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Supporting Information

Facile synthesis of nitrogen-doped carbon dots with robust fluorescence in strong alkali and reversible fluorescence 'off-on' switch between strong acid and alkali

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Experimental section

Materials

All used reagents were analytical-grade and used as received without further purification. Citric acid monohydrate (CA), ammonium hydroxide (25.0-28.0 wt%), hydrochloric acid (36-38 wt%), sodium hydroxide, sodium chloride, sodium sulfate anhydrous, magnesium chloride hexahydrate, sodium bicarbonate, potassium chloride, potassium phosphate dibasic, potassium chloride , calcium chloride anhydrous and sodium carbonate were purchased from Beijing Chemical Work (Beijing, china). Tris(hydroxymethyl)aminomethane was purchased from Aladdin Chemistry Co, Ltd. (Shanghai, China).

Characterization

UV-vis absorption spectra were recorded on a Shimadzu UV 3600 UV-VIS-NIR spectrophotometer. The fluorescence spectra were measure on a Hitachi F-7000 fluorescence spectrometer. FT-IR spectra were performed on a Bruker Tensor 27 FT-IR spectrometer in the range of 400-4000 cm^{-1}. Fluorescence lifetime was measured by using a steady state and time resolved fluorescence spectrometer (FLSP-920, Edinburgh Instruments).Transmission electron microscope (TEM) analyses were performed on a FEI TECnai G^2 F20 instrument. X-ray diffraction (XRD) pattern was performed on a Bruker D8 Focus powder diffractometer with Cu-Kα radiation.

Synthesis of fluorescent nitrogen doped-carbon dots

CA (1.054 g) and 1800 μL ammonium hydroxide were dissolved in 10 mL de-ionized water. Then the solution was transferred in 25 mL Teflon-lined autoclave and heated

at 200℃ for 6 hours. After reaction, the reactor was cooled to room temperature by water. The product was dialyzed (3500 Da) against de-ionized water.

Preparation of saturated sodium carbonate (Na_2CO_3) solution

The saturated Na_2CO_3 solution at 20℃ was prepared by dissolving 21.5 g Na_2CO_3 into 100 mL de-ionized water.

Preparation of simulated body fluid (SBF)

The SBF was prepared according to the literature.[1] Briefly, $CaCl_2$, $KH_2PO_4 \cdot 3H_2O$, KCl, NaCl, $MgCl \cdot 6H_2O$, $NaHCO_3$, and Na_2SO_4 were dissolved in de-ionized water and buffered at pH = 7.4 using tris(hydroxymethyl)aminomethane at 36.5℃.Chemical composition of SBF (1000 mL) were listed in Table S1.

Table S1. Chemical composition, amount and purity of the prepared 1000 mL SBF.

Reagents	Amount	Purity (%)
NaCl	8.035 g	99.5
$NaHCO_3$	0.355 g	99.5
KCl	0.255 g	99.5
$K_2HPO_4 \cdot 3H_2O$	0.231 g	99.0
$MgCl_2 \cdot 6H_2O$	0.311 g	98.0
1.0 M HCl	39 mL	-
$CaCl_2$	0.292 g	95.0
Na_2SO_4	0.072 g	99.0
TRIS	6.118 g	99.0
1.0 M HCl	0-5 mL	-

Quantum yield (QY) measurements

The QYs of the as-prepared N-CDs using different amounts of ammonium hydroxide were determined by a relative method by the reference of quinine sulfate (QY = 54% in 0.1 M H_2SO_4). The QY of the as-prepared N-CDs was calculated according to the following equation:[2]

$$\phi_{CDs} = \phi_{\mathrm{Re}\,f} \times \frac{A_{ref}}{I_{ref}} \times \frac{I_{CDs}}{A_{CDs}} \times \frac{\eta_{CDs}^2}{\eta_{\mathrm{Re}\,f}^2}$$

Where Φ is the QY of testing sample, A is the optical absorbance, I is the integrated fluorescence intensity and η is the refractive index. The subscript 'CDs' refers to the testing samples and 'Ref' refers to the referenced quinine sulfate. To minimize the reabsorption effects, the optical absorbance values were kept under 0.1 under 340 and 350 nm excitation.

