Electronic Supplementary Information

for

Urea-doped carbon dots as fluorescent switch for the selective detection of iodide ions and mechanistic study

Kai Wang,* Cuihuan Geng, Fang Wang, Yajun Zhao and Zongling Ru*

Table of Contents

1. Preparation of urea-doped carbon dots

0.50 g white cotton was dispersed into 20 mL distilled water under stirring. Aferward, the mixture was transterred into a 50 mL poly(tetrafluoroethylene) autoclave, heated at 210 ºC for 12 h. After the reaction, the reactors were cooled to room temperature by water or naturally. The yellow fluorescent CDs suspension was collected by removing the large dots with 0.22 μM filter membrane. The filtrate were dialyzed against distilled water through a dialysis membrane, with a molecular weight cut off of 1000 to remove salt and impurities. After feeze-drying, the cotton-based carbon dots (C-CDs) was kept in a dark and cool bottle for further study.

0.50 g white cotton and urea (various mass ratios (cotton:urea) from 1:1 to 1:10) were dispersed into 20 mL distilled water under stirring. Aferward, the mixture was transterred into a 50 mL poly(tetrafluoroethylene) autoclave, heated at 210 ºC for 12 h. After the reaction, the reactors were cooled to room temperature by water or naturally. The yellow fluorescent CDs suspension was collected by removing the large dots with 0.22 μM filter membrane. The filtrate were dialyzed against distilled water through a dialysis membrane, with a molecular weight cut off of 1000 to remove salt and impurities. After feeze-drying, these Urea-doped carbon dots (N-CDs) were kept at 4 ºC for further study.

Fluorescence quantum yield measurements

The slope method[S1] was used to calculate the QYs of N-CDs using the equation:

$$\Phi_x = \Phi_{st}(K_x/K_{st})(\eta_x/\eta_{st})^2$$

Where Φ is the quantum yield, K is the slope determined by the curves and η is the refractive index of the corresponding solution.

