

Supporting Information

Liquid and Solid-State Tunable Fluorescent Carbon Dots for Trace Water Detection

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Experimental Section

Materials

L-arginine and *o*-Phenylenediamine were purchased from Aladdin Chemical Company Limited (Shanghai, China). Sulfuric acid, sodium hydroxide, toluene, dichloromethane (DCM), ethyl acetate (EA), acetonitrile (ACN), acetone, N, N-dimethylformamide (DMF), N-methyl pyrrolidone (NMP), methanol (MeOH), ethanol (EtOH), and ethylene glycol (EG) were purchased from Sinopharm Chemical Reagent Company (Beijing, China). γ -(2,3-epoxypropoxy) propyltrimethoxysilane (GPTMS), 3-aminopropyltriethoxysilane (APTES), methyltriethoxysilane (MTES), polyvinyl pyrrolidone (PVP), polymethylmethacrylate (PMMA), polystyrene (PS) were purchased from Beijing InnoChem Science & Technology Co., Ltd. All materials were used directly without further purification. Deionized water was used throughout the study.

Instrumentation

The fluorescence spectra of CDs were tested with an F-4500 fluorescence spectrometer (scanning speed: 1200 nm/min, slit: 5 nm); UV-Vis absorption spectra were tested with a U-3000 and a Cary 5000 spectrophotometers (scanning speed: 600 nm/min). The morphologies of CDs (TEM) were tested by JEM-2100F transmission electron microscope (accelerating voltage of 200 kV), and the samples were observed when diluted and dropped on the ultrathin carbon film after drying. The height of CDs was measured by Dimension Fastscan Bio (Bruker, Germany) atomic force microscope

(AFM). The surface groups of CDs were tested by Excalibur-3100 FTIR spectrometer with wave number accuracy $< 0.01 \text{ cm}^{-1}$ and EscaLab 250Xi X-ray photoelectron spectrometer (XPS). The carbonization degree of CDs was characterized by D8 focus X-ray diffractometer and inVia-Reflex micro confocal Raman spectrometer. The absolute quantum yields and fluorescence lifetimes of CDs were tested by FLS1000 steady-state/transient fluorescence spectrometer.

Preparation of O-CDs

The *o*-Phenylenediamine (0.16 g) and L-arginine (0.11 g) were dissolved in 30 mL of sulfuric acid (7.36 M), and sonicated for 20 min to make it homogeneous. The solution was transferred into a 100 mL autoclave and heated at 200°C for 12 h. Then, it was cooled to room temperature and centrifuged at 10,000 rpm for 10 min to remove insoluble large particles. The liquid was added to 50 mL of NaOH (1.25 M) solution and stirred at room temperature for 30 min. The processed solution was centrifuged at 10,000 rpm for 10 minutes to collect the precipitate, which was washed with deionized water and centrifuged several times until the supernatant was clear. The precipitate was lyophilized to obtain the desired carbon dots, named as O-CDs.

Detection of trace water in organic solvents

0.5 mg of O-CDs were dissolved in 5 mL solutions containing different organic solvents (acetone, acetonitrile, DMF) and water contents (0-10%) by ultrasonication. Then, the fluorescence spectra were measured under optimal excitation.

Preparation of carbon dot fluorescent films

1 g of PS powder and 10 mL of toluene were mixed well. Then, O-CDs powders with the different masses according to the amount of PS powder were added in the solvent system. After stirring for uniform dispersion, the mixtures were poured into the mold. PS fluorescent films with different O-CDs doping concentrations were obtained after drying and curing at room temperature.

PMMA and PVP fluorescent films were prepared in the same way as PS fluorescent films. The only difference was that we replaced toluene with DMF and NMP, respectively.

Preparation of carbon dot gel glass

42.5 mL of MTES and 150 mL of ethanol were mixed evenly. Then 13.5 mL of aqueous acetic acid solution (pH=2.5) was added to the mixed solution. After overnight stirring, half volume of solvent was removed by rotary evaporation and stirred for one week at room temperature to achieve hydrolysis and condensation. 7.32 mL of the solution and different masses of O-CDs powder were stirred thoroughly and poured into the mold. Finally, the MTES based gel glasses with different O-CDs doping concentrations were obtained after curing at room temperature.

GPTMS and APTES based gel glasses were prepared in the same way as MTES based gel glasses. Only 42.5 mL of MTES was replaced with 47.6 mL of GPTMS and 50 mL of APTES, respectively; 7.32 mL of the solution was replaced with 7.84 mL and 8.4 mL, respectively.

