Supplementary Information

Structure and photoluminescence evolution of nanodots during pyrolysis of citric acid: From molecular nanocluster to carbogenic nanoparticles

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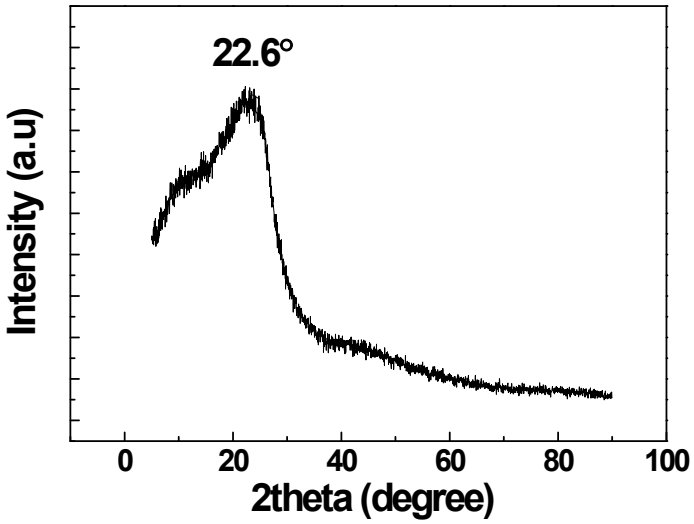

Figure S1 XRD pattern of Dots-300 powder.