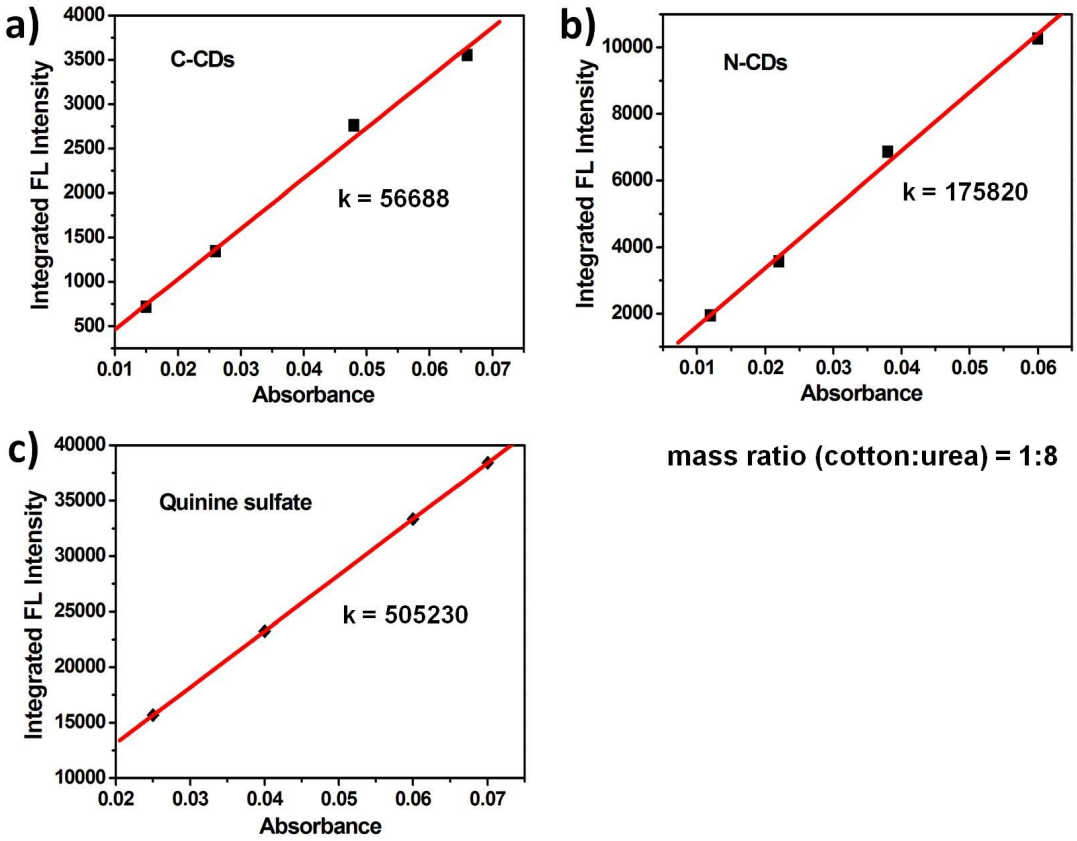

Figure S1 Fluorescence and absorbance of the C-CDs (a), N-CDs (b) and quinine sulfate (c), respectively.

Table S1 QYs of N-CDs of various mass ratios with different urea content.

Sample	N-CDs1	N-CDs2	N-CDs3	N-CDs4	N-CDs5
Mass ratio (cotton:urea)	1:1	1:2	1:6	1:8	1:10
QY(%)	7.32	11.84	17.28	18.79	16.53

2. Characterization of N-CDs

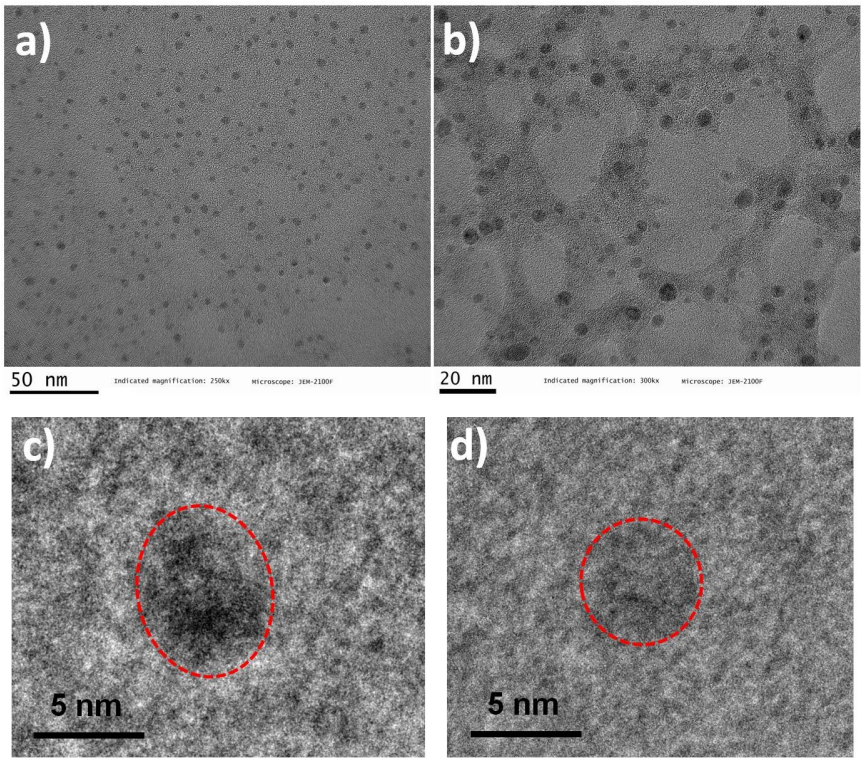

Figure S2 TEM (a and b) and HR-TEM (c and d) images of prepared N-CDs.

