Electronic Supplementary Information (ESI)

Fluorescent carbon dots with dual emissions and solvent-dependent properties for water detection in organic solvents

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Table S1. Quenching efficiency of the CDs synthesized under various conditions, at different concentrations of water. Molar ratio is written as mPDA:phenolphthalein.

molar ratio	Temperature (°C)	3% (v/v) water	25% (v/v) water
1:2	110	0.101	0.45
1:1	110	0.074	0.395
2:1	110	0.096	0.438
1:2	150	0.121	0.461
1:1	150	0.093	0.442
2:1	150	0.088	0.43
1:2	200	0.096	0.429
1:1	200	0.092	0.423
2:1	200	0.091	0.421

Table S2. Quantum yields (QYs) of CDs' green emissions in 10 different solvents and their relative polarity (E_T^N)

	Toluene	THF	DCM	Acetone	DMF	MeCN	DMSO	EtOH	MeOH	EG
E_T^N	0.1	0.21	0.309	0.355	0.386	0.45	0.46	0.654	0.762	0.79
QY (%)	1.14	1.79	0.97	0.95	0.77	0.93	1.28	0.81	1.47	3.01

Table S3. Summary of reports on fluorescent carbon dots for water detection in organic solvents.

References	Emission colors	Solvents	LoD	Sensing modes	Detection range (v/v)
1	blue	EtOH	0.052%	FL ratiometric	0-10%
2	purple	DMF	0.29%	FL quenching	0-4%
		MeOH	0.65%	FL quenching	0-10%
		acetone	0.57%	FL quenching, colorimetric	0-5%
3	green	EtOH	0.006%	FL quenching	0-1%
4	red	EtOH	N/A	absorption, circular dichroism	0-100%
5	red	EtOH	0.090%	FL quenching, colorimetric	0-100%
6	red	EtOH	0.38%	FL quenching	0-60%
		MeCN	1.05%	FL quenching	0-60%
		THF	2.97%	FL quenching	0-70%
		MeOH	0.41%	FL quenching	0-50%
7	yellow	EtOH	0.01%	FL quenching	0-10%
8	red	EtOH	0.50%	FL enhancement	0-50%
		DMF	N/A	FL enhancement	0-40%
		DMSO	N/A	FL enhancement	0-50%
		n-propanol	N/A	FL enhancement	0-50%
9	yellow	acetone	0.085%	FL quenching	0-4%
		THF	0.256%	FL quenching	0-6%
		EtOH	0.399%	FL quenching	0-4%
		DMF	0.189%	FL quenching	0-4%
10	blue-green	1,4-dioxane	0.000001%	FL quenching	0-0.5%
11	blue-green	THF	N/A	colorimetric	0-5%
12	blue-green	EtOH	1.667%	colorimetric	0-40%
		DMF	12.34%	colorimetric	0-40%
		MeCN	8.921%	colorimetric	0-40%
13	yellow-red	DMF	0.076%	colorimetric	0-0.8%
		ethyl acetate	0.037%	colorimetric	0-0.8%
		THF	0.072%	colorimetric	0-0.8%
14	blue-green	1,4-dioxane	0.046%	colorimetric	0-100%
		MeOH	7.06%	colorimetric	0-40%
		EtOH	5.38%	colorimetric	0-10%
15	yellow and orange	EtOH	N/A	FL ratiometric	10-80%
16	blue and red	EtOH	0.07%	FL ratiometric	0-5%
		MeOH	0.13%	FL ratiometric	0-2.4%
		MeCN	0.17%	FL ratiometric	0-5%
This study	blue and green	EtOH	0.12%	FL quenching, FL ratiometric	0-25%
		DMSO	0.01%	FL quenching	0-1%
		MeCN	0.006%	FL enhancement	0-2%

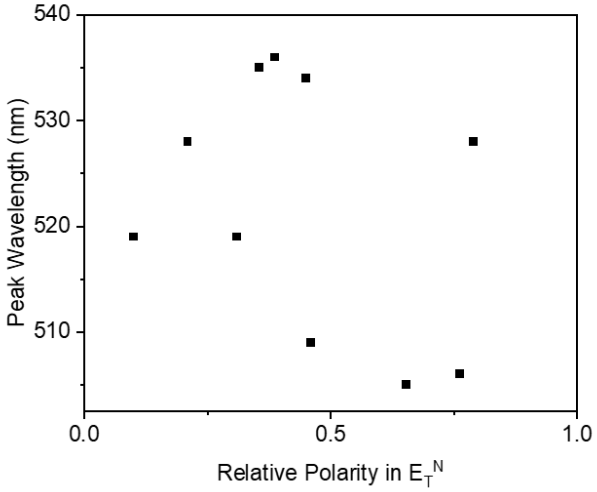

Figure S1. Peak wavelengths of green emissions in various solvents vs the solvents' relative polarity.

