

1 **Supplementary Information (SI)**

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

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7 ***Qing Zhang<sup>1,2\*</sup>, Ruoyu Wang<sup>1</sup>, Bowen Feng<sup>1</sup>, Xiaoxia Zhong<sup>1\*</sup>, Kostya (Ken) Ostrikov<sup>3</sup>***

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11 <sup>1</sup>State Key Laboratory of Advanced Optical Communication Systems and Networks, Key  
12 Laboratory for Laser Plasmas (Ministry of Education), School of Physics and Astronomy,  
13 Shanghai Jiao Tong University, Shanghai 200240, China.

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16 <sup>2</sup>Institute of Molecular Medicine, Renji Hospital, School of Medicine, Shanghai Jiao Tong  
17 University, Shanghai 200127, China.

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20 <sup>3</sup>School of Chemistry and Physics and QUT Centre for Materials Science, Queensland  
21 University of Technology (QUT), Brisbane QLD 4000, Australia.

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23 E-mail: qingzhang@sjtu.edu.cn; xxzhong@sjtu.edu.cn.

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39 **Table Caption:**

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

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

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44 **Figure Caption:**

45 **Supplementary Fig. 1** | Raman spectra of CDs

46 **Supplementary Fig. 2** | Zoomed  $^{13}\text{C}$ -NMR spectra of the CDs.

47 **Supplementary Fig. 3** | Zoomed  $^1\text{H}$ -NMR spectra of the CDs.

48 **Supplementary Fig. 4** |  $^{13}\text{C}$ -NMR spectra of 2,3-diaminophenazine (2,3-DAPN), Modified from  
49 “2,3-diaminophenazine is the product from the horseradish peroxidase-catalyzed oxidation of  
50 o-phenylenediamine” with permission from Elsevier.<sup>17</sup>

51 **Fig. 5** |  $^1\text{H}$ -NMR spectra of 2,3-DAPN, Modified from “2,3-diaminophenazine is the product from the  
52 horseradish peroxidase-catalyzed oxidation of o-phenylenediamine” with permission from Elsevier.<sup>17</sup>

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

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

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

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

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

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

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

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

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

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80 **Section 1: Supplementary Information of Tables.**

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

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

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

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

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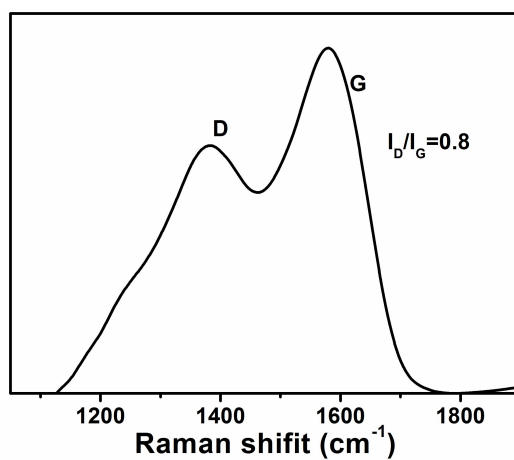
90 **Supplementary Table 3.** FL QYs of CDs, and 2,3-DAPN molecular.

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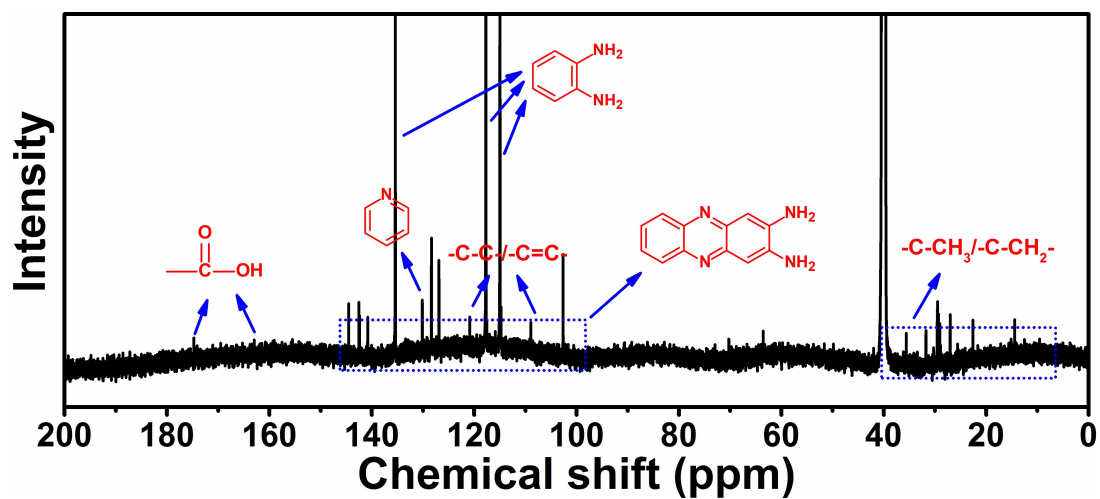
Reference	NIR Organic dye	QYs (%)
1	IR-1061 (Commercial dye)	1.7% <sup>9</sup>
2	LZ1105	1.6% <sup>10</sup>
2	IR-E1	0.7% <sup>11</sup>
3	IR-FTP	0.02% <sup>12</sup>
4	IR-FTTP	0.1% <sup>13</sup>
5	CH1055-PEG	0.3% <sup>14</sup>
6	CH-4T	1.1% <sup>15</sup>
7	SCH1100	0.2% <sup>16</sup>

