Electronic Supplementary Information (ESI)

for

Carbon Dots with Aggregation Induced Emission Enhancement for Visual Permittivity Detection

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Contents in ESI

1. Experimental Section

1.1 Materials

1.2 Synthesis of carbonaceous nanospheres

1.3 Characterizations

1.4 Quantum yield calculation

1.5 Calculation of fluorescence lifetime

2. Results

2.1 Figures

Fig.S1 UV-vis absorption spectra and PL spectra of TA-CDs and TA.

Fig.S2 PL spectra of TA in water/THF mixture solution.

Fig.S3 XRD pattern of TA-CDs.

Fig.S4 Raman Spectra of TA-CDs.

Fig.S5 XPS spectra of CDs.

Fig.S6 Fourier transformed infrared spectrum of the CDs.

2.2 Tables

2.3 Schemes

3. Notes and references

1. Experimental Section

1.1 Materials

Tanic acid (99%) was purchased from Xiya Reagent (Chengdu, China). THF (99.0 wt%, MV=72.11) was purchased from Aladdin (USA). Cefotaxime sodium salt was purchased from Aladdin (USA). NaCl, KCl, $ZnSO_4$, K_2SO_4, $Pb(NO_3)_2$, KNO_3 and other reagents were of analytical reagent grade. The solutions were prepared using Milli-Q purified water (18.2 MΩ).

1.2 Synthesis of carbonaceous nanospheres

First, 0.17 g tannic acid was added into 4 mL purified water and then dissolved sufficiently in ultrasonic condition. Next, the solution was transferred to a 25 mL teflon-lined stainless-steel autoclave and heated at 150 ℃ for 120 min. The color of the solution turned from light yellow to dark brown. After cooling the solution to room temperature, small molecules were detached through a dialysis membrane (1000 MWCO). Solid CDs were then concentrated by freezing at -80 ℃ and dried under vacuum for quantitative use. Characterizations of the TA-CDs were carried on by UV-Vis spectrophotometer, fluorescence spectrophotometer, scanning transmission electron microscopy and fourier transform infrared spectroscopy. To eliminate the effect of remaining TA, UV-vis absorption spectra and photoluminescence spectra of TA and TA-CDs were measured (Fig.S1). The emission intensity of TA-CDs was about 20 times of TA with the same concentration. What is more, PL spectra of TA in glycerol/water mixture solutions with glycerol ratio of 0, 20%, 40%, 60%, 80% were measured. With the increase of glycerol ratio, PL intensity of TA also enhanced, but until dispersed in 80% glycerol solution, PL intensity of TA was still quite weak. Thus, in subsequent use, such a weak PL emission of TA could be ignored.

1.3 Characterizations

Fluorescence spectroscopy was performed with an F-2500 fluorescence spectrophotometer (Hitachi, Tokyo, Japan), and UV-vis absorption spectroscopy was

performed with a UV-3600 spectrophotometer (Hitachi, Tokyo, Japan). Functional group analyses were carried out using a Fourier transform infrared spectrometer (FTIR-8400S, Toyota, Japan). The fluorescence life time was measured with FLTCSPC fluorescence spectrophotometer (Horiba Jobin Yvon Inc., France). The scanning electron microscope image was performed with a S4800 scanning transmission electron microscope (Hitachi, Tokyo, Japan).

1.4 Quantum yield calculation

The fluorescence quantum yield (ϕ) of TA-CDs was calculated using the fluorescence intensity and absorbance values of quinine sulfate as reference. The TA-CDs was dissolved in ultrapure water (η =1.33) while quinine sulfate (literature ϕ_R= 0.54) was dissolved in 0.1 mol/L H_2SO_4 (refractive index η = 1.33). This method has been reported to measure the QY of carbon nanoparticles.[1-3]

Different concentrations of CDs and the quinine sulfate were made, all of which had absorbance less than 0.1 at the excitation wavelength of CDs. Then, According to Equation (1)

$$\phi = \phi_R \times \frac{m}{m_R} \times \frac{\eta^2}{\eta_R^2} \tag{1}$$

Where m is the slopes calculated in Fig.S1 and η is the refractive index of the solvent. For this CDs solution, $\frac{\eta}{\eta_R} = 1$, wherein the subscript of R refers to the reference. The

QY of TA-CDs was calculated to be 7.16%.

According to Equation (1), the QY of CDs was calculated to be 42.65% in 80% THF ($\eta_{80\%THF} = 1.390$) solution. Wherein $\eta_{80\%THF}$ was calculated by equation

$\eta_{80\%THF} = 20\% \eta_{water} + 80\% \eta_{THF}$, wherein $\eta_{THF} = 1.404$.