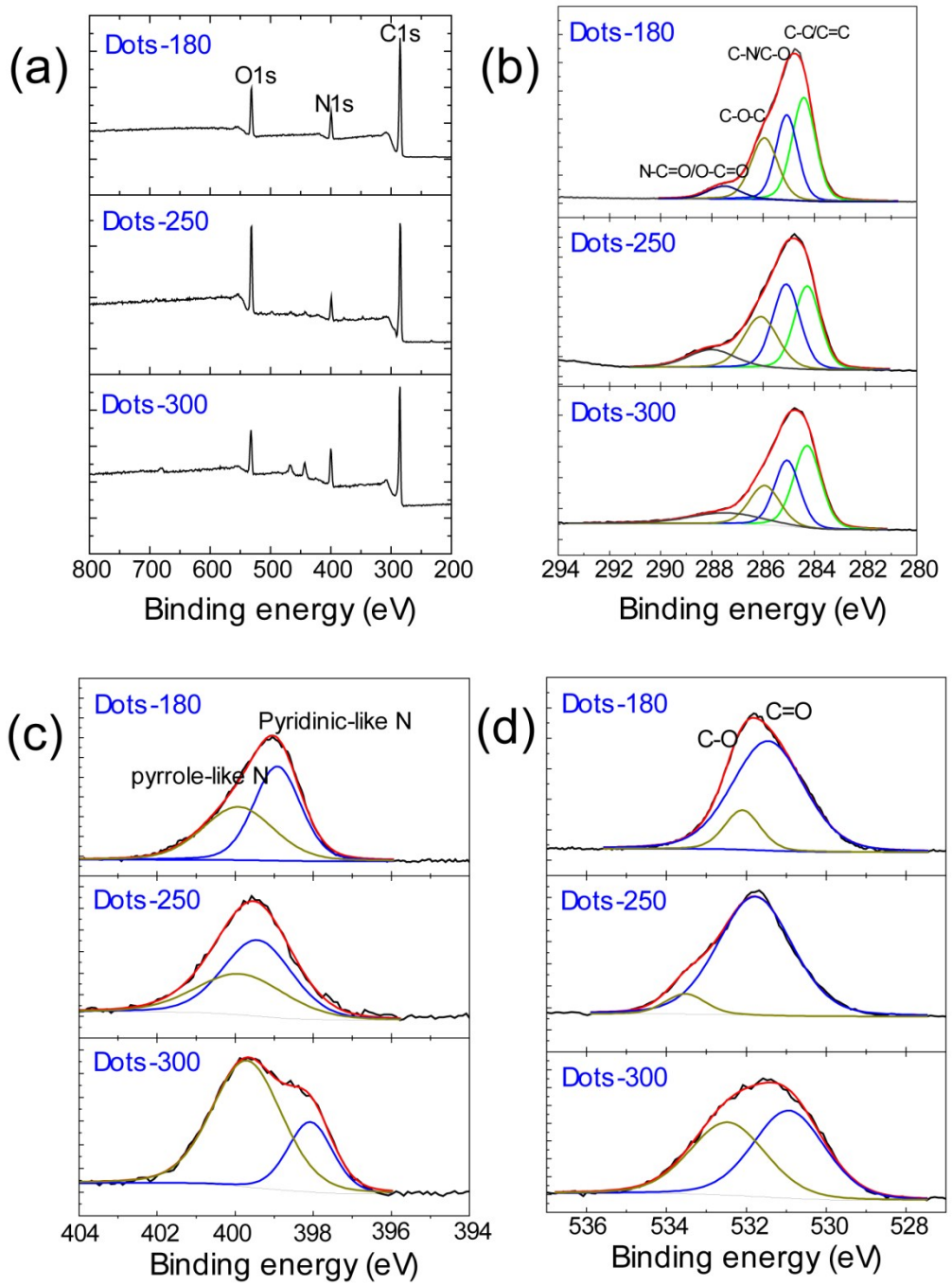

Figure S2 XRD analysis of nanodots. (a) full survey. (b) C1s spectra. (c) N1s spectra. (d) O1s spectra.

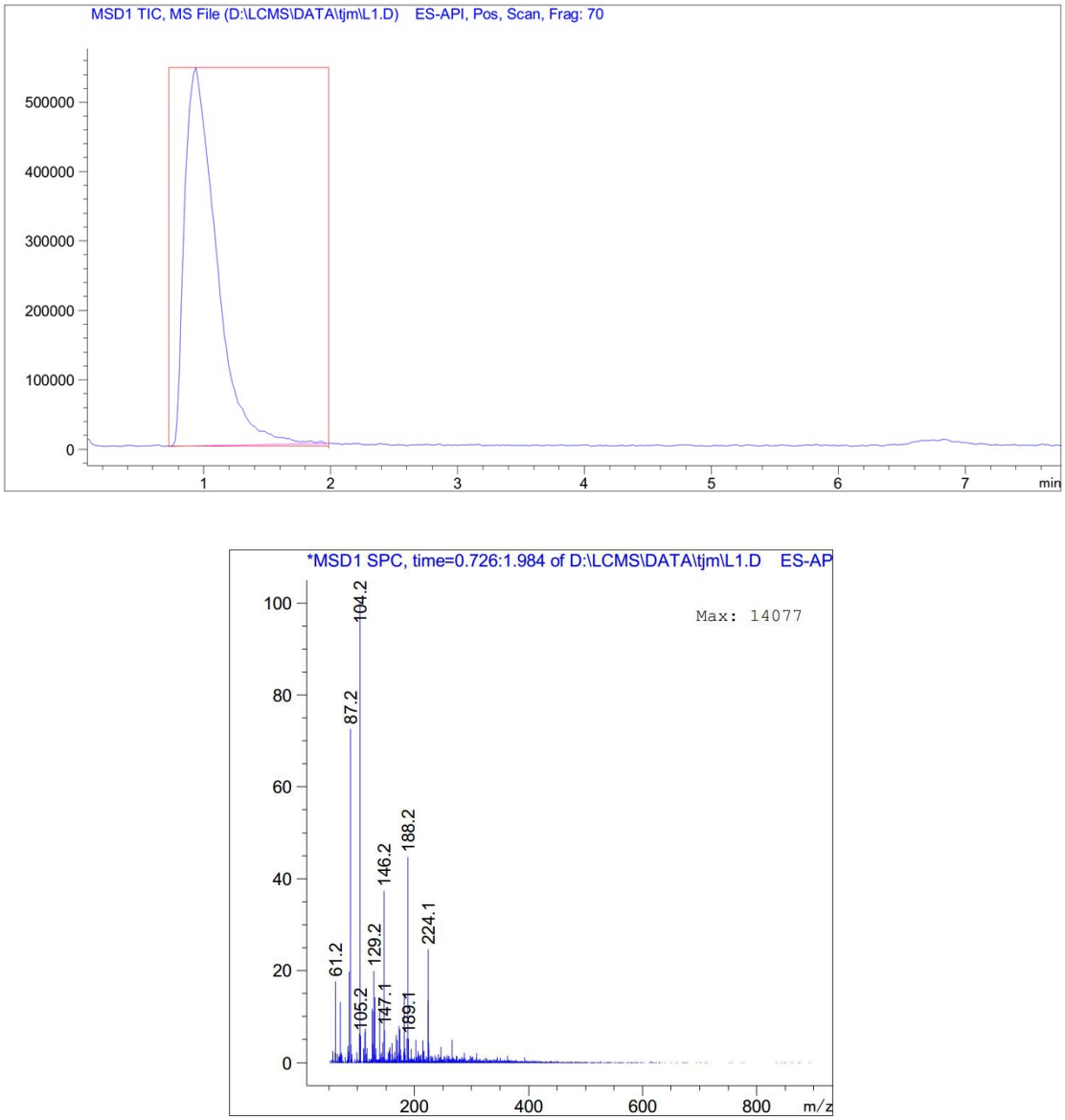

Figure S3 (Upper) Chromatograms for the elution of Dots-180 monitored by PDA at 254 nm. (Lower) Representative MS spectra from LC/MS analysis of the fraction in Dots-180. The presence of an ion with m/z = 224.1 correlates to the molecular formula of $C_{10}H_{14}N_3O_3^+$.

