Supporting Information

Luminescence modulation of carbon dots assemblies

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1. Experimental Section:

1.1 Materials

Analytic grade reagents of triethylenetetramine (TETA), diethylenetriamine (DTA), tetraethylenepentamine (TEPA), citric acid monohydrate (CA) ($C_6H_8O_7{\cdot}H2O$), anhydrous ethanol, glutaraldehyde (GA) (50 wt%), sodium borohydride ($NaBH_4$), formic acid (HCOOH) (>88%), formaldehyde solution (FA) (37-40 wt%), p-phenylenediamine, p-phthalaldehyde, rhodamine B (RhB), quinine sulfate, sulfuric acid (98%) as well as chemical grade of polyvinyl alcohol (mean degree of polymerization: 1750±50) (PVA) were from Beijing Chemical Reagent Co. 1, 8-diamine - 3,6-dioxaoctane (DADO) was purchased from J&K Scientific Ltd. Deuterium oxide Ultra-D (D_2O) (99.9%) from NMR Sigma-Aldrich was used to prepare NMR samples. Analytic grade of Nile blue A (>75%) was obtained from Shanghai Yuanye Biotechnology Co., Ltd. All the reagents were used as received without further purification. Deionized water was used in experiments.

1.2 The structures TETA and DADO

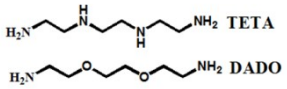

Fig. S1 the molecular structure of TETA and DADO

1.3 Synthesis of passivated Cdots

In the present work, TETA, DTA, TEPA and DADO were not only used as solvent but also as passivating agents to functionalize Cdots. The detailed synthesis of Cdots was described as follows. 1g of CA (carbon source) was added into 10 ml of different solvents and stirred about for 30 min. Then, it was transferred into Teflon-lined stainless autoclave and heated at 160 ^{o}C for 18h. The obtained solution was dialyzed against deionized water with dialysis bag (molecular weight cutoff (MWCO) of 1000) for 1 day to remove the free passivating agent, and the functionalized Cdots were obtained through rotary evaporation to remove the deionized water. Cdots functionalized with TETA, DTA, TEPA and DADO was named as TETA-Cdots, DTA-Cdots, TEPA-Cdots and DADO-Cdots.

1.4 Construction of Cdots assemblies by Cross-linking reaction between passivated Cdots and GA

Under stirring, 0.5 ml of the as prepared functionalized Cdots was added into 50ml of

deionized water and after stirring for about 15 min, 40 ml of 2 wt% GA aqueous solution was added and then maintained stirring at room temperature for 72h. After centrifugation, the obtained solution was dialyzed against deionized water in the dialysis bag (MWCO 8000-14000) for 2 days to remove the free GA and free Cdots and then the solution was concentrated through rotary evaporation. The product was named as Cdots assembly, for example TETA-Cdots assembly, DADO-assembly, TEPA-Cdots assembly and DTA-Cdots assembly.

1.5 Characterization

Transmission electron microscopy (TEM) images were recorded with JEOL JEM-2100 microscope operating at accelerating voltage of 200 kV. The IR spectra of the product were measured by the Hitachi Fourier transform infrared (FT-IR) spectroscopy with the resolution of 4 cm^{-1} and scan times of 49. Shimadzu UV-1601 spectrophotometer has been used to measure UV-Vis spectra. Fluorescence spectra were recorded with F-4500 fluorescence spectrophotometer. NMR measurements were conducted in the Bruker nuclear magnetic resonance spectrometer (NMR) (AVNANCE 400). The NMR samples were prepared by dispersing Cdots or Cdots assemblies in D_2O. The relative fluorescence quantum yield (QY) at λ_{ex} of 630, 530 and 360 nm was estimated with Nile Blue anhydrous ethanol (QY ~27%), [1,2] RhB anhydrous ethanol (QY ~ 70%) [3,4] and quinine sulfate in 0.5 M sulfuric acid solution (QY ~ 54%) [2-4] as references, respectively. Optical densities of the solution of the samples and reference were kept smaller than 0.05 to avoid re-absorption. Time-resolved PL spectroscopy was performed with a time-correlated single photon counting (TCSPC) module (Edinburgh Instruments F900). The hydrodynamic sizes of the samples were recorded with Dynamic Light Scattering (DLS) technique on a Dynapro NanoStar (Wyatt, USA). To prepare TETA-Cdots assembly/PVA ink, different volume of concentrated TETA-Cdots solution was added into 10 wt% PVA aqueous solution and then mixed thoroughly. To eliminate the bubbles during the mixture, 2 3 drop of ethanol was also introduced. To explore the color change of letters (written on parchment paper) with light source, pocket lamp emitting UV, blue and green light had been used. During taking picture of the letters under irradiation of blue and green lamp, orange filter had been applied to decrease the interference of incident light.