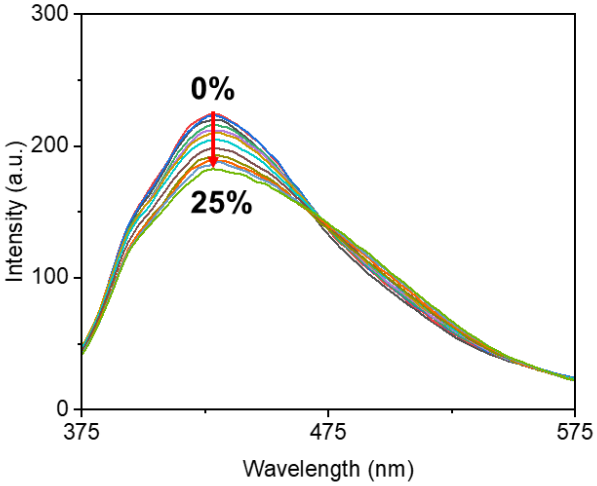

Figure S2. Fluorescence spectra of the CDs in ethanol at increasing concentrations of water (from 0 to 25%) under irradiation of 360 nm.

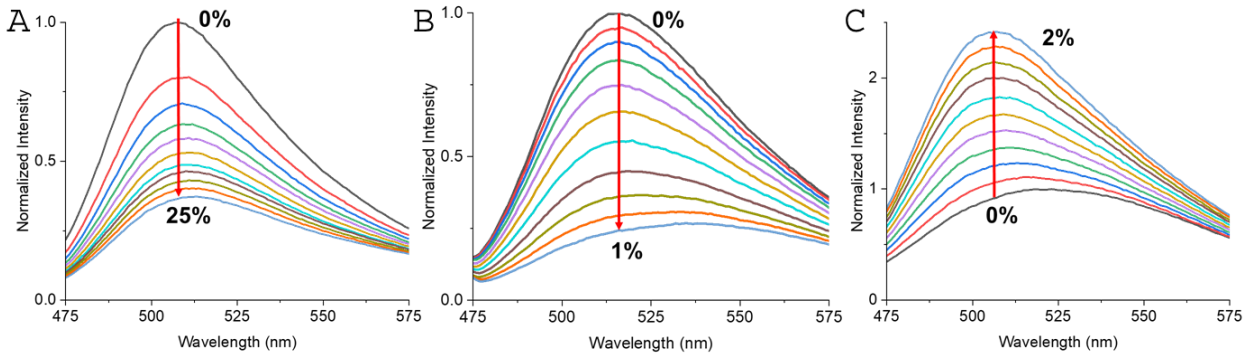

Figure S3. Normalized emission spectra of the CDs' green peak in different organic solvents (A. EtOH, B. DMSO, C. MeCN) upon addition of water.

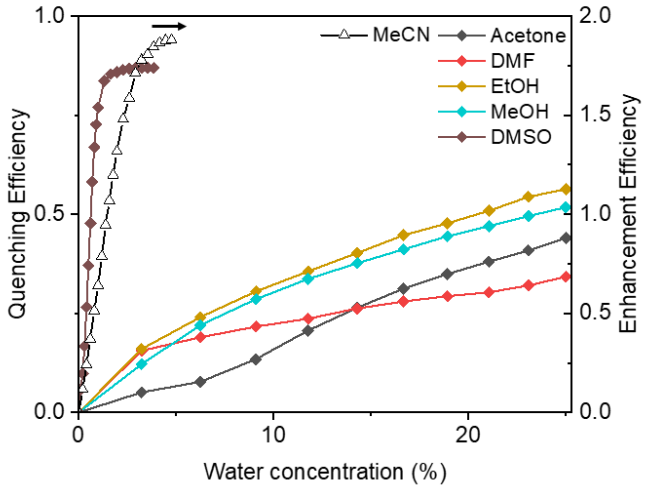

Figure S4. Quenching and enhancement efficiencies of the green emission peak in various solvents under the optimal excitation wavelengths.

