



HAL
open science

Modulating carbon dots from aggregation-caused quenching to aggregation-induced emission and applying them in sensing, imaging and anti-counterfeiting

Shengtao Zhang, Jinhong Li, Pengyue Xu, Jieyu Zhou, Yan Li, Yongmin Zhang, Shaoping Wu

► To cite this version:

Shengtao Zhang, Jinhong Li, Pengyue Xu, Jieyu Zhou, Yan Li, et al.. Modulating carbon dots from aggregation-caused quenching to aggregation-induced emission and applying them in sensing, imaging and anti-counterfeiting. *Talanta*, 2025, 282, pp.126983. 10.1016/j.talanta.2024.126983. hal-04738631

HAL Id: hal-04738631

<https://hal.sorbonne-universite.fr/hal-04738631v1>

Submitted on 15 Oct 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **Modulating carbon dots from aggregation-caused quenching**
2 **to aggregation-induced emission and applying them in**
3 **sensing, imaging and anti-counterfeiting**

4 Shengtao Zhang^{a,b,§}, Jinhong Li^{c,§}, Pengyue Xu^a, Jieyu Zhou^a, Yan Li^{b,*}, Yongmin
5 Zhang^{a,d}, Shaoping Wu^{a,*}

6 ^a Key Laboratory of Resource Biology and Biotechnology in Western China, Ministry
7 of Education, Biomedicine Key Laboratory of Shaanxi Province, Northwest
8 University, 229 Taibai Road, Xi'an, Shaanxi, 710069, P. R. China.

9 ^b Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of the
10 Ministry of Education, College of Chemistry and Materials Science, Northwest
11 University, Xi'an, 710069, P. R. China.

12 ^c Shaanxi Hantang Pharmaceutical Co., Ltd. Xi'an, 710021, P. R. China.

13 ^d Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, UMR 8232, 4
14 place Jussieu, 75005, Paris, France.

15 [§] These authors contributed equally to this work.

16 ^{*}Corresponding author: wushaoping@nwu.edu.cn

17 **ABSTRACT**

18 Aggregation Induced Emission Carbon Dots (AIE-CDs) address the problem of
19 conventional CDs being quenched in the solid-state. However, there are still
20 challenges in comprehending the luminescence mechanism. This work proposed a
21 strategy for preparing green, yellow, and near-infrared CDs by modifying the
22 functional groups on the precursor from hydroxyl and amino to *p*-methylenediamine,
23 in which electronic supply capacity determined the redshift. Additionally, The CDs'
24 properties transformed from Aggregation-Caused Quenching (ACQ) to AIE was
25 realized by substituting non-rotatable hydroxyl or amino groups with the rotatable *p*-

26 methylenediamine on the precursor. The resulting CDs were then applied in multifield.
27 C-CDs was used for ratiometric detection of Al^{3+} and F^- in pure water through three
28 methods including fluorometer, test strip and smartphone. R-CDs was used for
29 imaging cell nucleus and zebrafish. NIR-CDs ($\lambda_{\text{em}}= 676 \text{ nm}$) exhibits dual emission,
30 AIE and phosphorescent characteristics was used for triple anti-counterfeiting and
31 binary information encryption. In summary, our finding presented a strategy for
32 preparing multicolor CDs, proposed a mechanism for the transition of CDs from ACQ
33 to AIE, and explore their multiple applications in anti-counterfeiting, information
34 encapsulation, sensing and imaging.

35 **Keywords:** carbon dots, aggregation-induced emission (AIE), aluminum, fluoride;
36 phosphorescence, anti-counterfeiting

37 **1. Introduction**

38 The Nobel prize in chemistry 2023 was awarded to three scientists cultured in
39 quantum dots (QDs), the appearance of QDs adds color to nanotechnology, and
40 quantum effect gives it novel optical and electronic properties different from organic
41 dyes that can be applied in many important fields [1-4]. Carbon dots (CDs) not only
42 inherits the excellent properties of QDs, including emission-dependent excitation, up-
43 conversion photoluminescence, photobleaching and blinking [5, 6], but also solved
44 the disadvantage of greater toxicity of transition metal QDs, and had been widely used
45 in anti-counterfeiting [7, 8], bioimaging [9, 10], drug delivery [11], nanozyme [12-14],
46 catalysis [15, 16] and optical devices [17]. Traditional fluorescent CDs exhibit bright

47 fluorescence in dispersed state but undergo excessive energy transfer and π - π stacking
48 effects in aggregated state, causing to fluorescence quenching and limiting their
49 practical application [17, 18]. Based on this, researchers prepared aggregation induced
50 emission CDs (AIE CDs) to overcome this limitation [19]. AIE CDs was firstly
51 realized in 2013 by incorporating CDs into a matrix of cetyltrimethylammonium
52 bromide to inhibit the aggregation of CDs [20]. However, AIE CDs obtained by this
53 method still experience quenching at higher concentrations, which still limits its
54 practical applications. In 2019, a solid-state AIE CDs without matrix was obtained by
55 utilizing dithio-2-phenylacetate with rotatable units of disulfide bond as a precursor
56 and this development holds distinct advantages for anti-counterfeiting and bioimaging
57 [21]. Subsequently, many researchers regulated the structure of raw materials to
58 obtain AIE CDs [22], which triggered a wave of research [23-25]. Very recently,
59 yellow solid-state CDs by vibration suppression was prepared from trimellitic acid
60 and piperazine [26]. However, despite some success in the synthesis of AIE CDs,
61 there is still a large gap in insights into their luminescence mechanisms.

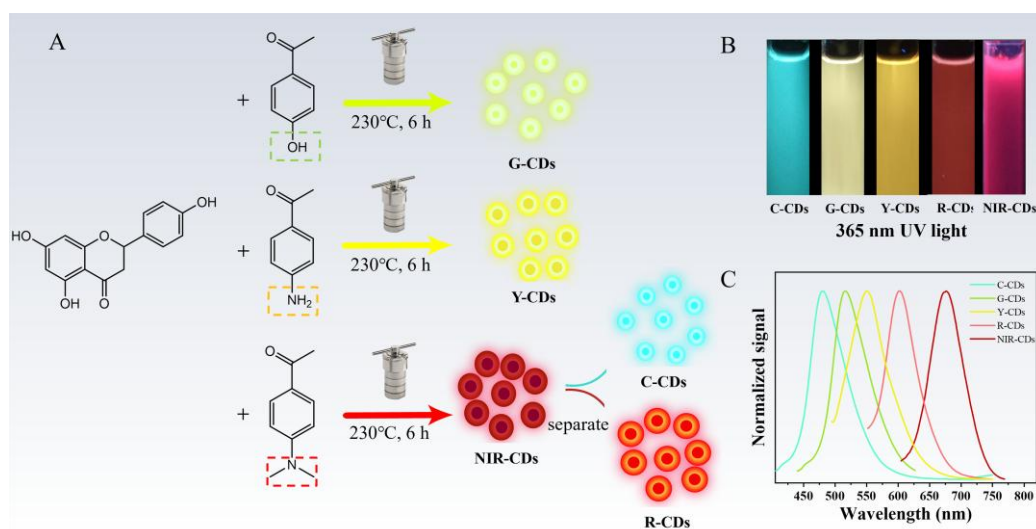
62 Additionally, the luminescence modes of CDs were still single and the
63 wavelength was short, which needs a breakthrough to meet the higher demands in
64 complex application scenarios. Such as anti-counterfeiting and information
65 encapsulation materials need to be easily synthesized, have high production yields,
66 possess a long lifetime, be environmentally friendly and resistant to replication [23,
67 27-29]. To cater diverse application scenarios, various approaches had been employed

68 for the synthesis of multicolor CDs encompassing adjustments of the quantity or type
69 of acids, reaction solvents, and proportions of reactants [30-35]. However, there were
70 limited reports on the modulation of fluorescence through subtle changes of
71 functional groups, which is pivotal to explore the luminescence mechanism of CDs.

72 Aluminum ions (Al^{3+}) and fluoride ions (F^-) play pivotal roles in various fields,
73 while excessive exposure to Al^{3+} can cause damage to the nervous system, and the
74 overuse of F^- can result in fluorosis and dental fluorosis. Literature reported the
75 detection of Al^{3+} using CDs with either AIE enhancement (AIEE) or Aggregation-
76 Caused Quenching (ACQ) characteristics, which suffered from high background
77 interference or pose toxicity concerns due to the use of organic solvents, respectively
78 [36-40], and even CDs with turn on detection face the problem of low yield [41].
79 Therefore, high yields of CDs and low background detection are two key points to
80 improve the sensing performance and practical ability in the detection of Al^{3+} and F^- .
81 Testing real samples is more complex than laboratory testing and requires simpler
82 sample handling and faster testing. Recently, there has been a notable increase in
83 interest in smartphone-based detection, the portability of the device greatly reduces
84 the detection threshold. Therefore, the integration of the AIE CDs with smartphone to
85 detect Al^{3+} and F^- will further enhance the portability and be more suitable for a wider
86 range of applications.