2. The color of different Cdots Assemblies aqueous solution

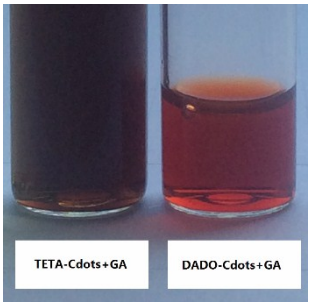

Fig. S2 After reacted with GA for 72h, the color of TETA-Cdots and DADO-Cdots aqueous solution

Comparing with the original functionalized Cdots, the introduction of GA made the color of pale-yellow TETA-Cdots and DADO-Cdots solution changed to dark brown and dark red, respectively.

3. The excitation spectra of TETA-Cdots and their assemblies

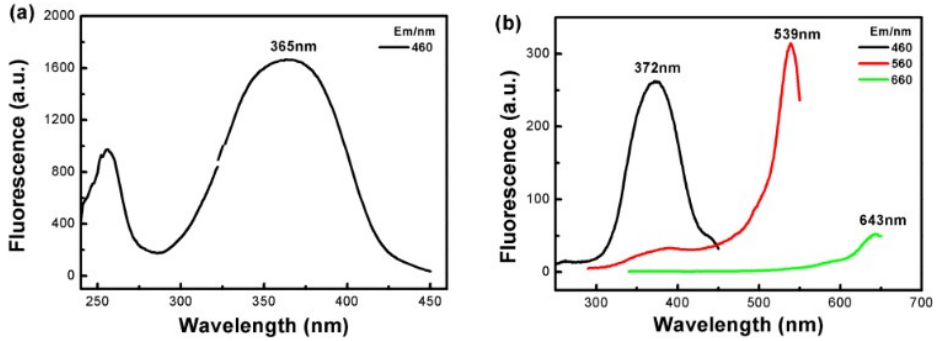

Fig. S3 Excitation spectra of dilute TETA-Cdots (a) and TETA-Cdots assemblies (b) aqueous solution

