Experiments

1.1 Chemicals and instruments

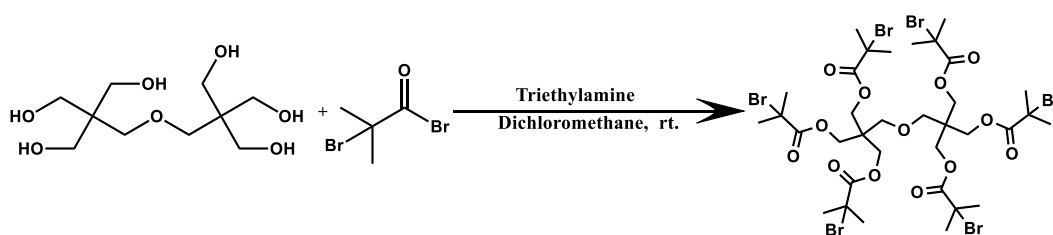
Triethylamine (TEA) (99%), dipentaerythritol (90%), α -bromoisobutyryl bromide (95%), trifluoroacetic acid (TFA, 99.9%), methacryloyl chloride (95%, stabilized by 200 ppm MEHQ), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC.), *N*-hydroxysuccinimide (NHS), dipentaerythritol (90%), *N, N, N', N'', N'''*-Pentamethyldiethylenetriamine (98%) (PMDETA) and anisole (99%) were purchased from Aladdin (Shanghai, China) and were used as received. Methyl methacrylate (MMA) (99%) and tert-butyl methacrylate (tBMA) (99%) were purchased from Macklin (Shanghai, China) and were distilled from CaH₂ under reduced pressure before use. All the solvents were purchased from Aladdin (Shanghai, China) and were distilled from CaH₂ before use. CuBr (99%) (Aladdin, Shanghai, China) was stirred in acetic acid for 15 h, washed subsequently with ethanol and diethyl ether, and then dried under vacuum before use.

Molecular weight and polydispersity were determined by using GPC-MALLS system (GPC: gel permeation chromatography) with three identical columns (5 μ m, 10 μ m, 10 μ m) equipping with a multiangle laser light scattering detector (MALLS) (Wyatt DAWN HELEOS LS II, Wyatt Technology Corp., Santa Barbara, USA) (λ = 658 nm), viscometer (Wyatt ViscoStar III, Wyatt Technology Corp., Santa Barbara, The USA) and refractometer (Wyatt Optilab T-rEX, Wyatt Technology Corp., Santa Barbara, USA) (λ =690 nm). THF (35 C, 1 mL/min) was used as the mobile phase. ASTRA software (Wyatt Technology Corp., Wyatt Technology Corp., Santa Barbara, USA) was used to process the data. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were measured on a Bruker AVANCE II 400 spectrometer operating at 400 MHz (Bruker, Karlsruhe, Germany). Deuterated chloroform (CDCl₃) was used as a solvent with 1% TMS as an internal reference. Atomic force microscopy (AFM) was performed on Bruker Scanning Probe Microscope (Bruker, Karlsruhe, Germany) by using a clean silica wafer as a

substrate. The dilute nanogel solution was spin-coated onto the clean silica wafer by (3000 r/min for 1 min) and was visualized by using a tapping mode. Fourier-transform infrared (FTIR) spectra were recorded on a Thermo Nicolet IR200 FT-IR spectrometer (Thermo Fisher Scientific China Co. Ltd, Shanghai, China) in the solid-state in KBr. Fluorescent emission and excitation spectra were recorded on a Lengguang F98 fluorescence spectrophotometer (Lengguang Technology Co. Ltd., Shanghai, China). Dynamic light scattering (DLS) measurement was performed on Zetasizer Nano ZS90 (Malvern Panalytical Shanghai Ltd., Shanghai, China). Quantum yield of the nanogel solution (1 mg/mL) was measured in a stoppered quartz cuvette (1 cm path length) on a HORIBA JOBIN YVON Fluoromax-4P spectrofluorometer (Jobin Yvon, Paris, France) by using an integrated sphere.

1.2 Synthesis of related products

1.2.1 Synthesis of hexa-functional Initiator



Scheme S1. Synthesis of routes of 6-functional initiator.

As shown in Scheme S1, dipentaerythritol (1.6g, 6.29mmol), and triethylamine (10mL, 75.5mmol) were mixed and dissolved in 100mL dichloromethane. After stirred for 15 min, Dilute 2-bromoisoobutyryl bromide (8mL, 56.6mmol) with dichloromethane (20mL) were added into the solution in the ice bath and stirring for 24 hours at 25°C. When the reaction was over, the solution was washed by saturated sodium bicarbonate solution and saturated sodium chloride solution and dried by anhydrous magnesium sulfate and then separated and purified by silica gel column. The final product was 3.23g (yield: 44.73%). The successful synthesis of the product was confirmed by the ¹H NMR (Figure S). In the ¹H NMR spectrum, all the proton chemical shifts were found with the right integration area. ¹H NMR (500MHz, Chloroform-d, ppm) δ=4.29(s,4H) δ=4.28(s, 4H), δ=4.27(s, 4H) δ=3.59(s, 2H), δ=3.58(s, 2H), δ=1.93(s, 12H)

1.2.2 Synthesis of 6-arm star-like poly (tert-butyl methacrylate) (star-like PtBMA)

Star-like PtBMA was synthesized by atom transfer radical polymerization of tert-butyl methacrylate monomers using 6-Br-initiator. Briefly, 0.287g of hexa-functional initiator, 90mL tert-butyl methacrylate (47mL of monomers), 0.0215g of CuBr were added into the schlenk bottle. After three times freeze-thaw degassing, and 100μL N,N,N',N'',N''-Pentamethyldiethylenetriamine (PMDETA) was added under argon atmosphere. The reactions were carried out at 30°C for 15 minutes to prepare polymers with low weight. Similarly, polymers with different weights were prepared by changing the temperature and reaction time. The solution passed through the alumina column to remove the catalyst and subsequently underwent precipitation with

methanol/water (v/v = 8/1, precipitator) to remove monomers and linear polymers. The product was then dried at 30°C under vacuum (yield: 9%). By using this method, two star-like PtBMA were synthesized with M_w of 2.10×10^4 and 5.14×10^4 determined by using GPC-MALLS and PDIs of 1.11 and 1.13 calculated from tradition GPC results calibrated by using a series of PS standards (Entry 1 and 2 in Table 1).

1.2.3 Synthesis of star-like poly (tert-butyl methacrylate)-block-poly (Methyl methacrylate) (star-like PtBMA-*b*-PMMA)

Star-like PtBMA-PMMA was synthesized by ATRP of methyl methacrylate monomers from star-like PtBMA initiator. Star-like PtBMA-Br (i.e., Br in PtBMA macroinitiator): CuBr : PMDETA : MMA = 1 : 0.4 : 0.8 : 600 (molar ratio) in toluene (6 mL solvent per 1 mL MMA): 0.6872g of poly (tert-butyl methacrylate) (PtBMA), 19mL of methyl methacrylate, 0.0172 g of CuBr and 114mL toluene were added into the schlenk bottle. After three times freeze-thaw degassing, and 100 μ L PMDETA was added against an argon flow. The schlenk bottle was then sealed and placed in an oil bath at 40°C for 30 minutes. The reaction was later quenched by cooling the schlenk bottle in liquid nitrogen. The crude products were firstly purified by column to remove cupric ions. The resultant solutions were concentrated and then precipitated from THF to methanol. The final products were dried in the vacuum oven (yield: 6%).

Table S1 Reaction conditions of like poly (tert-butyl methacrylate)-block-poly (Methyl methacrylate)

Number	MMA(mL)	Initiator(g)	CuBr(g)	PMDETA(μ L)	Toluene(mL)	T($^{\circ}$ C)	Time(min)	PDI ^a	M_n (g/mol) ^a	M_w (g/mol) ^b
1	19	0.6988	0.0172	50	114	40	30	1.14	22500	27800
2	11	0.4193	0.0258	75	66	40	30	1.18	34800	38900
3	26	0.2102	0.0086	25	13	60	60	1.12	111500	148400
4	20	0.2551	0.0043	13	6	60	90	1.20	141500	234100

^a M_n and polydispersity index (PDI) was measured on GPC equipped with a RI detector by using tetrahydrofuran (THF) as eluent which was calibrated with polystyrene standards by using the traditional method, ^b M_w s were calculated from static light scattering results determined by a GPC-MALLS system.