87 Herein we present a strategy to obtain multicolor CDs including G-CDs ($\lambda_{\text{em}} =$
88 520 nm), Y-CDs ($\lambda_{\text{em}} = 553$ nm) and NIR-CDs ($\lambda_{\text{em}} = 676$ nm) by employing

89 naringenin and acetophenone derivatives as precursors, the acetophenone derivatives
90 differ in the electron-donating capacity of functional groups (-OH, -NH₂, -N(CH₃)₂),
91 which determined the fluorescent color of CDs (Fig. 1A). Upon separating NIR-CDs,
92 C-CDs (λ_{em} = 480 nm) and R-CDs (λ_{em} = 602 nm) were obtained. G-CDs and Y-CDs
93 exhibited ACQ properties, while NIR-CDs (λ_{em} = 676 nm) possessed AIE and
94 phosphorescence properties, which was caused by the rotational functional group.
95 These CDs were applied in multifield. Firstly, NIR-CDs was fabricated into
96 fluorescent ink to achieve triple anti-counterfeiting and binary information encryption.
97 Secondly, gram scale of C-CDs was used to detect Al³⁺ and F⁻ in pure water, which
98 was integrated with test paper and smartphone platform for field detection. Lastly, R-
99 CDs exhibits low cytotoxicity and was successfully used for cellular and zebrafish
100 imaging, thereby demonstrating its potential in bioimaging.



101

102 **Fig. 1.** (A) Synthetic routes of full color CDs; (B) Photographs of C-CDs, G-CDs, Y-CDs, R-CDs

103 and NIR-CDs; (C) Fluorescence emission spectra of C-CDs, G-CDs, Y-CDs, R-CDs and NIR-CDs.

104 **2. Experimental Section**

105 **2.1. Synthesis of CDs**

106 Accurately weighed 2.0 g (7.34 mM) of naringin and 1.0 g (7.34 mM) of *p*-
107 hydroxyacetophenone into a 50 mL beaker, completely dissolved with 20 mL of EtOH,
108 which was heated at 230°C for 6 h in a 50 mL Teflon reactor. A yellow clarified
109 solution was obtained and the unreacted small molecules were removed by dialysis
110 (3500 Da) for 48 h. The product G-CDs was obtained after drying at 50°C, and the
111 calculated yield was 10.8%. Y-CDs was synthesized in the same way as G-CDs,
112 except that *p*-hydroxyacetophenone was replaced by *p*-aminoacetophenone, and the
113 yield was 15.7%. NIR-CDs was obtained by the same way except dialysis, with a high
114 yield of 75.7%, after dialysis and column chromatography of NIR-CDs in order, C-
115 CDs and R-CDs were obtained (DCM: MeOH= 80:1, 20:1, 5:1 sequentially) with
116 yields of 47.0% and 5.3%, respectively.

117 **2.2. Calculation of fluorescence quantum yield and fluorescence lifetime**

118 The methods were referred to our previous work [42], the details can be found in
119 the Supporting Information.

120 **2.3. Spectroscopic determination**

121 Weighed 10.0 mg of CDs prepared above and dissolved in 5.0 mL of EtOH to
122 obtain a master batch (2.0 mg/mL), then 50 µL of the master batch was transferred to
123 a colorimetric tube and fixed with EtOH to 5.0 mL to determine the spectral
124 properties. Mixtures of water and EtOH were used to measure the AIE properties of

125 NIR-CDs and C-CDs. Fluorescence spectra were detected at 405 nm.

126 **2.4. Triple anti-counterfeiting and binary information encryption experiment**

127 To obtain the fluorescent ink (0.5 mg/mL), 5.0 mg of NIR-CDs was accurately
128 weighed and dissolved in 10.0 mL of EtOH. The home-made fluorescent ink was
129 absorbed with a fountain pen and then written on the filter paper. The fluorescent
130 color was observed under a 365 nm UV lamp.

131 **2.5. Al³⁺ and F⁻ concentration titration experiments**

132 For the titration experiments of Al³⁺, 50 μL of C-CDs (0.5 mg/mL) was
133 transferred into a 10 mL colorimetric tube, then different volumes of Al³⁺ (1.0 mM, 0,
134 10, 20, 30, 40, 50, 60, 70 μL) were added and fixed to 5 mL with double-distilled
135 water. For F⁻ titration experiments, 50 μL of C-CDs was transferred to a 10 mL
136 colorimetric tube, then 70 μL of Al³⁺ (1.0 mM) and various F⁻ (1.0 mM, 0, 20, 40, 60,
137 80, 100, 120, 140, 160, 180, 200, 220, 240, 260, 280 μL) were added sequentially and
138 fixed to 5 mL with double-distilled water. The slits were chosen as 5 nm and 10 nm,
139 the voltage was 700 V and the excitation wavelength was set as 375 nm, all
140 fluorescence spectra were measured after the samples were mixed for 5 min.

141 **2.6. Selectivity titration experiments**

142 In the selectivity experiment of C-CDs to Al³⁺, Al³⁺ was replaced by other
143 possible co-existing ions (1.0 mM, Na⁺, Zn²⁺, Mg²⁺, K⁺, Hg²⁺, Fe³⁺, Fe²⁺, Cu²⁺, Ca²⁺,
144 Cu⁺, Sn²⁺, CO₃²⁻, F⁻, S²⁻, SO₄²⁻, NO₂⁻, Cl⁻, Br⁻, I⁻, CN⁻). And in the selectivity
145 experiment of C-CDs-Al³⁺ to F⁻, F⁻ was replaced by above possible co-existing ions.

146 **2.7. Competitive titration experiments**

147 In the competitive experiment of C-CDs to Al^{3+} , 50 μL of C-CDs (5.0 mg/mL),
148 70 μL of Al^{3+} (1.0 mM) and 70 μL of the above ions were added in sequence to the
149 colorimetric tube and then fixed to 5 mL with double-distilled water to detect their
150 fluorescence spectra. And in the competitive experiment of C-CDs- Al^{3+} to F^- , 50 μL
151 of C-CDs (5.0 mg/mL), 70 μL of Al^{3+} (1.0 mM), 280 μL F^- and 280 μL of the above
152 other ions were added in sequence to the colorimetric tube and then fixed to 5 mL
153 with double-distilled water to detect their fluorescence spectra.

154 **2.8. Al^{3+} test paper**

155 The methods details can be found in the Supporting Information.

156 **2.9. Smartphone sensing platform for Al^{3+} detection**

157 Weighed 1.5 mg of $[\text{Ru}(\text{bpy})_3]^{2+}$ dissolved in 5.0 mL of water at a concentration
158 of 0.4 mM. 10 μL $[\text{Ru}(\text{bpy})_3]^{2+}$, 30 μL C-CDs, and different volumes of Al^{3+} (1.0 mM,
159 0, 10, 20, 30, 40, 50, 60, 70, 80 μL) were aspirated and fixed to 5 mL. Fluorescence
160 pictures were taken with a smartphone and the RGB values were detected using the
161 Colorcoll APP.

162 **2.10. Smartphone sensing platform for F^- detection**

163 Weighed 1.5 mg of $[\text{Ru}(\text{bpy})_3]^{2+}$ dissolved in 5.0 mL of water at a concentration
164 of 0.4 mM. 10 μL $[\text{Ru}(\text{bpy})_3]^{2+}$, 30 μL C-CDs, 80 μL Al^{3+} and different volumes of F^-
165 (1.0 mM, 0, 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220, 240, 260, 280, 300 μL)
166 were aspirated and fixed to 5 mL. Fluorescence pictures were taken with a

167 smartphone and the RGB values were detected using the Colorcoll APP.

168 **2.11. Bioimaging**

169 Bioimaging experiments were performed with reference to our previous
170 work[43], the details can be found in the Supporting Information.

171 **3. Results and Discussions**

172 **3.1. Modulating fluorescence of CDs**

173 Using naringenin as main material, G-CDs, Y-CDs and NIR-CDs were prepared
174 by changing the functional groups on acetophenone derivatives from hydroxyl, amino
175 to *p*-methylenediamine. We presume that the modulation of fluorescence is a result of
176 distinct synthetic processes. The inductive effect gradually intensifies with the
177 heightened electron-donating capacity of para-substituted groups. This facilitates the
178 condensation reactions between naringenin and acetophenone derivatives, ultimately
179 increases the degree of conjugation. To confirm the fluorescence modulation wasn't
180 induced by the acetophenone derivatives itself, CDs synthesized solely from the
181 acetophenone derivatives were conducted. These CDs exhibited blue fluorescence
182 with no redshift (Fig. S5A), which demonstrated the redshift came from the reaction
183 between naringenin and acetophenone derivatives. Furthermore, control experiments
184 demonstrated that the fluorescence of the CDs prepared blue-shifted when the
185 precursor's para-position was altered from formyl group to carboxyl group (Fig. S5B).

