Supplementary Information (SI)

Photoluminescence Mechanism of Carbon Dots: Triggering High-colour-purity Red Fluorescence Emission through edge amino protonation

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Table Caption：

Supplementary Table 1. Comparison of photoluminescence red-shift mechanism of multi-color CDs between previous research and our work.

Supplementary Table 2. FL QYs of CDs, and 2,3-DAPN molecular.

Figure Caption：

Supplementary Fig. 1 | Raman spectra of CDs

Supplementary Fig. 2 | Zoomed ^{13}C-NMR spectra of the CDs.

Supplementary Fig. 3 | Zoomed ^{1}H-NMR spectra of the CDs.

Supplementary Fig. 4 | ^{13}C-NMR spectra of 2,3-diaminophenazine (2,3-DAPN), Modified from "2,3-diaminophenazine is the product from the horseradish peroxidase-catalyzed oxidation of o-phenylenediamine" with permission from Elsevier.[17]

Fig. 5 | ^{1}H-NMR spectra of 2,3-DAPN, Modified from "2,3-diaminophenazine is the product from the horseradish peroxidase-catalyzed oxidation of o-phenylenediamine" with permission from Elsevier.[17]

Supplementary Fig. 6 | (a)-(b) UV-vis absorption of OPD, 2,3-DAPN and CDs with or without protonation treatment.

Supplementary Fig. 7 |(a), (b) FL spectra of protonated OPD kept at deionized water for 6 hours excited by 480 nm and 808 nm femtosecond laser. (c), (d) ^{1}H-NMR and zoomed ^{1}H-NMR spectra of OPD molecular kept at deionized water for 6 hours. Due to the oxidation reaction, part of OPD molecular has converted into 2,3-DAPN analogues.

Supplementary Fig. 8 | (a), (b) UV-vis absorption of OPD with or without protonation treatment; (c), (d) FL emission of CDs, OPD and 2,3-DAPN samples with or without protonation treatment the identical excitation conditions.

Supplementary Fig. 9 | (a), (c) Up-conversion FL spectra of 2,3-DAPN at pH7 and pH 1 under 808 nm femtosecond laser excitation. (b), (d) Relationship of FL intensity and femtosecond (fs) laser power at pH 7 and pH 1.

Supplementary Fig. 10 | (a), (c) Up-conversion FL spectra of OPD at pH7 and pH 1 under 808 nm femtosecond (fs) laser excitation. (b), (d) Relationship of FL intensity and fs laser power at pH 7 and pH 1.

Supplementary Fig. 11 | (a), (b), and (c) Transmission electron microscopy imaging (TEM), high resolution image and Size distribution of CDs; (d), (g) UV-vis absorption spectra of CDs with or without protonation; (e), (h) FL spectra of CDs dissolved without protonation (excited at 400 nm) and with protonation (excited at 560 nm); (f), (i) FL excitation spectra of CDs with or without protonation.

Supplementary Fig. 12 | (a)-(d) Raman spectra of CDs prepared at 60,120, 180 and 220℃. (e) and (f) FL emission of CDs synthesized with or without protonation.

Supplementary Fig. 13 | (a) and (b) FL emission of the protonated CDs excited under 600 and 800 nm continuum light source; (c) and (d) NIR-II in vivo images of mice before and after vein injection.

Supplementary Fig. 14 | (a) Photograph of LED device fabricated using CDs; (b) FL emission spectrum of the LED device excited by UV light-emitting chips; (c) Color coordinates picture of the LED device (0.26, 0.59).

Section 1: Supplementary Information of Tables.

Supplementary Table 1. Comparison of photoluminescence red-shift mechanism of multi-color CDs between previous research and our work.

Reference	Journal	Mechanism of PL red-shift
1[1]	Carbon 2014, 70, 279.	Increasing degree of COO^-
2[2]	Advanced Materials 2015, 27, 1663	Increasing degree of oxidation
3[3]	Angew. Chem. - Int. Ed. 2015, 54, 2970	Increasing degree C-O-C & C-O
4[4]	Acs Nano 2016, 10, 484	Increasing degree of COO-
5[5]	Nanoscale 2016, 8, 729	Increasing degree of N content
6[6]	ACS Nano 2017, 11, 12402.	Increasing degree of graphitic-N
7[7]	Green Chem. 2017, 19, 3611.	Increasing degree of oxidation
8[8]	Advanced Materials, 2018, 30.	Increasing degree of graphitization and surface modification of -COOH
Our work		Protonation of 2,3-Diaminophenazine

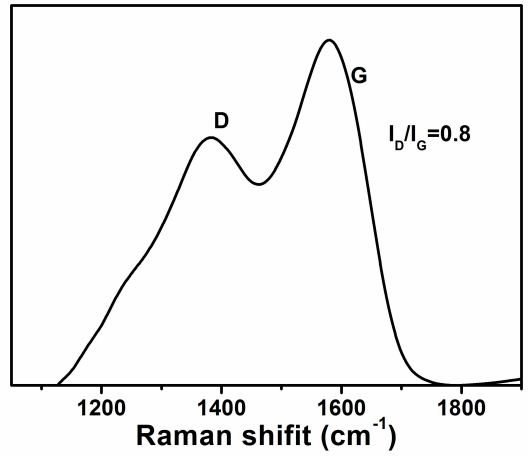
Supplementary Table 2. FL QYs of CDs, and 2,3-DAPN molecular.