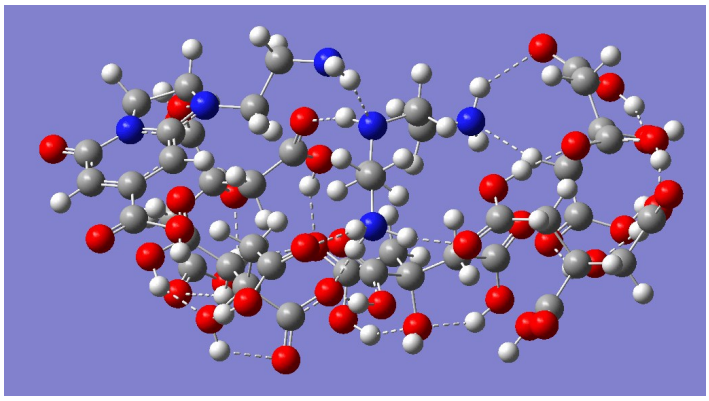

Figure S4 Optimized geometries of AEIOP coupled with DETA@5CA at the B3LYP-D3/6-31G level.

Table S1 Atomic coordinates of optimized geometries of AEIOP coupled with DETA@5CA.

C	-0.09366600	1.97804700	1.26178300
C	-0.07945500	0.46871500	0.99223200
H	-0.98421200	2.24892400	1.83322700
H	0.78690400	2.27097100	1.83636700
H	-0.91200000	0.22451700	0.31462700
H	0.83762400	0.19315800	0.46169000
N	-0.11176300	2.75990300	-0.03520900
H	-1.09408600	2.92912100	-0.32895900
H	0.40146900	3.65723300	0.05665200
N	-0.17363200	-0.27663200	2.25562700
H	0.58717300	-0.94967800	2.35314400
C	-1.47753400	-0.91164700	2.53287700
C	-1.64352700	-2.25182200	1.79429700
H	-2.27524800	-0.22810300	2.22173900
H	-1.57667000	-1.06386100	3.61495700
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H	-3.27171500	-3.40456800	1.13673000
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C	-5.94051000	3.46610200	-0.97573300
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O	4.50836500	2.65870300	-2.76474200
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C	-6.07103300	-3.44398400	3.19094000
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C	5.59761900	2.84127800	1.93134100
C	6.77654900	3.29890200	1.27496900
C	7.92650800	2.54088100	1.20532800
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C	6.55808400	-0.57692800	2.85237200
C	5.07966400	-0.56086300	3.31473700
H	4.73273800	3.47720100	2.02746100
H	8.80215600	2.89668600	0.68153100