1.2.4 Synthesis of star-like poly (acrylic acid)-block-poly (methyl methacrylate) (star-like PMAA-*b*-PMMA))

Star-like PMAA-*b*-PMMA was synthesized by hydrolysis of tert-butyl ester groups of PtBMA blocks of star-like PtBMA-*b*-PMMA to acrylic acid groups. Star-like PtBMA-*b*-PMMA (0.2g) was fully dissolved in dichloromethane (40 mL), followed by the addition of trifluoroacetic acid (5 mL). The reaction proceeded at room temperature for 48 hours. After hydrolysis, the solvent was evaporated under reduced pressure. The final product underwent precipitation with diethyl ether, and thoroughly dried under vacuum at 40 $^{\circ}$ C for 24 hours.

1.2.5 Synthesis of C-dots

The chemical reaction produced between carboxyl groups (-COOH) of the inner hydrophilic PAA blocks of star-like PMAA-*b*-MMA and the amino group of polyamines. Then, the mixture was heated at 210°C for 3 hours. The brown solution was added into water slow and brown floc formed that easily be separated from water by filter paper. The crude products were purified with silica column chromatography using tetrahydrofuran as eluents. After removing the solvents and further drying under a vacuum,

the purified CDs were obtained.

1.2.6 Synthesis of crosslinked polymer dots (P-dots-CL)

Using catalyst 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS) to complete the amidation reaction between carboxyl groups (-COOH) of the inner hydrophilic PAA blocks of star-like PMAA-*b*-MMA and the amino group of polyamines. 60mg of star-like PMAA-PMMA was dissolved in 100mL THF and added 0.1526g of EDC, 0.0457g of NHS. The solution stirring for 1 hour in the ice bath and added ethylenediamine (0.0389g). The reaction mixture was stirred at room temperature for 10 h and the solvent was evaporated under reduced pressure. After the mixture was partitioned between dichloromethane and H₂O. Then washed with 5% aqueous HCl (3 × 15mL), 5% aqueous NaHCO₃ (20 mL). The organic layer was washed with H₂O, dried over MgSO₄, and concentrated under reduced pressure. The crosslinked polymer dots final product underwent precipitation with methyl alcohol.

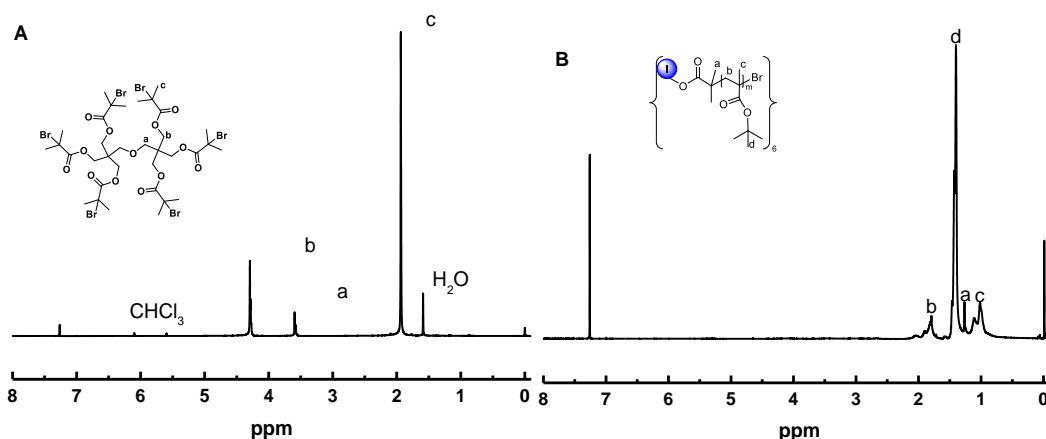
1.2.7 Synthesis of crosslinked polymer dots with different crosslinking density

50 mg of star-like PMAA-*b*-PMMA was dissolved in 250mL THF and added 0.4662 g of EDC, 0.1398 g of NHS. The solution stirring for 1h in the ice bath and added ethylenediamine (0.1216 g). The reaction mixture was stirred at room temperature. Similarly, different crosslinking density polymers were prepared by changing reaction time. After the concentrated mixture was partitioned between EtOAc and H₂O. The organic layer was washed with H₂O, dried over MgSO₄, and concentrated under reduced pressure. Purification by flash chromatography (THF) afforded crosslink star-like polymer.