QYs	CDs	2,3-DAPN
Without protonation	14%	24%
With protonation	1.9%	0.2%

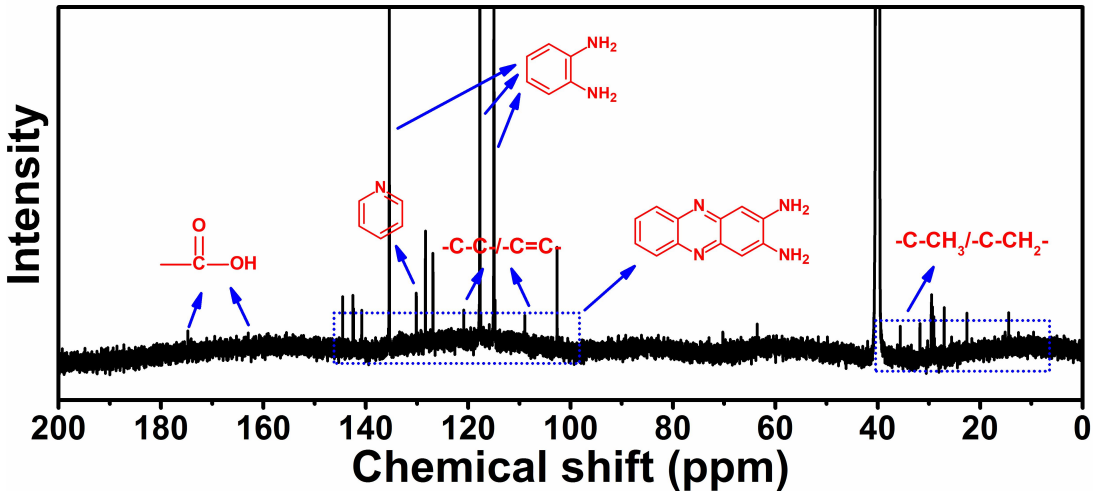
Supplementary Table 3. FL QYs of CDs, and 2,3-DAPN molecular.

Reference	**NIR Organic dye**	**QYs (%)**
1	IR-1061 (Commercial dye)	**1.7%**[9]
2	LZ1105	**1.6%**[10]
2	IR-E1	**0.7%**[11]
3	IR-FTP	**0.02%**[12]
4	IR-FTTP	**0.1%**[13]
5	CH1055-PEG	**0.3%**[14]
6	CH-4T	**1.1%**[15]
7	SCH1100	**0.2%**[16]