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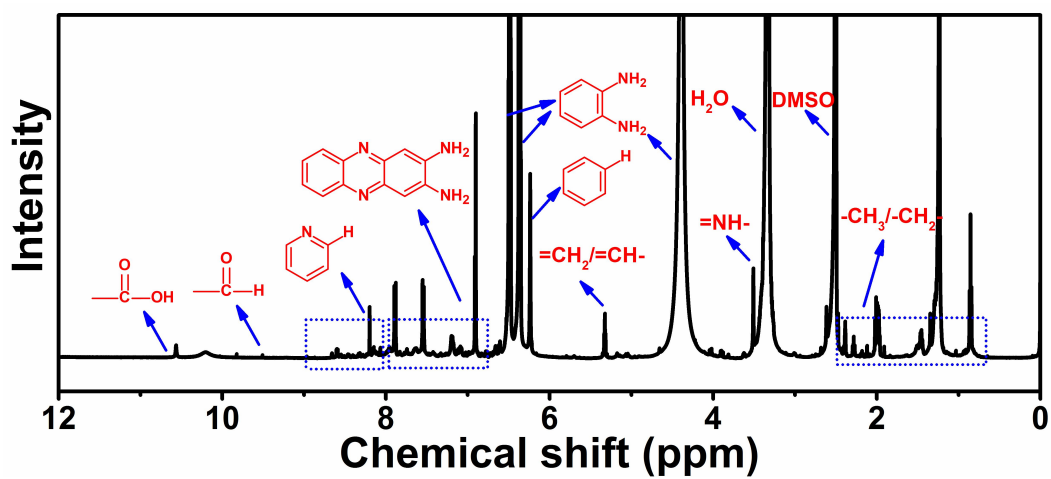


**Supplementary Fig. 1** Raman spectra of CDs.



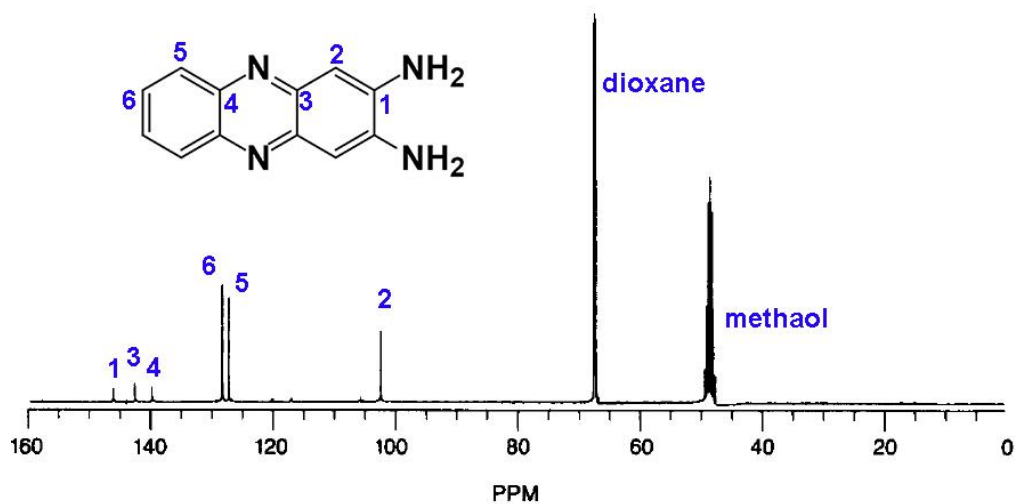
Supplementary Fig. 2 | Zoomed <sup>13</sup>C-NMR spectra of the CDs.

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Supplementary Fig. 3| Zoomed <sup>1</sup>H-NMR spectra of the CDs.