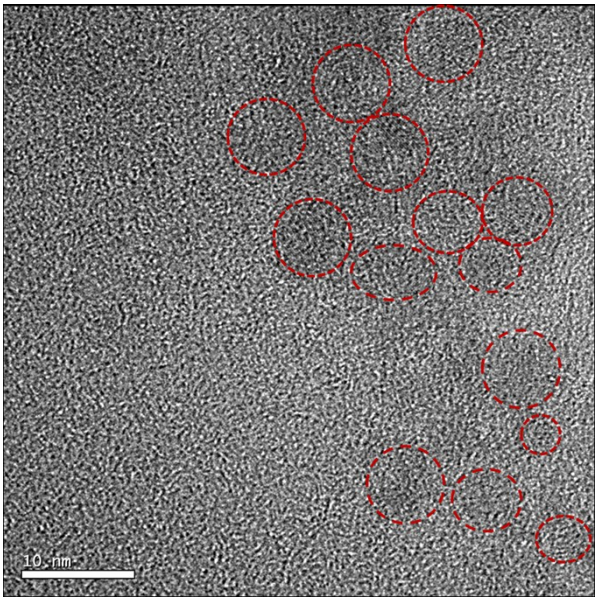


Fig. S1 HR-TEM image of N-CDs.

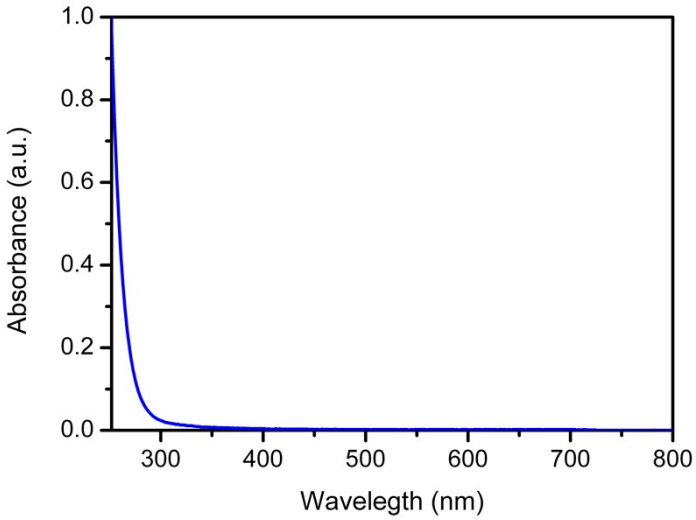


Fig. S2 Absorption spectra of citric acid under the hydrothermal treatment at 200℃ for 6 h.

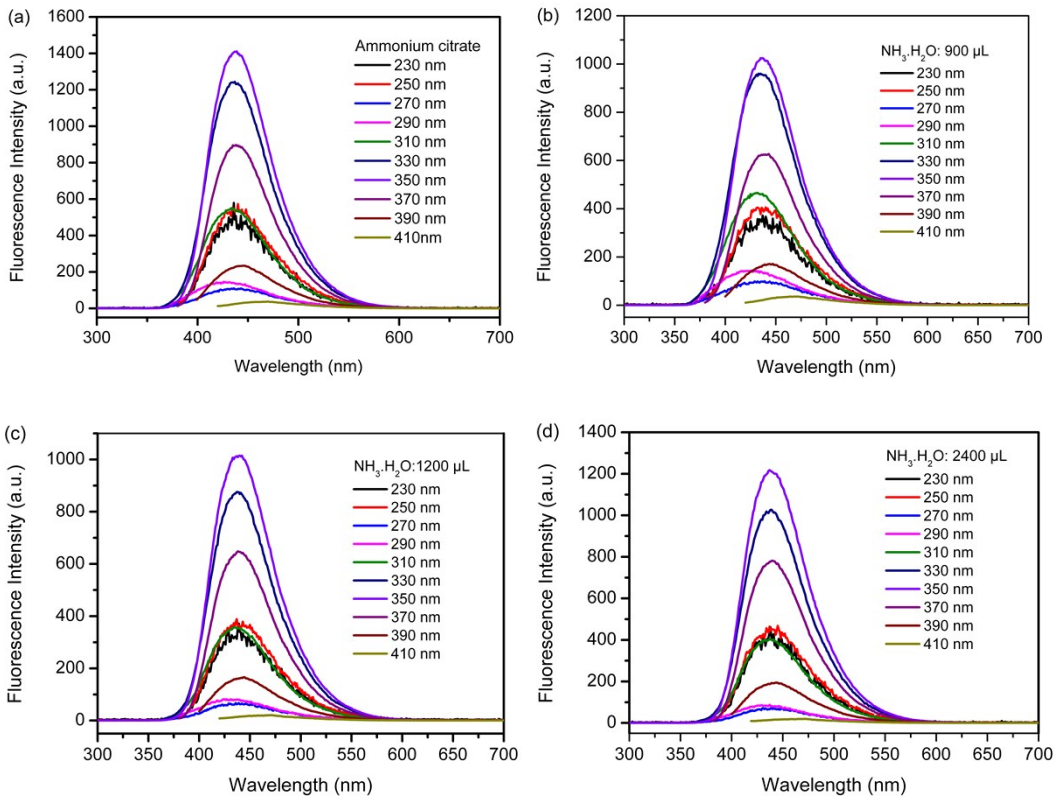
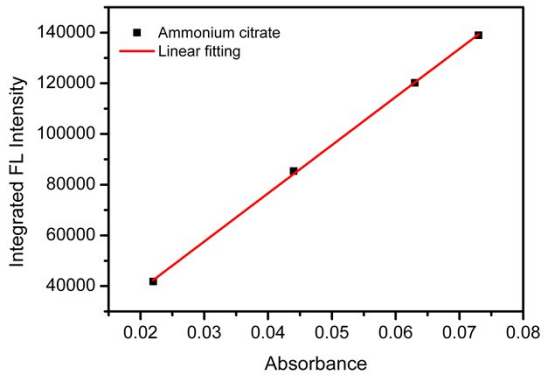