3. Sensitive detection for I⁻

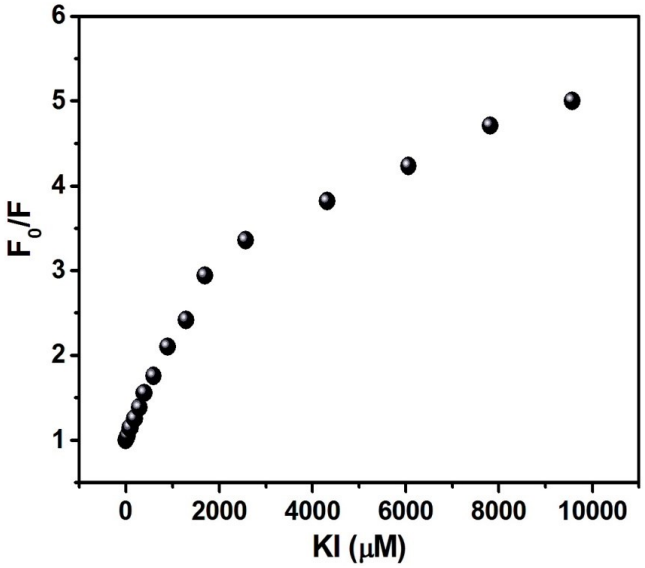

Figure S3 The relationship between F_0/F and KI concentrations, F_0 and F represent the PL intensity of N-CDs when the KI solutions were absence and presence, respectively.

4. Fluorescent quenching mechanism

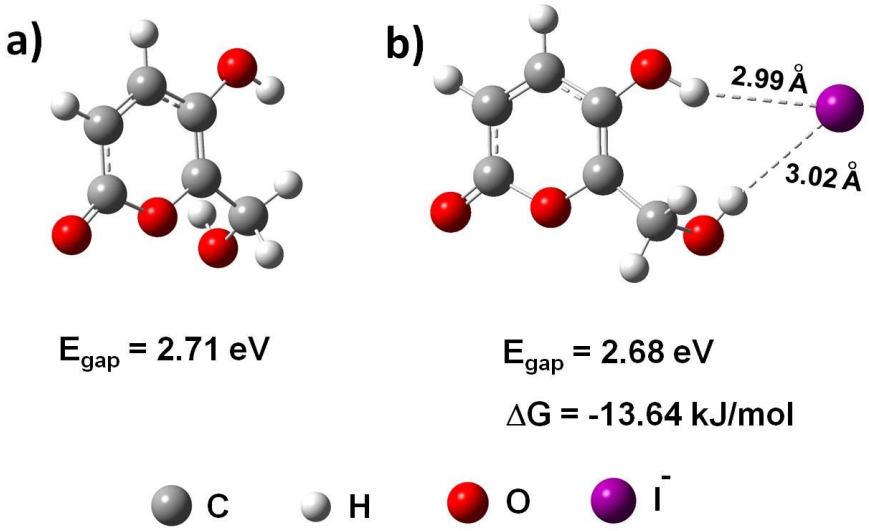

Figure S4 The optimized molecular geometry of chromophore unit of C-CDs. (b) The optimized molecular geometry between C-CDs and I^-.

The optimized molecular geometry of chromophore units of C-CDs and C-CDs/I^- are shown in Figure S5. On the basis of HOMO and LUMO energies, the energy gaps value (E_g) of optimized C-CDs geometry is 2.71 eV. While N-CDs and I^- can form stable complex, the distances between I^- and **H** atoms of hydroxyl (-OH), and methylene hydroxyl (-CH_2OH) groups of C-CDs are 2.99 Å, and 3.02 Å, indicating that there exist duple O-H···I^- and CH_2O-H···I^- interactions between two moieties.

Table S2 Relative Gibbs free energies and corresponding binding energy obtained by means of DFT calculations.

	Gibbs Free Energy (hatree)	**Binding Energy (kJ/mol)**
N-CDs	-681.870	/
I^-	-11.624	/
N-CDs/I^-	-693.485	/
		-23.63
C-CDs	-533.044	/
I^-	-11.624	/
C-CDs/I^-	-544.663	/
		−13.64