1.5 Calculation of fluorescence lifetime

Average fluorescence lifetime of CDs was calculated according to Equation (2)

$$\overline{\tau} = \frac{A_1\tau_1 + A_2\tau_2 + A_3\tau_3}{A_1 + A_2 + A_3} \qquad (2)$$

Wherein A_i is the fractional contributions of time-resolved decay lifetime of τ_i. The average fluorescence lifetime of CDs in aqueous solution and 80% THF solution was calculated to be 1.85 ns and 1.21 ns.
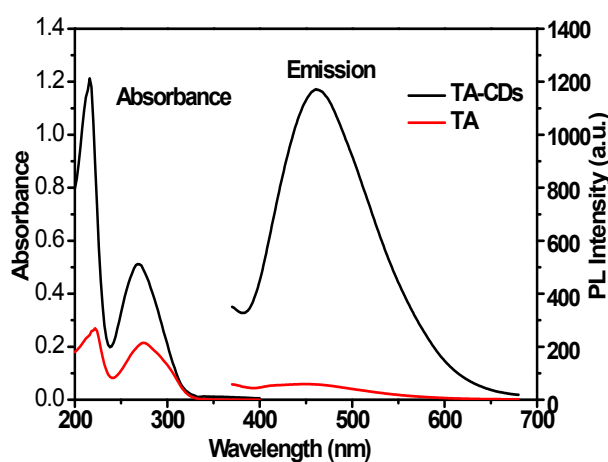
2. Results

2.1 Figures

Fig.S1 UV-vis absorption spectra and PL spectra of TA-CDs and TA. 0.05 mg/ml TA-CDs and TA were prepared to acquire PL spectra and the PL spectra were measured with excitation wavelength of 350 nm. The UV-vis absorption spectra were normalized.
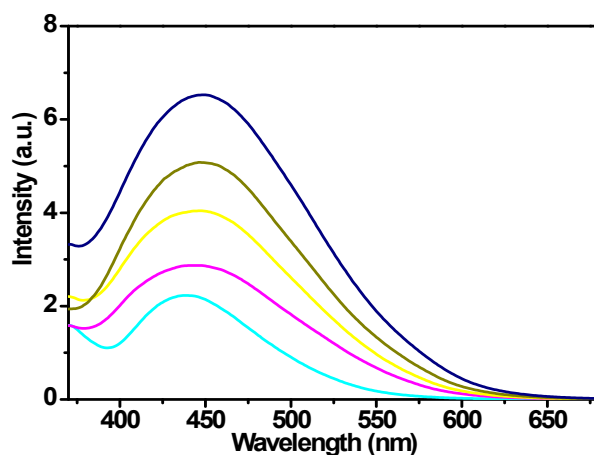

Fig.S2 PL spectra of TA in glycerol and water mixture solutions with glycerol ratio of 0, 20%, 40%, 60%, 80%. TA was prepared to 2 μg/ml in water/glycerol for PL measurement.
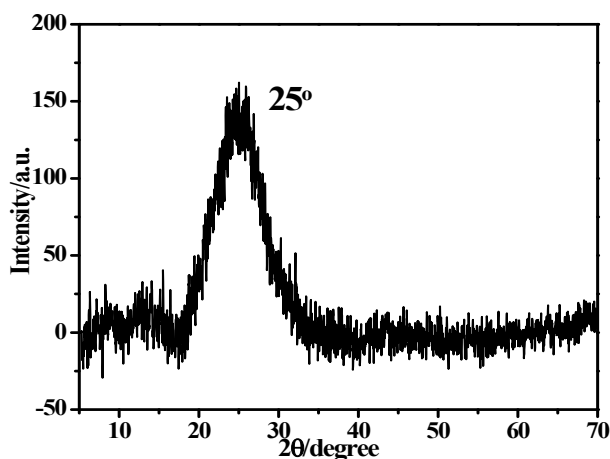
Fig.S3 XRD pattern of TA-CDs. The XRD pattern with a broad peak centered at 25° is attributed to the graphite lattice spacing and highly disordered carbon atoms, which is consistent with HRTEM image.[4]
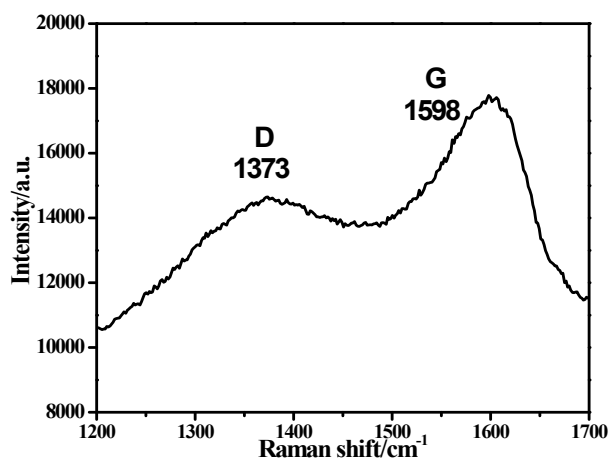