186 **3.2. Characterization of CDs**

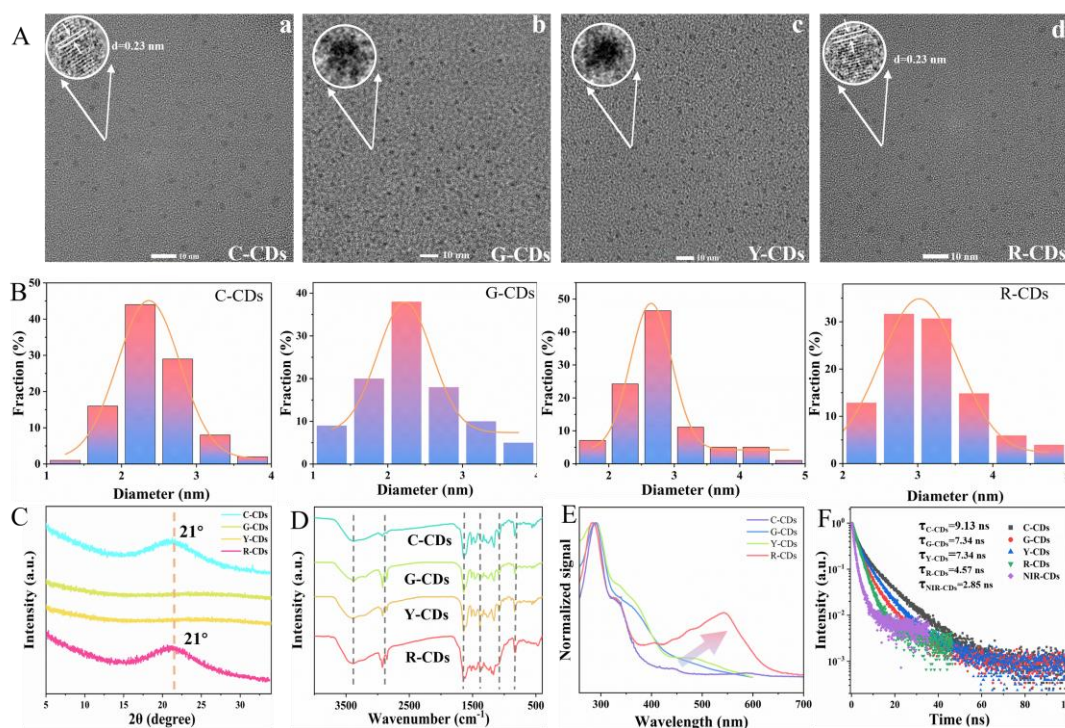
187 To explore the morphology and structure of CDs, Transmission electron

188 microscopy (TEM) and X-ray powder diffraction (XRD) were employed. As shown in
189 Fig. 2A-B, the average particle sizes of C-CDs, G-CDs, Y-CDs and R-CDs are 2.4 nm,
190 2.3 nm, 2.8 nm, 3.2 nm, respectively, which exhibit a distinct pattern and indicate that
191 the fluorescence modulation of these CDs is follows to Quantum Confinement Effect
192 (QCE). C-CDs and R-CDs show clear lattice structures with a lattice spacing of 0.23
193 nm corresponding to (100) planes of graphite C, while both G-CDs and Y-CDs lack
194 lattice structures that represent amorphous CDs indicate different degrees of reaction
195 compared with C-CDs and R-CDs [44, 45]. This observation was corroborated by the
196 X-ray diffraction (XRD) pattern (Fig. 2C), where C-CDs and R-CDs exhibited peaks
197 at 21° , whereas G-CDs and Y-CDs didn't display obvious peaks. It is hypothesized
198 that this phenomenon is associated with the extent of surface oxidation. The X-ray
199 photoelectron spectroscopy (XPS) indicate that G-CDs and Y-CDs exhibit a lower
200 oxygen content and a higher carbon content in comparison to C-CDs and R-CDs
201 (Table S1), which results in the formation of amorphous CDs.

202 Fourier transform infrared spectra (FT-IR) and XPS were then investigated to
203 affirm the character of these CDs (Fig. 2D). All CDs contained -OH/-NH₂ ($\sim 3379\text{ cm}^{-1}$)
204 ¹), -CH₃ ($\sim 2923\text{ cm}^{-1}$), C=C ($\sim 1640\text{ cm}^{-1}$), benzene ring ($1500\text{ cm}^{-1}\sim 1450\text{ cm}^{-1}$ except
205 G-CDs), C-OH ($1200\sim 1000\text{ cm}^{-1}$). It is noteworthy that C-CDs and R-CDs exhibit
206 stronger absorption peaks in the regions of C=C/C=N, C=O, C-N and benzene rings
207 between 1650 and 800 cm^{-1} compared to G-CDs and Y-CDs. Furthermore, there is an
208 overall enhancement in the FT-IR absorption peaks within this region from G-CDs to

209 Y-CDs and ultimately to R-CDs, which serves as additional evidence for the gradual
210 increase in the degree of conjugation within CDs. Subsequently, the investigation of
211 the elemental composition of G-CDs, Y-CDs, and R-CDs were carried out by XPS,
212 (Table S1). It was observed that the carbon content from G-CDs, Y-CDs to R-CDs
213 gradually decreased in parallel the oxygen content increased, correlating with the
214 redshift of UV absorption spectra (UV-vis) absorption (Fig. 2E).

215 To further investigate the properties of these CDs, the fluorescence decay curves
216 (Fig. 2F) and the average amplified fluorescence lifetimes (Table S2) of these CDs
217 were fitted. It can be seen that the fluorescence lifetimes and luminescence
218 efficiencies tend to decrease with the increasing wavelength [46]. And the radiative
219 decay efficiency of G-CDs, Y-CDs and R-CDs gradually increases, with less energy
220 absorbed by the electrons under the same conditions, corresponding to the redshift of
221 fluorescence.



222

223 **Fig. 2.** Characterization of C-CDs, G-CDs, Y-CDs and R-CDs. (A) TEM and HR-TEM (inset)

224 images of C-CDs, G-CDs, Y-CDs, R-CDs are presented from left to right; (B) Particle size

225 distribution plots for C-CDs, G-CDs, Y-CDs and R-CDs are displayed from left to right; (C) XRD

226 patterns of C-CDs, G-CDs, Y-CDs and R-CDs; (D) FT-IR spectra of C-CDs, G-CDs, Y-CDs and

227 R-CDs; (E) UV-vis spectra of C-CDs, G-CDs, Y-CDs and R-CDs; (F) Fluorescence decay curves

228 of C-CDs ($\lambda_{\text{em}}=480$ nm), G-CDs ($\lambda_{\text{em}}=520$ nm), Y-CDs ($\lambda_{\text{em}}=553$ nm), R-CDs ($\lambda_{\text{em}}=602$ nm) and

229 NIR-CDs ($\lambda_{\text{em}}=676$ nm), respectively.

230 3.3. Optical properties of synthesized CDs

231 Table S3 presents the spectral properties of these CDs, which exhibit cyan, green,

232 yellow, red and NIR fluorescence with QYs of 68.8%, 19.2%, 34.3%, 26.9% and

233 3.5%, respectively. Notably, G-CDs, Y-CDs and R-CDs exhibit ACQ properties, while

234 C-CDs and NIR-CDs with AIE properties. To explore the reason for this transition

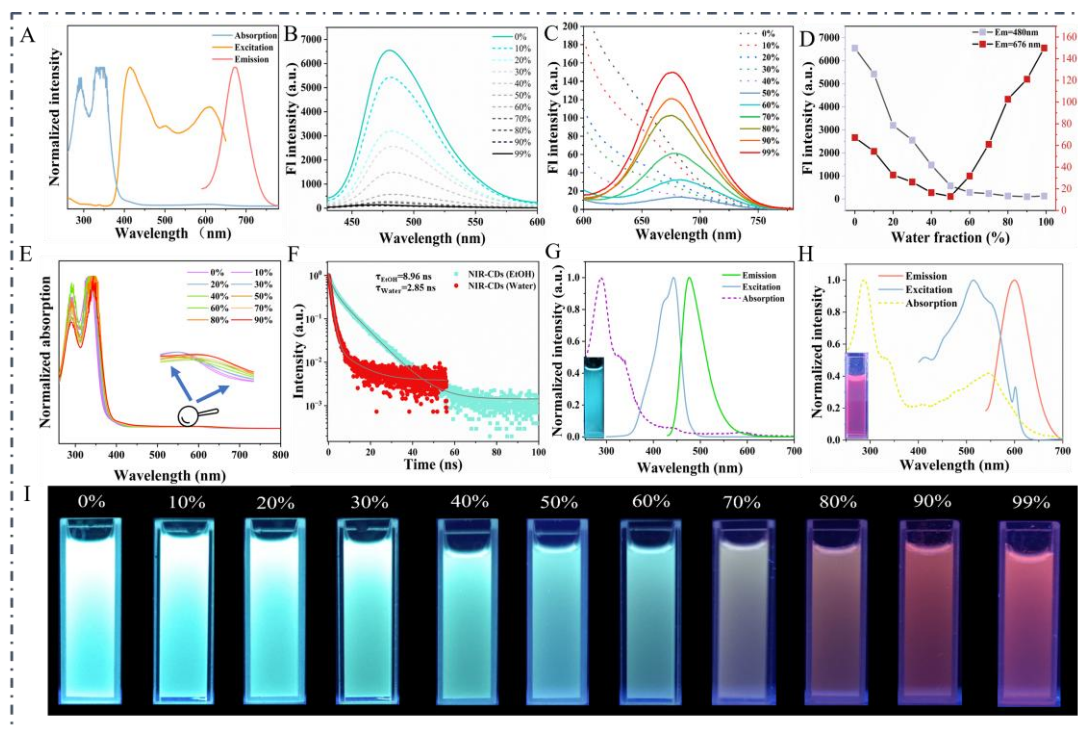
235 from ACQ to AIE, a series of experiments were performed next.