1.2.8 Preparation of fluorescent epoxy resin by using C-dots as nanoadditive

The epoxy resins were prepared by using commercial A and B monomers. 15.00 g of liquid A monomer was mixed with 5.00 g of liquid B monomer followed by addition of 0.10 g of C-dots. After gently stirring, a transparent viscous solution was obtained and was transferred into the mould after being degased in vacuum for 1.0 h. After 24 h, a rigid and transparent fluorescent epoxy resin was obtained. The pure epoxy resin were prepared in the same way for blank control.

2. Characterization of the products and their fluorescence behaviors



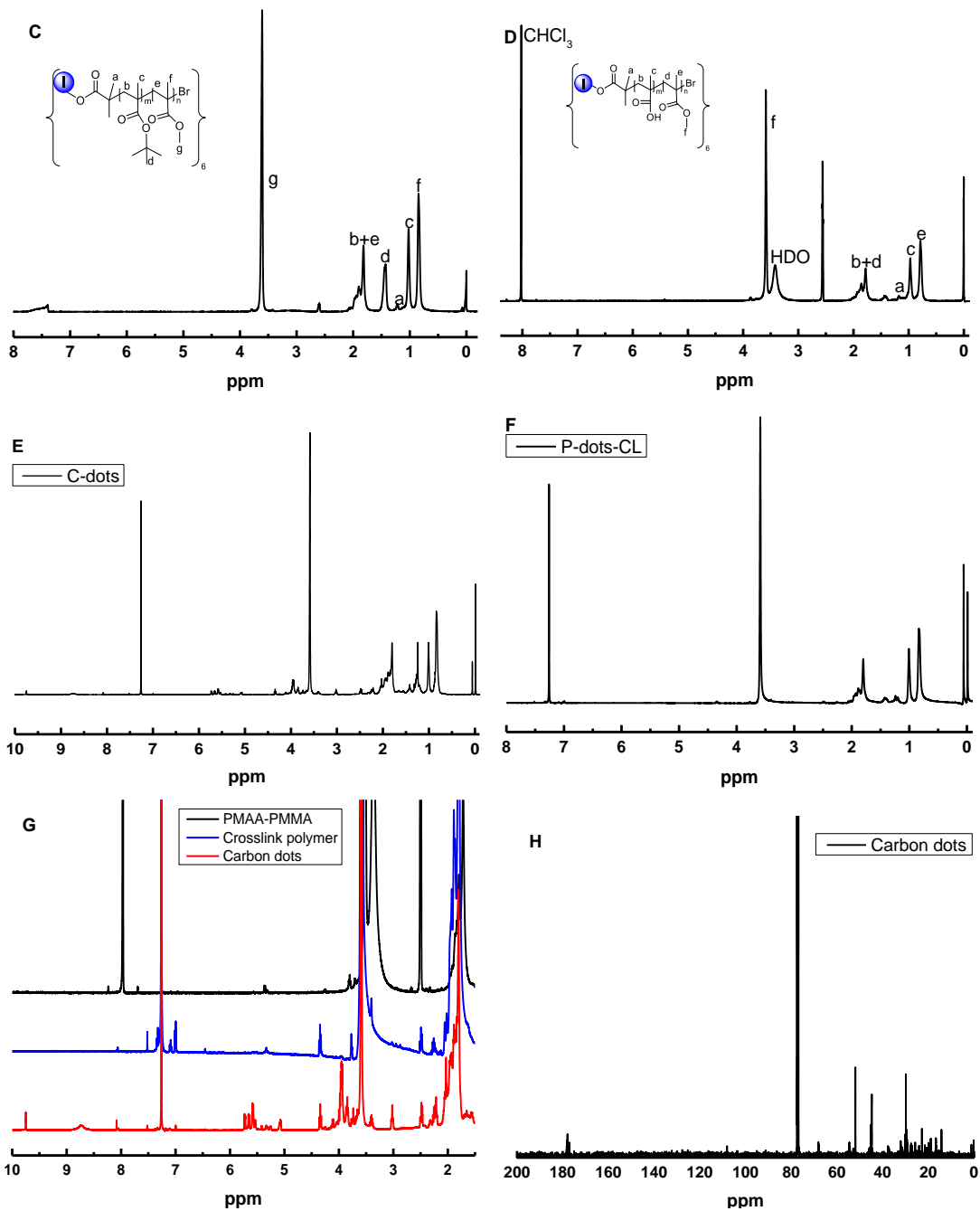