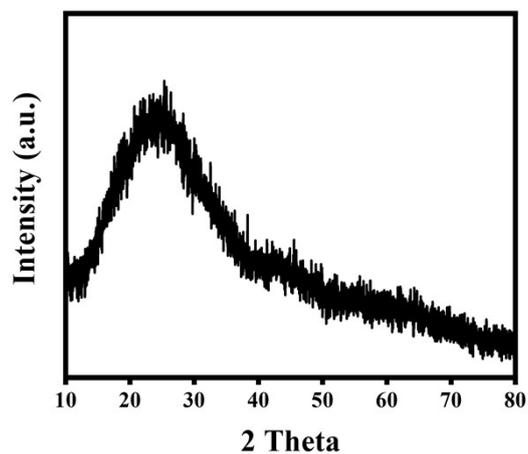


Fig. S1 XRD spectrum of O-CDs.

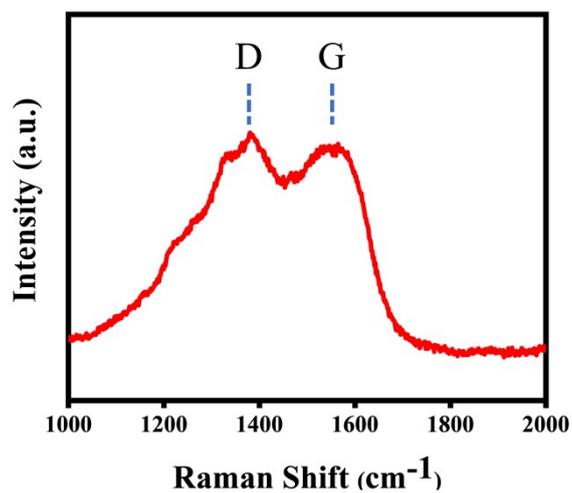


Fig. S2 Raman spectrum of O-CDs.

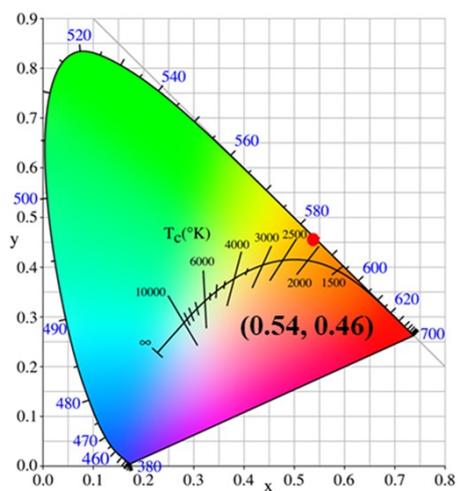


Fig. S3 CIE coordinates of O-CDs.

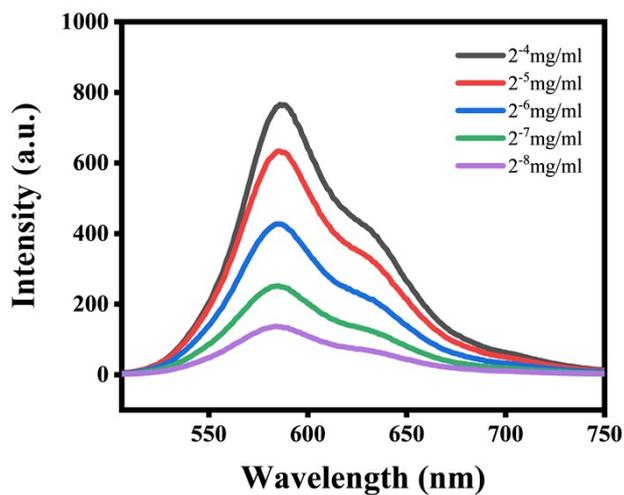


Fig. S4 Fluorescence spectra of O-CDs at different concentrations in DMF.

