*Supporting information for*

# Uncovering the p$K_a$ dependent fluorescence quenching of carbon dots by chlorophenols

Yu Zhang, Yu Wang, Yafeng Guan and Liang Feng*†

† Key Laboratory of Separation Science for Analytical Chemistry, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, Liaoning 116023, P. R. China

Corresponding Author:

Liang Feng

E-mail: fengl@dicp.ac.cn

# ***Contents***

## 1. Determination of the experimental concentration of NSCDs

With the aim of setting the most suitable concentration of NSCDs in the whole experiments, the fluorescent intensities of various levels of NSCDs were recorded. As shown in Figure S2 (Supporting information, SI), the fluorescent intensity increases first, reaches maximum at 0.23 mg/mL, and goes down as the concentration of NSCDs rises. This phenomenon testifies the occurrence of collisional quenching behavior in the high concentration of CDs solution. Since the concentration of NSCDs below 0.02 mg/mL correlates well with fluorescent intensity (Figure S2 inset), 0.02 mg/mL is selected as the suitable experimental concentration.

## 2. Materials

Thiomalic acid (TMA, purity > 98%) and ethanolamine (EOA, purity > 99%) were obtained from Aladdin Industrial Corporation (Shanghai, China). DL-malic acid (MA, purity > 99.5%) and sodium chloride (NaCl, purity > 99.5%) were supplied by Tianjin Bodi Chemical co., Ltd (China). Ethylene glycol (EG, purity > 99%), sodium hydroxide (NaOH, purity > 96%) and hydrochloric acid (HCl, wt. 36-38%) were purchased from Sinopharm Chemical Reagent co., Ltd (Shanghai, China). 2-Chlorophenol (2-CP, purity > 99.5%), 3-chlorophenol (3-CP, purity > 98%), 4-chlorophenol (4-CP, purity > 99%), 2,4-dichlorophenol (2,4-DCP, purity > 99.5%), 3,5-dichlorophenol (3,5-DCP, purity > 98%), 2,6-dichlorophenol (2,6-DCP, purity > 99%), 2,4,6-trichlorophenol (2,4,6-TCP, purity > 98%), pentachlorophenol (2,4,6-TCP, analytical standard), 2-chlorotoluene (2-CT, purity > 99.5%), 1,2-dichlorobenzene (1,2-DCB, purity > 98%), 1,3,5-trichlorobenzene (1,3,5-TCB, purity > 99%) and 2-chlorobenzonic acid (2-CBA, purity > 98%) were all obtained from Aladdin Industrial Corporation (Shanghai, China). Analytically pure phenol was purchased from Tianjin Kermel Chemical Reagent co., Ltd (China). All chemicals were used as received. And ultra-purified water was used throughout the work.

## 3. Measurement of quantum yield (QY)

For calculations of QY, four concentrations of synthesized NSCDs, CDs, NCDs, and SCDs were prepared and their UV absorbance was controlled to less than 0.1 at respective maximum excitation wavelength and 320 nm as well to minimize the re-absorption effect. The integrated fluorescent intensity of each determinant was recorded at the same excitation wavelengths as corresponding UV absorbance. Quinine sulfate in 0.1 mol/L of $H_2SO_4$ was taking as a standard of which quantum yield is 54 %. The quantum yield was calculated using the following equation:

$$\Phi_X = \Phi_{st}\left(\frac{Grad_X}{Grad_{st}}\right)\left(\frac{\eta_X^2}{\eta_{st}^2}\right)$$

where the subscripts st and X denote standard group and test group, respectively; $\Phi$ is the fluorescence quantum yield; Grad is the gradient from the plot of integrated fluorescent intensity versus absorbance; and $\eta$ is the refractive index of the solvent (the values of both 0.1 mol/L of $H_2SO_4$ and pure water are 1.33).