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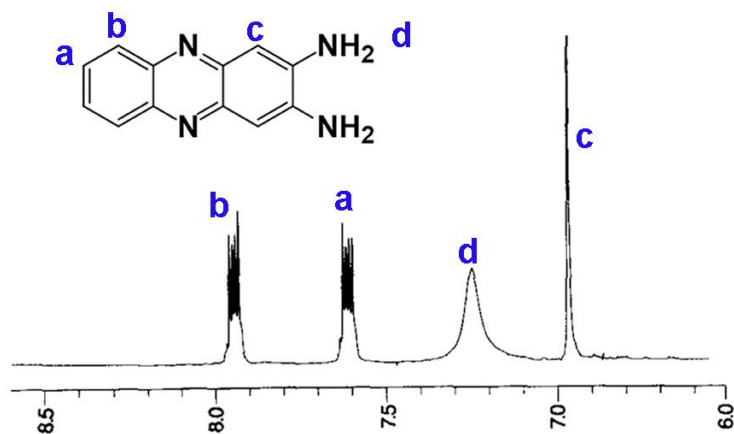


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**Supplementary Fig. 4** | <sup>13</sup>C-NMR spectra of 2,3-diaminophenazine (2,3-DAPN), Modified from “2,3-diaminophenazine is the product from the horseradish peroxidase-catalyzed oxidation of o-phenylenediamine” with permission from Elsevier <sup>17</sup>.

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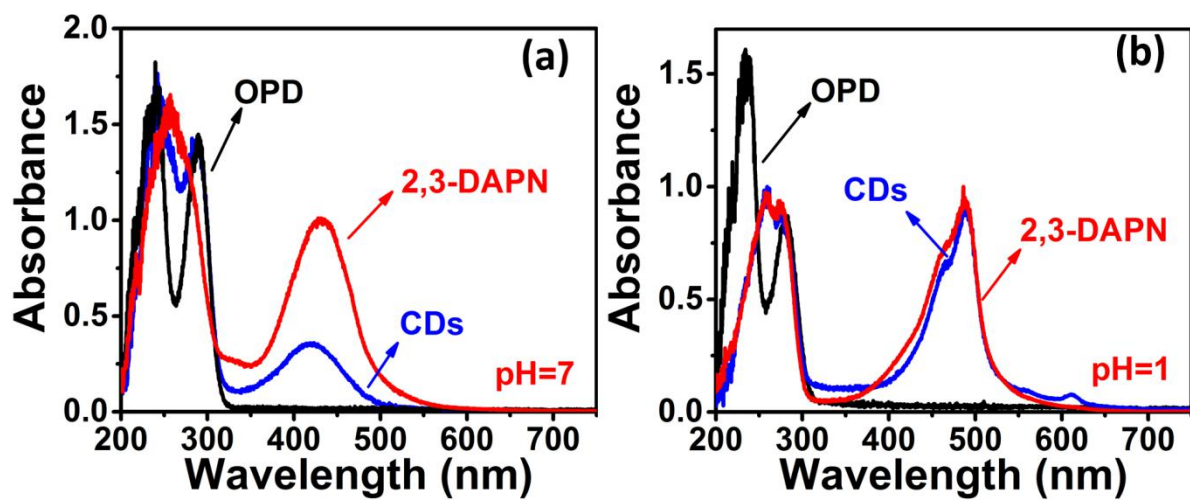
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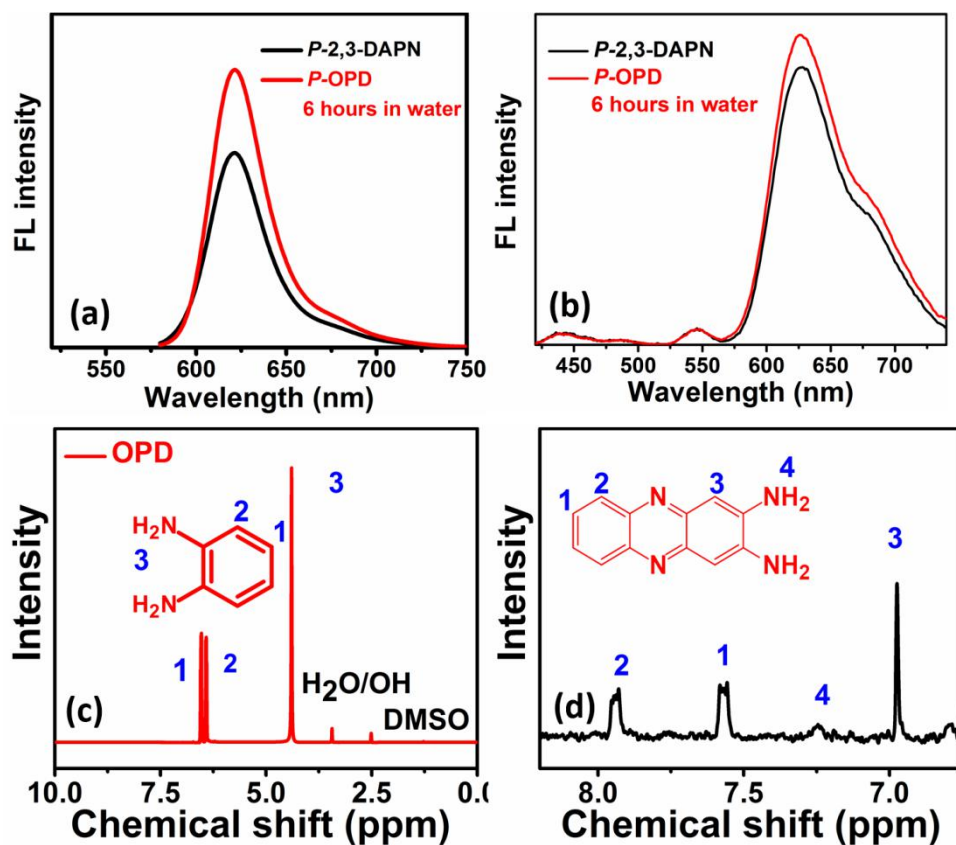