Figure S1. ^1H NMR spectrum of (A) hexa-functional Initiator, (B) PtBMA, (C) star-like PtBMA-*b*-PMMA, (D) star-like PMAA-*b*-PMMA, (E) carbon dots, (F) crosslink polymer, (G) comparison of ^1H NMR spectra of star-like PMAA-*b*-PMMA in mixed solvent of DMSO- D_6 and CHCl_3 , crosslink polymer, and carbon dots in CDCl_3 , (H) ^{13}C NMR spectrum of carbon dots.

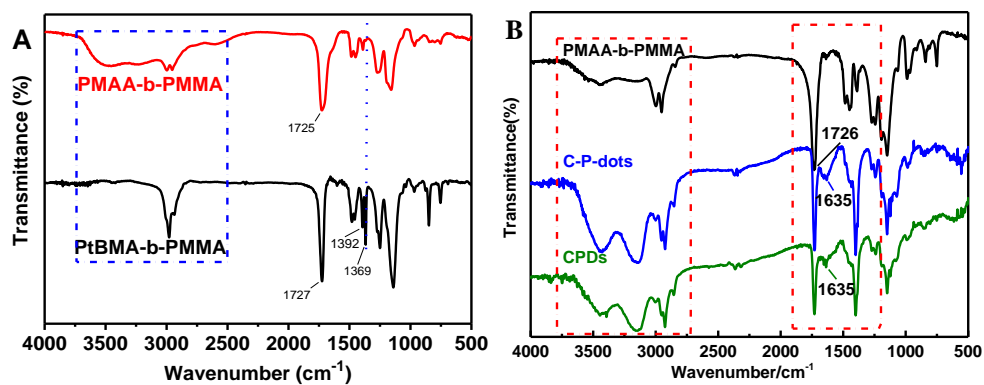


Figure S2. FT-IR spectra of PtBMA-*b*-PMMA and PMAA-*b*-PMMA.



Figure S3. Fluorescent behaviors of PMAA-*b*-PMMA and crosslinked polymer dots with different polymer weight in solid state under a UV light ($\lambda_{\text{ex}}=365$ nm).