236 NIR-CDs display two emission centers at 480 nm and 676 nm (Fig. 3A), which
237 are both excitation-independent (Fig. S6). To investigate the origin of the dual
238 emission of NIR-CDs, thin-layer chromatography was performed. It was found that
239 NIR-CDs is a mixture of C-CDs ($\lambda_{em}= 480$ nm), R-CDs ($\lambda_{em}= 602$ nm) and unreacted
240 raw materials (Fig. S7). Fluorescence scans were performed at varying water fractions.
241 As shown in Fig. 3B, the fluorescence intensity of NIR-CDs at 480 nm experienced a
242 decrease as the water fraction increased from 0% to 99%, which was attributed to the
243 quenching of carbon-core caused by excessive resonance energy transfer in the
244 aggregated state. Meanwhile, the NIR fluorescence at 676 nm gradually increased,
245 which is achieved by inhibiting the rotation of *N,N*-dimethyl groups on the surface of
246 CDs (Fig. 3C). These findings are supported by the UV absorption spectra (Fig. 3E)
247 and fluorescence lifetime plots. Fig. 3F and Table S4 show a decrease in absorption at
248 290 nm and 340 nm with increasing water fraction, while absorption at 560 nm
249 gradually increased and red-shifted, confirming the presence of π - π stacking
250 interaction and the formation of *J*-aggregates [21]. The average amplified
251 fluorescence lifetimes of NIR-CDs in Ethanol (EtOH) and in water were 8.96 ns and
252 2.85 ns, respectively, suggesting that NIR-CDs has different emission centers in water
253 and EtOH [22]. The AIE phenomena was further confirmed by DLS (Table S5). The
254 size of NIR-CDs was 8.7 nm with a zeta potential of -1.7 mV in EtOH. However, in
255 water, the size increased to 31.0 nm and the zeta potential increased to 34.1 mV,
256 which is consistent with the TEM (Fig. S8) and Atomic Force Microscope (AFM)

257 images. To verify the AIE mechanism of NIR-CDs, control experiments using *p*-
258 aminoacetophenone and *p*-diethylaminobenzaldehyde as acetophenone derivatives
259 were conducted. As depicted in Fig. S9, *p*-aminoacetophenone did not exhibit any
260 AIE properties, whereas *p*-diethylaminobenzaldehyde demonstrated AIE properties. It
261 is suggested that the rotation of *N,N*-dimethyl was inhibited by the increasing content
262 of water, which in turn reduced the non-radiative transition and caused AIE.
263 Conversely, the non-rotating amino group could not induce AIE.

264 It is noteworthy that C-CDs also possesses AIE properties and emits cyan
265 fluorescence in dispersed state and red fluorescence in solid state (Fig. S10 and Fig.
266 S11). Fig. S12A shows that the fluorescence intensity of C-CDs at 480 nm gradually
267 decreased with the increasing of water fraction, while the fluorescence intensity at
268 600 nm started to increase when the water fraction reached 80%. The AIE properties
269 of C-CDs were verified by UV absorption, DLS, fluorescence lifetime. The UV
270 absorption (Fig. S12B) of C-CDs at 340 nm and 425 nm steadily increases and
271 undergoes a redshift with the increasing of water fraction, indicating the existence of
272 AIE and the formation of *J*-aggregates [21]. Furthermore, C-CDs exhibits size of 2.4
273 nm in EtOH and 65.2 nm in water, which is consistent with the TEM and AFM
274 images (Fig. S14). Accompanied by zeta potentials of 4.5 mV and -16.9 mV,
275 respectively, this indicates that C-CDs was well dispersed in EtOH but poorly
276 dispersed in water (Table S7). The fluorescence lifetimes of C-CDs in EtOH and
277 water were 9.13 ns and 1.85 ns, respectively (Table S8), demonstrating that C-CDs

278 has different emission centers in the dispersed and solid states. Furthermore, the
 279 maximum emission peak shifts from 480 nm at pH 7.0 to 550 nm at pH 0.2,
 280 accompanied by a 595 nm shoulder peak (Fig. S15). The size of C-CDs increased
 281 from 2.4 nm to 1258 nm as the pH decreased (Table S7), indicating its aggregation in
 282 an acidic environment and the fluorescence color is relative with its degree of
 283 aggregation. R-CDs, which use the same raw materials as C-CDs, did not exhibit AIE
 284 properties. HR-XPS analysis (Table S6) shows the decrease of N-H and the increase
 285 of C-N=C of R-CDs compared to C-CDs, indicating an increasing conjugate structure
 286 and degree of reaction from C-CDs to R-CDs. This means that C-CDs has more
 287 starting functional groups (-N(CH₃)₂) on its surface, while R-CDs is more reactive
 288 and carry less -N(CH₃)₂, leading to ACQ properties.



289
 290 **Fig. 3.** Optical properties of NIR-CDs. (A) Absorption (blue), excitation (orange) and emission
 291 (red) curves of NIR-CDs; (B) Fluorescence emission curves of NIR-CDs at 480 nm in different

292 water contents ($\lambda_{\text{ex}}= 405$ nm); (C) Fluorescence emission curves of NIR-CDs at 676 nm in
293 different water contents ($\lambda_{\text{ex}}= 405$ nm); (D) Fluorescence intensity of NIR-CDs at 480 nm (purple
294 line) and 676 nm (red line) at different water contents; (E) Absorption spectra of NIR-CDs with
295 different water contents; (F) Fluorescence decay curves of NIR-CDs in EtOH ($\lambda_{\text{em}}=480$ nm) and
296 water ($\lambda_{\text{em}}= 676$ nm), respectively; (G) Absorption (purple), excitation (blue) and emission (green)
297 curves of C-CDs; (H) Absorption (yellow), excitation (blue) and emission (red) curves of C-CDs;
298 (I) Fluorescence photos of NIR-CDs at different water contents (0%-99%) under 365 nm UV lamp.

299 **3.4. Swiss knife applications of CDs**

300 *3.4.1. Feasibility study of Al^{3+} and F^- sensing*

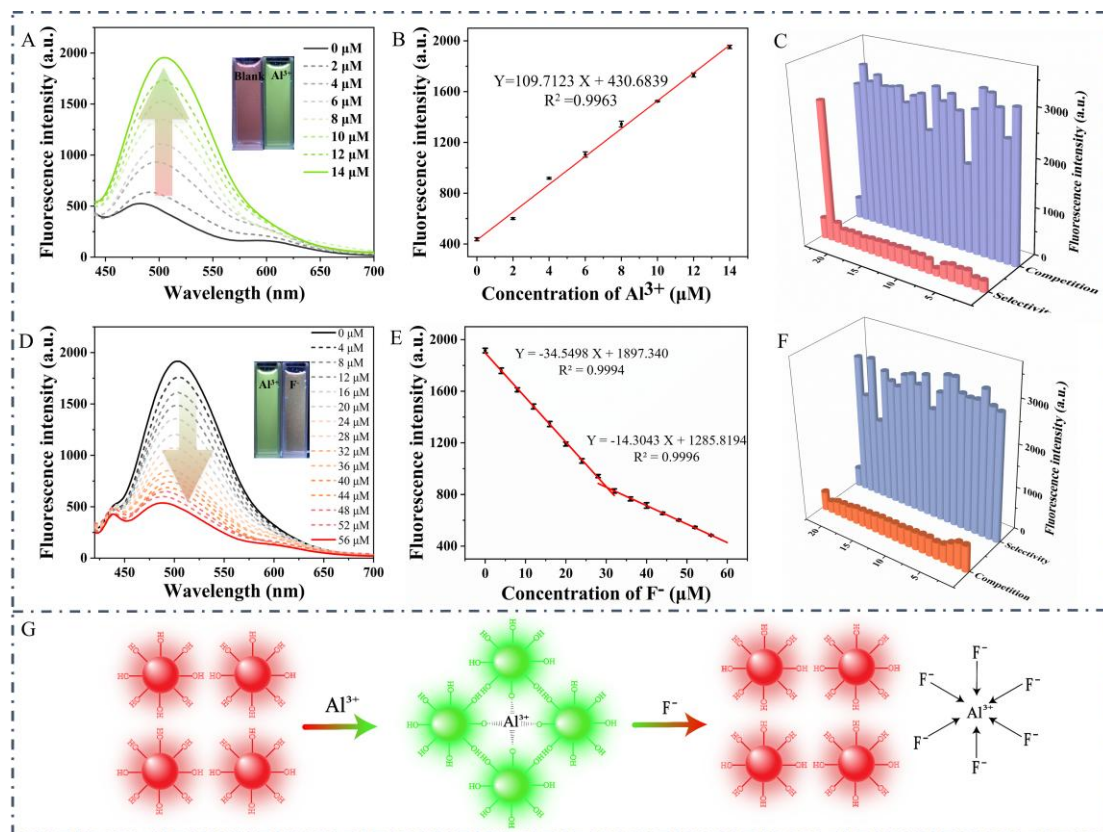
301 Based on the AIE properties, high yield and Al^{3+} -triggered aggregation of C-CDs, a
302 strong practically probe to detect Al^{3+} and F^- was developed. Table S9 and Table S10
303 demonstrate the comparative performance of Al^{3+} and F^- among C-CDs and reported
304 probes, the working detection process exhibited low toxicity and higher sensitivity.
305 Fig. 4A shows the fluorescence intensity of C-CDs at 480 nm gradually increased
306 after the addition of Al^{3+} , accompanied by a redshift to 505 nm. C-CDs exhibits red
307 fluorescence in pure water, while Al^{3+} enhanced the green fluorescence, showing good
308 linearity between 0-14 μM ($R^2= 0.9963$), and the limit of detection (LOD) was 0.081
309 μM . Some potential coexisting ions were used to detect the selectivity and
310 competitiveness of C-CDs. As shown in Fig. 4C, these ions didn't cause a significant
311 increase in fluorescence. In competitive experiments, almost no interference was
312 observed from substances other than Fe^{3+} , which caused a 37.3% reduction in the