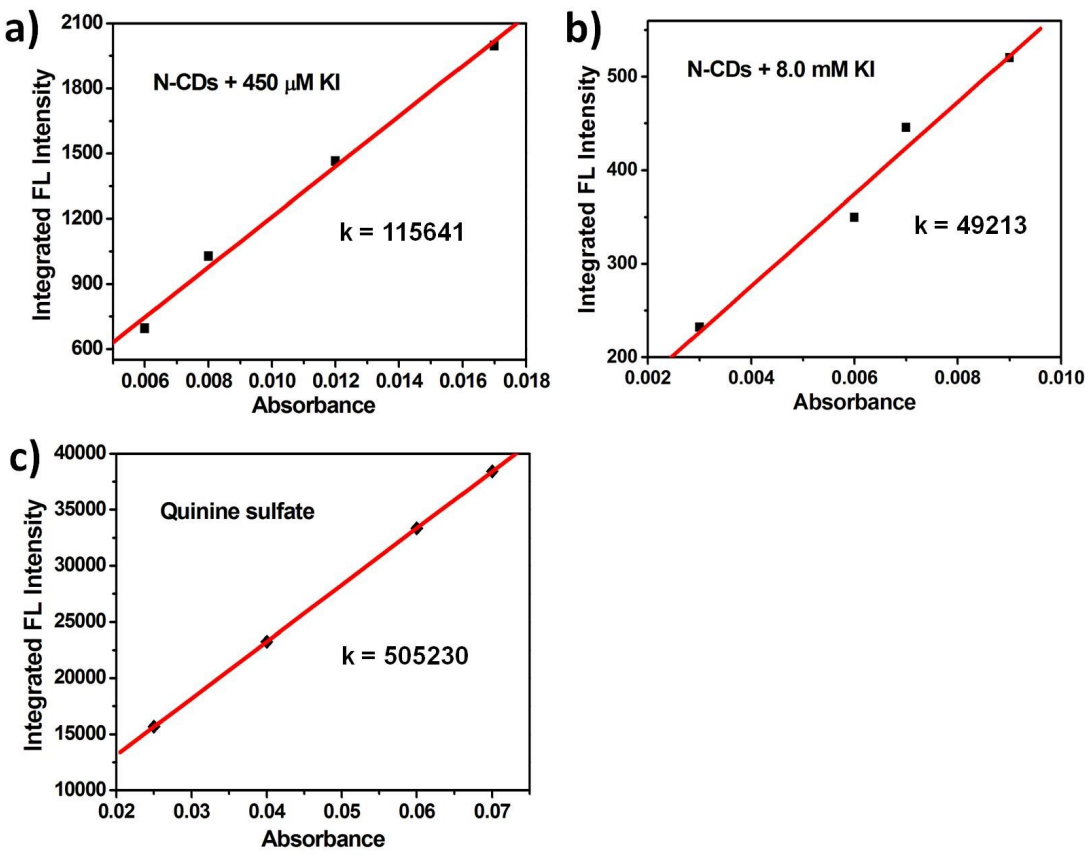

Figure S5 Fluorescence and absorbance of N-CDs with the addition of 450 μM KI (a), N-CDs with the addition of 8.0 mM KI (b) and quinine sulfate (c), respectively.

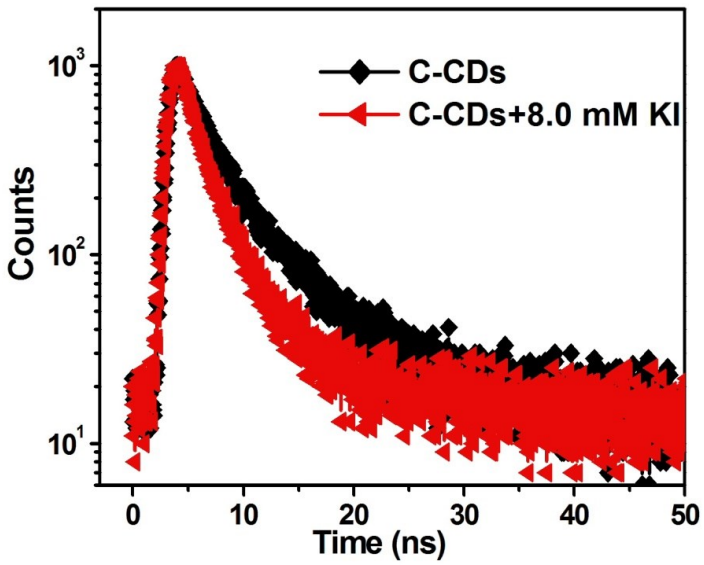

Figure S6 Time-resolved fluorescence decay spectra of C-CDs response to I^- (8.0 mM).

References

S1. H. Zheng, Q. Wang, Y. Long, H. Zhang, X. Huang and R. Zhu, *Chem. Commun.*, **2011**, *47*, 10650-10652.