Fig. S3 Fluorescence spectra of the as-prepared N-CDs in water using different amounts of ammonium hydroxide under the excitation wavelengths from 230 to 410 nm with 20 nm increment.



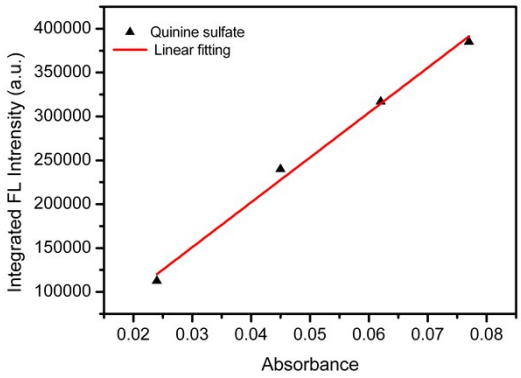


Fig. S4 Integrated fluorescence intensity of N-CDs prepared from ammonium citrate (λ_{ex} = 340 nm) as a function of absorbance values.

Table S2. QY of N-CDs prepared by using ammonium citrate.

	Abs-1	Abs-2	Abs-3	Abs-4	Integrated FL-1	Integrated FL-2	Integrated FL-3	Integrated FL-4	Slope (10^6)	QY
N-CDs	0.022	0.044	0.063	0.073	41788	85372	120163	138985	1.90	0.200
Quinine sulfate	0.024	0.045	0.062	0.077	112312	239748	316835	384866	5.11	0.54

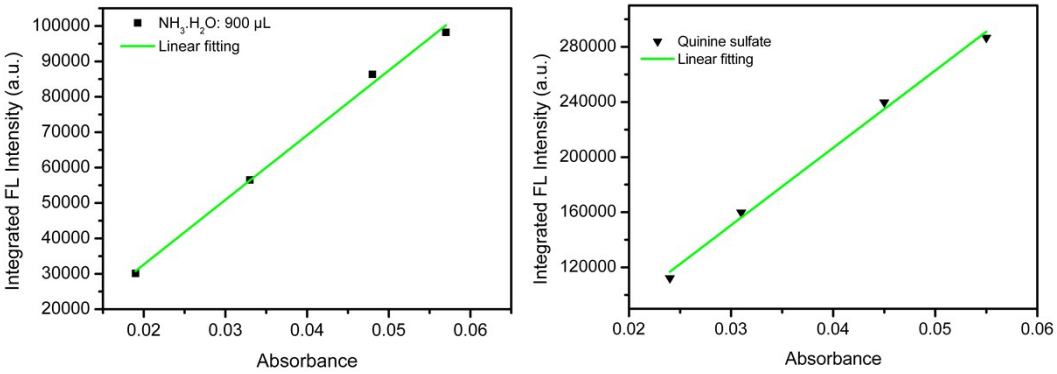


Fig. S5 Integrated fluorescence intensity of N-CDs prepared from 900 µL ammonium hydroxide (λ_{ex} = 340 nm) as a function of absorbance values.