4. The optical properties of TEPA-Cdots assembly

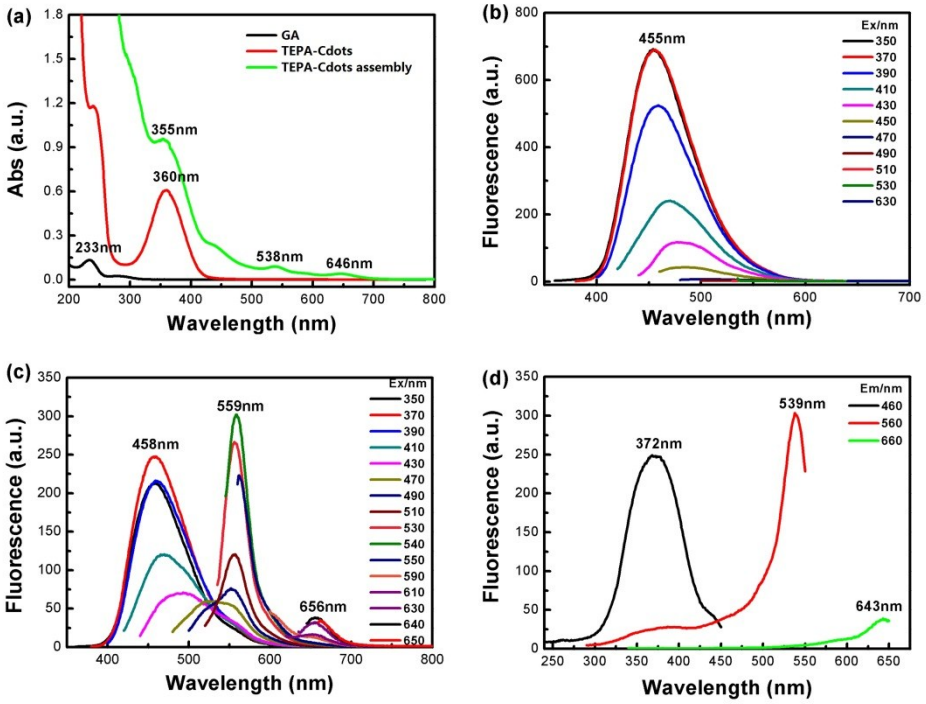

Fig. s4 a) UV-Vis absorption spectra of TEPA-Cdots, GA and TEPA-Cdots assemblies; b) fluorescent and excitation spectra of TEPA-Cdots; c) fluorescent spectra and d) excitation spectra of TEPA-Cdots assemblies aqueous solution

As demonstrated in Fig. S4a and b, TEPA-Cdots had a distinct absorption at 360 nm and blue emission at 454 nm. After the addition of GA aqueous solution, the color became deeper, very fast, then to orange, red and at last, dark brown. Correspondently, a shoulder and two new absorption bands appeared at 440, 538 and 635 nm. In the fluorescence spectrum, extra fluorescence at 559 and 656 nm presented (Fig. S4c). The QY of the blue emission at 450 nm decreased from 7.2% of TEPA-Cdots monomer to 2.4% of TEAP-Cdots assemblies. In addition, the QY of yellow (～560 nm) and red emission (656 nm) were about 5.8% and 21.6%, close to that of TETA-Cdots assemblies.

5. The optical properties of DTA-Cdots assembly

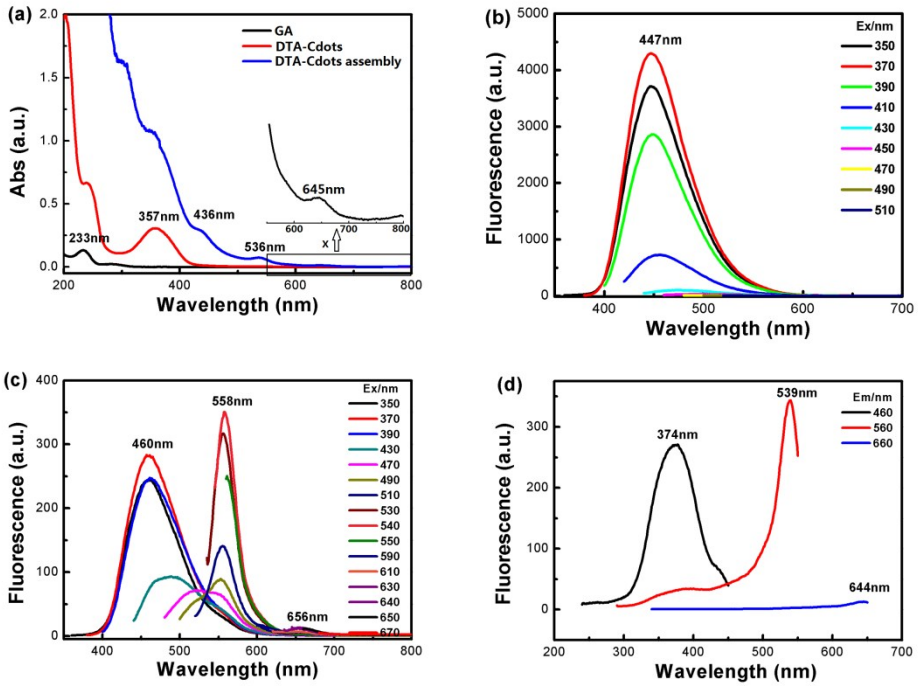

Fig. S5 a) UV-Vis absorption spectra of DTA-Cdots, GA and DTA-Cdots assemblies; b) fluorescence spectra of DTA-Cdots; c) fluorescent spectra and d) excitation spectra of DTA-Cdots assembly aqueous solution.

Different from TETA-Cdots and TEPA-Cdots assembly, for DTA-Cdots assembly, the absorption band at about 645 nm was very tiny (Fig. S5a and b). The QY corresponding to the blue emission damped from about 40% for DTA-Cdot monomer and to 2.6% for DTA-Cdots assemblies, confirming the agglomerates of DTA-Cdots. At the same time, the QY for yellow emission (～560 nm) was about 8.9%, higher than that of TETA-Cdots assemblies.

