

Supporting Information

Excitation Wavelength Independent Visible Color Emission of Carbon Dots

Hua Wang^{1,2}, Chun Sun¹, Xingru Chen^{1,3}, Yu Zhang¹, Vicki L. Colvin⁴, Quinton Rice⁵, Jaetae Seo⁵, Shengyu Feng⁶, Shengnian Wang², William W. Yu^{1,3,*}

1 State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun 130012, China

2 Institute for Micromanufacturing, Department of Chemical Engineering, Louisiana Tech University, Ruston, LA 71270, US

3 Department of Chemistry and Physics, Louisiana State University, Shreveport, LA 71115, US

4 Department of Chemistry, Brown University, Providence, RI 02912, US

5 Advanced Center for Laser Science and Spectroscopy, