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Supporting information

2 **Time-Dependent Phosphorescence Color of Carbon Dots in Boric**

3 **Acid Matrix for Dynamic Information Encryption**

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14 **Experiment section**

15 **Chemicals and reagents**

16 L-aspartic acid (AA) was purchased from Sinopharm Chemical Reagent Co., Ltd.

17 (Shanghai, China). Boric acid (BA) was purchased from HUSHI Reagent Co., Ltd.

18 (Shanghai, China). Potassium fluoride (KF), potassium chloride (KCl), potassium

19 bromide (KBr), and potassium iodide (KI) were purchased from Inno Chem Reagent

20 Co., Ltd. (Beijing, China) and Aladdin Reagent Co., Ltd. (Shanghai, China). All other

21 chemicals used were of analytical grade and used without further purification.

22 **Apparatus and characterization**

1 The synthesis of CDs and CDs-X (X = F, Cl, Br, I) was carried out using a
2 Yiheng DHG-9145A oven (Yiheng, China). Red-CDs and Blue-CDs were
3 synthesized using a Midea PC2321W microwave oven (Midea, China). Absorption
4 spectra in solution were obtained using a UV-2600 UV-visible spectrophotometer
5 (Shimadzu, Japan), while absorption spectra in solid were obtained using a Carry
6 5000 UV-Vis-NIR spectrophotometer (Agilent, USA). Fluorescence and
7 phosphorescence spectra were obtained using a HITACHI F-7000 fluorescence
8 spectrophotometer (Hitachi, Japan). Phosphorescence lifetimes were measured using
9 an FS5 fluorescence spectrophotometer (Edinburgh Instruments, UK). Quantum yield
10 and phosphorescence quantum yield were measured using an FLS1000 fluorescence
11 spectrophotometer (Edinburgh Instruments, UK). Morphological and size analysis
12 was conducted using a transmission electron microscope (TEM, FEI/ Talos F200X G2,
13 USA). X-ray diffraction (XRD) analysis was performed using a Smart La X-ray
14 powder diffractometer (Japan). X-ray photoelectron spectra (XPS) were recorded
15 using a K-alpha+ spectrometer (Thermo Fisher Scientific, USA). Fourier transform
16 infrared spectroscopy (FT-IR) spectra were obtained using a Nicolet iS50 FT-IR
17 spectrometer (Thermo Fisher, USA). Ultrapure water was prepared using a Milli-Q
18 water purification system (USA). Video and digital photos were obtained using a
19 smart phone Find X6 (OPPO, China).

20 **Synthesis of CDs**

21 A mixture of 50 mg AA and 3 g BA was dissolved in 40 mL of deionized water.
22 The solution was then heated to 240 °C for 5 hours in a covered beaker. After

1 naturally cooling to room temperature, CDs were obtained and ground into powder.

2 **Synthesis of CDs-X**

3 CDs-X (X = F, Cl, Br, I) was synthesized using a similar method as CDs. In
4 addition to 50 mg AA and 3 g BA, 50 mg KX (X = F, Cl, Br, I) was used as a
5 precursor.

6 **Synthesis of Red-CDs**

7 Red-carbon dots were synthesized referring to the literature [1].

8 **Synthesis of Blue-CDs**

9 To synthesize Blue-CDs, a mixture of citric acid (200 mg) and BA (1.2 g) was
10 dissolved in 20 mL of deionized water. The solution was then reacted for 180 seconds
11 using a microwave oven on high heat. After the reaction, Blue-CDs were obtained.

12 **Measurement of the phosphorescence lifetime of CDs**

13 The phosphorescent lifetime of powdered CDs was measured using an
14 Edinburgh FS5 fluorescence lifetime meter. The calculation formula for CDs
15 phosphorescence life is given by:

$$16 \quad (1) \tau = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i}$$

17 **Application of CDs in anti-counterfeiting and information encryption**

18 (1) QR code encryption application. The powder of CDs was evenly filled in the
19 mold of a QR code, and images were captured using a digital camera under visible
20 light, 365 nm UV light excitation, and visible light with 365 nm UV light off.

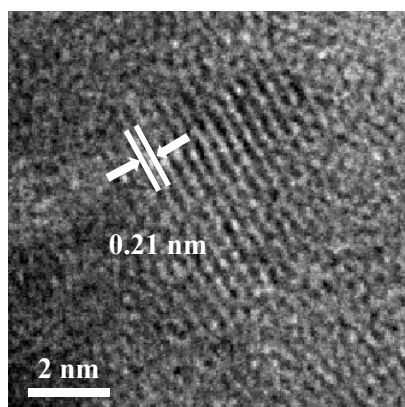
21 (2) Digital information encryption application. The powders of CDs, Blue-CDs,
22 and Red-CDs were filled into a template with the number 8888. Images were captured

1 using a digital camera under visible light, 365 nm UV light excitation, and visible
2 light with 365 nm UV light off.