Table S3. QY of N-CDs prepared by using 900 µL ammonium hydroxide.

	Abs-1	Abs-2	Abs-3	Abs-4	Integrated FL-1	Integrated FL-2	Integrated FL-3	Integrated FL-4	Slope (10^6)	QY
N-CDs	0.019	0.033	0.048	0.057	30138	56494	86333	98211	1.82	0.175
Quinine sulfate	0.024	0.031	0.045	0.055	112312	159920	239748	286719	5.61	0.54

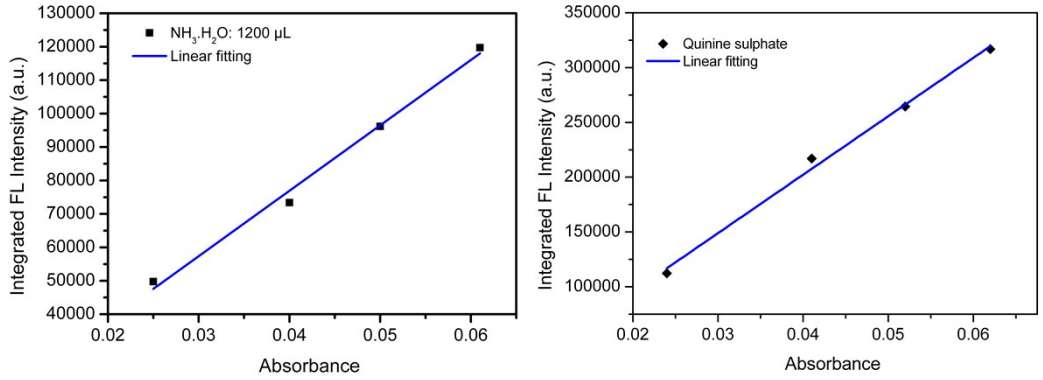


Fig. S6 Integrated fluorescence intensity of N-CDs prepared from 1200 µL ammonium hydroxide (λ_{ex} = 340 nm) as a function of absorbance values.

Table S4. QY of N-CDs prepared by using 1200 µL ammonium hydroxide.

	Abs-1	Abs-2	Abs-3	Abs-4	Integrated FL-1	Integrated FL-2	Integrated FL-3	Integrated FL-4	Slope (10^6)	QY
N-CDs	0.025	0.040	0.050	0.061	49764	73379	96162	119713	1.95	0.197
Quinine	0.024	0.041	0.052	0.062	112312	216955	264464	316835	5.33	0.54

sulfate

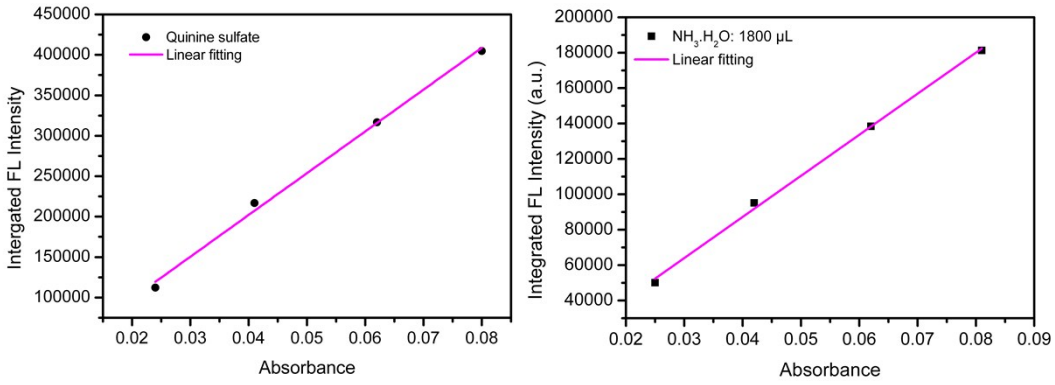


Fig. S7 Integrated fluorescence intensity of N-CDs prepared from 1800 µL ammonium hydroxide (λ_{ex} = 350 nm) as a function of absorbance values.

Table S5. QY of N-CDs prepared by using 1800 µL ammonium hydroxide.