Fig.S4 Raman Spectra of TA-CDs. The Raman spectrum showed the G-band at 1598 cm^{-1} and the D-band at 1373 cm^{-1} which attribute to sp^2 and sp^3 carbons respectively. The relative intensity (I_D/I_G) of the Raman peaks for the TA-CDs is around 0.82, indicating that they have a similar structure to graphite.[5]
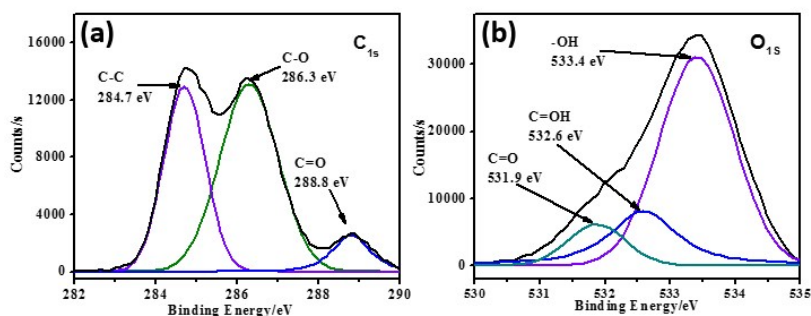

Fig.S5 XPS spectra of CDs. (a) C$_{1s}$ spectra, (b) O$_{1s}$ spectra of CDs. The C1s spectrum shows

three peaks at 284.7, 286.3 and 288.8, which are attributed to C=C, C-O and C=O, respectively.[6, 7] While the O1s spectrum exhibits three peaks at 531.9, 532.6 and 533.4 eV, which are attributed to O=C, C-OH and -OH groups, respectively.[8-10]
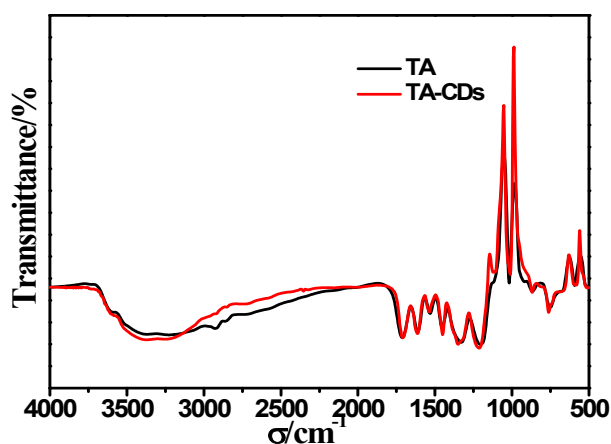

Fig.S6 Fourier transformed infrared spectrum of the CDs. The FTIR spectrum exhibited characteristic absorption bands of O-H, C=C, O-H and C-O stretching at about 3300 cm^{-1}, 1612 cm^{-1}, 1535 cm^{-1}, 1450 cm^{-1}, 1350 cm^{-1} and 1211 cm^{-1}. Usually, the stretching vibration peaks after 1000 cm^{-1} are indicated for aromatic rings. The FTIR results indicated that there are aromatic rings and phenolic hydroxyl groups.
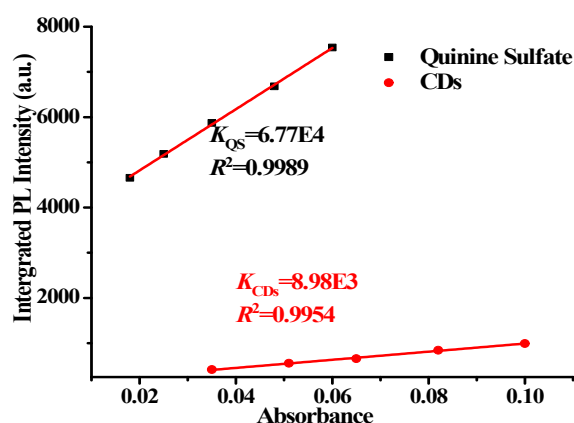