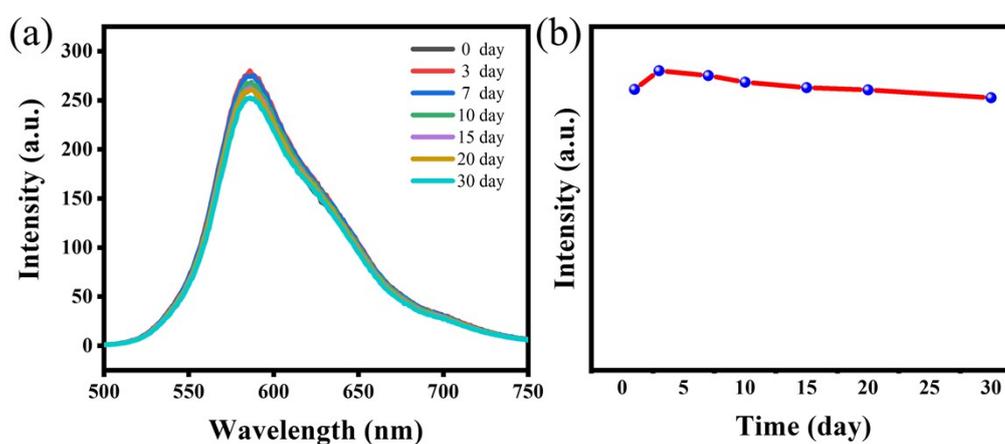


Fig. S5 Fluorescence spectra (a) and fluorescence intensity change curve (b) of O-CDs placed at room temperature for 30 days.

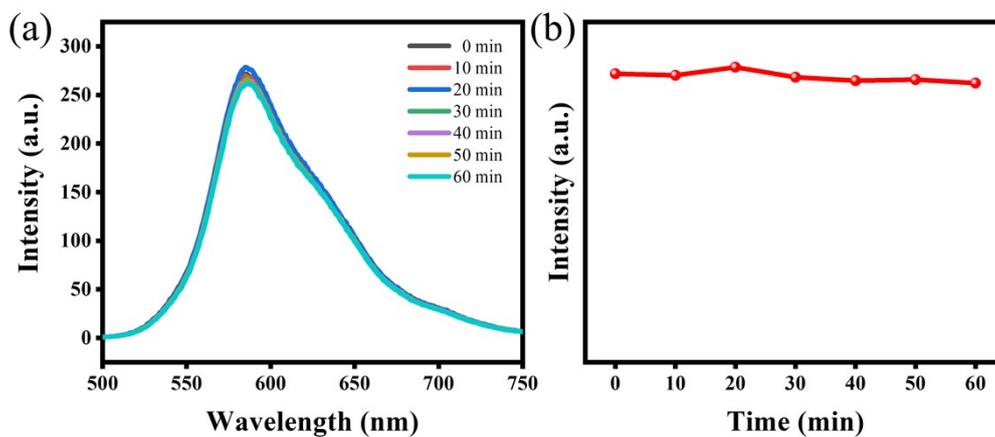


Fig. S6 Fluorescence spectra (a) and fluorescence intensity change curve (b) of O-CDs under continuous UV lamp irradiation for 1h.