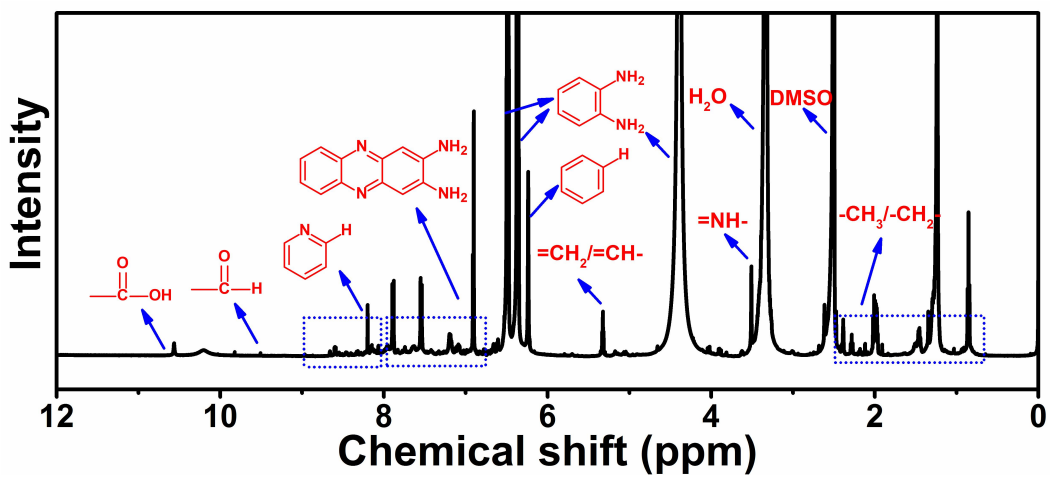
Section 2: Supplementary Figures



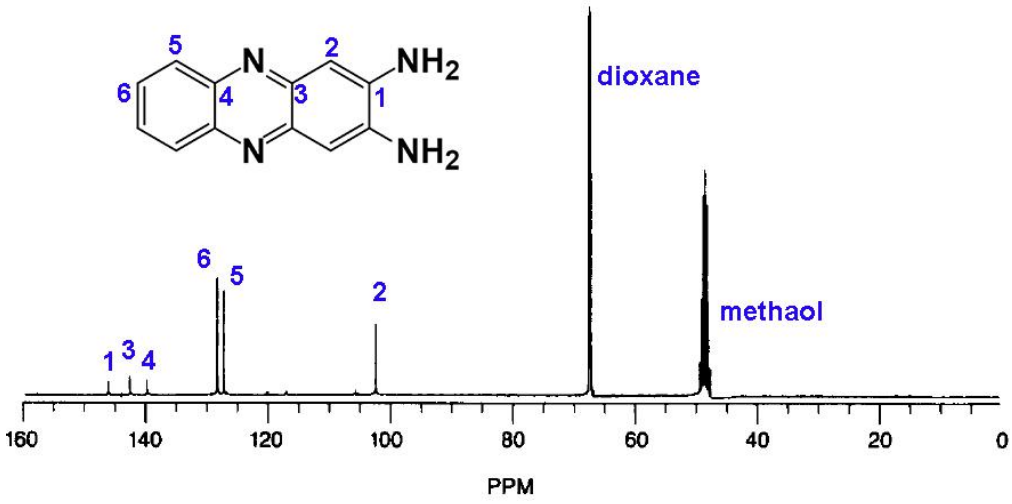
Supplementary Fig. 1 Raman spectra of CDs.



Supplementary Fig. 2 | Zoomed ^{13}C-NMR spectra of the CDs.



Supplementary Fig. 3| Zoomed ^{1}H-NMR spectra of the CDs.



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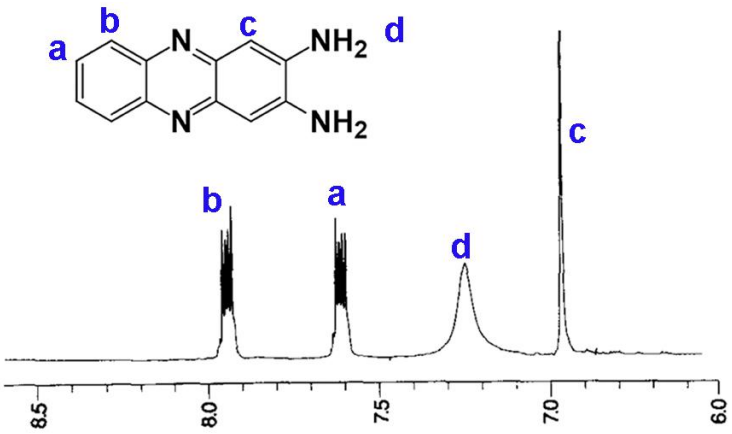

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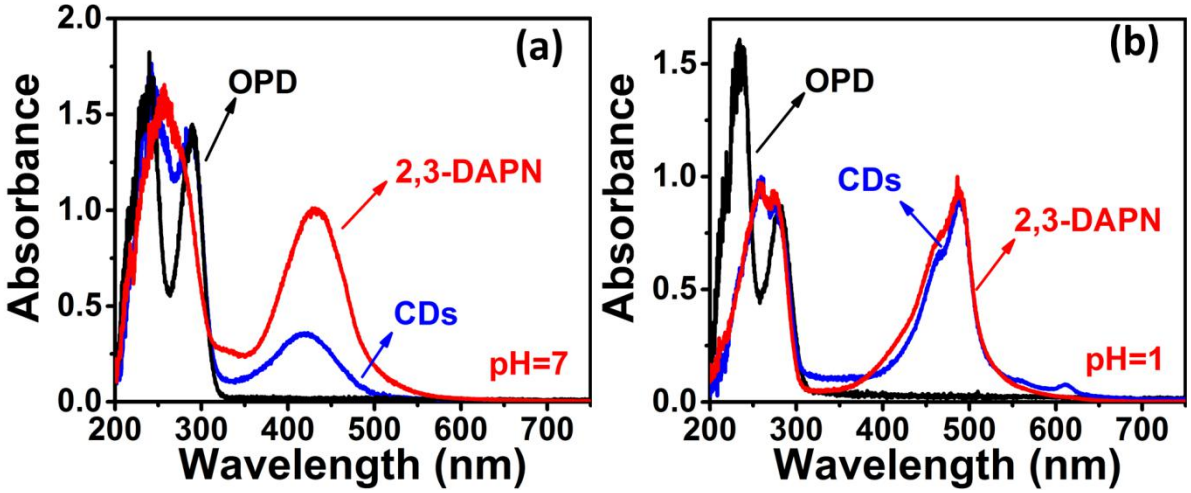