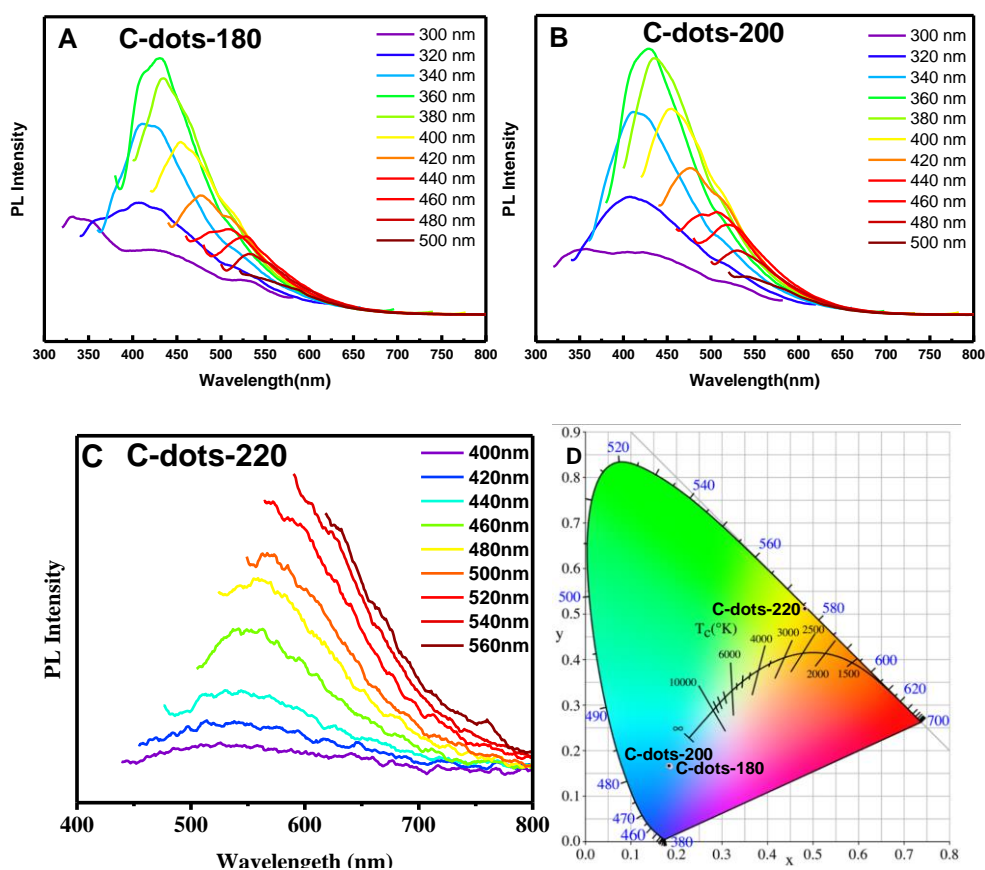


Figure S4. (A) Solution fluorescent spectra of C-dots synthesized by carbonization of star-like PMAA-*b*-PMMA with ethylenediamine with different excitation wavelengths. (A) Solution fluorescent spectra of C-dots-200°C. (C) Solution fluorescent

spectra of C-dots-180°C. (B) Solution fluorescent spectra of C-dots-200°C. (C) Solution fluorescent spectra of C-dots-220°C. (D) The CIE chromaticity diagram of C-dots, P-dots-CL and P-dots-EL, C-dots-180 °C, C-dots-200 °C, C-dots-220°C solutions in THF (c = 6.0 mg/mL)

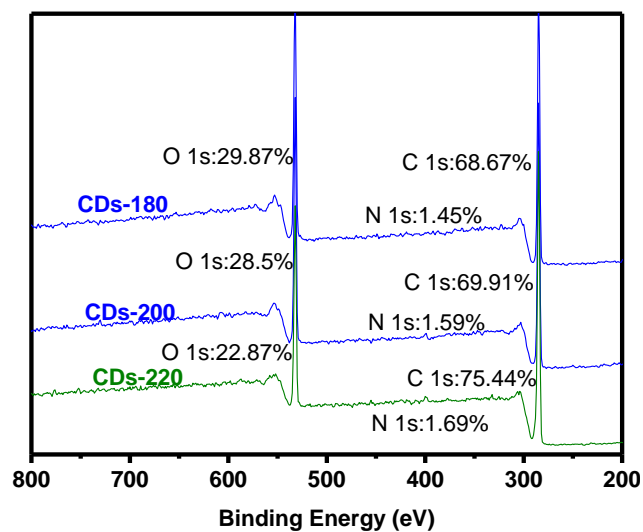


Figure S5. Full-scale XPS spectra of C-dots-180 °C, C-dots-200 °C and C-dots-220 °C.

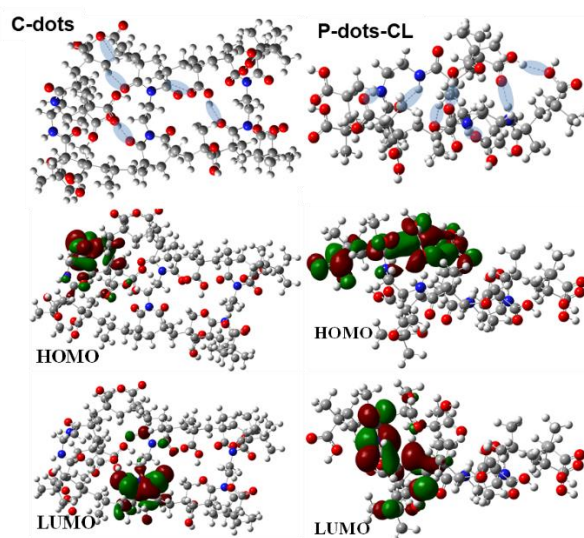


Figure S6. Theoretical conformations and hydrogen bonding of C-dots and P-dots-CL and their molecular orbital surfaces of HOMO and LUMO revealed by DFT-D3 computation on B3LYP/TZVP level