3 (3) Time-dependent afterglow information encryption application. Different CDs
4 and CDs-I were filled into the cap template. Images were captured using a digital
5 camera after visible light, 365 nm UV light excitation, and visible light with 365 nm
6 UV light off.

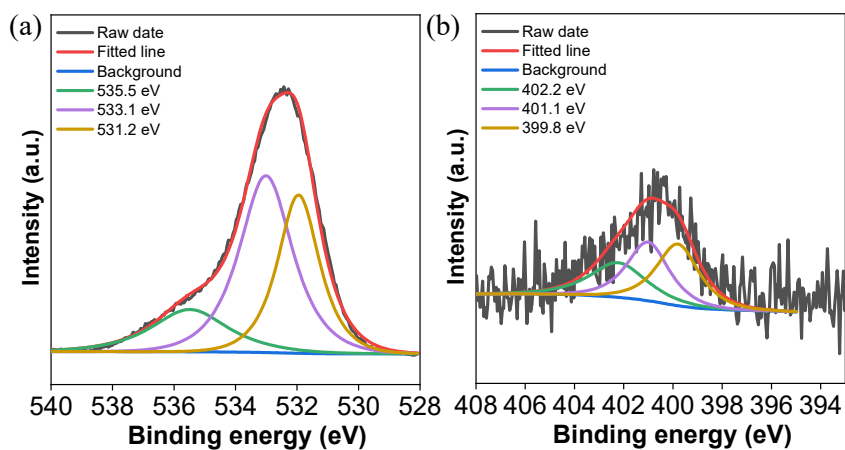
7 (4) Multiple information encryption application. Different CDs, CDs-F, CDs-Cl,
8 CDs-Br, and CDs-I were filled into the template of HQU. Images were captured using
9 a digital camera after 365 nm UV light excitation and 365 nm UV light off.

10 Result



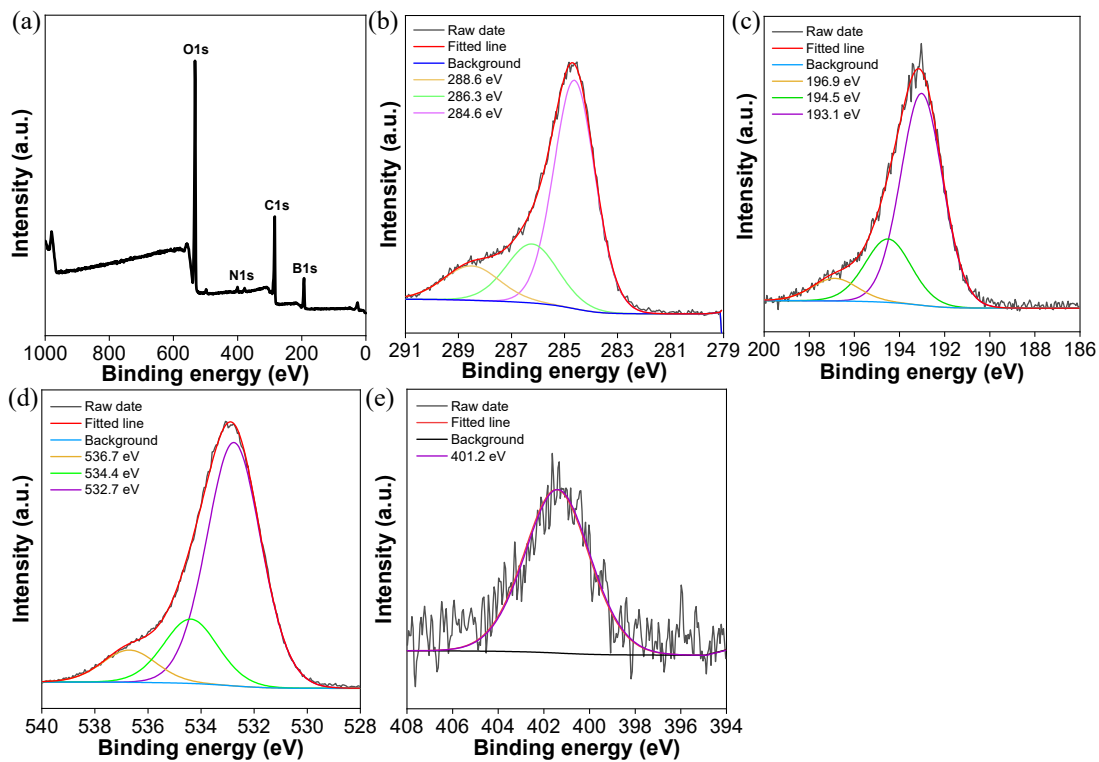
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12 Figure S1 The corresponding HRTEM images of CDs.