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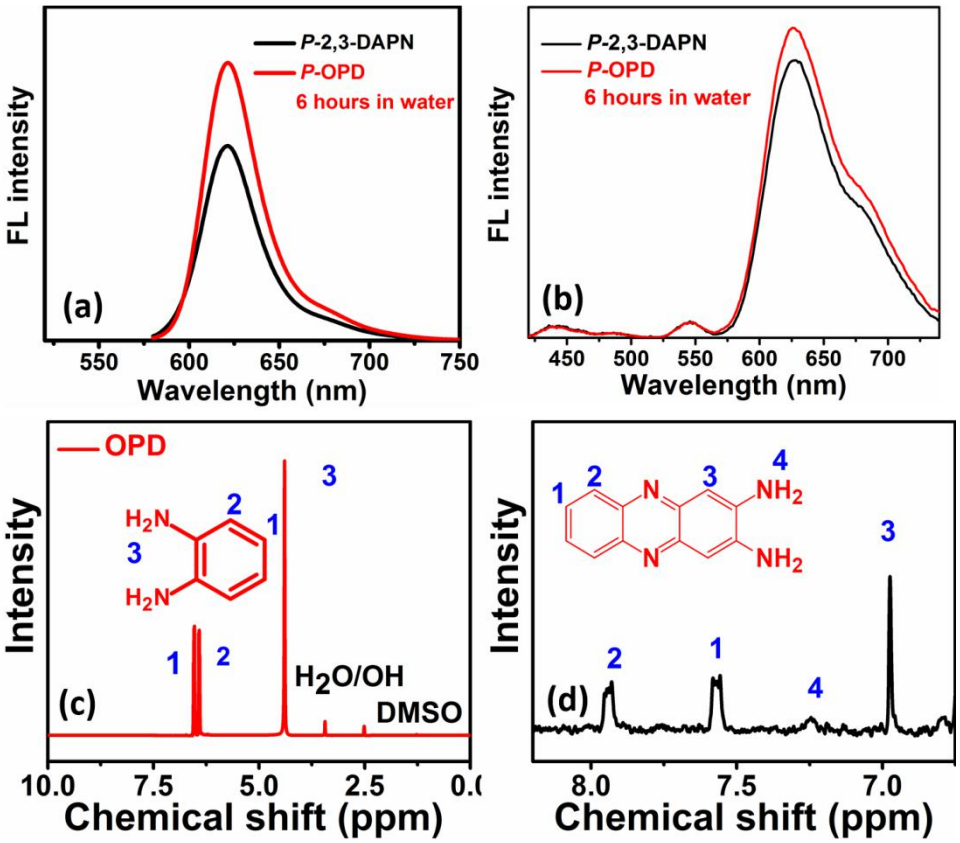

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275 **Supplementary Fig. 7 |** (a), (b) FL spectra of the protonated OPD kept in deionized water for 6 hours
276 excited by 480 nm and 808 nm femtosecond laser. (c), (d) ^{1}H-NMR and magnified ^{1}H-NMR spectra of
277 the OPD molecular kept in deionized water for 6 hours. Due to the oxidation reaction, a part of the
278 OPD molecular has converted into 2,3-DAPN analogues.