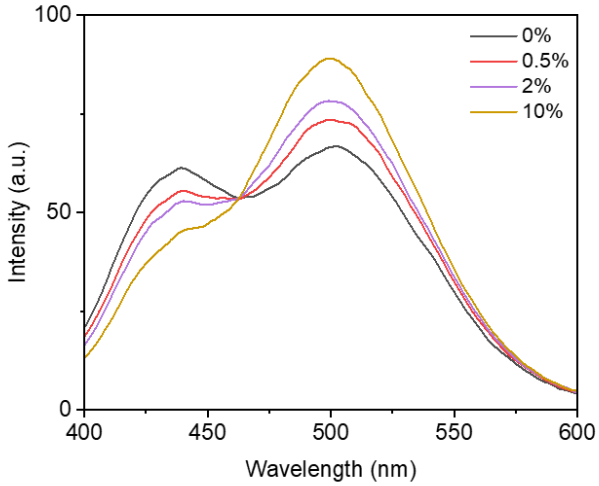

Figure S5. Emission spectrum of CDs in DMSO at different concentrations of water excited at 380 nm showing ratiometric signals for sensing.

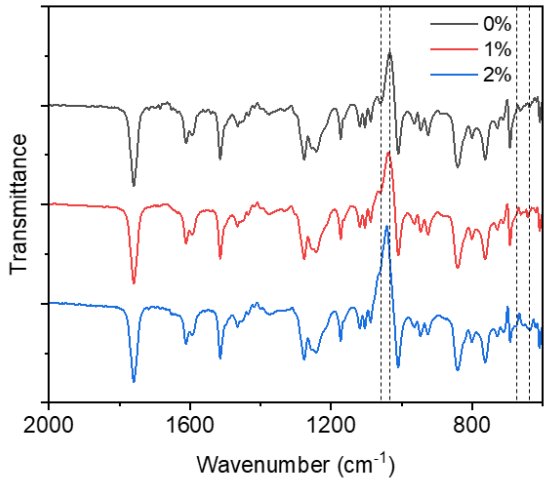

Figure S6. FTIR spectra with different water concentrations in DMSO/CDs.

References

(1) Qin, Y.; Bai, Y.; Huang, P.; Wu, F.-Y. Dual-Emission Carbon Dots for Ratiometric Fluorescent Water Sensing, Relative Humidity Sensing, and Anticounterfeiting Applications. *ACS Appl. Nano Mater.* **2021**, *4* (10), 10674–10681. https://doi.org/10.1021/acsanm.1c02148.

(2) Zhang, K.; Chen, T.-T.; Shen, Y.-J.; Zhang, L.-F.; Ma, S.; Huang, Y. Luminescent Macrocyclic Sm(III) Complex Probe for Turn-off Fluorescent and Colorimetric Water Detection in Organic Solvents and Liquid Fuels. *Sens. Actuators B Chem.* **2020**, *311*, 127887. https://doi.org/10.1016/j.snb.2020.127887.

(3) Ye, C.; Qin, Y.; Huang, P.; Chen, A.; Wu, F.-Y. Facile Synthesis of Carbon Nanodots with Surface State-Modulated Fluorescence for Highly Sensitive and Real-Time Detection of Water in Organic Solvents. *Anal. Chim. Acta* **2018**, *1034*, 144–152. https://doi.org/10.1016/j.aca.2018.06.003.

(4) Hallaji, Z.; Bagheri, Z.; Ranjbar, B. One-Step Solvothermal Synthesis of Red Chiral Carbon Dots for Multioptical Detection of Water in Organic Solvents. *ACS Appl. Nano Mater.* **2023**, *6* (5), 3202–3210. https://doi.org/10.1021/acsanm.2c04466.

(5) Meng, Y.; Cui, S.; Lei, P.; Guo, J.; Wang, Q.; Shuang, S.; Dong, C. Design of Polarity-Dependence Orange Emission Multifunctional Carbon Dots for Water Detection and Anti-Counterfeiting. *Mater. Today Chem.* **2023**, *33*, 101669. https://doi.org/10.1016/j.mtchem.2023.101669.