## 4. Supporting figures and tables

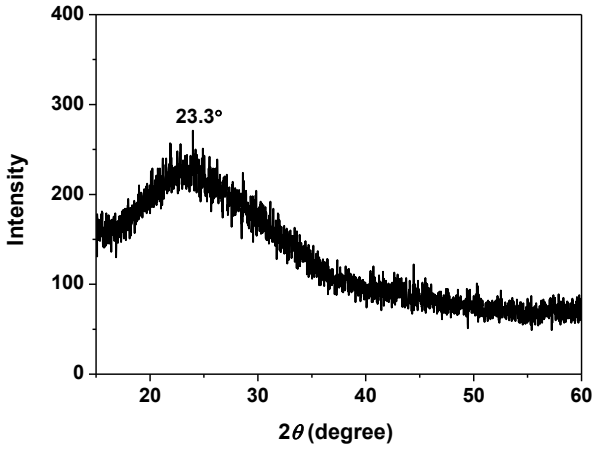



*Figure S1*. XRD pattern of NSCDs.

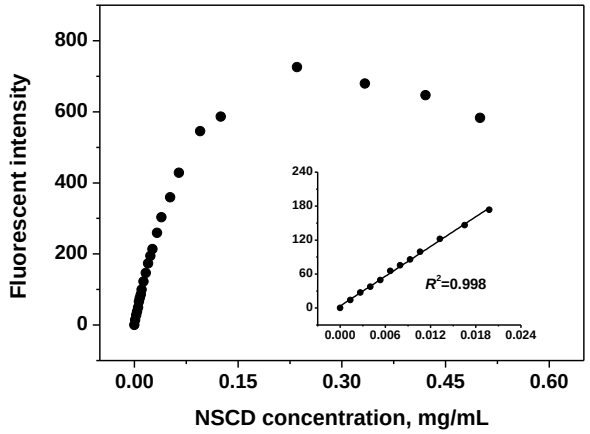



***Figure S2***. Concentration dependent fluorescent intensity of NSCDs. Inset: linear relationship of certain concentration of NSCDs (below 0.02 mg/mL) and their fluorescent intensity.