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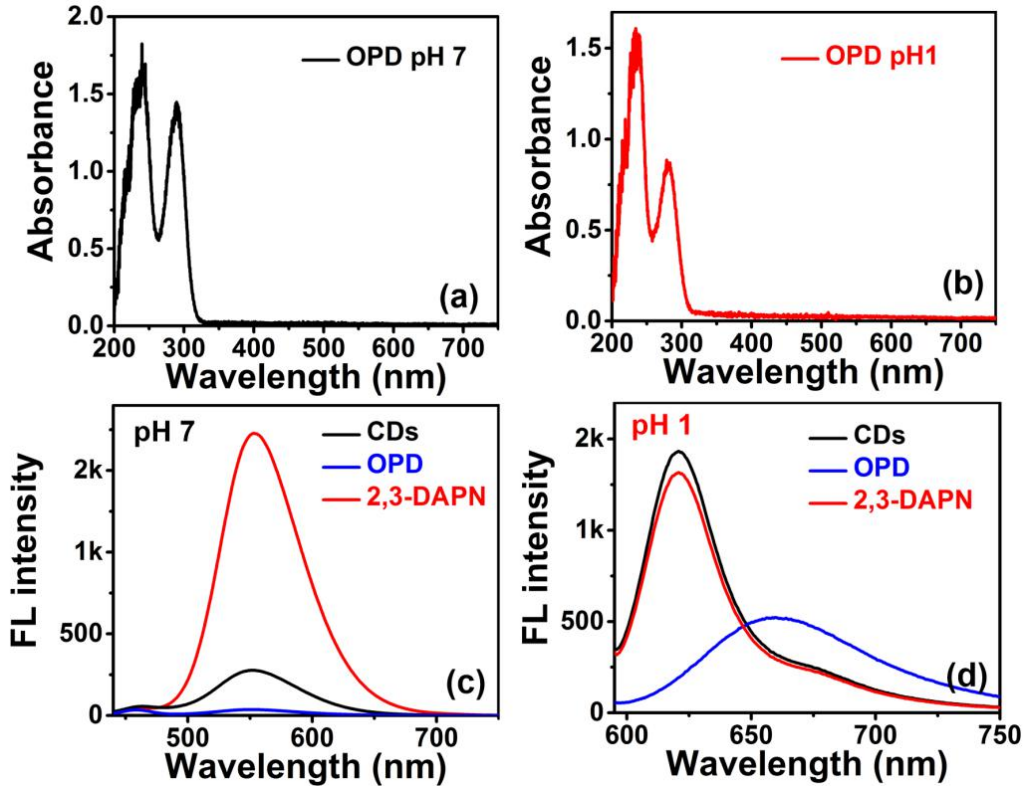

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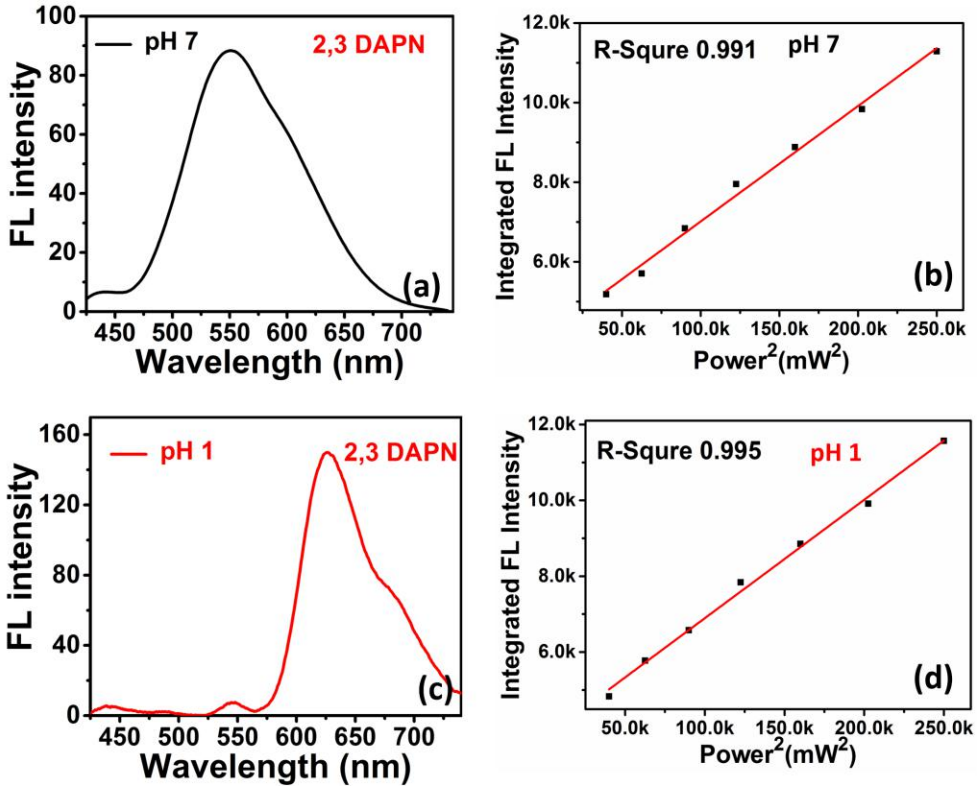