Fig.S7 Linear fitting for quantum yield calculation of CDs and Quinine sulfate. TA-CDs was dissolved in ultrapure water while quinine sulfate was dissolved in 0.1 mol/L H_2SO_4. All the TA-CDs and quinine sulfate solutions had absorbance less than 0.1 at the excitation wavelength of 350 nm.
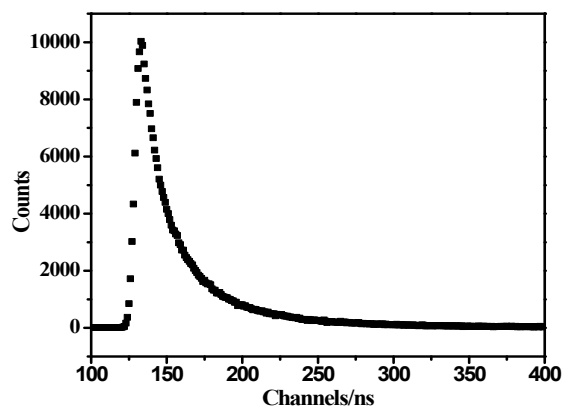
Fig.S8 Fluorescence lifetime intensity decay of CDs in aqueous solution (excitation at 350 nm, emission at 455 nm). According to equation 2, fluorescence lifetime of TA-CDs was calculated to be 1.85 ns.
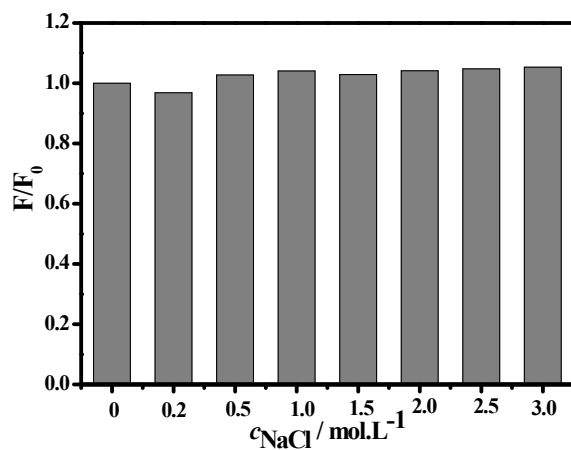

Fig.S9 PL intensity of TA-CDs measured at 350 nm in different ionic strengths. All NaCl concentrations were final concentrations after CDs' addition.
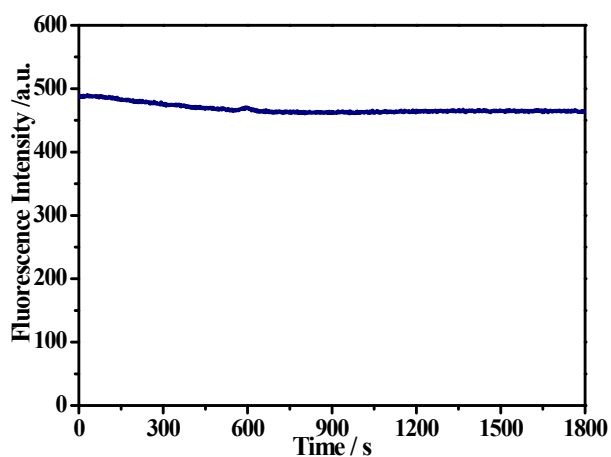

Fig.S10 Fluorescence Intensity for the as-prepared TA-CDs under continuous excitations.

The excitation wavelength was 350nm and emission wavelength was 455 nm. After exposed under continuous excitations, fluorescence intensity of TA-CDs did not show an obvious decrease.
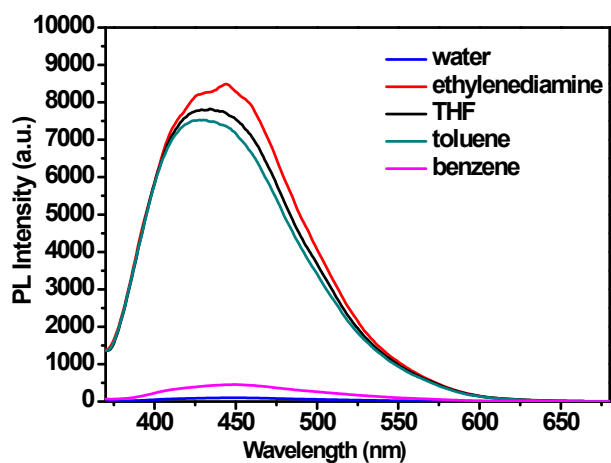