313 fluorescence of C-CDs- Al^{3+} . To solve this problem, the masking agent ascorbic acid
314 was introduced into the system, which can reduce Fe^{3+} to Fe^{2+} (Fig. S19). Accuracy
315 assessment experiments exhibited a high degree of overlap with reference method
316 (Table S11).

317 The stability and kinetics of C-CDs in response to Al^{3+} were next investigated,
318 C-CDs responds well to Al^{3+} at high ionic strength (NaCl concentration of 200 mM).
319 Kinetic experiment was shown in Fig. S20, where the response of C-CDs to Al^{3+}
320 could reach stability at 4 min with a 9-fold increase in fluorescence intensity. The
321 response of C-CDs- Al^{3+} to F^- was verified based on the chelation reaction of Al^{3+} and
322 F^- , and F^- restored the fluorescence of C-CDs- Al^{3+} from green to red (Fig. 4D). The
323 analytical response of C-CDs- Al^{3+} to F^- show good linearity between 0-28 μM ($R^2=$
324 0.9994) and 30-56 μM ($R^2= 0.9996$) [47], with a LOD of 0.67 μM (Fig. 4E). Fig. 4F
325 shows good selectivity of C-CDs- Al^{3+} to detect F^- .

326 Finally, a possible mechanism was proposed that C-CDs aggregates in water to
327 emit red fluorescence, while Al^{3+} can chelate with hydroxyl groups on C-CDs, then
328 entrapping between C-CDs and reducing its aggregation to emit green fluorescence,
329 while F^- takes away Al^{3+} and the fluorescence returns to red (Fig. 4G). To validate this
330 mechanism, the size of C-CDs in different systems were investigated (Table S7), the
331 size of C-CDs in water was 65.2 nm, while reached 481.5 nm when Al^{3+} was present,
332 providing evidence that Al^{3+} chelate with hydroxyl groups and insert between C-CDs
333 to prevent the aggregation among C-CDs. Additionally, owing to the structural

334 similarity between R-CDs and C-CDs, Al^{3+} is also capable of inducing aggregation of
 335 R-CDs (Fig. S21). Since R-CDs didn't has AIE properties, the addition of Al^{3+} leads
 336 to (ACQ). Fluorescence decay curves demonstrate that the lifetime of C-CDs at τ_2
 337 remained, while τ_1 increased from 0.551 ns to 0.827 ns after the addition of Al^{3+} ,
 338 which revealed a reduction in the degree of aggregation of C-CDs (Table S12 and Fig.
 339 S22). Above observation proved that the addition of Al^{3+} reduces the aggregation of
 340 C-CDs.



341
 342 **Fig. 4.** (A) Fluorescence emission curves of C-CDs with the addition of Al^{3+} (0-14 μM); (B)
 343 Linearity of concentration of Al^{3+} and fluorescence intensity; (C) Fluorescence emission intensity
 344 of C-CDs (purple bar) and C-CDs+ Al^{3+} (14 μM , red bar) in the presence of Zn^{2+} , Sn^{2+} , Pb^{2+} , Mg^{2+} ,
 345 Na^+ , K^+ , Fe^{3+} , Ba^{2+} , Ca^{2+} , Co^{2+} , Cu^+ , Fe^{2+} , Cu^{2+} , CO_3^{2-} , F^- , S^{2-} , SO_4^{2-} , NO_2^- , Cl^- , Br^- , I^- , CN^- ; (D)
 346 Fluorescence emission curves of C-CDs+ Al^{3+} (14 μM) with different concentrations of F^- (0-56

347 μM); (E) Linearity of concentration of F^- and fluorescence intensity; (F) Fluorescence emission
348 intensity of C-CDs+ Al^{3+} (blue bar) and C-CDs+ Al^{3+} + F^- (14 μM , red bar) in the presence of Zn^{2+} ,
349 Sn^{2+} , Pb^{2+} , Mg^{2+} , Na^+ , K^+ , Fe^{3+} , Ba^{2+} , Ca^{2+} , Co^{2+} , Cu^+ , Fe^{2+} , Cu^{2+} , CO_3^{2-} , S^{2-} , SO_4^{2-} , NO_2^- , Cl^- , Br^- ,
350 I^- , CN^- ; (G) Possible response mechanism diagram of C-CDs toward Al^{3+} and F^- .

351 3.4.2. Field detection of Al^{3+} and F^-

352 The fluorescence method is more sensitive and accurate, but it requires
353 complicated instrumentation to test, which is not suitable to field analysis. Therefore,
354 two methods for the rapid detection of Al^{3+} and F^- were proposed. Firstly, test paper
355 for Al^{3+} was prepared (Fig. 5A), the control group showed red fluorescence, while the
356 addition of Al^{3+} changed red fluorescence to green and enhanced gradually. For more
357 sensitive detection, C-CDs was combined with Nile Red to enable ratiometric
358 detection of Al^{3+} , which resulted in a more intuitive display of Al^{3+} -induced
359 fluorescence color change (Fig. 5B). In addition, selectivity and competitiveness
360 experiments were conducted, demonstrating high selectivity and anti-interference (Fig.
361 5C and Fig. S23). To enhance the detection sensitivity and visualization of Al^{3+} and F^-
362 concentrations, a method to visualize Al^{3+} and F^- concentrations with smartphone was
363 developed. As shown in Fig. 5D and 5E, Al^{3+} alters the fluorescence from red to green,
364 while F^- alters the fluorescence from green to red. The RGB values were captured
365 with a smartphone and plotted against the concentrations of Al^{3+} and F^- using B/R
366 with R^2 of 0.9970 and 0.9971 (Fig. 5F and 5G), respectively. The smartphone sensing
367 platform based on C-CDs demonstrated good sensing performance, which is expected

368 to be used for the fast detection of Al^{3+} and F^- .

369 3.4.3. Detection of Al^{3+} and F^- in lake water.

370 The insoluble impurities in the lake water were removed by filtration, and then
371 ascorbic acid was added to remove Fe^{3+} . C-CDs was used to detect Al^{3+} and F^- in real
372 samples (Table 1). The standard recovery rate of C-CDs for the detection of Al^{3+} was
373 in the range of 98.0-104.0%, with relative standard deviations below 2.6%. For F^-
374 assay, the standard recovery rate was in the range of 98.2-100.2%, with relative
375 standard deviations below 3.5%. The results demonstrated the ability of C-CDs to
376 detect Al^{3+} and F^- in real samples.

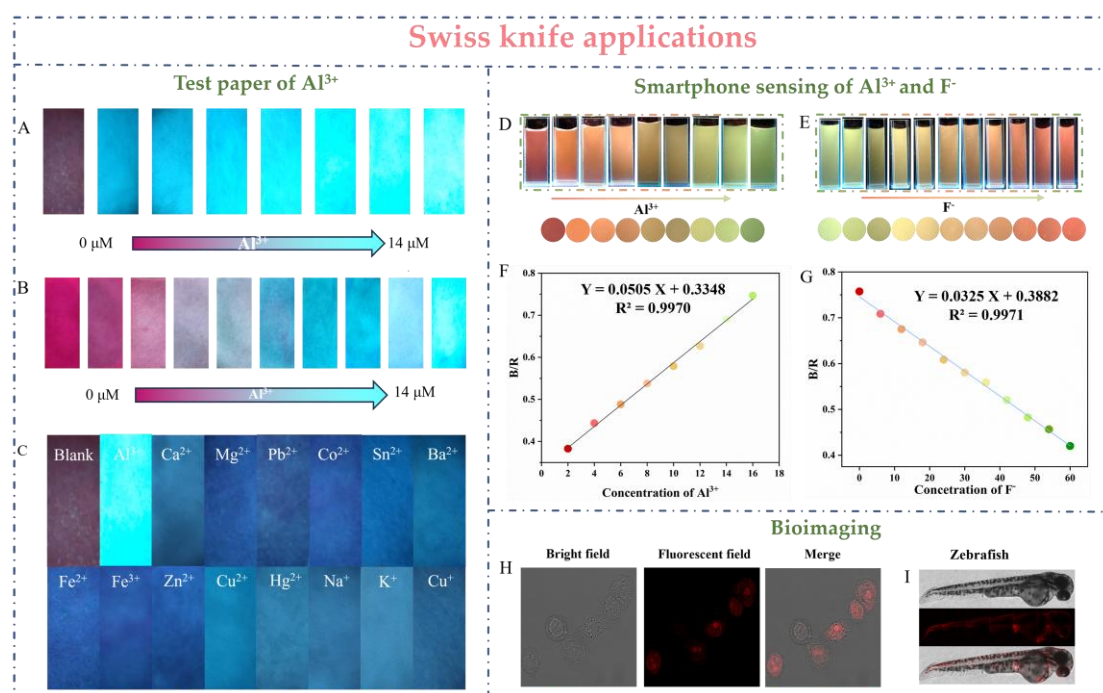
377 **Table 1.** Proposed method used to detect Al^{3+} and F^- in lake water