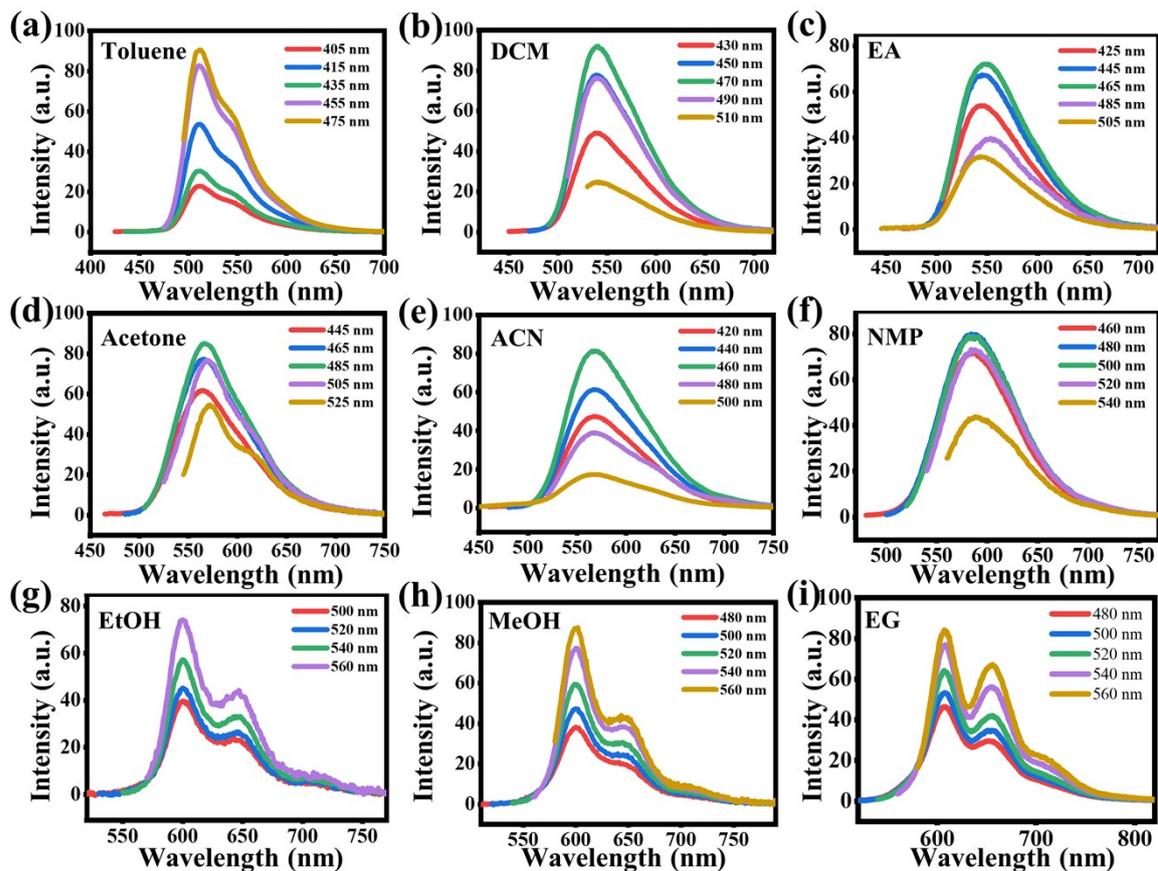


Fig. S7 PL spectra of O-CDs in different solvents under different excitations. (a) Toluene (b) DCM (c) EA (d) Acetone (e) ACN (f) NMP (g) EtOH (h) MeOH (i) EG

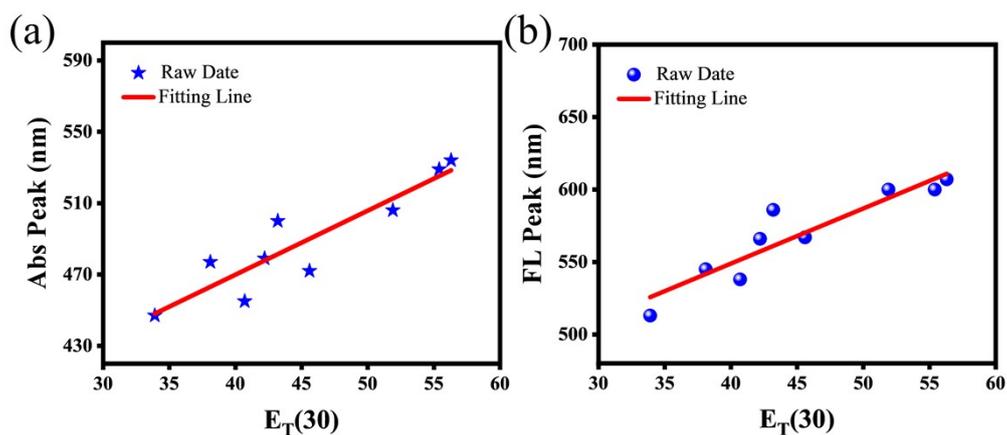


Fig. S8 The linear relationship between solvent polarity parameter $E_T(30)$ and UV-Vis absorption peak (a), fluorescence peak (b).

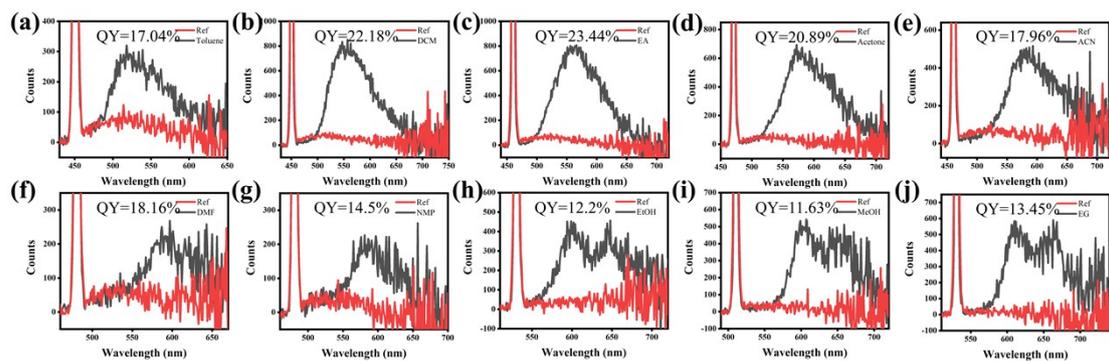


Fig. S9 Absolute quantum yields of O-CDs in different solvents. (a) Toluene (b) DCM (c) EA (d) Acetone (e) ACN (f) DMF (g) NMP (h) EtOH (i) MeOH (j) EG