Fig.S11 PL spectra of TA-CDs in water, ethylenediamine, THF, toluene and benzene. The permittivity of ethylenediamine, toluene and benzene was smaller than THF. The PL intensity of TA-CDs in ethylenediamine and toluene did not show a notable difference, but PL intensity of TA-CDs in benzene was only about 5 times of that in water, which had such a decrease comparing with that in THF.
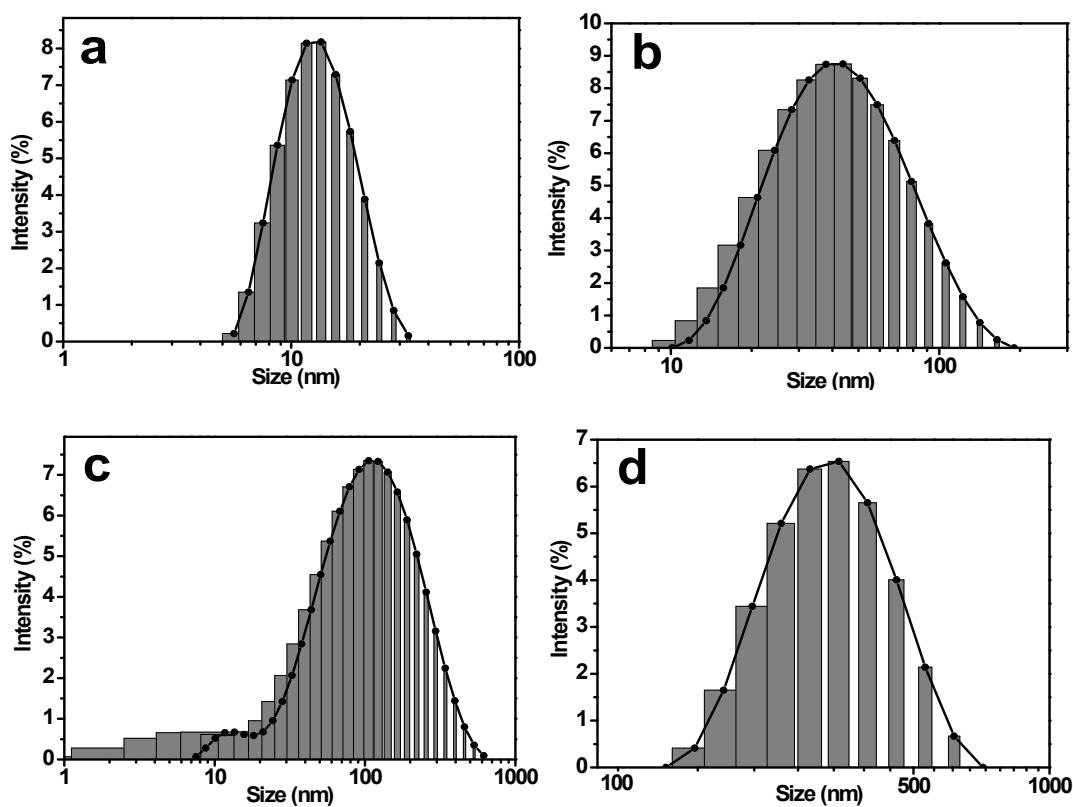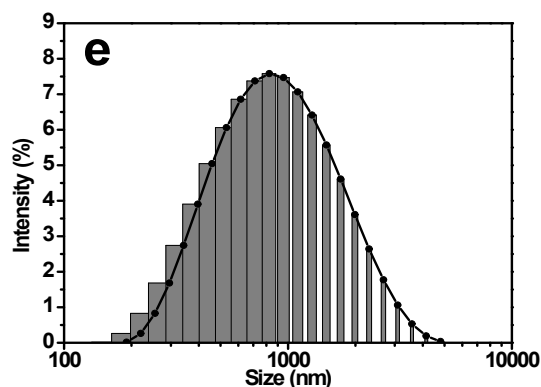
Fig.S12 Aggregation features of TA-CDs in the presence of THF. a-e represent for diameters of TA-CDs in the aqueous medium of 0, 10%, 20%, 30% and 50% THF through dynamic light scattering (DLS), respectively.
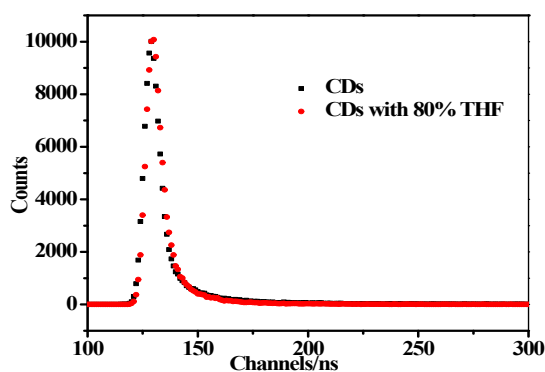
Fig.S13 Fluorescence lifetime intensity decay of CDs in aqueous solution and 80% THF solution (excitation at 350 nm, emission at 455 nm). Fluorescence lifetime of CDs in 80% THF solution decreased from 1.85 ns to 1.21 ns comparing with CDs in aqueous solution.