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243 **Supplementary Fig. 6** | (a)-(b) UV-vis absorption of OPD, 2,3-DAPN and CDs with or without  
244 protonation treatment.

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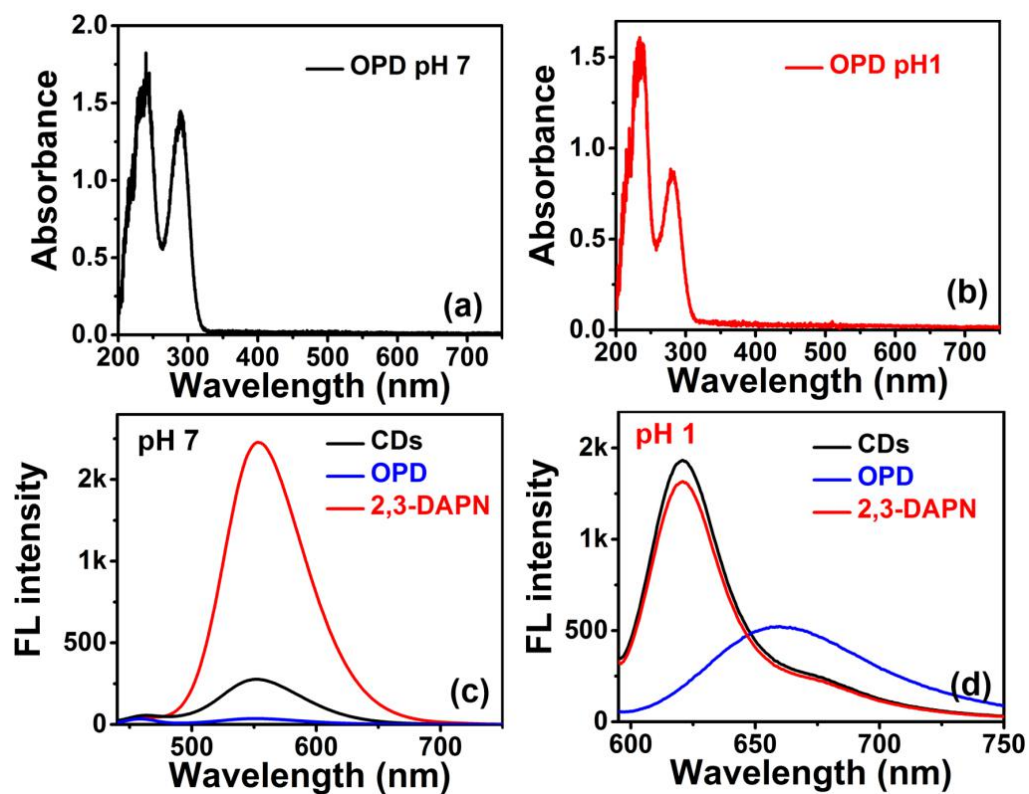
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275 **Supplementary Fig. 7** | (a), (b) FL spectra of the protonated OPD kept in deionized water for 6 hours  
 276 excited by 480 nm and 808 nm femtosecond laser. (c), (d) <sup>1</sup>H-NMR and magnified <sup>1</sup>H-NMR spectra of  
 277 the OPD 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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283 **Supplementary Fig. 8** | (a), (b) UV-vis absorption of OPD with or without protonation treatment; (c),  
284 (d) FL emission of CDs, OPD and 2,3-DAPN samples with or without protonation treatment the  
285 identical excitation conditions.