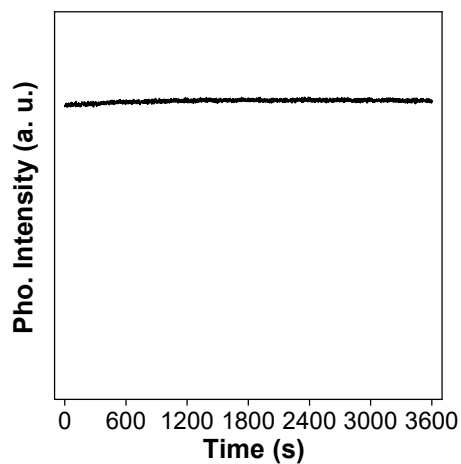
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14 Figure S2 HR XPS O 1s (a) and N 1s (b) spectra of CDs.



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2 Figure S3 Full scan XPS spectrum of CDs. HR XPS C 1 s (b), B 1 s (c) O 1s (d) and
3 N 1s (e) spectra of CDs-I.

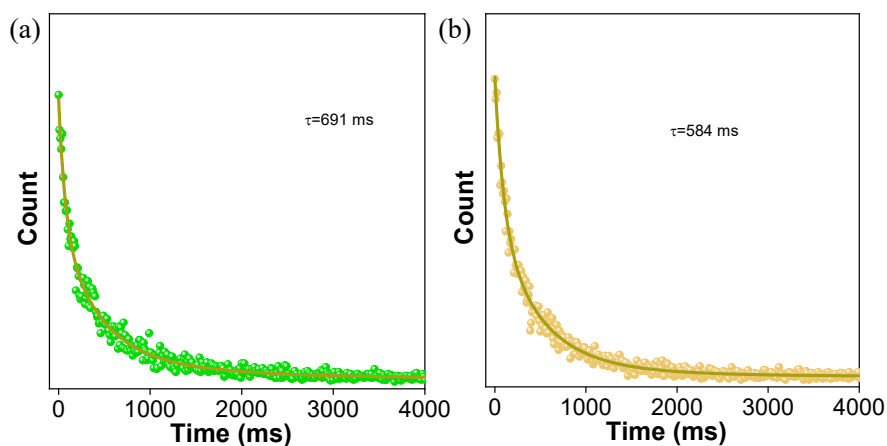
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6 Figure S4 Photobleaching spectrum of CDs.

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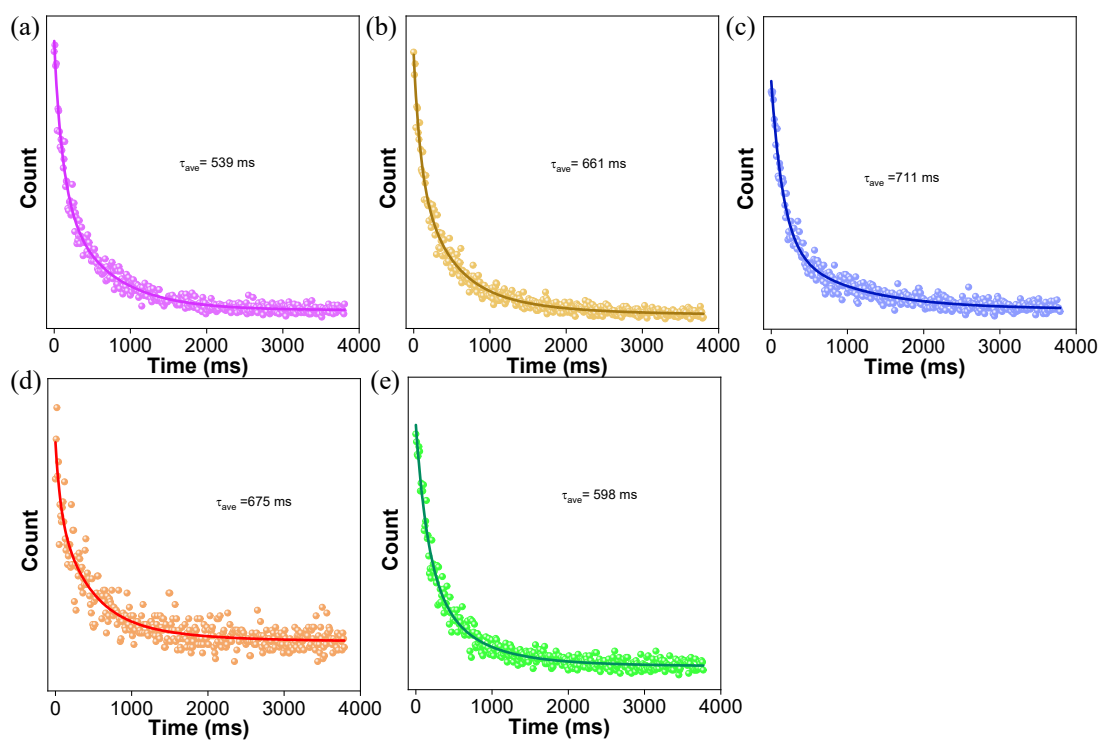