	Abs-1	Abs-2	Abs-3	Abs-4	Integrated FL-1	Integrated FL-2	Integrated FL-3	Integrated FL-4	Slope (10^6)	QY
N-CDs	0.025	0.042	0.062	0.081	50115	95133	138389	181308	2.32	0.242

Quinine sulfate	0.024	0.041	0.062	0.08	112312	216955	316835	404955	5.16	0.54

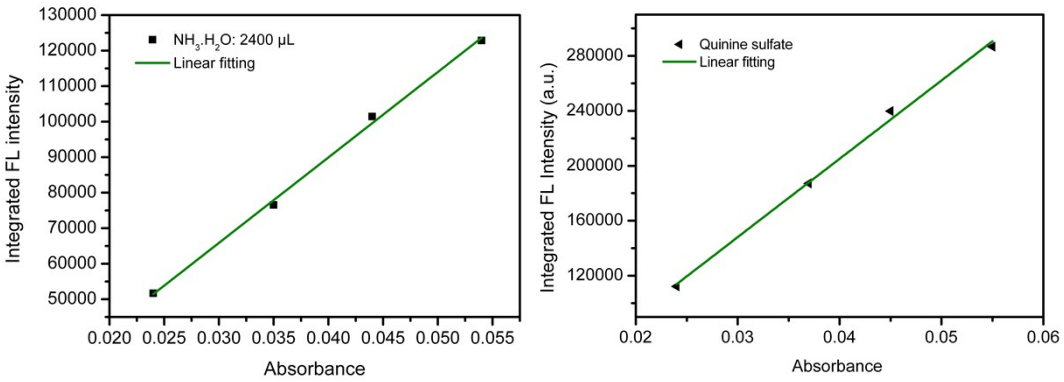


Fig. S8 Integrated fluorescence intensity of N-CDs prepared from 2400 µL ammonium hydroxide (λ_{ex} = 350 nm) as a function of absorbance values.

Table S6. QY of N-CDs prepared by using 2400 µL ammonium hydroxide.

	Abs-1	Abs-2	Abs-3	Abs-4	Integrated FL-1	Integrated FL-2	Integrated FL-3	Integrated FL-4	Slope (10^6)	QY
N-CDs	0.024	0.035	0.044	0.054	51675	76514	101432	122859	2.40	0.227

Quinine sulfate	0.024	0.037	0.045	0.055	112312	187198	239748	286719	5.70	0.54

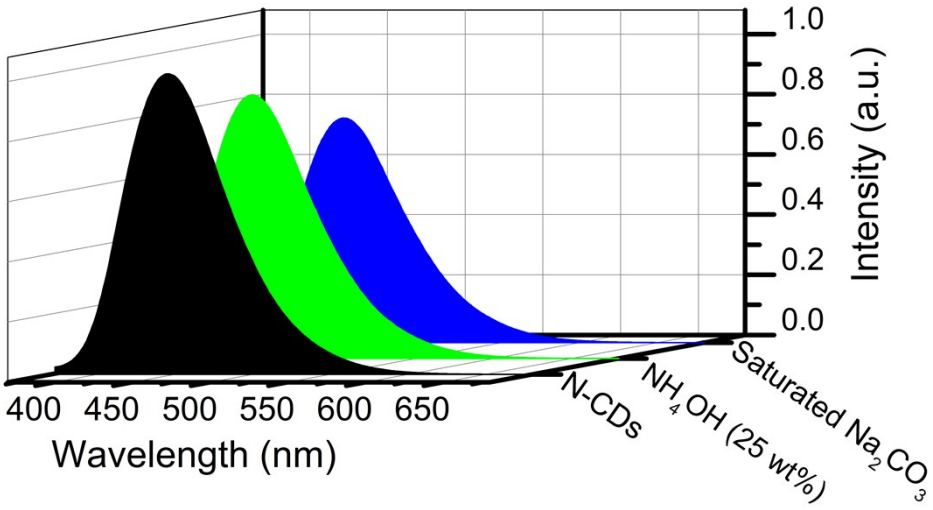


Fig. S9 3D fluorescence spectra of N-CDs in saturated Na_2CO_3 (20℃) and concentrated NH_4OH (25 wt %) solutions.