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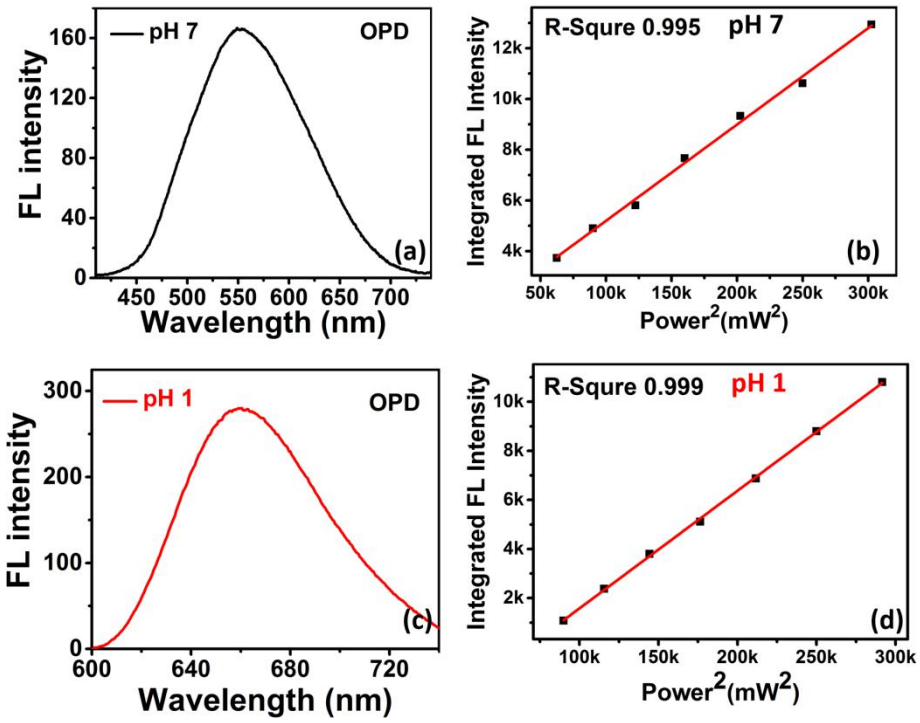

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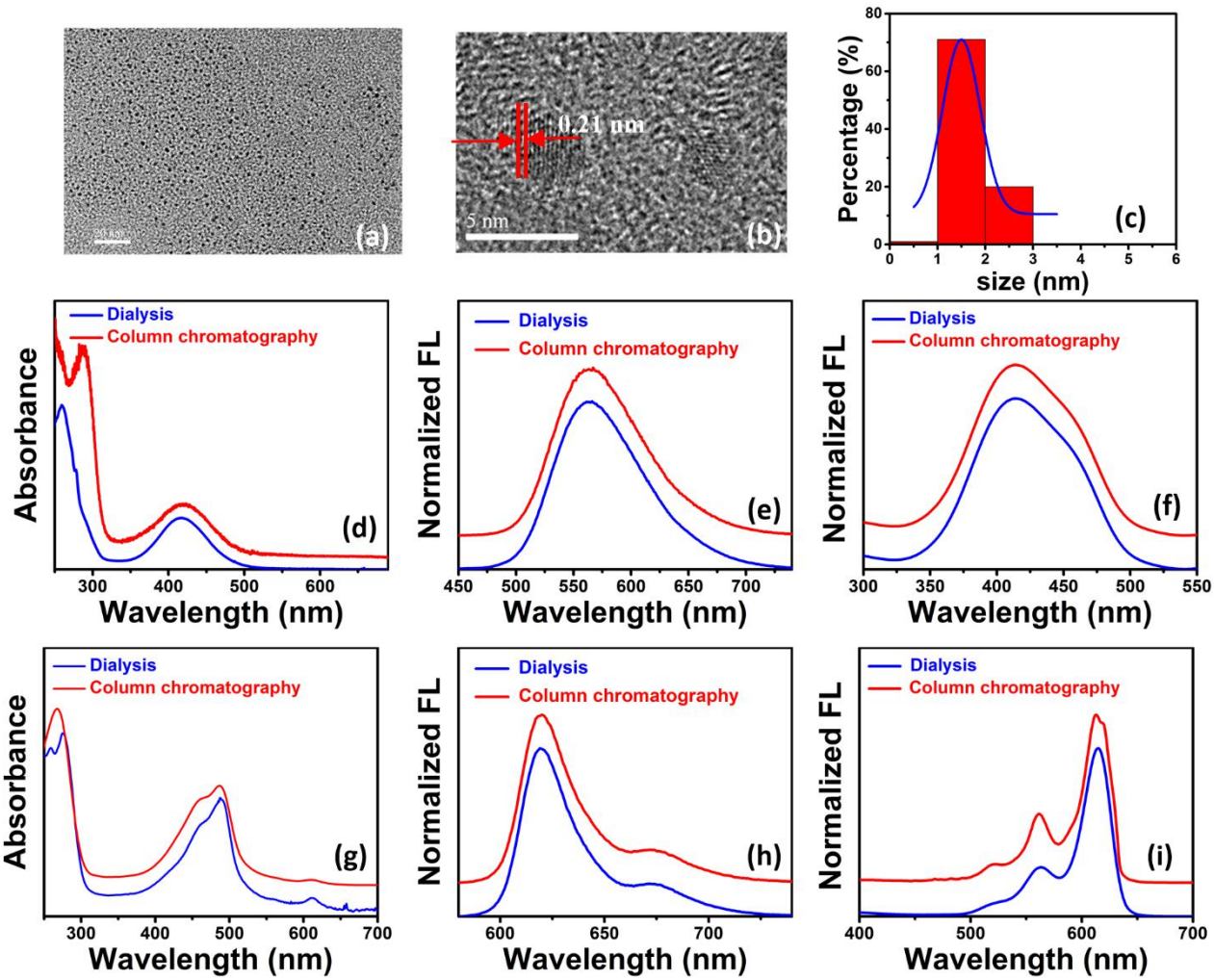