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2 Figure S5 (a) 500 nm and (b) 580 nm wavelength time-resolved afterglow decay

3 curve of CDs.

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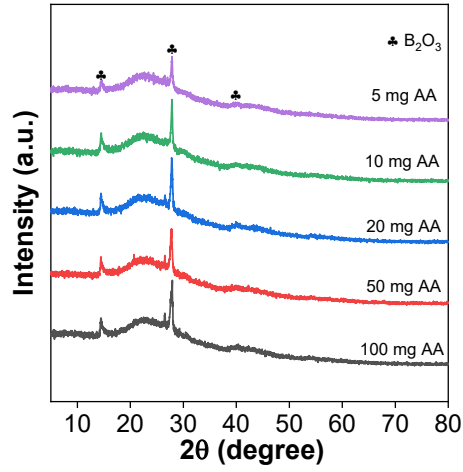


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6 Figure S6 Time-resolved afterglow decay curve of CDs synthesized with different

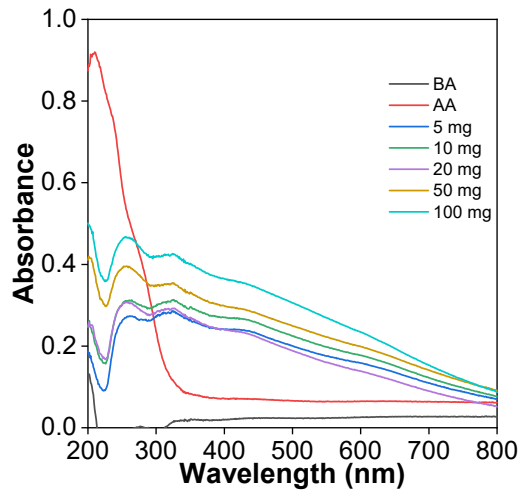
7 quality AA (a) 5 mg, (b) 10 mg (c) 20 mg (d) 50 mg (e) 100 mg.

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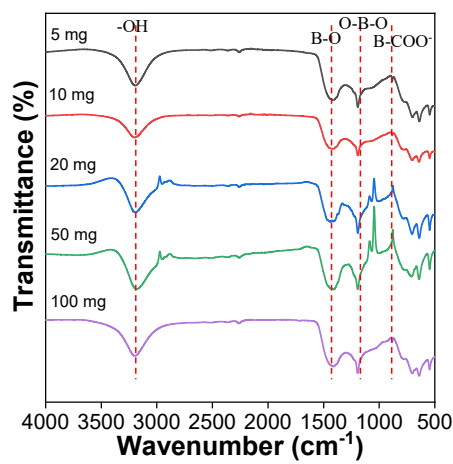
2 Figure S7 XRD spectra of CDs synthesized with different quality AA.



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4 Fig S8 UV-vis absorption spectra of CDs synthesized with different quality AA.