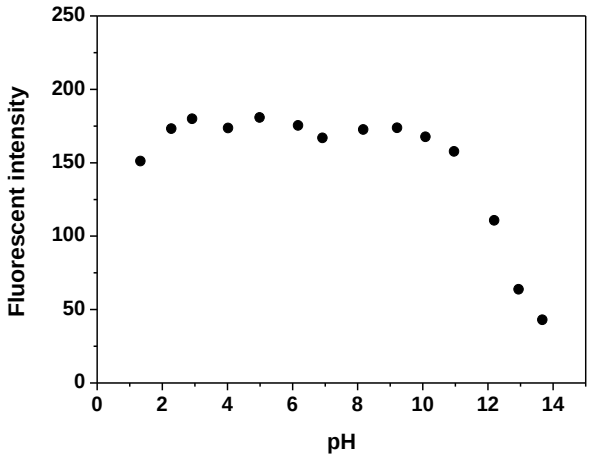



***Figure S3***. pH effect on fluorescence of NSCDs at 0.02 mg/mL.

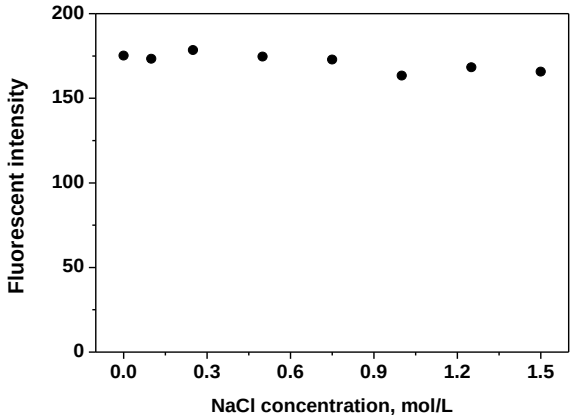



***Figure S4***. Salinity effect on fluorescence of NSCDs at 0.02 mg/mL.

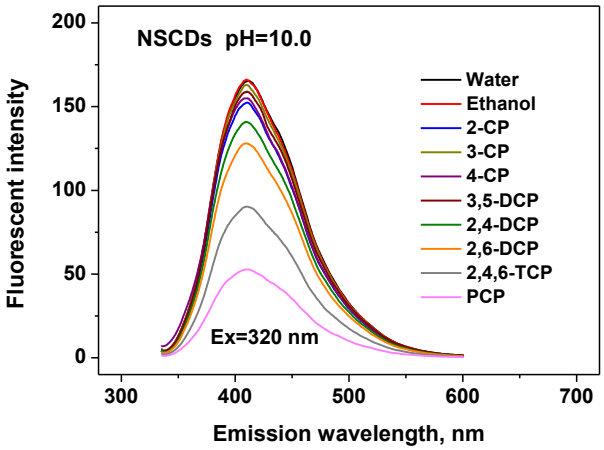