H	6.72824300	-1.27512400	2.03319900
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C	3.23718000	1.19004000	3.07909000
C	2.53457400	0.92992800	4.43410600
H	2.71434600	0.61794800	2.29164300
H	3.14017800	2.25430700	2.84253800
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H	0.99882300	2.36995600	4.55211300
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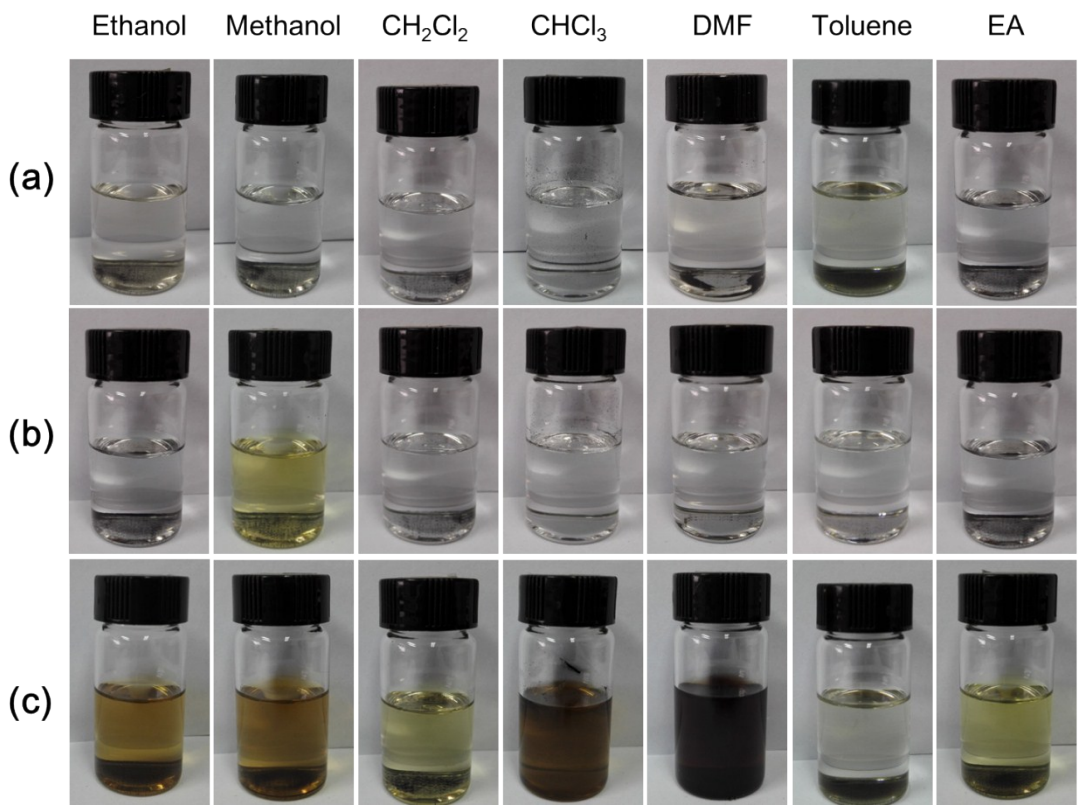

Figure S5 Photographs of nanodots dispersed in various solvents. (a) Dots-180; (b) Dots-250; (c) Dots-300.