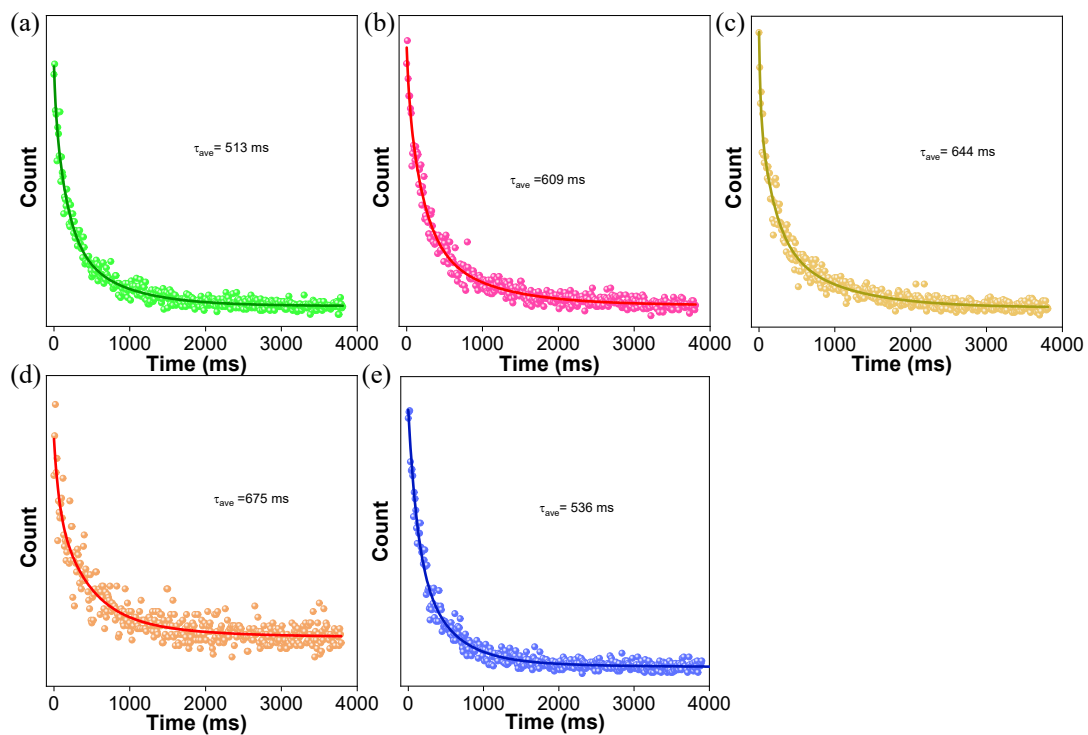
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7 Figure S9 FT-IR spectra of CDs synthesized with different quality AA.

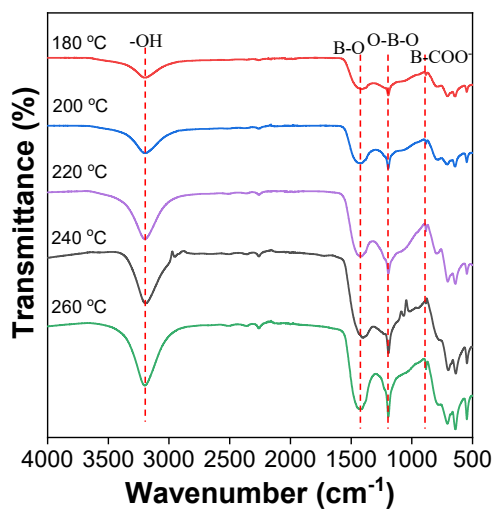
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3 Figure S10 Time-resolved afterglow decay curve of CDs synthesized with different
4 temperature (a) 180 °C, (b) 200 °C, (c) 220 °C, (d) 240 °C, (e) 260 °C.

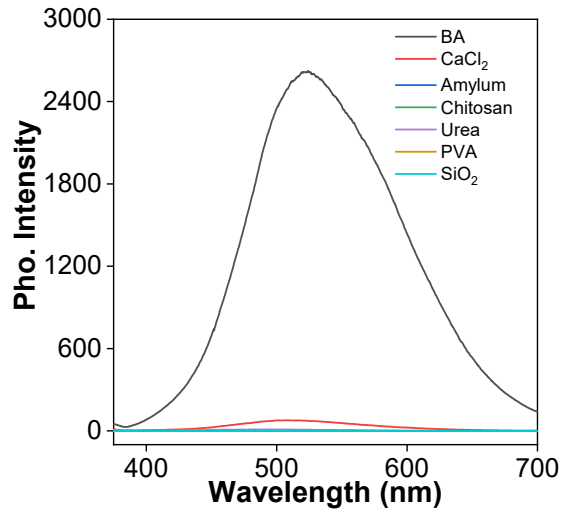
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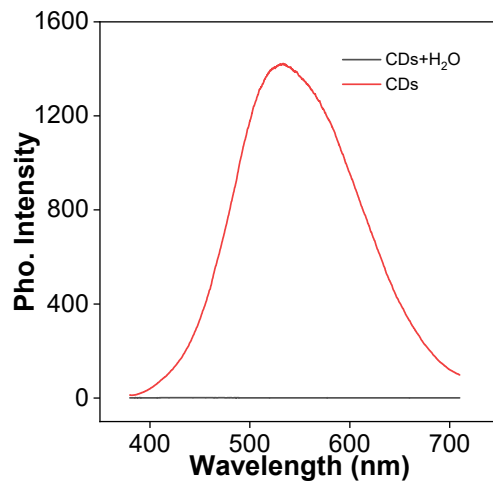
7 Figure S11 FT-IR spectra of CDs synthesized with different temperature.