***Figure S5***. CPs induced fluorescence quenching of NSCDs (0.02 mg/mL, 3 mL) at pH 10.0. The concentrations of CPs were finally set as $1\times10^{-4}$ mol/L. Water and ethanol were added in the same volume (30.4 μL) as CPs to exclude the dilution and solvent effect.

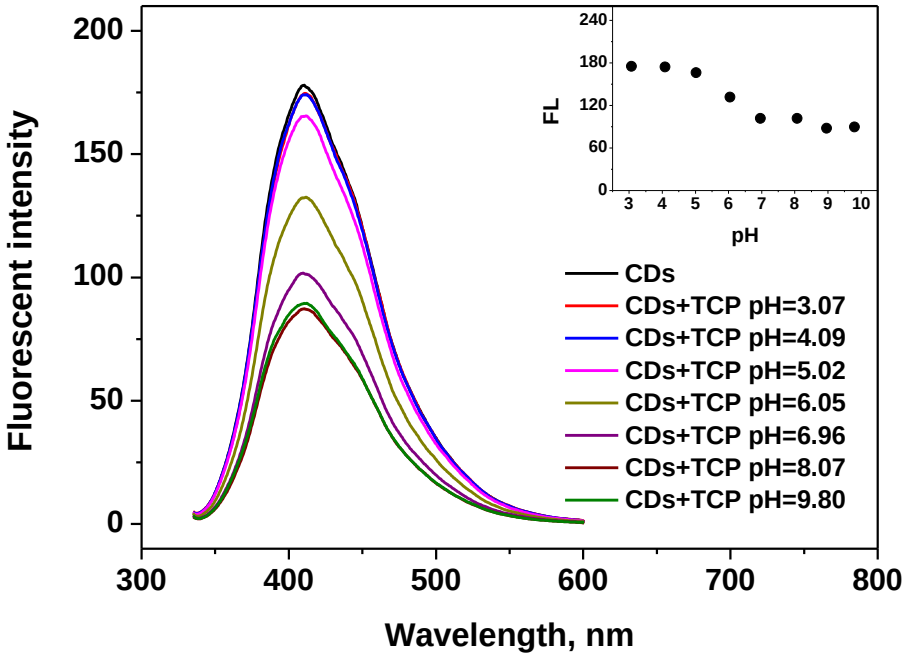
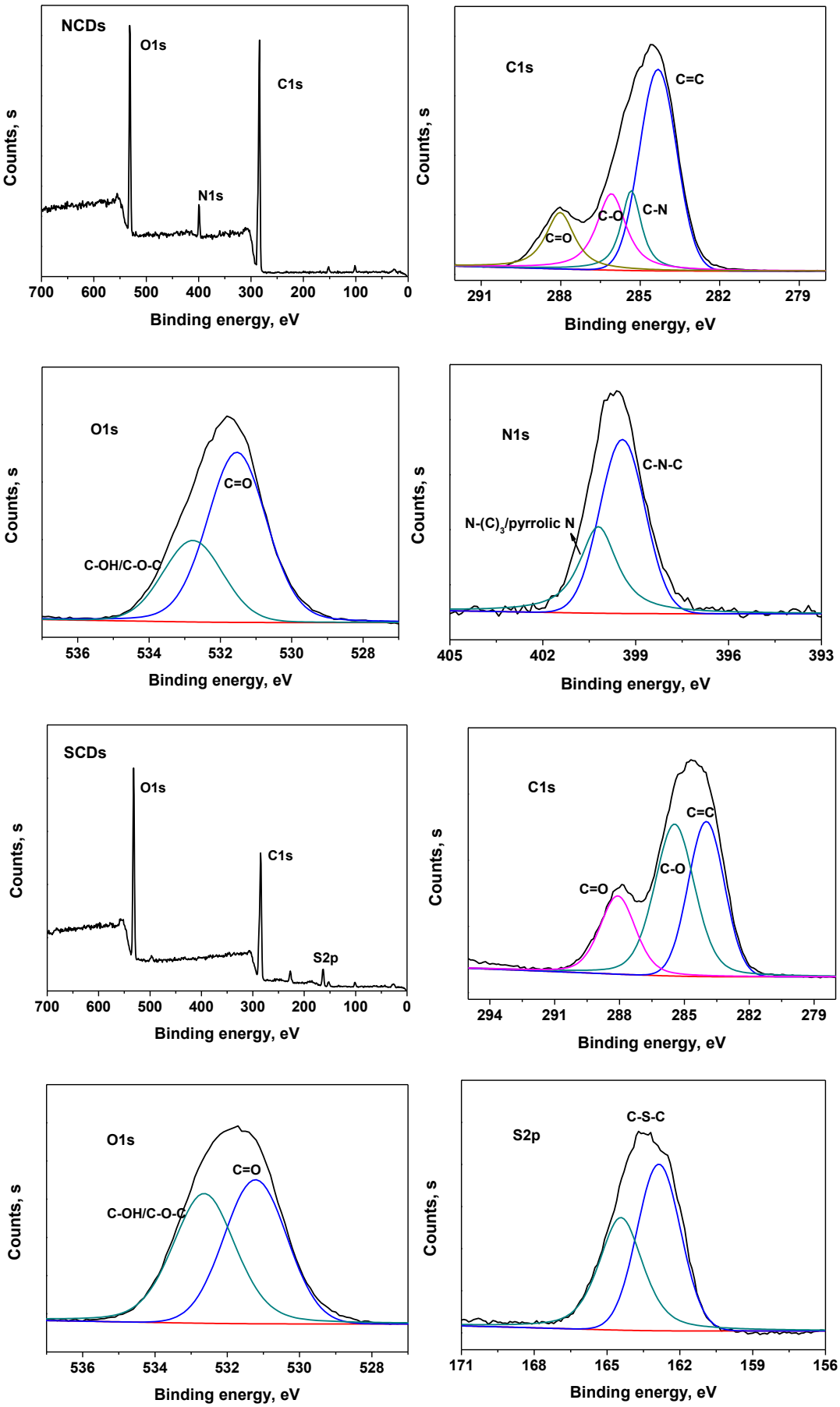