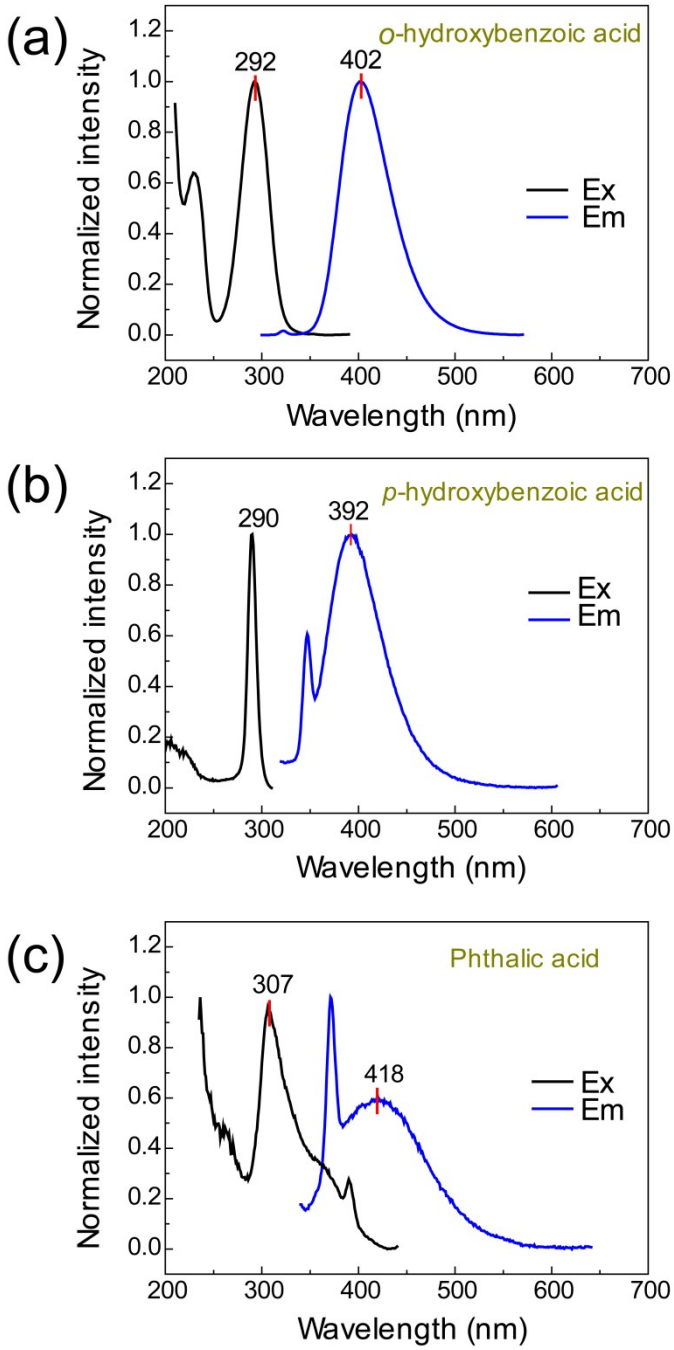

Figure S6 PL spectra of (a) *o*-hydroxybenzoic acid, (b) *p*-hydroxybenzoic acid and (c) phthalic acid as the model compounds of QMF. All regents are purchased from the Sinopharm Chemical Reagent Co., Ltd.

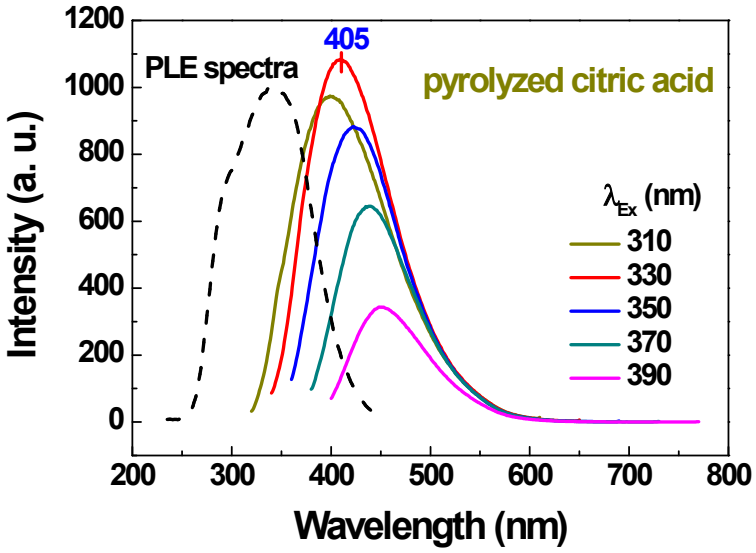

Figure S7 PL spectra of pyrolyzed citric acid. The pyrolysis process of citric acid follows the method in this paper in the absence of amines.

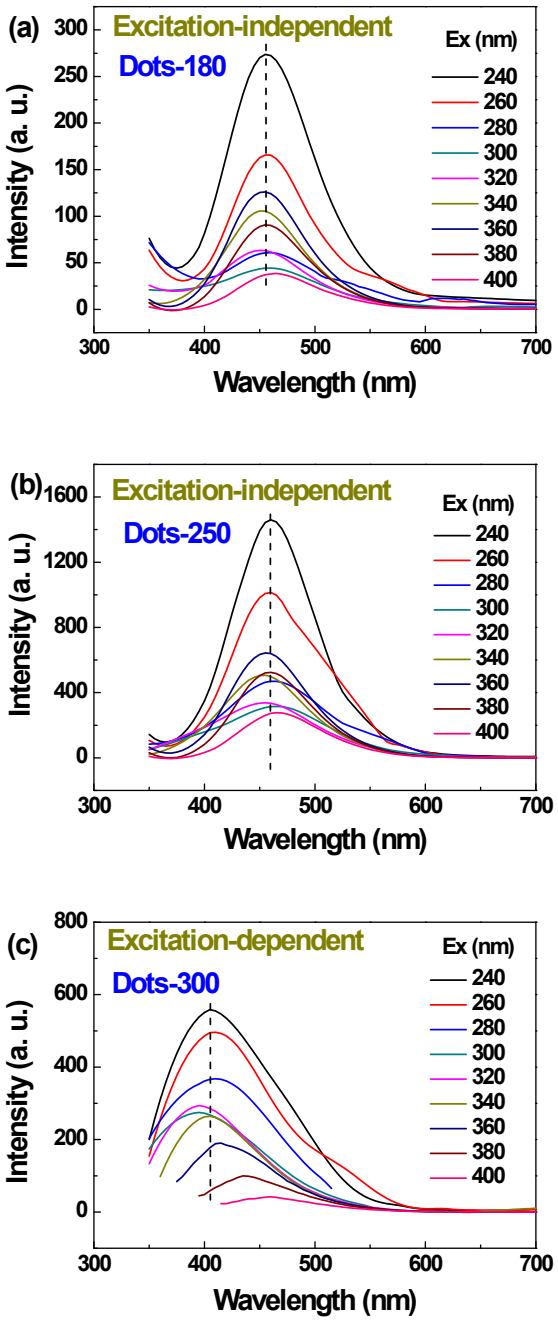

Figure S8 PL spectra of (a) Dots-180, (b) Dots-250 and (c) Dots-300 at different excitation wavelengths.