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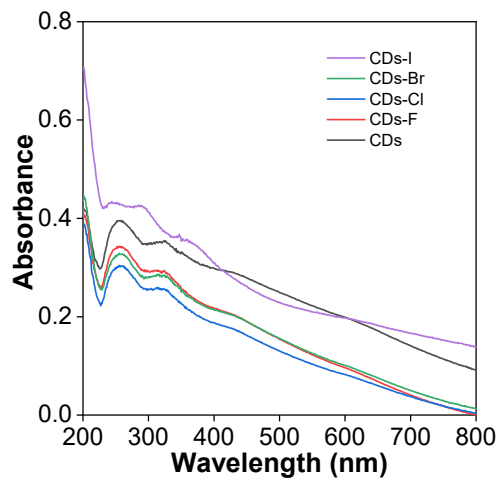
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2 Figure S12 Phosphorescent spectra of another matrix.



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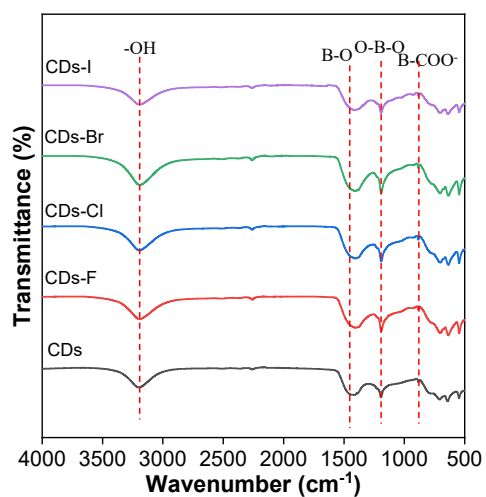
4 Figure S13 Phosphorescent spectra of CDs and CDs with H₂O.



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6 Figure S14 UV-vis absorbance spectra of CDs and CDs-X (X=F, Cl, Br, I).

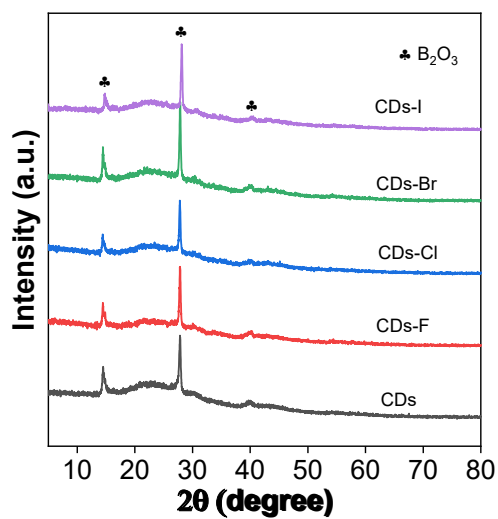
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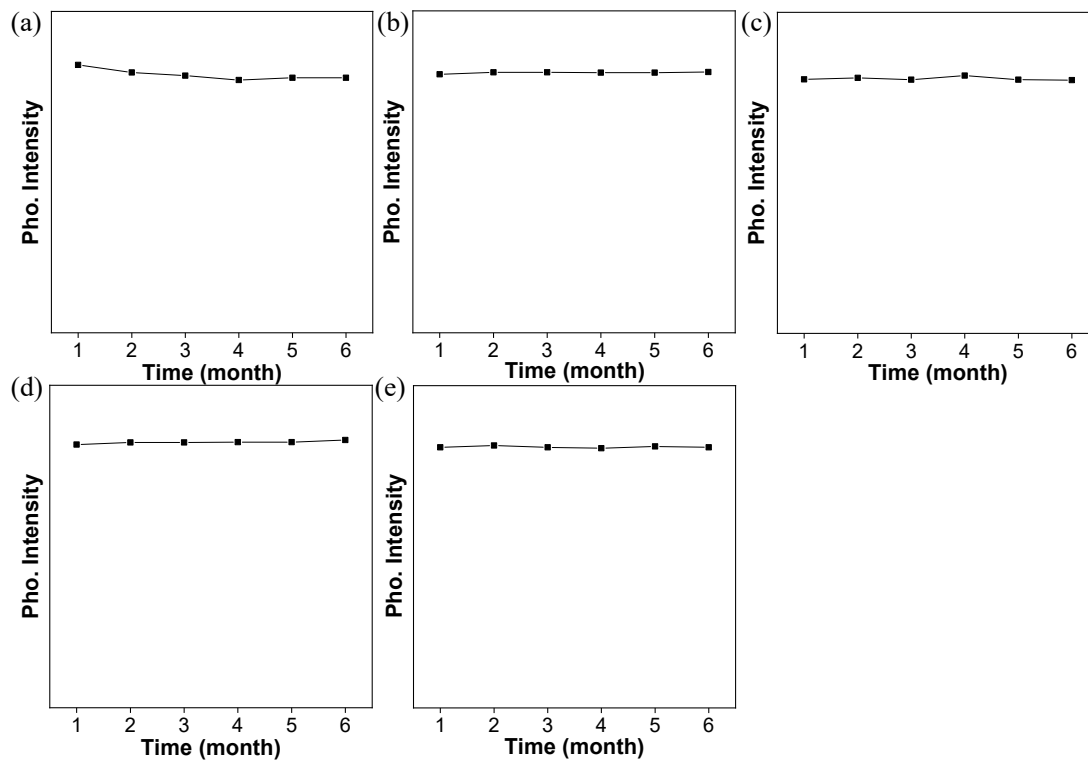
2 Figure S15 FT-IR spectra of CDs and CDs-X (X=F, Cl, Br, I).