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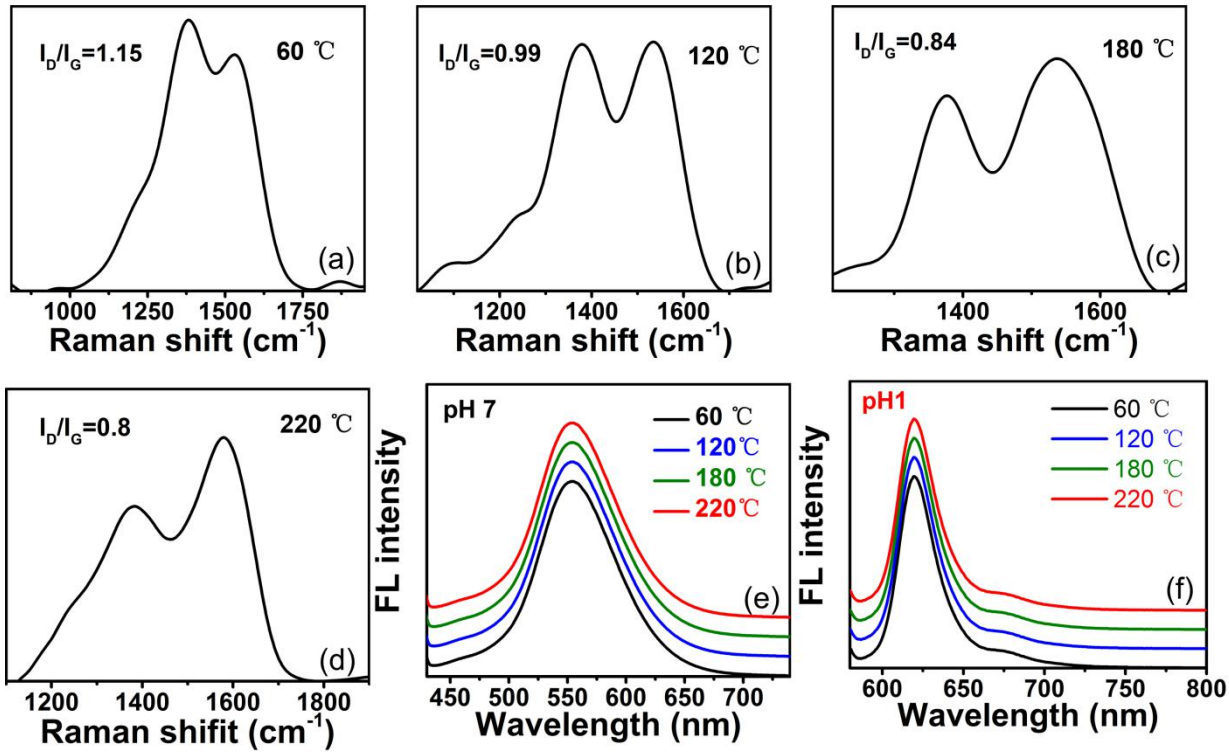

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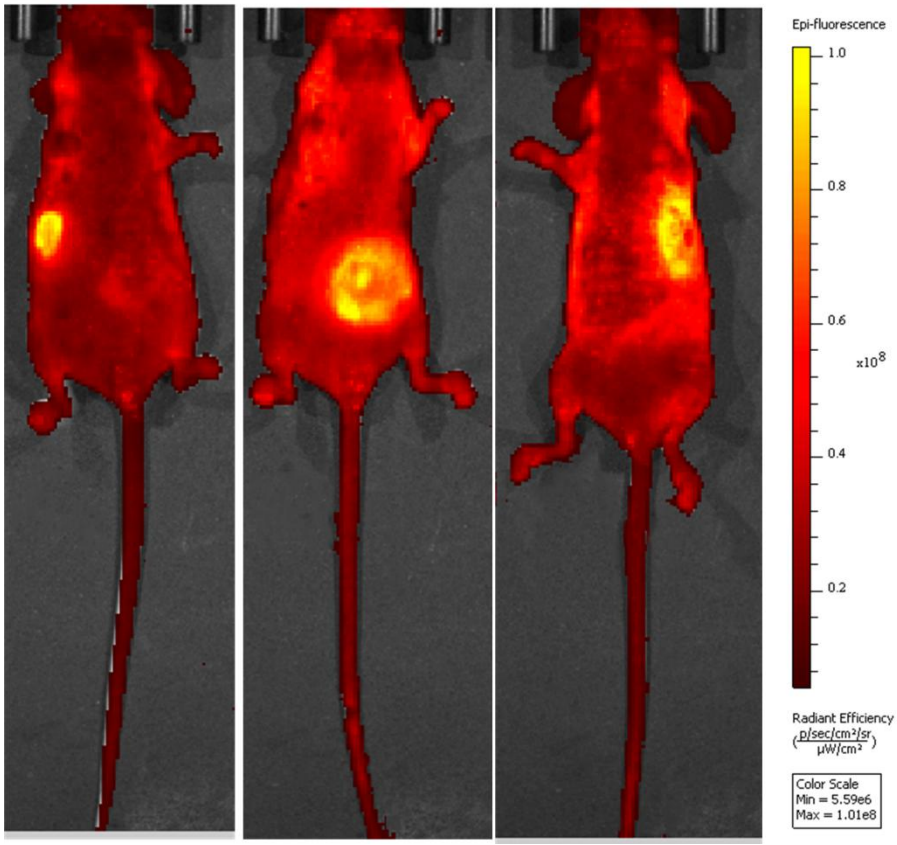