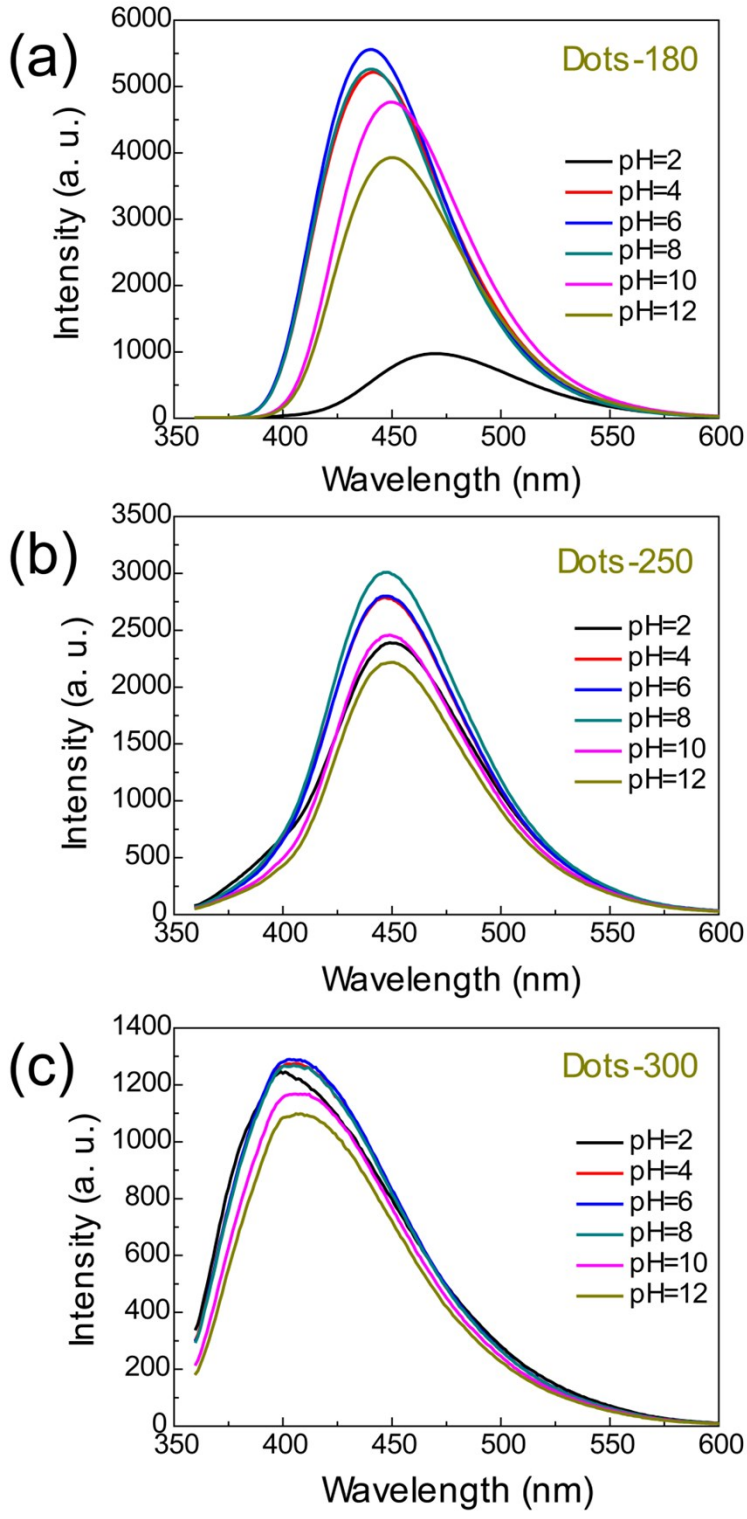

Figure S9 The pH-dependent PL spectra of nanodots.