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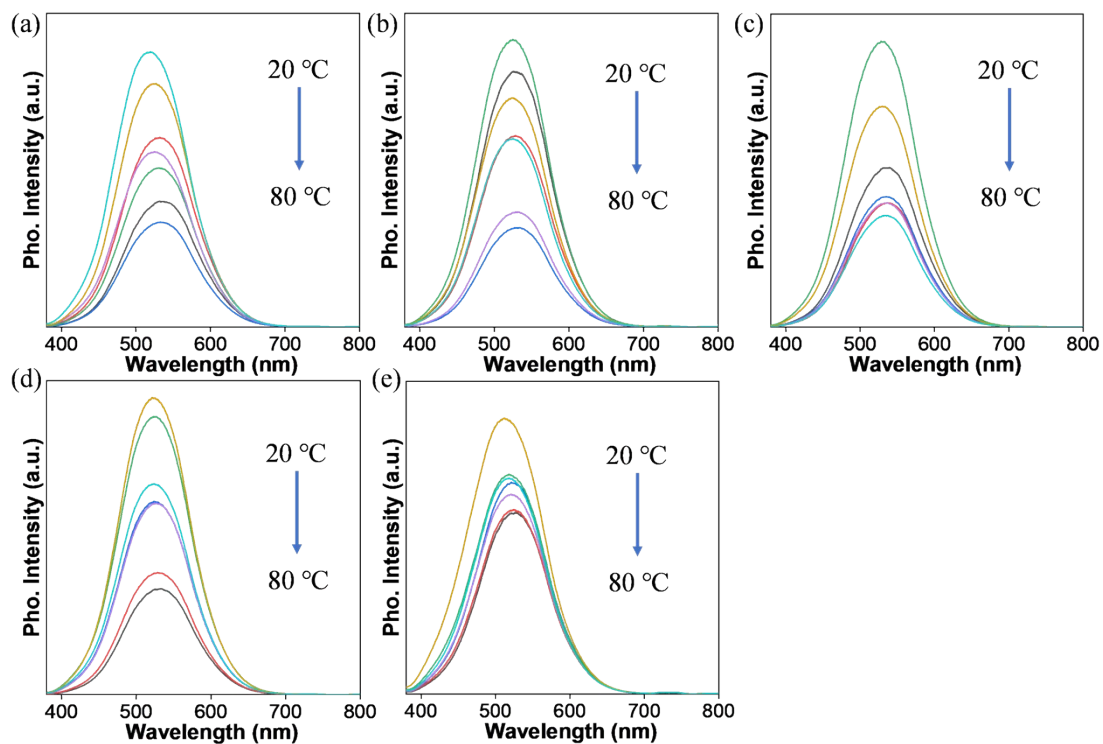
5 Figure S16 XRD spectra of CDs and CDs-X (X=F, Cl, Br, I).