Testing items	added (μM)	Measured (μM)	Recovery (%)	RSD (%)
Al^{3+}	2.0	2.08	104.0	2.6%
	7.0	6.95	99.3	1.2%
	12.0	11.76	98.0	1.9%
	20.0	19.89	99.5	1.7%
F^-	30.0	30.07	100.2	0.9%
	40.0	39.29	98.2	3.5%

378 3.4.4. Bioimaging

379 Due to the longer wavelength and brighter fluorescence QYs, R-CDs has been
380 applied to cellular imaging. As shown in Fig. 5H, R-CDs emits bright fluorescence in
381 HepG2 cells and has enhanced brightness in the nucleus, suggesting its potential for
382 nuclear staining [48]. Furthermore, R-CDs demonstrates superior tissue penetration
383 capabilities and has been applied in zebrafish imaging (Fig. 5I). The cytotoxicity of
384 both R-CDs and C-CDs was minimal, the cell survival rate of HepG2 reached 98%

385 when the concentration of R-CDs or C-CDs was 200.0 $\mu\text{g/mL}$ (Fig. S24). In
 386 conclusion, R-CDs is a potentially nanoprobe that can be used for bioimaging.



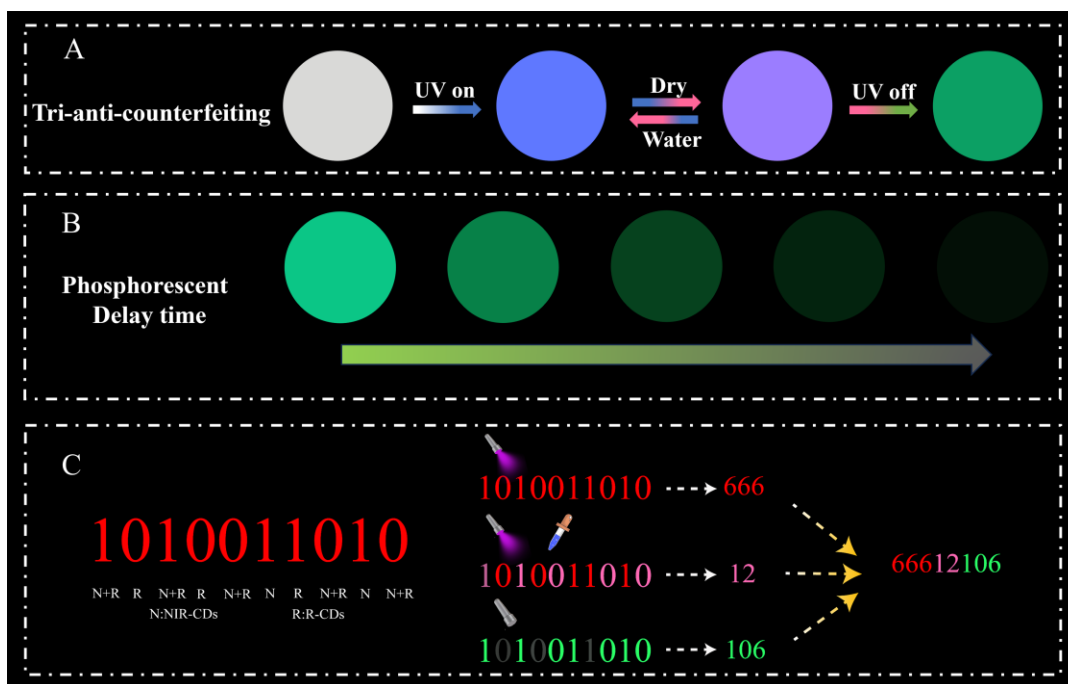
387
 388 **Fig. 5.** (A) Test paper of Al^{3+} under different concentrations of Al^{3+} ; (B) Ratiometric test paper of
 389 Al^{3+} under different concentrations of Al^{3+} ; (C) Test paper of C-CDs immersed in various ions; (D)
 390 Photos of C-CDs and $[\text{Ru}(\text{bpy})_3]^{2+}$ in the addition of Al^{3+} (0-16 μM); (E) Photos of C-CDs and
 391 $[\text{Ru}(\text{bpy})_3]^{2+}$ with 16 μM Al^{3+} in the addition of F^- (0-60 μM); (F) Linearity of concentration of
 392 Al^{3+} and B/R; (G) Linearity of concentration of F^- and B/R; (H) Fluorescent confocal photographs
 393 of HepG2 cells in the presence of R-CDs (10.0 $\mu\text{g/mL}$); (I) Fluorescent confocal photographs of
 394 zebrafish in the presence of R-CDs (10.0 $\mu\text{g/mL}$).

395 3.4.5. Triple anti-counterfeiting and binary information encryption

396 NIR-CDs was made it into a triple anti-counterfeit ink due to its fascinating
 397 optical properties. As shown in Fig. 6A, writing on the filter paper with a pen filled
 398 with fluorescent ink is not visible under daylight. However, due to the aggregation of

399 NIR-CDs on the filter paper, it emitted red fluorescence under 365 nm UV lamp,
400 constituting the first layer of anti-counterfeiting. Spraying water onto the filter paper
401 disperses NIR-CDs and generates blue fluorescence, representing the second level of
402 anti-counterfeiting. The change in fluorescence color from cyan to blue may be
403 attributed to the physical interaction between NIR-CDs and the filter paper[40]. After
404 the filter paper dries and the UV lamp was turned off, a green phosphorescence lasting
405 for 7 seconds could be observed (Fig. 6B), constituting the third level of anti-
406 counterfeiting. Phosphorescence forms due to the filter paper restricts the motion of
407 NIR-CDs and facilitates the stabilization of excited triplet electrons[49, 50].

408 Furthermore, a binary-to-decimal information encryption system was developed.
409 The code number '1010011010' was sprayed with NIR-CDs, R-CDs, or a mixture of
410 both (Fig. 6C). Upon turning on the UV lamp, red fluorescence was employed to
411 display the numeral "1010011010". After activating the water spray system, the digit
412 '11000' was showcased using pink fluorescence. Finally, upon deactivating the light
413 source, the numeral '1101010' was indicated using green fluorescence. Convert these
414 numbers into decimal codes corresponding to 666, 12 and 106. Furthermore, it is
415 possible to change the coloring agent to modify the code, and different combinations
416 of codes can be obtained by changing the sequence of turning the light on and off.
417 Due to the flexibility and complexity of the secure system, it is almost impossible to
418 break it without getting the correct order.



419

420 **Fig. 6.** Triple anti-counterfeiting and information encryption of NIR-CDs. (A) Tri-anti-

421 counterfeiting of NIR-CDs on filter paper; (B) Phosphorescent duration of NIR-CDs on filter

422 paper; (C) Binary information encryption system diagram.

423 **4. Conclusion**

424 In conclusion, we prepared cyan, green, yellow, red, and near-infrared CDs using

425 naringenin and acetophenone derivatives as raw materials. Characterization and

426 control experiments demonstrated that the color of the CDs can be modulated by the

427 electron supplying ability of functional group. Furthermore, a method for producing

428 AIE CDs was proposed, and it was discovered that the CDs underwent a transition

429 from ACQ to AIE when the functional group of the precursor changed from a non-

430 rotatable -OH or -NH₂ to a rotatable -N(CH₃)₂. These CDs exhibit excellent optical

431 properties and have been applied in various fields. NIR-CDs was employed in ink for

432 triple anti-counterfeiting and binary information encryption. C-CDs was used for

433 ratiometric quantitative sensing of Al^{3+} and F^- using portable devices such as
434 smartphone and test paper. R-CDs was successfully used for cellular and zebrafish
435 imaging, demonstrating its potential in the field of bioimaging applications. This work
436 offers a new approach for comprehending the mechanism of AIE CDs and lays a
437 foundation for the development of AIE CDs.

438 **CRedit authorship contribution statement**

439 **Shengtao Zhang**: Conceptualization, Investigation, Formal analysis, Writing-
440 original draft. **Jinhong Li**: Conceptualization, Funding acquisition, Writing-original
441 draft. **Pengyue Xu**: Investigation, Methodology. **Jieyu Zhou**: Writing-review &
442 editing. **Yan Li**: Writing-review & editing, Funding acquisition, Resources. **Yongmin**
443 **Zhang**: Writing-review & editing. **Shaoping Wu**: Writing-review & editing, Funding
444 acquisition, Resources.