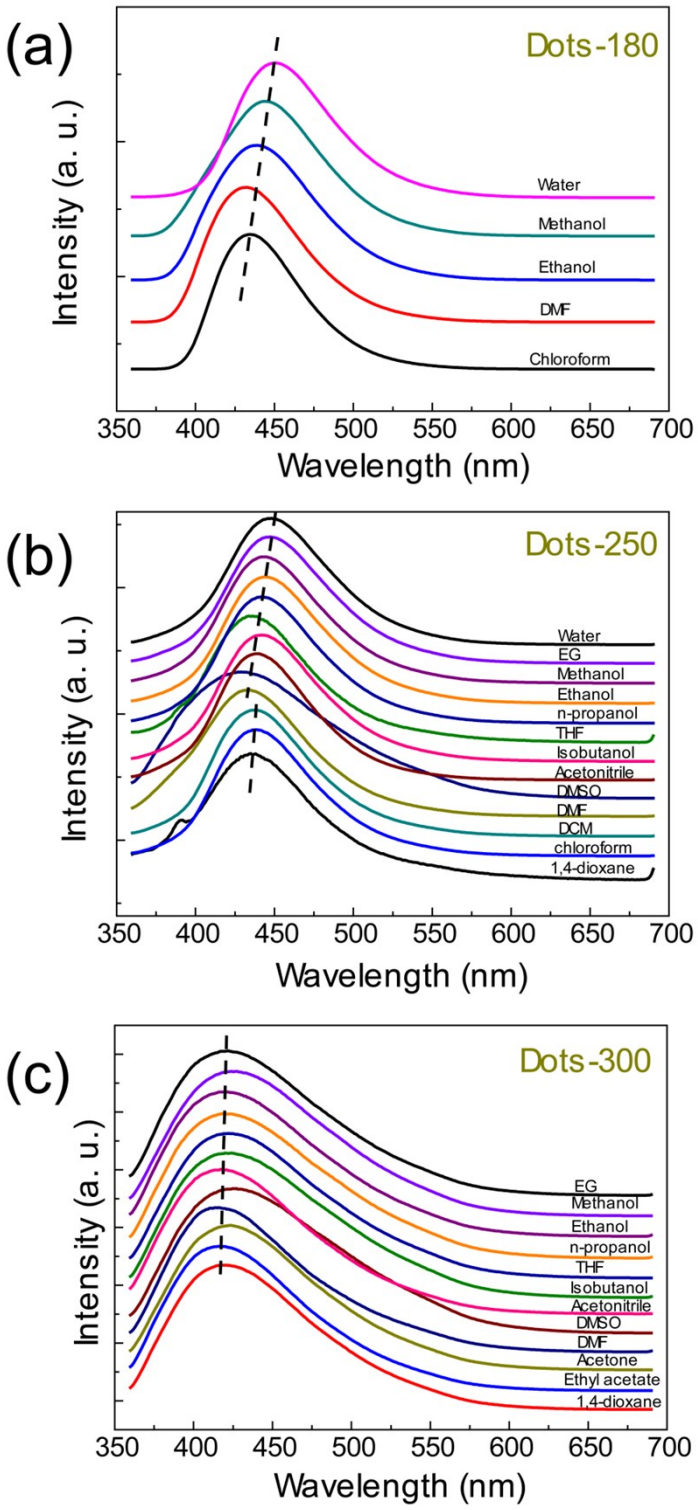

Figure S10 PL spectra of nanodots in solvents of increasing polarity under 350 nm excitation at neutral pH.

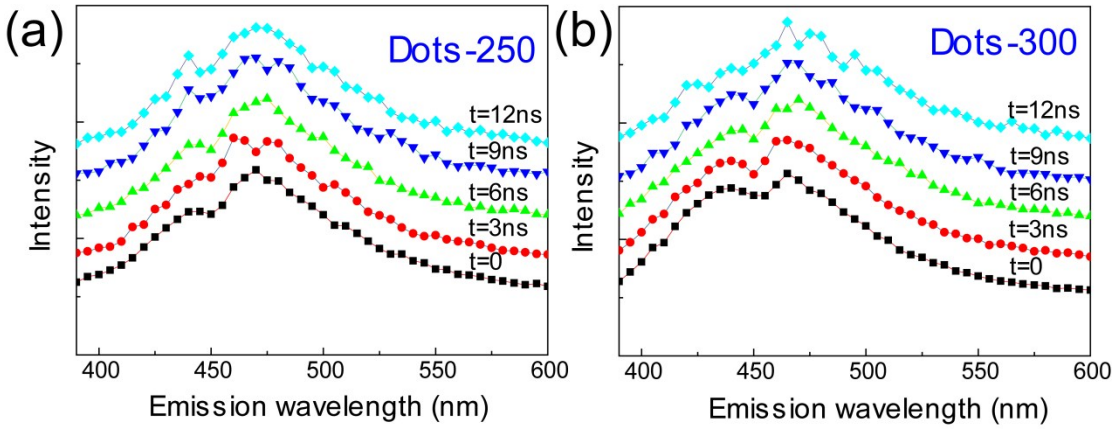

Figure S11 Extracted PL spectra at different time delays for (a) Dots-250 and (b) Dots-300.