6. Investigation on the quantum yield (QY) and fluorescent lifetime (τ) of C-dots and their assembly

Table S1 the QY and average τ (τ_{av}) of original C-dots and their assembly at different λ_{em}

λ_{em}	460/nm		560/nm		660/nm	
	QY/%	τ_{av}/ns	QY/%	τ_{av}/ns	QY/%	τ_{av}/ns
TETA-Cdots	11.8	9.57				
TETA-Cdots assembly	2.8	4.79	6.1	1.59	23.4	2.11
DADO-Cdots	40.9	11.26				
DADO-Cdots assembly	0.69	3.86	17.6	2.61		

The fluorescence decay curves were fitted with the double exponential model and two fluorescence lifetimes were obtained. The average fluorescence lifetime (τ_{av}) was calculated with the following equation:[5]

$$\tau_{av} = \Sigma B_i \tau_i^2 / \Sigma B_i \tau_i$$

where the B_i is the fractional weights of the various decay time components τ_i of the multi-exponential fitting.

To estimate the QY of original C-dots and their assemblies for blue, yellow and red emission the λ_{ex} were 360, 530 and 630 nm with quinine sulfate, RhB and Nile blue as references, respectively.

7. NMR measurements of primary Cdots and their assemblies

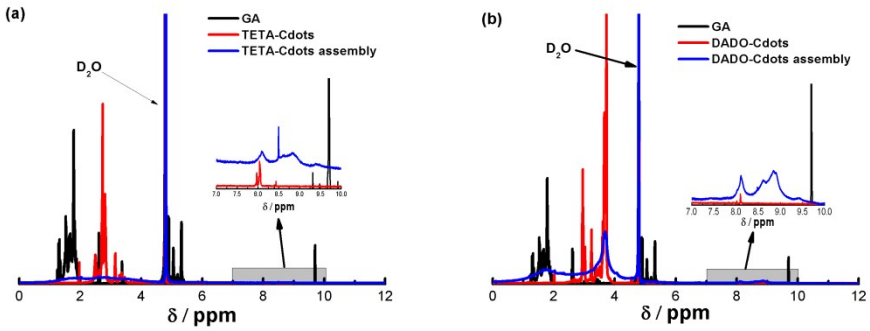

Fig. S6 ^{1}H NMR spectra of Cdots and Cdots assembly

8. The optical change of TETA-Cdots assemblies with the addition of different agents

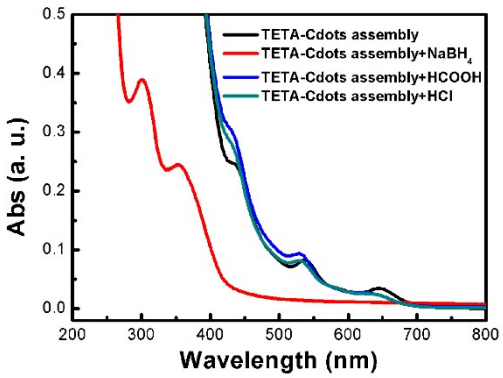

Fig. S7 UV-Vis spectra of TETA-Cdots assembly aqueous solution in the presence of different reactive agents

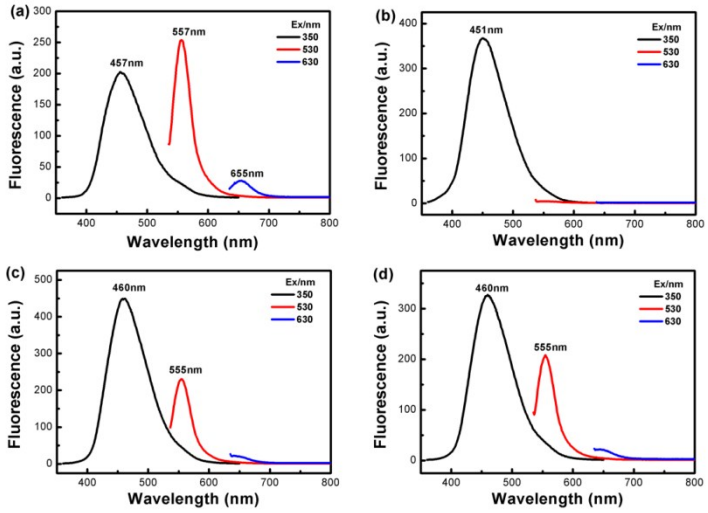

Fig. S8 Fluorescence spectra of the TETA-Cdots assembly aqueous solution (a) and in the presence of $NaBH_4$ (b), HCOOH (c) and HCl (d)