(6) Wang, W.; Wu, J.; Xing, Y.; Wang, Z. Solvent-Dependent Red Emissive Carbon Dots and Their Applications in Sensing and Solid-State Luminescence. *Sens. Actuators B Chem.* **2022**, *360*, 131645. https://doi.org/10.1016/j.snb.2022.131645.

(7) Wei, J.; Li, H.; Yuan, Y.; Sun, C.; Hao, D.; Zheng, G.; Wang, R. A Sensitive Fluorescent Sensor for the Detection of Trace Water in Organic Solvents Based on Carbon Quantum Dots with Yellow Fluorescence. *RSC Adv.* **2018**, *8* (65), 37028–37034. https://doi.org/10.1039/C8RA06732E.

(8) Yang, M.; Liu, M.; Wu, Z.; He, Y.; Ge, Y.; Song, G.; Zhou, J. Fluorescence Enhanced Detection of Water in Organic Solvents by One-Pot Synthesis of Orange-Red Emissive Polymer Carbon Dots Based on 1,8-Naphthalenediol. *Micro Nano Lett.* **2020**, *15* (7), 469–473. https://doi.org/10.1049/mnl.2019.0170.

(9) Geng, B.; Wang, X.; Li, P.; Shen, W.; Qin, H.; Fang, F.; Yin, L.; Shen, L.; Pan, D. Multifunctional Carbon Dots for Trace Water Detection, White LEDs, and Bioimaging. *ChemistrySelect* **2019**, *4* (48), 14162–14168. https://doi.org/10.1002/slct.201904133.

(10) Ma, G.; Wang, R.; Zhang, M.; Dong, Z.; Zhang, A.; Qu, M.; Gao, L.; Wei, Y.; Wei, J. Solvothermal Preparation of Nitrogen-Doped Carbon Dots with PET Waste as Precursor and Their Application in LEDs and Water Detection. *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.* **2023**, *289*, 122178. https://doi.org/10.1016/j.saa.2022.122178.

(11) Senthamizhan, A.; Fragouli, D.; Balusamy, B.; Patil, B.; Palei, M.; Sabella, S.; Uyar, T.; Athanassiou, A. Hydrochromic Carbon Dots as Smart Sensors for Water Sensing in Organic Solvents. *Nanoscale Adv.* **2019**, *1* (11), 4258–4267. https://doi.org/10.1039/C9NA00493A.

(12) Lee, H. J.; Jana, J.; Thi Ngo, Y.-L.; Wang, L. L.; Chung, J. S.; Hur, S. H. The Effect of Solvent Polarity on Emission Properties of Carbon Dots and Their Uses in Colorimetric Sensors for Water and Humidity. *Mater. Res. Bull.* **2019**, *119*, 110564. https://doi.org/10.1016/j.materresbull.2019.110564.

(13) Kumari, R.; Sahu, S. K. Effect of Solvent-Derived Highly Luminescent Multicolor Carbon Dots for White-Light-Emitting Diodes and Water Detection. *Langmuir* **2020**, *36* (19), 5287–5295. https://doi.org/10.1021/acs.langmuir.0c00631.
(14) Huo, Z.; Xu, W.; Wang, Z.; Xu, S. A Carbonized Polymer Dot (CPD) Nanosensor for Trace Water Detection with a Wide Detection Range. *Dyes Pigments* **2021**, *196*, 109805. https://doi.org/10.1016/j.dyepig.2021.109805.
(15) Zou, H.; Liao, X.; Lu, X.; Hu, X.; Xiong, Y.; Cao, J.; Pan, J.; Li, C.; Zheng, Y. Fluorescence Studies of Double-Emitting Carbon Dots and Application in Detection of H2O in Ethanol and Differentiation of Cancer Cell and Normal Cell. *J. Photochem. Photobiol. Chem.* **2023**, *441*, 114746. https://doi.org/10.1016/j.jphotochem.2023.114746.
(16) Liu, X.; Zhou, Z.; Wang, T.; Deng, P.; Yan, Y. Visual Monitoring of Trace Water in Organic Solvents Based on Ecofriendly b/r-CDs Ratiometric Fluorescence Test Paper. *Talanta* **2020**, *216*, 120958. https://doi.org/10.1016/j.talanta.2020.120958.