***Figure S6***. 2,4,6-TCP induced fluorescence quenching of NSCDs (0.02 mg/mL, 3 mL) at various pH conditions. Inset: fluorescence quenching tendency of NSCDs by 2,4,6-TCP as pH rises. Fluorescent intensity data were recorded at emission wavelength of 410 nm.


NCDs
O1s
C1s
N1s
Counts, s
Binding energy, eV
C1s
C=C
C-O
C-N
C=O
O1s
C=O
C-OH/C-O-C
N1s
C-N-C
N-(C)3/pyrrolic N
SCDs
S2p
C-S-C

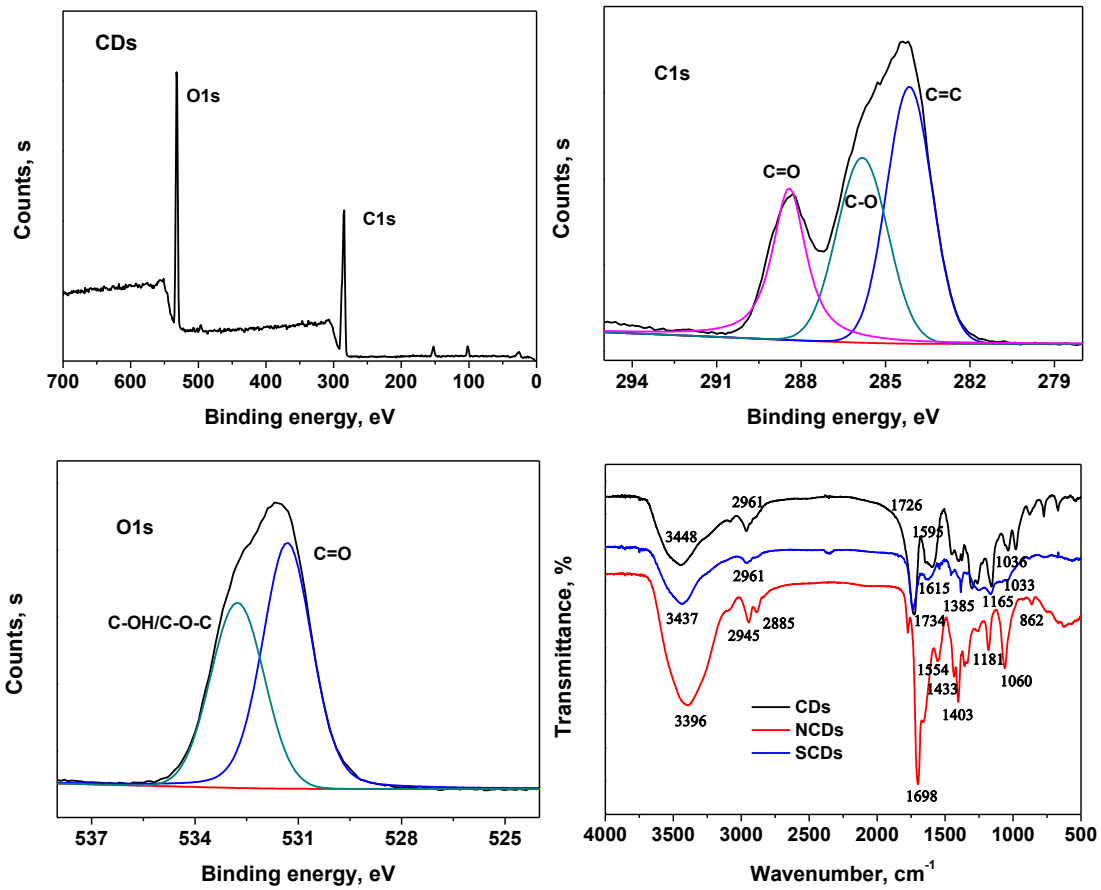



***Figure S7***. Structural characterizations of NCDs, SCDs and bare CDs by XPS and FTIR. Relative interpretations of these characterizations were listed in Tables S2 and S3.

