Electronic Supplementary Material (ESI) for Analyst.

Supporting Information

Carbon dots with hydrogen bond-controlled aggregation behavior

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Experimental Section

Materials: Tannic acid (TA) and N-methylpyrrolidone (NMP) are obtained from Aladdin Reagent Co., Ltd (Shanghai, China). Ethylenediamine (EDA) and isopropanol are purchased from Titan Scientific Co., Ltd (Shanghai, China). Methanol, ethanol and acetone are acquired from Sinopharm chemical reagent Co., Ltd (Shanghai, China). DMSO is obtained from Lingfeng chemical reagent Co., Ltd (Shanghai, China). Dialysis membrane for the purification of hydrophilic carbon dots (H-CDs) is purchased from Solarbio Co., Ltd (Beijing, China). All solutions are prepared using 18.2 MΩ.cm ultrapure water from Millipore-Q ultrapure water system.

Apparatus: The morphology and size of H-CDs are obtained by a JEM-2100 high-resolution transmission electron microscope (TEM). The Fourier transform infrared (FT-IR) spectrum of H-CDs is measured through a Hitachi FTIR-8400S FT-IR spectrometer. UV-vis absorption spectrum of H-CDs is collected from a 759S UV-vis spectrophotometer. Fluorescence (FL) spectra of H-CDs in different solvents are measured by a F97pro FL spectrophotometer. The FL lifetimes of H-CDs in different solvents are determined using an FLS1000 FL spectrometer.

Preparation of H-CDs: H-CDs are synthesized with a minor revision as previously reported.[22] A brief procedure is presented as follows: 50 mg of TA is firstly dissolved in 4.8 mL ultrapure water. Dark brown H-CDs solution can be observed within 3 days after the addition of 0.2 mL of EDA at room temperature. The H-CDs are further purified by dialyzing (cellulose ester dialysis membrane, 100-500 MWCO) and then stored at 4 °C.

Solvent-dependent FL experiment of H-CDs: Protic solvents (methanol, ethanol and isopropanol) and aprotic solvents (NMP, DMSO and acetone) with different volume fractions are introduced into the H-CDs aqueous solution for investigating the effect of hydrogen bonding on the FL emission and dispersion of H-CDs. The FL spectra of H-CDs (4 g/mL, 5 mL) in aqueous solution with different volume fraction (0% - 100%) of organic solvents are measured by exciting at 350 nm.

Supplementary Note 1. A magnified TEM image of H-CDs

TEM image of H-CDs is obtained by a JEM-2100 TEM. Results show that H-CDs have an amorphous nanostructure.

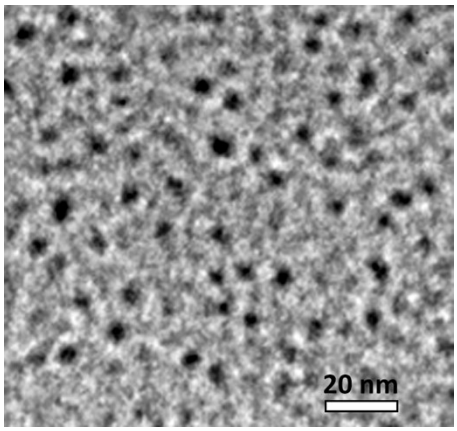

Fig. S1. A magnified TEM image of H-CDs.

Supplementary Note 2. FT-IR spectrum of H-CDs

FT-IR spectrum of H-CDs is measured through a Hitachi FTIR-8400S FT-IR spectrometer. FT-IR spectrum strongly proves that the surface of H-CDs is rich in O–H/N–H (3307 cm^{-1}), C=N (1647 cm^{-1}), C=C (1582 cm^{-1}), C–N (1386 cm^{-1}), and C–OH (1105 cm^{-1}) groups.

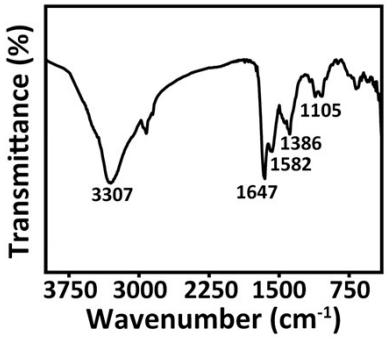

Fig. S2. FT-IR spectrum of H-CDs.

Table S1. Element composition of H-CDs by XPS spectrum.

Elements	Atomic percentage
C	57.41%
N	17.93%
O	24.66%

Supplementary Note 3. High-resolution XPS spectra of H-CDs

High-resolution XPS spectra of H-CDs are measured by a Thermo Scientific Escalab 250Xi X-ray photoelectron spectrometer. The C1s spectrum shows four peaks at 284.3, 285.3, 285.9 and 287.3 eV, which can be ascribed to C–C/C=C, C–N, C–O and C=O/C=N bonds, respectively. The N1s spectrum shows two peaks at 399.0 and 400.4 eV, which can be ascribed to C–N and C=N bonds, respectively. The O1s spectrum shows two peaks at 530.6 and 531.9 eV, which can be ascribed to C=O and C–OH bonds, respectively.