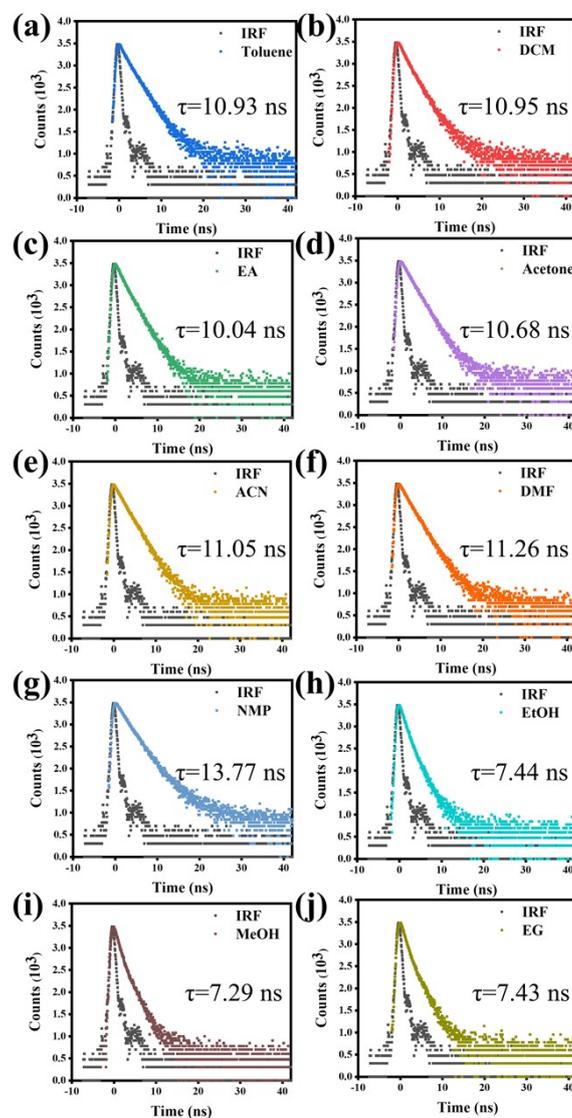


Fig. S10 The fluorescence lifetime of O-CDs in different solvents. (a) Toluene (b) DCM (c) EA (d) Acetone (e) ACN (f) DMF (g) NMP (h) EtOH (i) MeOH (j) EG

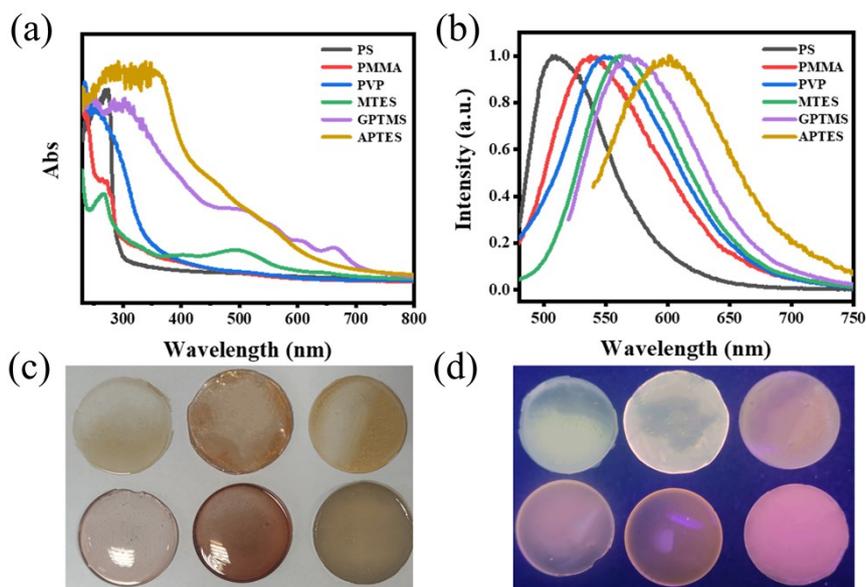


Fig. S11 Absorption spectra (a) and fluorescence spectra (b) of O-CDs in different substrates. Photographs of O-CDs in different substrates under daylight (c) and UV light (d), the above from left to right are PS, PMMA, PVP fluorescent films and the below from left to right are MTES, GPTMS, APTES based gel glasses.