445 **Conflict of Interest**

446 There are no conflicts to declare.

447 **Acknowledgements**

448 This work was supported by the National Natural Science Foundation of China
449 (No. 22074119), the Key Research and Development Program of Shaanxi Province
450 (No. 2021ZDLSF03-03), Biomedicine Key Laboratory of Shaanxi Province (No.
451 2018SZS41).

452 **References**

453 [1] R. Rossetti, S. Nakahara, L. Brus, Quantum size effects in the redox potentials, resonance
454 Raman spectra, and electronic spectra of CdS crystallites in aqueous solution, J. Chem. Phys.

- 455 79(2) (1983) 1086-1088, 10.1063/1.445834.
- 456 [2] H. Lu, G. Carroll, N. Neale, M. Beard, infrared quantum dots: progress, challenges, and
457 opportunities, *ACS Nano*. 13(2) (2019) 939-953, 10.1021/acsnano.8b09815.
- 458 [3] F. García de Arquer, D. Talapin, V. Klimov, Y. Arakawa, M. Bayer, E. Sargent, Semiconductor
459 quantum dots: technological progress and future challenges, *Science*. 373(6555) (2021)
460 eaaz8541, doi:10.1126/science.aaz8541.
- 461 [4] H. Guo, Y. Lu, Z. Lei, H. Bao, M. Zhang, Z. Wang, C. Guan, B. Tang, Z. Liu, L. Wang,
462 Machine learning-guided realization of full-color high-quantum-yield carbon quantum dots,
463 *Nat. Commun.* 15(1) (2024) 4843, 10.1038/s41467-024-49172-6.
- 464 [5] X. Xu, R. Ray, Y. Gu, H. Ploehn, L. Gearheart, K. Raker, W. Scrivens, Electrophoretic analysis
465 and purification of fluorescent single-walled carbon nanotube fragments, *J. Am. Chem. Soc.*
466 126(40) (2004) 12736-12737, 10.1021/ja040082h.
- 467 [6] Z. Yang, T. Xu, H. Li, M. She, J. Chen, Z. Wang, S. Zhang, J. Li, Zero-dimensional carbon
468 nanomaterials for fluorescent sensing and imaging, *Chem. Rev.* 123(18) (2023) 11047-11136,
469 10.1021/acs.chemrev.3c00186.
- 470 [7] X. Yu, H. Zhang, J. Yu, Luminescence anti-counterfeiting: from elementary to advanced,
471 *Aggregate*. 2(1) (2021) 20-34, <https://doi.org/10.1002/agt2.15>.
- 472 [8] Q. Feng, Z. Xie, M. Zheng, Room temperature phosphorescent carbon dots for latent
473 fingerprints detection and in vivo phosphorescence bioimaging, *Sens. Actuators B Chem.* 351
474 (2022) 130976, <https://doi.org/10.1016/j.snb.2021.130976>.
- 475 [9] C. Zhou, R. Cheng, B. Liu, Y. Fang, K. Nan, W. Wu, Y. Xu, Cascade selective recognition of
476 H₂O₂ and ascorbic acid in living cells using carbon-based nanozymes with peroxidase-like
477 activity, *Sens. Actuators B Chem.* 402 (2024) 135118,
478 <https://doi.org/10.1016/j.snb.2023.135118>.
- 479 [10] J. Yang, H. Liu, Y. Huang, L. Li, X. Zhu, Y. Ding, One-step hydrothermal synthesis of near-
480 infrared emission carbon quantum dots as fluorescence aptamer sensor for cortisol sensing
481 and imaging, *Talanta*. 260 (2023) 124637, <https://doi.org/10.1016/j.talanta.2023.124637>.
- 482 [11] M. Liu, B. Chen, C. Li, C. Huang, Carbon dots: synthesis, formation mechanism,

483 fluorescence origin and sensing applications, *Green Chem.* 21(3) (2019) 449-471,
484 10.1039/C8GC02736F.

485 [12] G. Hutton, B. Reuillard, B. Martindale, C. Caputo, C. Lockwood, J. Butt, E. Reisner, Carbon
486 dots as versatile photosensitizers for solar-driven catalysis with redox enzymes, *J. Am. Chem.*
487 *Soc.* 138(51) (2016) 16722-16730, 10.1021/jacs.6b10146.

488 [13] L. Haiyang, L. Guantong, Z. Nan, Y. Zhanye, J. Xinge, Z. Bing, Y. Tian, Ag-carbon dots with
489 peroxidase-like activity for colorimetric and SERS dual mode detection of glucose and
490 glutathione, *Talanta.* 273 (2024) 125898, <https://doi.org/10.1016/j.talanta.2024.125898>.

491 [14] Y. Zhu, R. Zhang, Z. Hu, F. Wu, B. N co-doped carbon dots as efficient nanozymes for
492 colorimetric and fluorometric dual-mode detection of cholesterol, *Talanta.* 278 (2024)
493 126471, <https://doi.org/10.1016/j.talanta.2024.126471>.

494 [15] H. Guo, J. Raj, Z. Wang, T. Zhang, K. Wang, L. Lin, W. Hou, J. Zhang, M. Wu, J. Wu, L.
495 Wang, Synergistic effects of amine functional groups and enriched-atomic-iron sites in
496 carbon dots for industrial-current-density CO₂ electroreduction, *Small.* 20(32) (2024)
497 2311132, <https://doi.org/10.1002/sml.202311132>.

498 [16] B. Hu, K. Huang, B. Tang, Z. Lei, Z. Wang, H. Guo, C. Lian, Z. Liu, L. Wang, Graphene
499 quantum dot-mediated atom-layer semiconductor electrocatalyst for hydrogen evolution,
500 *Nanomicro Lett.* 15(1) (2023) 217, 10.1007/s40820-023-01182-7.

501 [17] B. Wang, S. Lu, The light of carbon dots: from mechanism to applications, *Matter.* 5(1) (2022)
502 110-149, <https://doi.org/10.1016/j.matt.2021.10.016>.

503 [18] H. Li, Y. Chen, H. Wang, H. Wang, Q. Liao, S. Han, Y. Li, D. Wang, G. Li, Y. Deng, Amide (n,
504 π^*) transitions enabled clusteroluminescence in solid-state carbon dots, *Adv. Funct. Mater.*
505 33(37) (2023) 2302862, <https://doi.org/10.1002/adfm.202302862>.

506 [19] Y. Jia, Z. Cheng, G. Wang, S. Shuang, Y. Zhou, C. Dong, F. Du, Nitrogen doped biomass
507 derived carbon dots as a fluorescence dual-mode sensing platform for detection of
508 tetracyclines in biological and food samples, *Food Chem.* 402 (2023) 134245,
509 <https://doi.org/10.1016/j.foodchem.2022.134245>.

510 [20] M. Gao, C. Liu, Z. Wu, Q. Zeng, X. Yang, W. Wu, Y. Li, C. Huang, A surfactant-assisted

511 redox hydrothermal route to prepare highly photoluminescent carbon quantum dots with
512 aggregation-induced emission enhancement properties, *Chem. Commun.* 49(73) (2013)
513 8015-8017, 10.1039/C3CC44624G.

514 [21] H. Yang, Y. Liu, Z. Guo, B. Lei, J. Zhuang, X. Zhang, Z. Liu, C. Hu, Hydrophobic carbon
515 dots with blue dispersed emission and red aggregation-induced emission, *Nat. Commun.* 10(1)
516 (2019) 1789, 10.1038/s41467-019-09830-6.

517 [22] X. Xu, L. Mo, Y. Li, X. Pan, G. Hu, B. Lei, X. Zhang, M. Zheng, J. Zhuang, Y. Liu, C. Hu,
518 Construction of carbon dots with color-tunable aggregation-induced emission by nitrogen-
519 induced intramolecular charge transfer, *Adv. Mater.* 33(49) (2021) 2104872,
520 <https://doi.org/10.1002/adma.202104872>.

521 [23] Y. Ru, G. Waterhouse, S. Lu, Aggregation in carbon dots, *Aggregate.* 3(6) (2022) e296,
522 <https://doi.org/10.1002/agt2.296>.

523 [24] S. Zhang, B. Li, J. Zhou, J. Shi, Z. He, Y. Zhao, Y. Li, Y. Shen, Y. Zhang, S. Wu, Kill three
524 birds with one stone: Mitochondria-localized tea saponin derived carbon dots with AIE
525 properties for stable detection of HSA and extremely acidic pH, *Food Chem.* 405 (2023)
526 134865, <https://doi.org/10.1016/j.foodchem.2022.134865>.

527 [25] Z. Yang, H. Li, T. Xu, M. She, J. Chen, X. Jia, P. Liu, X. Liu, J. Li, Red emissive carbon dots
528 as a fluorescent sensor for fast specific monitoring and imaging of polarity in living cells, *J.*
529 *Mater. Chem. A.* 11(6) (2023) 2679-2689, 10.1039/D2TA09462B.