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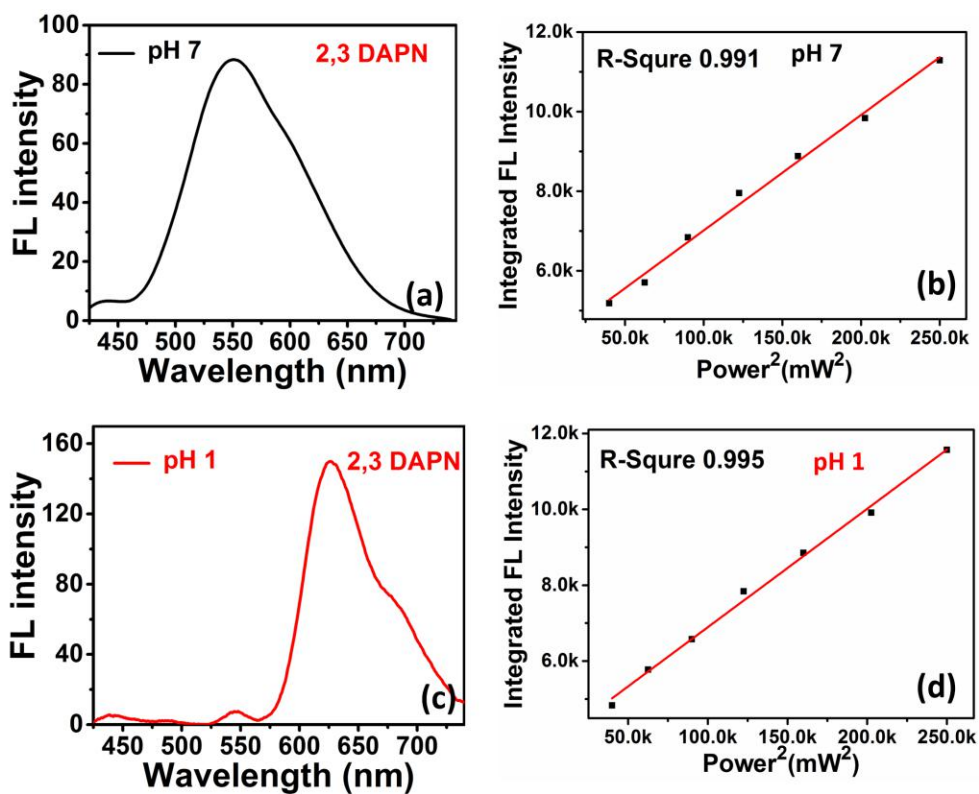
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307 **Supplementary Fig. 9** | (a), (c) Up-conversion FL spectra of 2,3-DAPN at pH7 and pH 1 under 808  
 308 nm femtosecond laser excitation. (b), (d) Relationship of FL intensity and femtosecond (fs) laser  
 309 power at pH 7 and pH 1.

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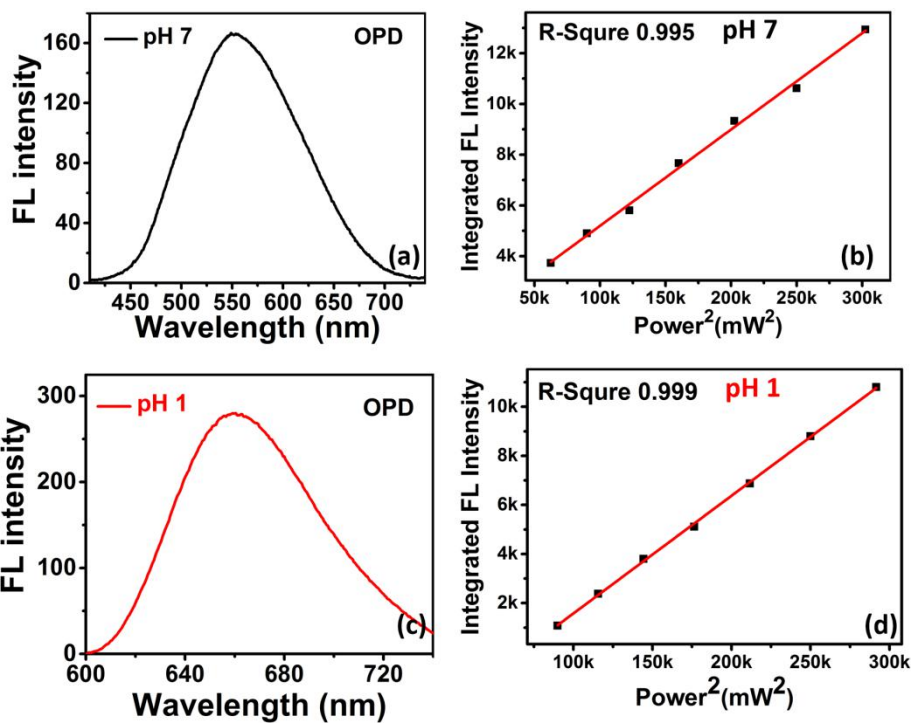
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324 **Supplementary Fig. 10** | (a), (c) Up-conversion FL spectra of OPD at pH7 and pH 1 under 808 nm  
 325 femtosecond (fs) laser excitation. (b), (d) Relationship of FL intensity and fs laser power at pH 7 and  
 326 pH 1.