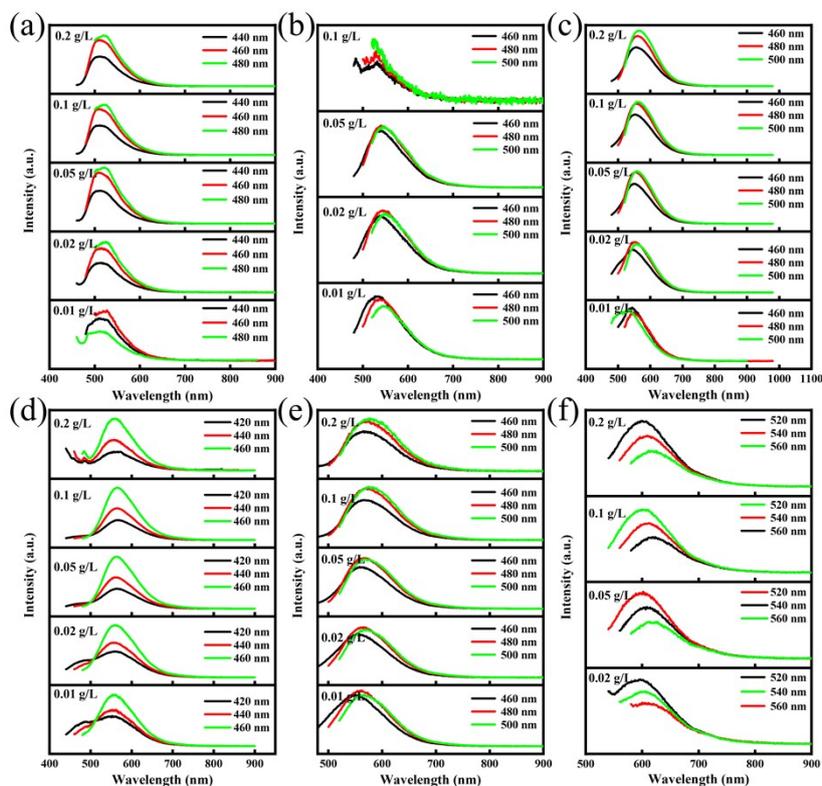


Fig. S12 Fluorescence spectra of solid-state substrates with different O-CDs doping concentrations and under different excitation wavelengths. (a) PS, (b) PMMA, (c) PVP fluorescent films; (d) MTES, (e) GPTMS, (f) APTES based gel glasses.

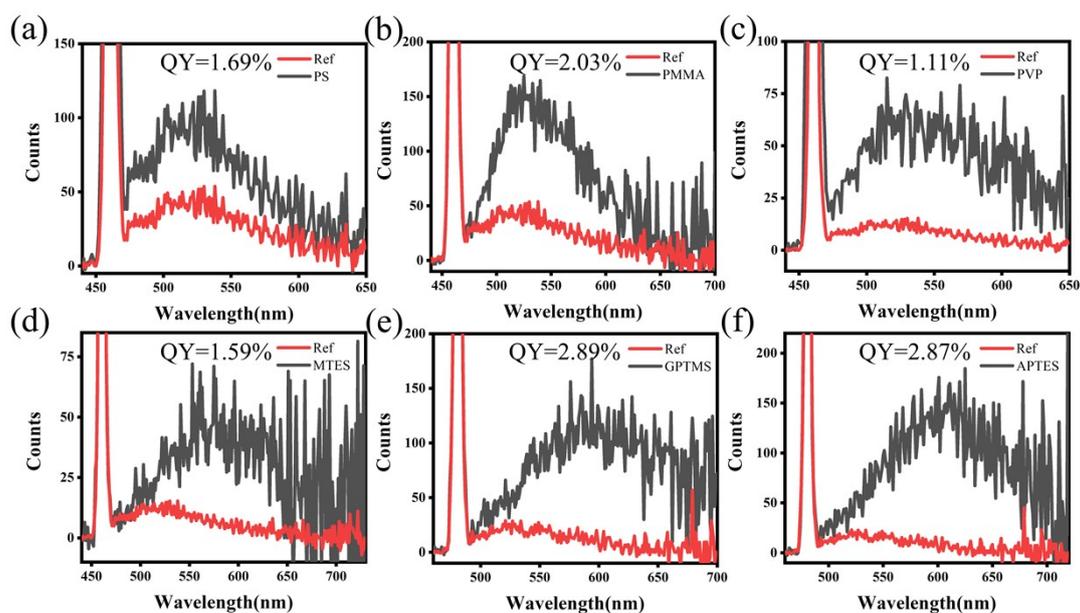


Fig. S13 Absolute quantum yields of O-CDs in different substrates. (a) PS, (b) PMMA, (c) PVP fluorescent films; (d) MTES, (e) GPTMS, (f) APTES based gel glasses.