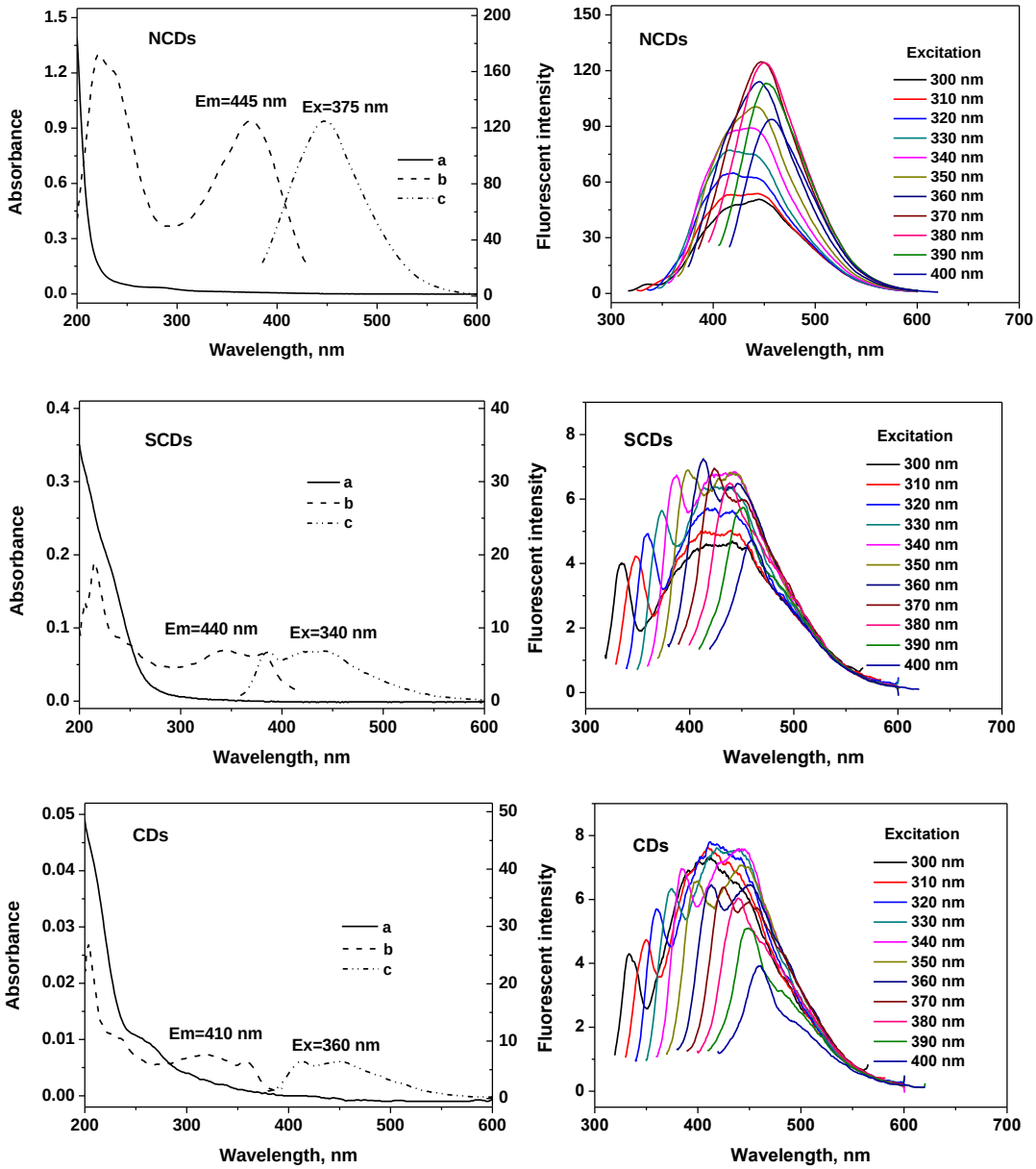



***Figure S8***. Optical properties of NCDs, SCDs and CDs (0.02 mg/mL).

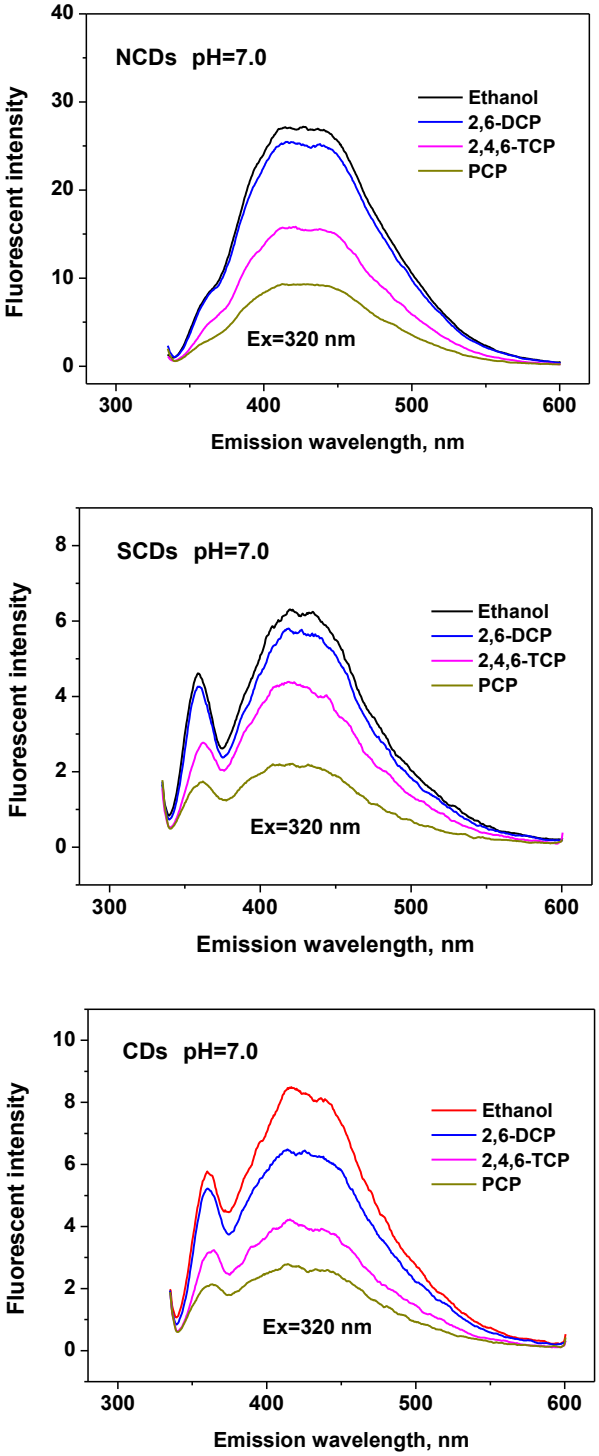



***Figure S9***. Fluorescence quenching of three synthesized CDs (0.02 mg/mL) induced by CPs at pH 7.0. The emission spectra were all monitored at excitation wavelength of 320 nm.

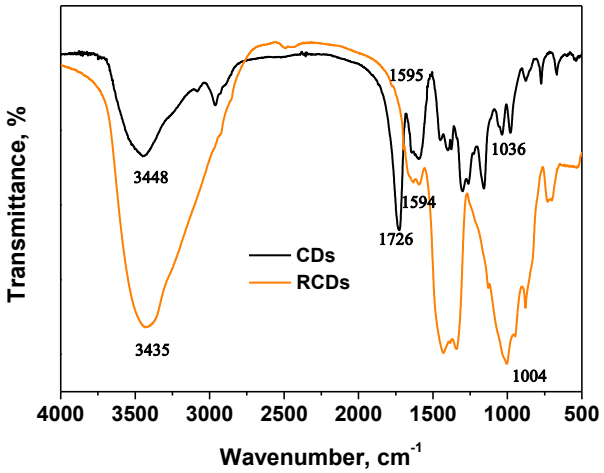



***Figure S10***. FTIR spectra of bare CDs and RCDs. The vibrational absorption band of C=O at 1726 $cm^{-1}$ disappears, and that of –OH at 3448 $cm^{-1}$ shifts to 3435 $cm^{-1}$ and becomes extremely strong upon the reduction of the CDs, which indicates that the surface carbonyl groups of the CDs were reduced to –OH groups. Moreover, the stretching peak of C=C at 1595 $cm^{-1}$ remains unchanged. These results are in accord with previous reports.

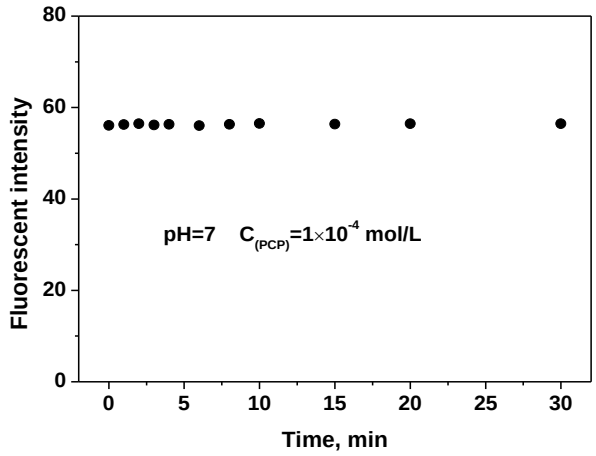



***Figure S11***. Quenching dynamic study of NSCDs (0.02 mg/L) with the addition of $1 \times 10^{-4}$ mol/L of PCP at pH 7.0. As seen, the fluorescent intensity kept unchanged as time went by, indicating interaction between NSCDs and PCP was quickly completed.

***Table S1***. Fluorescence quenching degree of NSCDs at various excitation wavelengths after treated with PCP.

| | 310 nm | 320 nm | 330 nm | 340 nm | 350 nm |
|---|---|---|---|---|---|
| NSCDs | 143.98 | 176.62 | 204.56 | 196.72 | 152.04 |
| NSCDs + PCP-1 | 139.71 | 166.82 | 186.91 | 185.77 | 149.48 |
| FL quenching degree-1 | 4.27 | 9.80 | 17.65 | 10.95 | 2.56 |
| NSCDs + PCP-2 | 99.52 | 124.22 | 153.81 | 167.54 | 142.26 |
| FL quenching degree-2 | 44.46 | 52.40 | 50.75 | 29.18 | 9.78 |