530 [26] Z. Wan, Y. Li, Y. Zhou, D. Peng, X. Zhang, J. Zhuang, B. Lei, Y. Liu, C. Hu, High-efficiency
531 solid-state luminescence from hydrophilic carbon dots with aggregation-induced emission
532 characteristics, *Adv. Funct. Mater.* 33(11) (2023) 2207296,
533 <https://doi.org/10.1002/adfm.202207296>.

534 [27] K. Muthamma, D. Sunil, P. Shetty, Carbon dots as emerging luminophores in security inks for
535 anti-counterfeit applications - an up-to-date review, *Appl. Mater.* 23 (2021) 101050,
536 <https://doi.org/10.1016/j.apmt.2021.101050>.

537 [28] S. Zhang, J. Wang, Y. Ni, Y. Li, H. Zhang, W. Zhang, Z. Xie, S. Zhou, Modulation of carbon
538 dots hybrids lasers for high security flexible multi-level anti-counterfeiting, *J. Alloys Compd.*

- 539 957 (2023) 170307, <https://doi.org/10.1016/j.jallcom.2023.170307>.
- 540 [29] Y. Wang, X. Li, S. Zhao, B. Wang, X. Song, J. Xiao, M. Lan, Synthesis strategies,
541 luminescence mechanisms, and biomedical applications of near-infrared fluorescent carbon
542 dots, *Coordin Chem Rev.* 470 (2022) 214703, <https://doi.org/10.1016/j.ccr.2022.214703>.
- 543 [30] L. Wang, W. Li, L. Yin, Y. Liu, H. Guo, J. Lai, Y. Han, G. Li, M. Li, J. Zhang, R. Vajtai, P.
544 Ajayan, M. Wu, Full-color fluorescent carbon quantum dots, *Sci. Adv.* 6(40) (2020)
545 eabb6772, doi:10.1126/sciadv.abb6772.
- 546 [31] Z. He, Y. Sun, C. Zhang, J. Zhang, S. Liu, K. Zhang, M. Lan, Recent advances of solvent-
547 engineered carbon dots: a review, *Carbon.* 204 (2023) 76-93,
548 <https://doi.org/10.1016/j.carbon.2022.12.052>.
- 549 [32] J. Wang, J. Zheng, Y. Yang, X. Liu, J. Qiu, Y. Tian, Tunable full-color solid-state fluorescent
550 carbon dots for light emitting diodes, *Carbon.* 190 (2022) 22-31,
551 <https://doi.org/10.1016/j.carbon.2022.01.001>.
- 552 [33] K. Jiang, S. Sun, L. Zhang, Y. Lu, A. Wu, C. Cai, H. Lin, Red, green, and blue luminescence
553 by carbon dots: full-color emission tuning and multicolor cellular imaging, *Angew. Chem. Int.*
554 *Ed.* 54(18) (2015) 5360-5363, <https://doi.org/10.1002/anie.201501193>.
- 555 [34] L. Ai, Z. Song, M. Nie, J. Yu, F. Liu, H. Song, B. Zhang, G. Waterhouse, S. Lu, Solid-state
556 fluorescence from carbon dots widely tunable from blue to deep red through surface ligand
557 modulation, *Angew. Chem. Int. Ed.* 62(12) (2023) e202217822,
558 <https://doi.org/10.1002/anie.202217822>.
- 559 [35] S. Wang, Y. Wang, Y. Ning, W. Wang, Q. Liu, Multicolor emissive carbon dot-based
560 fluorometric analysis platform for rapid quantification and discrimination of nitroimidazole
561 antibiotic residues, *Talanta.* 271 (2024) 125679, <https://doi.org/10.1016/j.talanta.2024.125679>.
- 562 [36] Y. Sang, K. Wang, X. Kong, F. Cheng, C. Zhou, W. Li, Color-multiplexing europium doped
563 carbon dots for highly selective and dosage-sensitive cascade visualization of tetracycline
564 and Al^{3+} , *Sens. Actuators B Chem.* 362 (2022) 131780,
565 <https://doi.org/10.1016/j.snb.2022.131780>.
- 566 [37] J. Liu, Y. Zhan, B. Qiu, Z. Lin, L. Guo, Portable smartphone platform based on aggregation-

567 induced enhanced emission carbon dots for ratiometric quantitative sensing of fluoride ions,
568 ACS Sens. 8(2) (2023) 884-892, 10.1021/acssensors.2c02589.

569 [38] X. Li, L. Zhao, Y. Wu, A. Zhou, X. Jiang, Y. Zhan, Z. Sun, Nitrogen and boron co-doped
570 carbon dots as a novel fluorescent probe for fluorogenic sensing of Ce^{4+} and ratiometric
571 detection of Al^{3+} , Spectrochim. Acta. A. 282 (2022) 121638,
572 <https://doi.org/10.1016/j.saa.2022.121638>.

573 [39] X. Tang, Y. Zhao, H. Yu, S. Cui, H. Temple, E. Amador, Y. Gao, M. Chen, S. Wang, Z. Hu, W.
574 Chen, Concentration-regulated multi-color fluorescent carbon dots for the detection of
575 rifampicin, morin and Al^{3+} , Mater. Today Adv. 18 (2023) 100383,
576 <https://doi.org/10.1016/j.mtadv.2023.100383>.

577 [40] X. Bao, E.V. Ushakova, E. Liu, Z. Zhou, D. Li, D. Zhou, S. Qu, A.L. Rogach, On-off
578 switching of the phosphorescence signal in a carbon dot/polyvinyl alcohol composite for
579 multiple data encryption, Nanoscale. 11(30) (2019) 14250-14255, 10.1039/C9NR05123F.

580 [41] L. Yan, B. Zhang, Z. Zong, W. Zhou, S. Shuang, L. Shi, Artificial intelligence-integrated
581 smartphone-based handheld detection of fluoride ion by Al^{3+} -triggered aggregation-induced
582 red-emission enhanced carbon dots, J. Colloid Interface Sci. 651 (2023) 59-67,
583 <https://doi.org/10.1016/j.jcis.2023.07.125>.

584 [42] W. Zhao, P. Xu, Y. Ma, Y. Song, Y. Wang, P. Zhang, B. Li, Y. Zhang, J. Li, S. Wu, Old trees
585 bloom new flowers, lysosome targeted near-infrared fluorescent probe for ratiometric sensing
586 of hypobromous acid in vitro and in vivo based on Nile red skeleton, Bioorg. Chem. 143
587 (2024) 107031, <https://doi.org/10.1016/j.bioorg.2023.107031>.

588 [43] W. Zhao, S. Zhang, J. Yan, P. Xu, B. Li, Y. Zhang, J. Li, S. Wu, A dual-emission fluorescent
589 probe for simultaneous detection of singlet oxygen and hypochlorous acid in lipid droplets,
590 Sens. Actuators B Chem. 412 (2024) 135813, <https://doi.org/10.1016/j.snb.2024.135813>.

591 [44] Y. Yang, N. Xiao, S. Liu, L. Han, N. Li, H. Luo, pH-induced aggregation of hydrophilic
592 carbon dots for fluorescence detection of acidic amino acid and intracellular pH imaging,
593 Mater. Sci. Eng: C. 108 (2020) 110401, <https://doi.org/10.1016/j.msec.2019.110401>.

594 [45] M. Liu, L. Yang, R. Li, B. Chen, H. Liu, C. Huang, Large-scale simultaneous synthesis of

595 highly photoluminescent green amorphous carbon nanodots and yellow crystalline graphene
596 quantum dots at room temperature, *Green Chem.* 19(15) (2017) 3611-3617,
597 10.1039/C7GC01236E.

598 [46] Z. Wang, F. Yuan, X. Li, Y. Li, H. Zhong, L. Fan, S. Yang, 53% Efficient red emissive carbon
599 quantum dots for high color rendering and stable warm white-light-emitting diodes, *Adv.*
600 *Mater.* 29(37) (2017) 1702910, <https://doi.org/10.1002/adma.201702910>.

601 [47] S. Zhang, Y. Gu, Z. Shi, N. Lu, H. Xu, A novel reversible fluorescent probe based on
602 naphthalimide for sequential detection of aluminum (Al^{3+}) and fluoride (F^-) ions and its
603 applications, *Anal Methods.* 13(44) (2021) 5360-5368, 10.1039/D1AY01545A.

604 [48] H. Liu, X. Geng, X. Wang, L. Wei, Z. Li, S. Lin, L. Xiao, A carbonized fluorescent nucleolus
605 probe discloses RNA reduction in the process of mitophagy, *CCS Chem.* 4(8) (2022) 2698-
606 2710, doi:10.31635/ccschem.021.202101371.

607 [49] J. Tan, J. Zhang, W. Li, L. Zhang, D. Yue, Synthesis of amphiphilic carbon quantum dots with
608 phosphorescence properties and their multifunctional applications, *J. Mater. Chem. C.* 4(42)
609 (2016) 10146-10153, 10.1039/C6TC03027K.

610 [50] M. Fu, L. Lin, X. Wang, X. Yang, Hydrogen bonds and space restriction promoting long-lived
611 room-temperature phosphorescence and its application for white light-emitting diodes, *J.*
612 *Colloid Interface Sci.* 639 (2023) 78-86, <https://doi.org/10.1016/j.jcis.2023.02.040>.

613