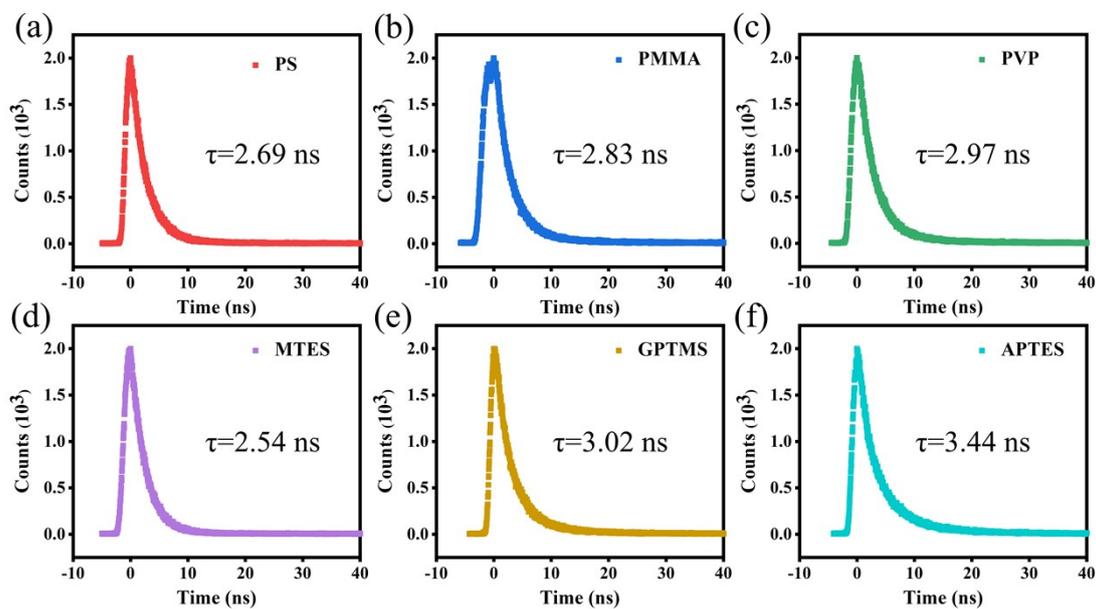


Fig. S14 Fluorescence lifetime of O-CDs in different substrates. (a) PS, (b) PMMA, (c) PVP fluorescent films; (d) MTES, (e) GPTMS, (f) APTES based gel glasses.

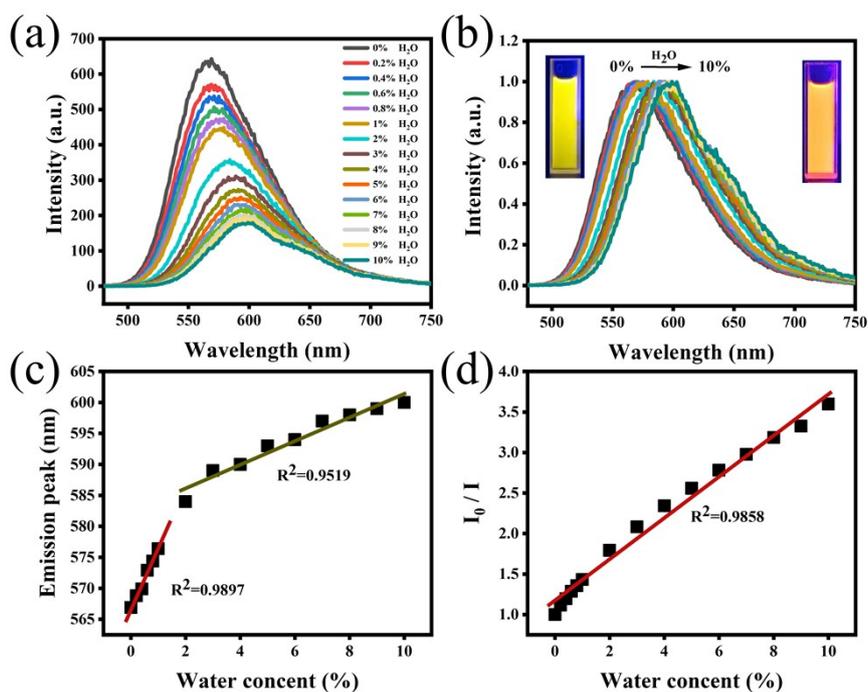


Fig. S15 (a) Fluorescence spectra of CDs in ACN with different water content. (b) Normalized fluorescence spectra. Illustrations are photos of solutions with 0% and 10% water content under UV light. (c-d) Fitting of maximum emission peak and I_0/I .