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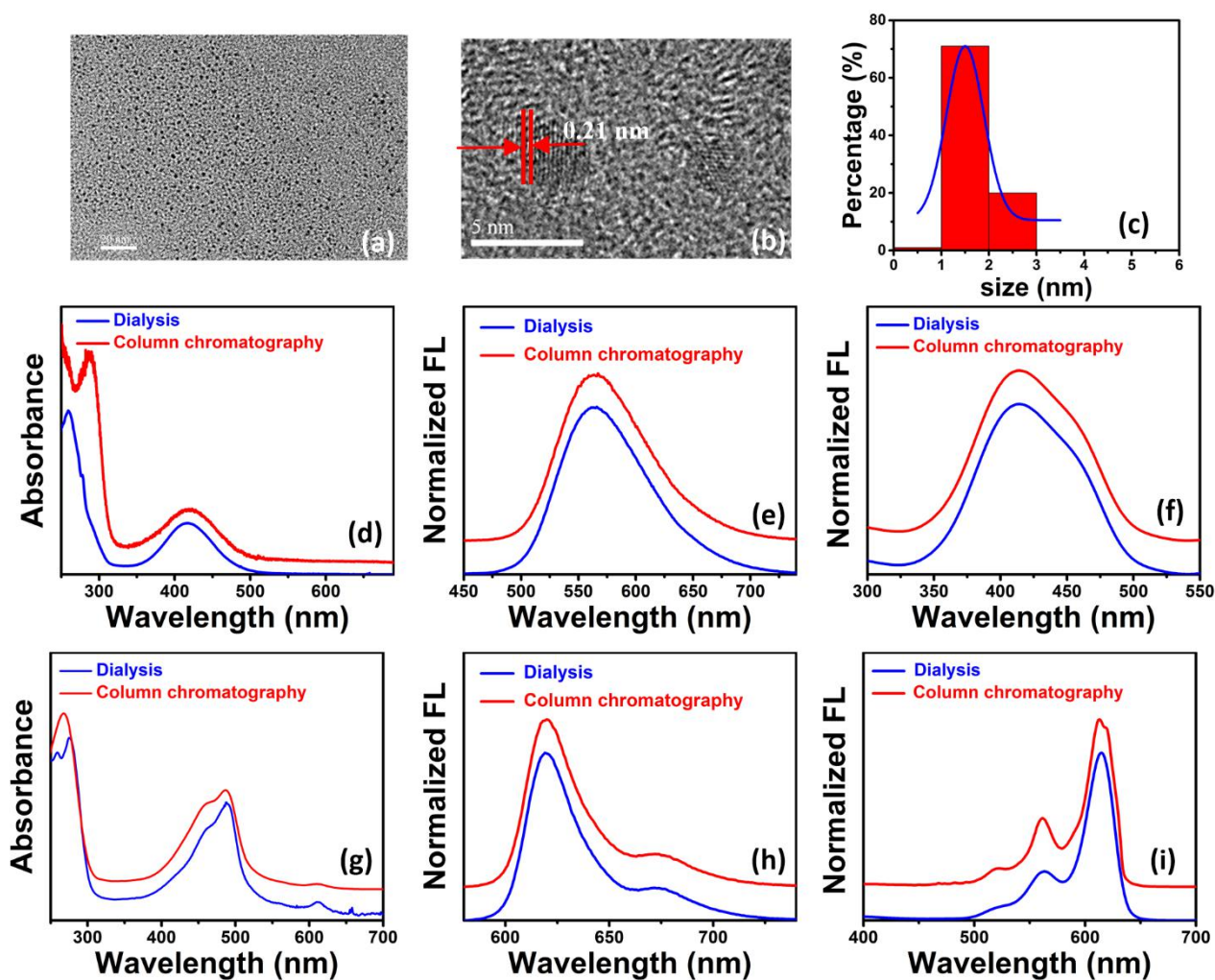
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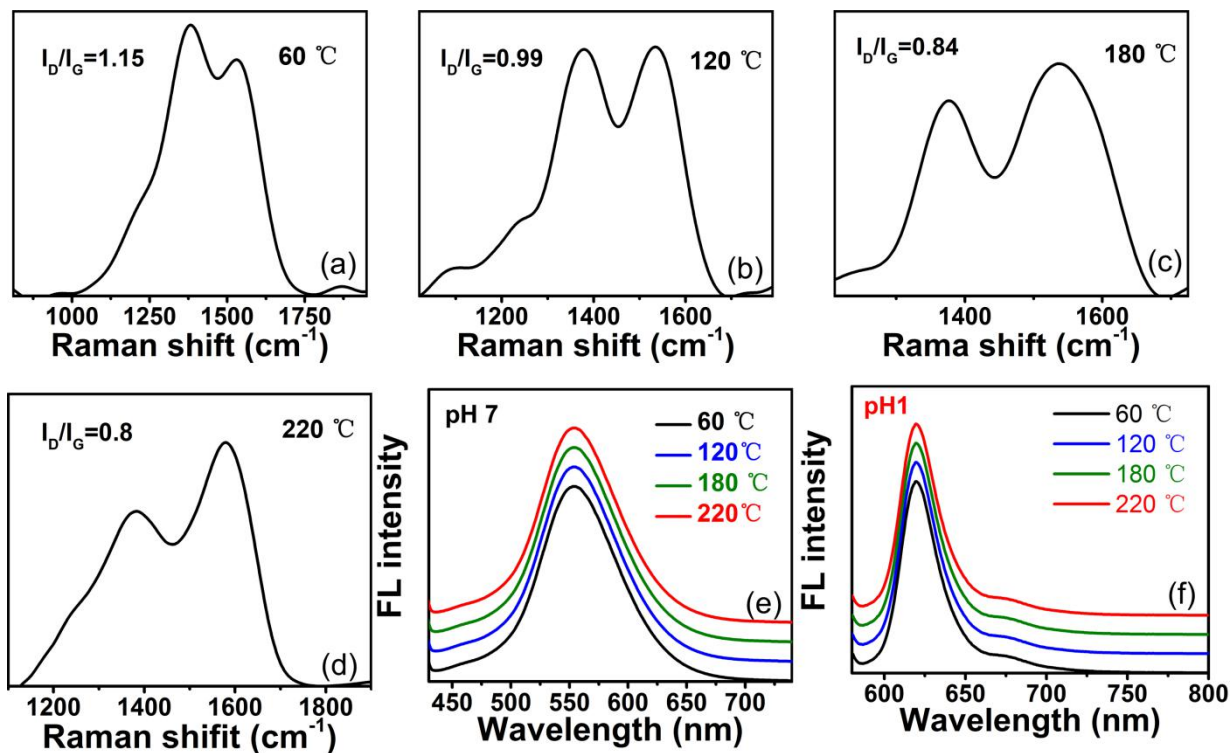
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**Supplementary Fig. 11** | (a), (b), and (c) Transmission electron microscopy imaging (TEM), high resolution image and size distribution of CDs; (d), (g) UV-vis absorption spectra of CDs with or without the protonation; (e), (h) FL spectra of CDs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