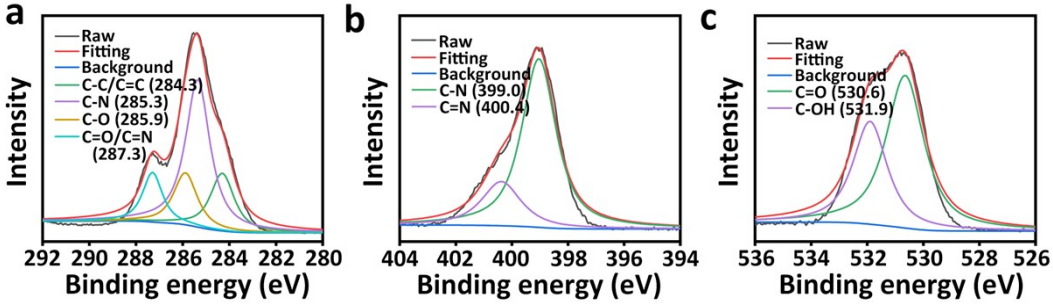

Fig. S3. High-resolution XPS spectra of H-CDs. High-resolution (a) C1s, (b) N1s and (c) O1s spectra of H-CDs.

Supplementary Note 4 The TEM images of H-CDs in different volume fractions of methanol.

The TEM images of H-CDs in different volume fractions of methanol are measured by a JEM-2100 high-resolution TEM. Results show that H-CDs begin to aggregate continuously as the volume fraction increase of methanol.

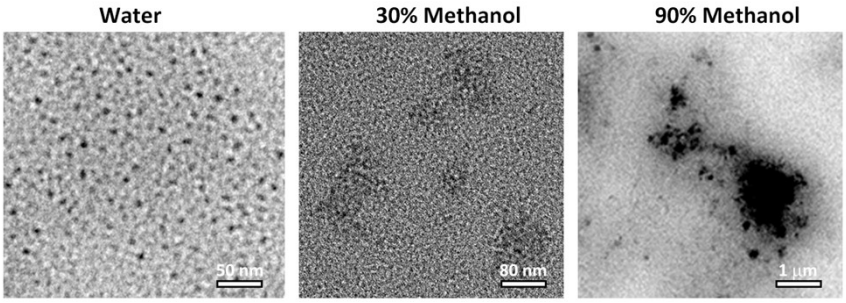

Fig. S4 The TEM images of H-CDs in different volume fractions of methanol.

Supplementary Note 5. The FL intensities of H-CDs in different volume fractions of protic solvents.

The FL intensities of the H-CDs in different volume fractions of protic solvents are measured by a F97pro FL spectrophotometer. Other protic solvents such as ethanol **(Fig. S5a)** and isopropanol **(Fig. S5b)** are also similar to methanol, which can cause the FL quenching of H-CDs with the increasing of protic solvents.

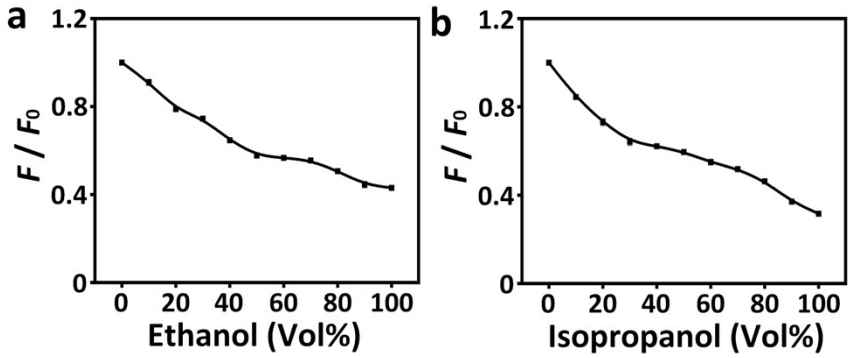

Fig. S5. The FL intensities of H-CDs in different volume fractions of protic solvents. (a) Ethanol and (b) isopropanol.

Supplementary Note 6 The TEM images of H-CDs in different volume fractions of DMSO.

The TEM images of H-CDs in different volume fractions of DMSO are measured by a JEM-2100 high-resolution TEM. Results show the behavior of H-CDs aggregation first and then dispersion with the increase of DMSO.

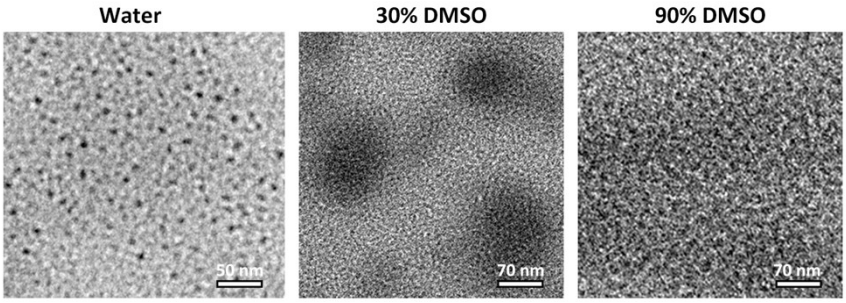

Fig. S6 The TEM images of H-CDs in different volume fractions of DMSO.

Supplementary Note 7 The FL intensities of H-CDs in different volume fractions of aprotic solvents.

The FL intensities of the H-CDs in different volume fractions of aprotic solvents are measured by a F97pro FL spectrophotometer. Other aprotic solvents such as acetone **(Fig. S7a)** and NMP **(Fig. S7b)** are also similar to DMSO. Results show that the FL intensity of H-CDs firstly decreases and then increases with the increasing of aprotic solvents.

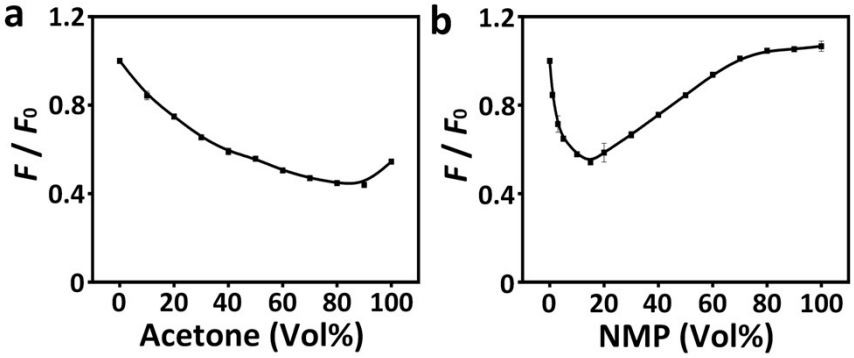

Fig. S7 The FL intensities of H-CDs in different volume fractions of aprotic solvents. (a) Acetone and (b) NMP.

Supplementary Note 8 The FL lifetimes of H-CDs in different volume fractions of methanol and DMSO solvents.

The FL lifetimes of the H-CDs in different volume fractions of methanol and DMSO solvents are measured by an FLS1000 FL spectrometer. Results show that the FL lifetime of H-CDs is about 4.5 ns, which is almost unchanged in different methanol contents **(Fig. S8a)**. While the FL lifetime of H-CDs decreases with the increase of DMSO content **(Fig. S8b)**.

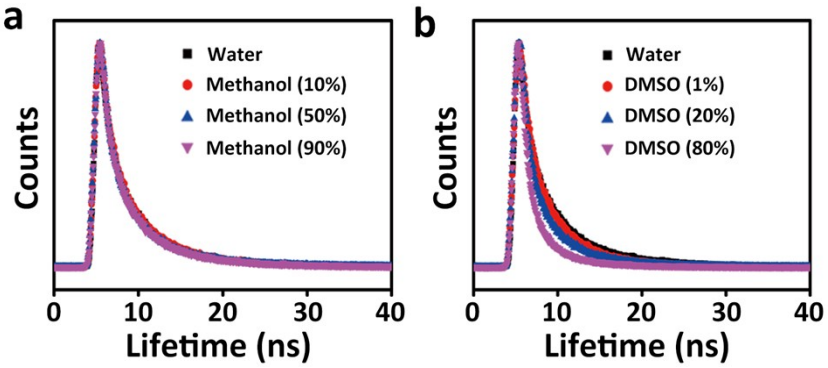

Fig. S8 The FL lifetimes of H-CDs in different volume fractions of (a) methanol and (b) DMSO solvents.

Table S2 Lifetimes from the time-resolved decay profiles of H-CDs in different solvents.

Solvents	τ_1 (ns)	Pct. (%)	τ_2 (ns)	Pct. (%)	Ave. τ (ns)
Water	1.633	44.53	6.753	55.47	4.473
1% DMSO	1.660	48.84	5.762	51.16	3.758
20% DMSO	1.254	51.88	5.610	48.12	3.345
80% DMSO	1.022	70.09	5.969	29.91	2.420
10% Methanol	1.609	44.12	6.725	55.88	4.468
50% Methanol	1.634	49.75	7.032	50.25	4.346
90% Methanol	1.575	48.37	7.028	51.63	4.390

Table S3 The comparison of the determination methods of DMSO.

Probes	Linear detection range	Detection limit	Ref.
Ferrocene-conjugated iridium(III) complex	0.5 – 60%	0.393%	1
Ln^{3+} metal–organic frameworks	10 – 100%	1.68%	2
Cd-based metal–organic framework	0 – 5%	/	3
Fluorescent Au(I)@(Ag_2/Ag_3)-thiolate particles	/	0.0178%	4
H-CDs	0.005 – 0.75%	0.001%	This work

References

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