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372 **Supplementary Fig. 13** | In vivo fluorescence images of nude mice injected with different
373 subcutaneous location.

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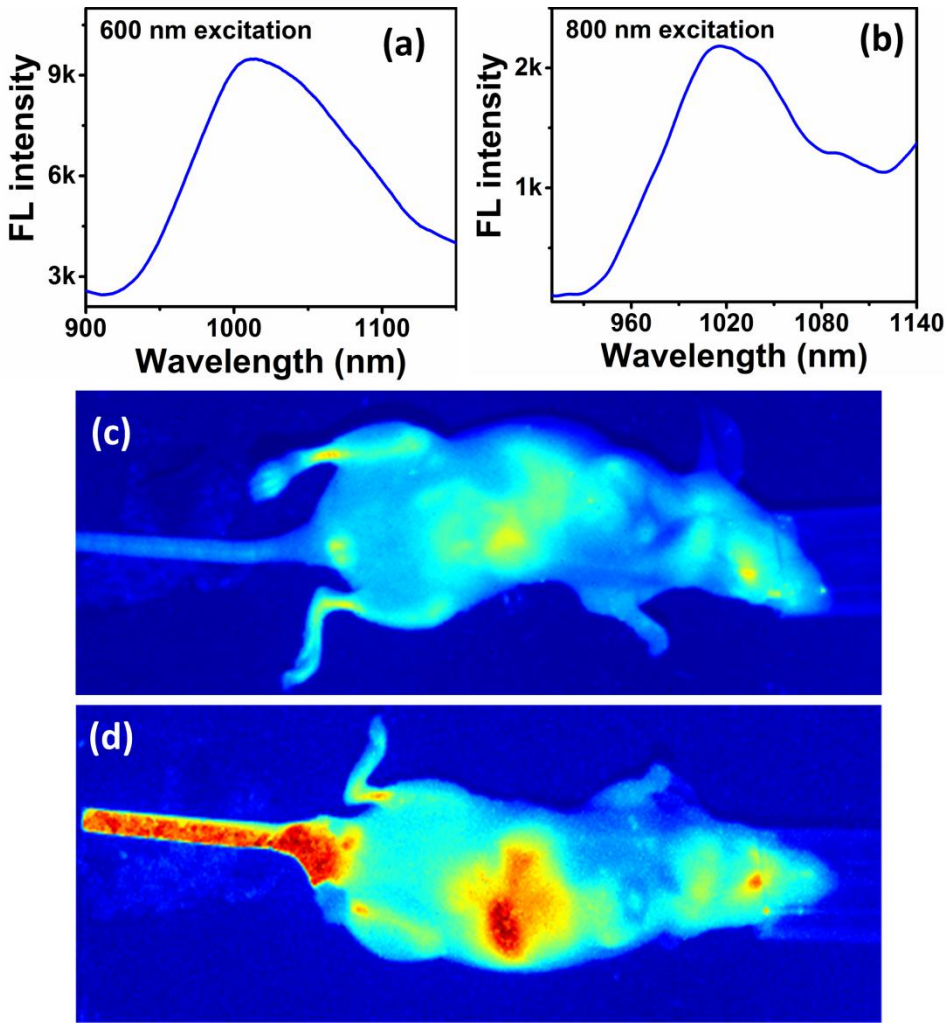

Supplementary Fig. 14 | (a) and (b) FL emission of the protonated CDs excited under 600 and 800 nm continuum light source; (c) and (d) NIR-II in vivo images of mice before and after vein injection.

Reference

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