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

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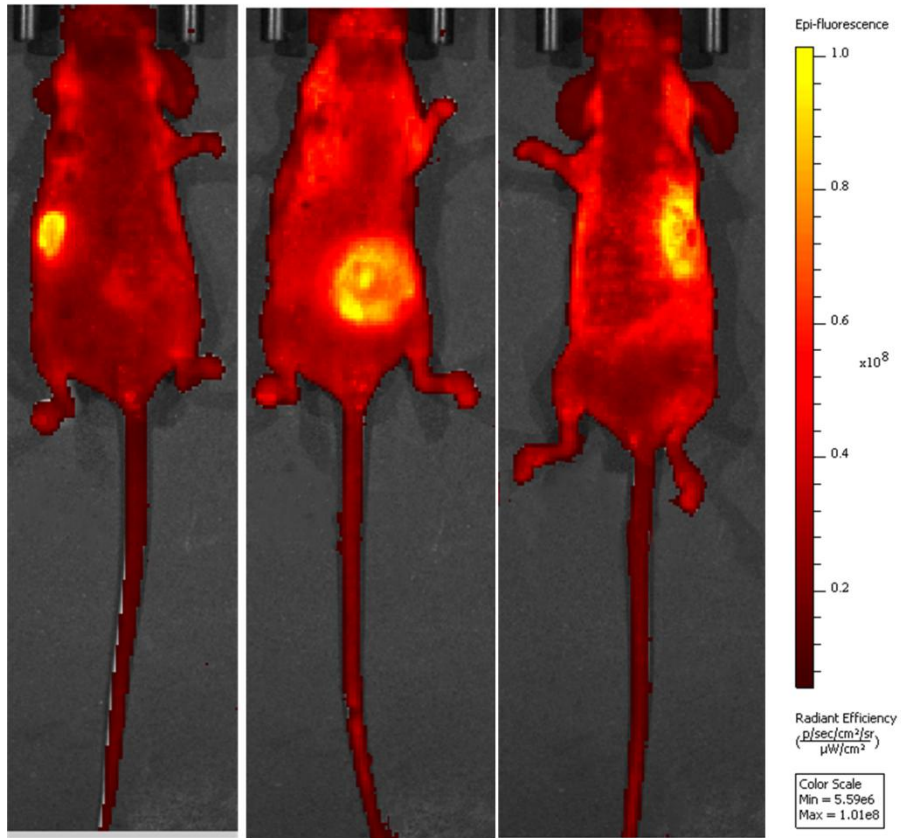
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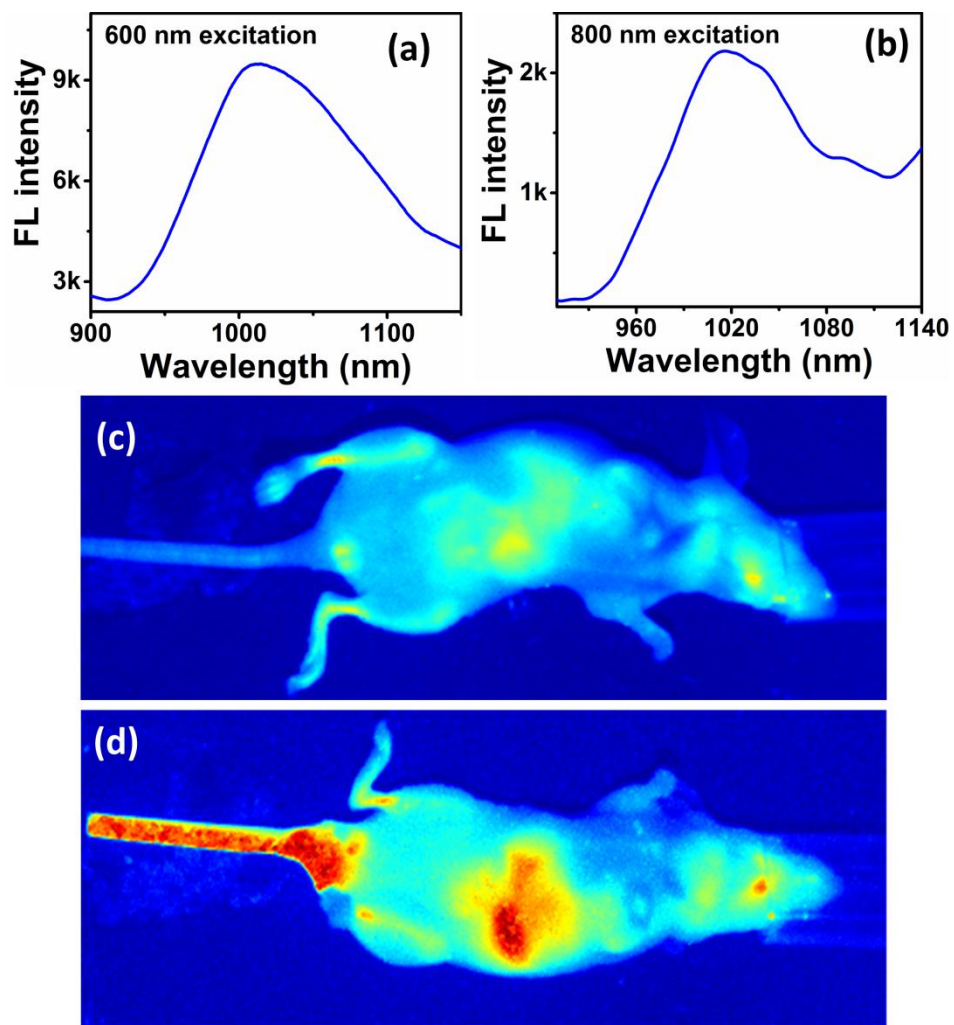
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372 **Supplementary Fig. 13** | In vivo fluorescence images of nude mice injected with different  
373 subcutaneous location.

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

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