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2 Figure S17 Phosphorescence intensity stability spectra of (a) CDs, (b) CDs-F, (c)

3 CDs-Cl, (d) CDs-Br, and (e) CDs-I.



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5 Figure S18 Phosphorescence intensity stability spectra of (a) CDs, (b) CDs-F, (c)

6 CDs-Cl, (d) CDs-Br, and (e) CDs-I at different temperatures.

1 Table S1. Photophysical characteristics of carbon dots under 365 nm UV light.

Quality (mg)	λ_{em} (nm)	A_1 (%)	τ_1 (s)	A_2 (%)	τ_2 (s)	A_3 (%)	τ_3 (s)	τ_{ave} (s)
5	525	6.551	0.037	51.19	0.127	42.26	0.642	0.54
10	525	41.98	0.087	43.40	0.389	14.62	1.083	0.66
20	525	48.15	0.157	22.96	0.156	28.89	0.938	0.71
50	525	6.551	0.106	51.19	0.405	42.26	1.322	0.68
100	530	54.81	0.152	37.50	0.475	7.690	1.225	0.60

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3 Table S2. Photophysical characteristics of carbon dots under 365 nm UV light.

Temperatur e (°C)	λ_{em} (nm)	A_1 (%)	τ_1 (s)	A_2 (%)	τ_2 (s)	A_3 (%)	τ_3 (s)	τ_{ave} (s)
180	510	31.25	0.065	54.17	0.397	14.58	1.118	0.67
200	510	35.44	0.229	24.05	0.229	40.50	0.957	0.77
220	525	14.93	0.033	57.14	0.209	27.92	0.828	0.61
240	525	6.551	0.106	51.19	0.405	42.26	1.322	0.68
260	525	37.16	0.093	46.62	0.409	16.22	1.151	0.72

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1 Table S3. Photophysical characteristics of CDs and CDs-X (X=F, Cl, Br, I) under 365

2 nm UV light.

Sample	λ_{em} (nm)	A_1 (%)	τ_1 (s)	A_2 (%)	τ_2 (s)	A_3 (%)	τ_3 (s)	τ_{ave} (s)
CDs	525	6.551	0.106	51.19	0.405	42.26	1.322	0.68
CDs-F	521	41.98	0.038	43.40	0.306	14.62	1.511	0.83
CDs-Cl	525	54.81	0.119	37.50	0.520	7.690	1.809	0.82
CDs-Br	520	34.02	0.131	56.70	0.510	9.280	1.540	0.81
CDs-I	520	48.51	0.136	22.96	0.601	28.89	1.640	0.71

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5 Table S4. Photophysical characteristics of CDs and CDs-X (X=F, Cl, Br, I) under 254

6 nm UV light.

Sample	λ_{em} (nm)	A_1 (%)	τ_1 (s)	A_2 (%)	τ_2 (s)	A_3 (%)	τ_3 (s)	τ_{ave} (s)
CDs	486	6.551	0.012	51.19	0.262	42.26	1.118	0.85
CDs-F	480	41.98	0.104	43.40	0.484	14.62	1.972	1.22
CDs-Cl	470	48.15	0.074	22.96	0.390	28.89	1.723	1.13
CDs-Br	470	34.02	0.082	56.70	0.366	9.280	1.620	1.11
CDs-I	460	54.81	0.175	37.50	0.473	7.690	1.503	0.93

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1 Table S5. The FL emission peaks, phosphorescent emission peaks, and calculated

2 ΔE_{ST} QY and PQY of CDs and CDs-X (X=F, Cl, Br, I) excited at 365 nm UV light.

Sample	FL (nm)	RTP (nm)	ΔE_{ST} (eV)	QY (%)	PQY (%)
CDs	450	525	0.39	7.43	2.91
CDs-F	454	521	0.35	8.95	3.64
CDs-Cl	453	525	0.38	9.49	6.30
CDs-Br	438	520	0.45	8.00	7.31
CDs-I	438	520	0.45	2.77	1.00

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5 Table S6. Relative contents of B, C, N, O and C/O in CDs and CDs-I.

sample	B (%)	C (%)	N (%)	O (%)	C/O
CDs	27.78	33.44	1.36	37.42	0.89
CDs-I	28.49	32.26	1.54	37.72	0.85

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1 Table S7. Relative contents of B, C, N and O related functional groups in CDs and
 2 CDs-I.

sample	B			O	
	B-CO ₂	B ₂ O ₃	B-O	C=O	O-B
CDs	59.07	20.09	20.84	77.47	22.53
CDs-I	69.21	22.68	8.108	65.93	34.07
	C			N	
	C-C	C-O	C=O	N-H	Graphite N
CDs	65.52	19.53	14.95	35.16	28.68
CDs-I	65.31	21.17	13.42	0	100

3

4

5 Reference

- 6 [1] Y.-C. Liang, Q. Cao, K.-K. Liu, X.-Y. Peng, L.-Z. Sui, S.-P. Wang, S.-Y. Song,
 7 X.-Y. Wu, W.-B. Zhao, Y. Deng, Q. Lou, L. Dong, C.-X. Shan, *ACS Nano*, 2021,
 8 **15**(10), 16242-16254.