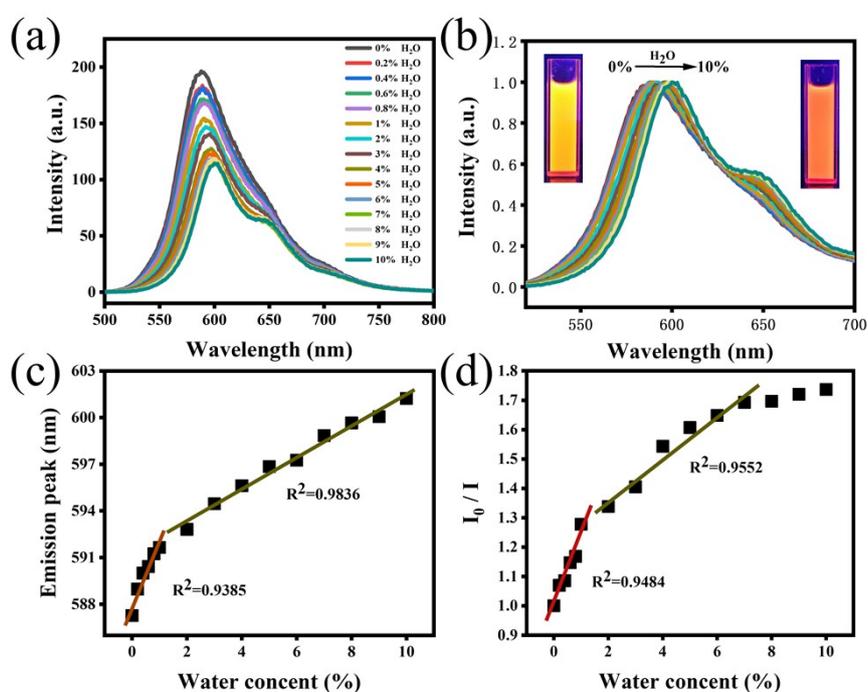


Fig. S16 (a) Fluorescence spectra of CDs in DMF with different water content. (b) Normalized fluorescence spectra. Illustrations are photos of solutions with 0% and 10% water content under UV light. (c-d) Fitting of maximum emission peak and I_0/I .

Table S1. Percentage of each element content of O-CDs.

Elements	Energy	Percentage (%)
C 1s	285 eV	72.20
N 1s	399 eV	12.24
O 1s	530 eV	13.26
S 2p	167 eV	2.30

Table S2. Presence of carbon in O-CDs in the form and percentage of content.

Form	Energy	Percentage (%)
HO-C=O	288.5 eV	4.31 %
C=O/C=N	286.0 eV	29.67 %
C-N/C-O/C-S	285.1 eV	28.19 %
C-C/C=C	284.6 eV	37.83 %

Table S3. Presence of nitrogen in O-CDs in the form and percentage of content.

Form	Energy	Percentage (%)
Pyrrolic N	401.3 eV	9.78 %
Aniline N	400.0 eV	49.86 %
Pyridinic N	398.6 eV	40.35 %

Table S4. Presence of oxygen in O-CDs in the form and percentage of content.

Form	Energy	Percentage (%)
C-O	533.0 eV	51.14 %
C=O	531.3 eV	48.86 %

Table S5. Data of O-CDs in different solvents.

Solvent	$\lambda_{\text{abs}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	QY/%	τ/ns
Toluene	447	513	17.04	10.93
DCM	455	538	22.18	10.95
EA	477	545	23.44	10.04
Acetone	479	566	20.89	10.68
ACN	472	567	17.96	11.05
DMF	500	586	18.16	11.26
NMP	494	590	14.5	13.77
EtOH	506	600	12.2	7.44
MeOH	529	600	11.63	7.29
EG	534	607	13.45	7.43

Table S6. Comparison of O-CDs with other reported CDs in trace water detection.

Method	Materials	Solvent	LOD (%)	Reference
Hydrothermal followed by reflux	β -Resorcylic acid Ethylenediamine	Acetone	0.37	[1]
		THF	0.36	
Solvothermal	1,1'-binaphthyl-2,2'-diamine	EtOH	0.38	[2]
		ACN	1.05	
		THF	2.97	
Hydrothermal	<i>o</i> -Phenylenediamine	MeOH	0.41	[3]
		Acetone	0.19	
		THF	0.13	
Solvothermal	<i>o</i> -Phenylenediamine	ACN	0.18	[4]
		EtOH	0.03	

Sulfamide				
Hydrothermal	Isophthalic acid Ethylenediamine	EtOH	0.071	[5]
		Acetone	0.027	
		ACN	0.021	
		THF	0.011	
Solvothermal	<i>o</i> -Phenylenediamine L-arginine	Acetone	0.042	This work
		ACN	0.129	
		DMF	0.132	

Notes and references

- 1 M. Moniruzzaman and J. Kim, *Sens. Actuators B Chem.*, 2019, **295**, 12-21.
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