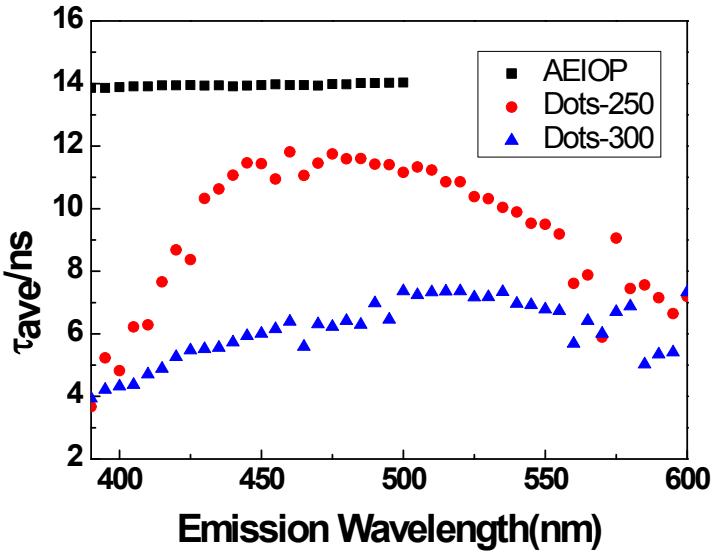

Figure S12 Average PL lifetime τave of Dots-250 and Dots-300 as a function of emission wavelength. $\tau_{ave} = \tau_1 \cdot f_1 + \tau_2 \cdot f_2$. PL lifetime of AEIOP are incorporated for comparison.[1]

Quantum Yield Measurements.

The quantum yield was determined by the slope method.

$$\emptyset_x = \emptyset_x\left(K_x/K_s\right)\left(\eta_x/\eta_s\right)^2$$

Where Φ is the relative quantum yield, K is the slope determined by the curves between the measured integrated emission intensity and the optical density, η is the refractive index of the solvent. For the aqueous solutions, η_x/η_s=1. The subscript "*s*" refers to quinine sulfate dissolved in 0.5 M H_2SO_4 with absolute quantum yield (0.54), and "*x*" for the sample. To minimize re-absorption effects, absorption in the 1.0 cm fluorescence cuvette was kept below 0.10 at the excitation wavelength (360 nm).

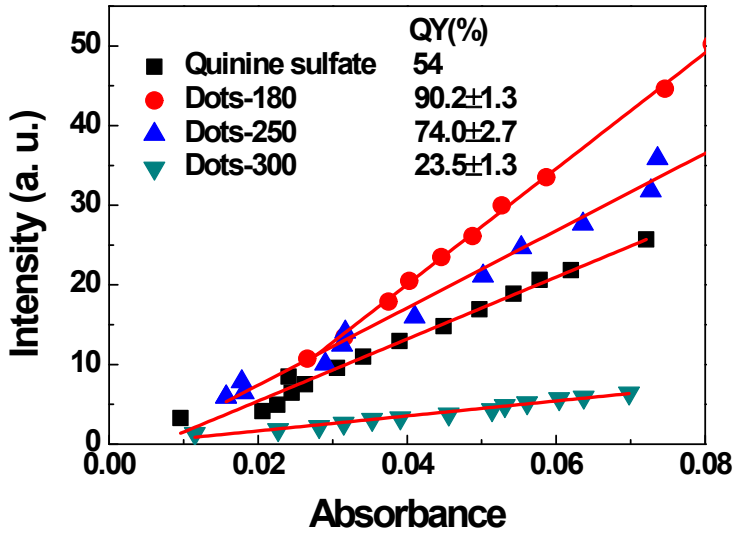

Figure S13 Fitting line between fluorescence peak area and absorbance of the nanodots. The quinine sulfate solution as a reference is also displayed for QY calculation.

REFERENCES:

(1) Wenkai Zhang, Lijuan Shi, Yingqiu Liu, Xianrui Meng, Hao Xu, Yuanqing Xu, Baoying Liu, Xiaomin Fang, Hai-Bei Li, Tao Ding, Supramolecular interactions via hydrogen bonding contributing to citric-acid derived carbon dots with high quantum yield and sensitive photoluminescence. *RSC Adv.*, 2017, 7, 20345-20353.