Fig.S14 The fluorescence emission spectra of the TA-CDs in aqueous solution and 50% glycerol solution. Fluorescence emission spectra achieved under excitation wavelength of 350 nm. Fluorescence intensity of TA-CDs in 50% glycerol was about 10 times of which in aqueous solution.

2.2 Schemes

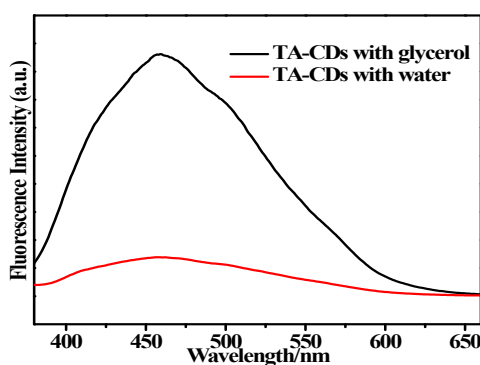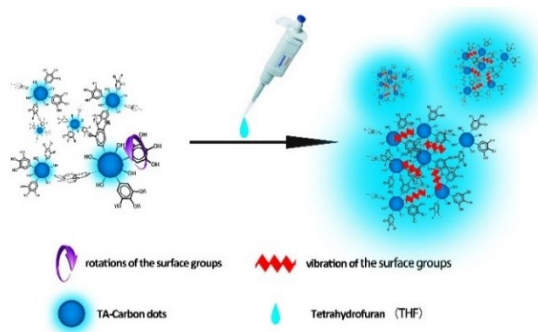**Scheme S1** State of surface groups before and after the addition of THF.

2.3 Tables

Table S1 Fluorescence lifetime of CDs in aqueous solution

	τ_i/ns	A_i/ %
τ_1	0.56	70.27
τ_2	2.59	22.37
τ_3	11.96	7.36

The fluorescence lifetime was fitted using a three-exponential decay function to yield the lifetime of TA-CDs. Wherein A_i is the fractional contributions of time-resolved decay lifetime of τ_i.

Table S2 Calculation of two items in the permittivity fitting curve.

ε	$9.53 \times 10^5 (e^{-\frac{\varepsilon}{4.82 \times 10^6}} - 1)$	$5.52 \times 10^3 e^{-\frac{\varepsilon}{1.68}}$
7.6	-1.503	78.645
10.4	-2.056	27.881
12.3	-2.432	22.877
12.79 (turning point)	-2.529	20.029
18.3	-3.618	16.812
20.7	-4.093	16.908
24.5	-4.844	16.853
26.3	-5.200	16.900
32.7	-6.465	17.654

36.7	-7.256	17.845
37.5	-7.414	17.708
47.2	-9.332	17.654
65	-12.852	17.841
80	-15.817	16.817

In the table, the first and the second term of the fitting curve (equation 1 in the main text) between permittivity (ε) and fluorescence intensity ratio ($\frac{I}{I_0}$) was calculated.

Table S3 Rate constants of CDs in aqueous solution and 80% THF solution.

	In aqueous solution	In 80% THF solution
ϕ/%	7.16	42.65
τ/ns	1.85	1.21
$k_r/10^6\text{s}^{-1}$	38.7	352.5
$k_{nr}/10^8\text{s}^{-1}$	5.02	4.74

Wherein, ϕ and τ represent for fluorescence quantum yield and fluorescence lifetime. According to equation 2 and 3 in the main text, k_r and k_{nr} represent for radiative rate and non-radiative rate, respectively.

3. Notes and references

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