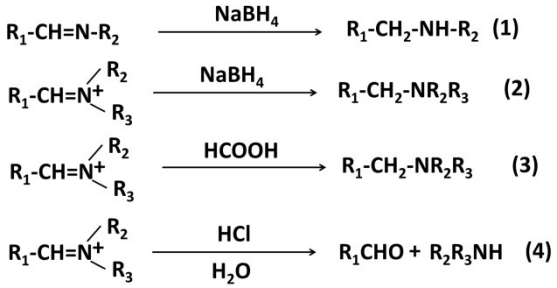

Fig. S9 Reactions between different imine bonds and various chemical agents

Adding $NaBH_4$, HCOOH and HCl into the TETA-Cdots assembly aqueous solution for about 30 - 60 min, the optical spectra of the mixture solution were recorded. As shown in Fig. S7 and S8b, $NaBH_4$ erased their visible absorption bands and yellow, red PL completely, through the reactions

1 and 2 (Fig. S9); HCOOH and HCl made the red absorption and PL weakened (Fig. S7, S8c, S8d) through reactions of 3 and 4 (Fig. S9).

9. The optical variation of TETA-Cdots upon the addition of FA

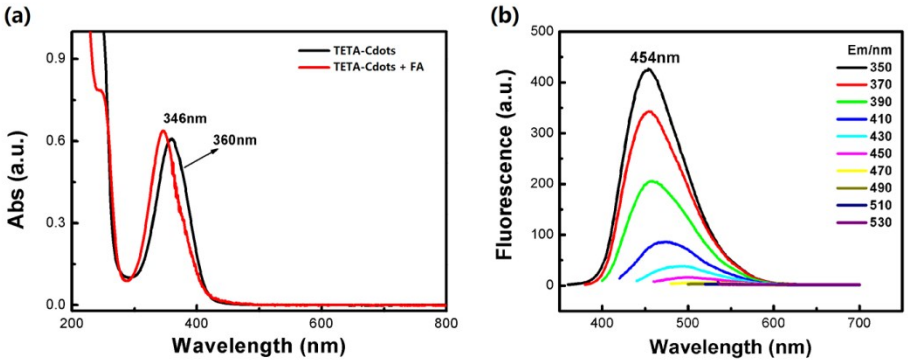

Fig. S10 Influence of FA on the optical property of TETA-Cdots. a) UV-Vis absorption spectra of TETA-Cdots aqueous solution, the mixture solution of TETA-Cdots and FA (insert was the image of these two solution); and b) fluorescence spectrum of the mixture solution of TETA-Cdots and FA.

Even after several days, the introduction of FA only made the absorption band at 360 nm blue shifted to some extent and the absorption in the range of 400~500nm was slightly upraised. In addition, the fluorescent property was almost no variation.

10. The optical properties of the reactive product of p-phenylenediamine and p-phthalaldehyde

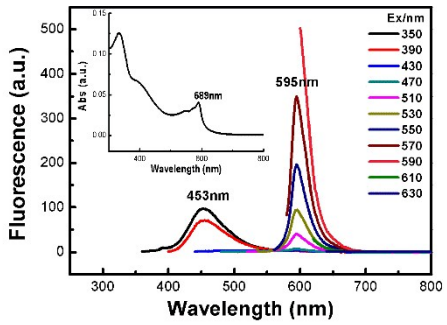

Fig. S11 The fluorescence spectra of reactive products of p-phenylenediamine and p-phthalaldehyde upon various excitation wavelengths (insert is the absorption spectrum)

Under stirring, a proper amount of p-phenylenediamine was added into the p-phthalaldehyde anhydrous ethanol solution and then the solution was maintained at 80 ^{o}C for about 12h. After filtered, the optical properties of the clear supernatant were measured. As shown in Fig. S11, the emission related to the imine bonds shifted from 556 to 595 nm, implying

that the PL of non-conjugated imine polymers could be tuned by the structure of aldehyde or amine used.

References

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