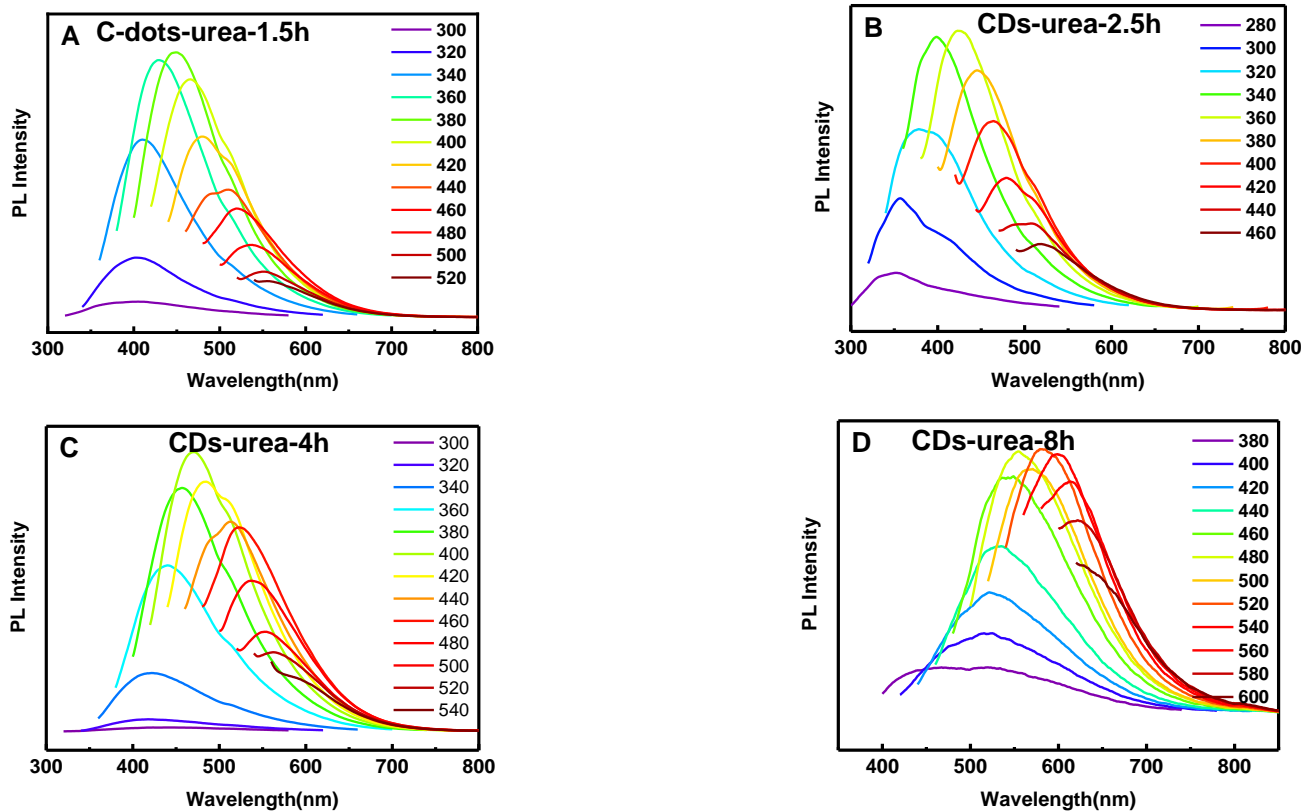


Figure S7. Excitation-dependent fluorescence of C-dot synthesized by co-carbonization of star-like PMAA-*b*-PMMA with urea for different times