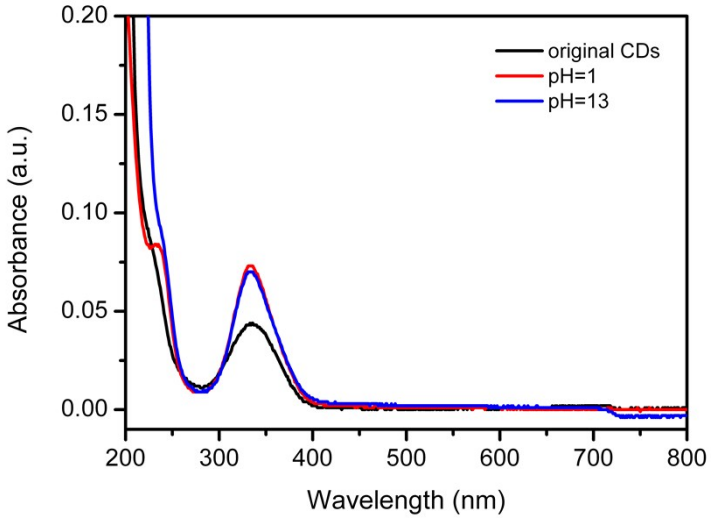


Fig. S10 Absorption spectra of N-CDs aqueous at pH=1 and 13.

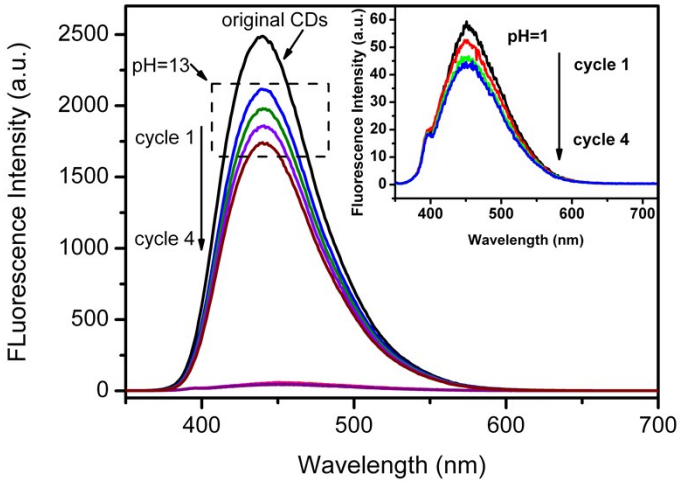


Fig. S11 The reversible and repeatable fluorescence spectra of N-CDs when modulating pH between 1 and 13.

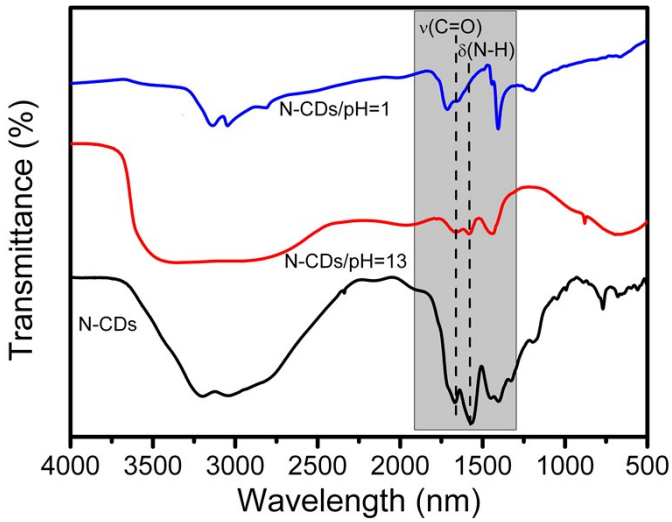


Fig. S12 Comparison of FT-IR spectra of the N-CDs with those at pH =1 and 13.

Table S7 Fluorescence lifetimes of the N-CDs alone and the N-CDs in pH=13 and 1 solutions.

Sample	τ_1 (ns)	Percentage	τ_2 (ns)	Percentage	τ_3 (ns)	Percentage	Averaged lifetime (ns)
N-CDs	6.33	60.24%	10.52	39.76%	-	-	7.99
N-CDs/pH=13	6.44	87.33%	9.78	12.67%	-	-	6.86
N-CDs/pH=1	0.69	11.58%	3.47	50.83%	9.40	37.59%	5.37

References:

1 A. Oyane, H. M. Kim, T. Furuya, T. Kokubo, T. Miyazaki and T. Nakamura, *J Biomedical Mater. Res. A,* 2003, **65**, 188.

2 M. Grabolle, M. Spieles, V. Lesnyak, N.Gaponik, A. Eychmüller and U. Resch-Genger, *Anal. Chem.* 2009, **81**, 6285.