[a] -1 and -2 represent respectively the concentrations of PCP are $1 \times 10^{-5}$ and $6.6 \times 10^{-5}$ mol/L

***Table S2***. XPS results of NCDs, SCDs and bare CDs.

| | | Full scan | | High resolution scan | |
|---|---|---|---|---|---|
| | | Binding energy, eV | At. % | Binding energy, eV | Attributed groups |
| NCDs | C1s | 284.6 | 73.37 | 284.3 | C=C |
| | | | | 285.3 | C–N |
| | | | | 286.1 | C–O |
| | | | | 288.1 | C=O |
| | O1s | 531.8 | 21.8 | 531.5 | C=O |
| | | | | 532.8 | C–OH/C–O–C |
| | N1s | 399.7 | 4.84 | 399.4 | C–N–C |
| | | | | 400.2 | Pyrrolic N |
| SCDs | C1s | 284.6 | 65.58 | 284.0 | C=C |
| | | | | 285.5 | C–O |
| | | | | 288.1 | C=O |
| | O1s | 531.8 | 29.90 | 531.2 | C=O |
| | | | | 532.6 | C–OH/C–O–C |
| | S2p | 163.3 | 4.52 | 162.9 | –C–S– 2p3/2 |
| | | | | 164.4 | –C–S– 2p1/2 |
| CDs | C1s | 284.6 | 67.28 | 284.1 | C=C |
| | | | | 285.8 | C–O |
| | | | | 288.4 | C=O |
| | O1s | 531.8 | 32.72 | 531.3 | C=O |
| | | | | 532.8 | C–OH/C–O–C |

***Table S3***. Surface group attributions of NCDs, SCDs and bare CDs characterized by FTIR.

| NCDs | | SCDs | | CDs | |
|---|---|---|---|---|---|
| Wavenumber, $cm^{-1}$ | Attributed groups | Wavenumber, $cm^{-1}$ | Attributed groups | Wavenumber, $cm^{-1}$ | Attributed groups |
| 3396 | υ(O–H)/ υ(N–H) | 3437 | υ(O–H) | 3348 | υ(O–H) |
| 2945, 2885 | υ(C–H) | 2961 | υ(C–H) | 2961 | υ(C–H) |
| 1698 | υ(C=O) | 1734 | υ(C=O) | 1726 | υ(C=O) |
| 1554 | υ(C=C) | 1615 | υ(C=C) | 1595 | υ(C=C) |
| 1433 | δ(C–N) | 1385 | δ(C–H) | 1036 | υ(C–O–C) |
| 1403 | δ(C–H) | 1165 | υ(S=O)/ υ(C–O) | | |
| 1181 | υ(C–N–C) | 1033 | δ(C–S)/ δ(C–O) | | |
| 1060 | δ(C–O–C) | | | | |
| 862 | δ(N–H) | | | | |

***Table S4***. Respective quantum yields of various CDs at 320 nm and their corresponding maximum excitation wavelength.

| | 320 nm | | 330 nm | | 340 nm | | 360 nm | | 375 nm | |
|---|---|---|---|---|---|---|---|---|---|---|
| | *K* | *Φ*, % | *K* | *Φ*, % | *K* | *Φ*, % | *K* | *Φ*, % | *K* | *Φ*, % |
| NSCDs | 92685 | 10.84 | 115299 | 12.97 | | | | | | |
| NCDs | 66229 | 7.74 | | | | | | | 187018 | 18.70 |
| SCDs | 20967 | 2.45 | | | 33765 | 4.09 | | | | |
| CDs | 40189 | 4.70 | | | | | 52446 | 5.70 | | |
| Quinine sulfate | 855263 | 54 | 888668 | 54 | 825272 | 54 | 920175 | 54 | $1\times10^6$ | 54 |

***Table S5***. Fluorescence quenching extent of various carbon dots (0.02 mg/mL) by 2,4,6-TCP ($1 \times 10^{-4}$ mol/L) at pH 7.0.

| | NSCDs | NCDs | SCDs | CDs | RCDs |
|---|---|---|---|---|---|
| FL quenching percent, % | 41 | 40 | 31 | 53 | 36 |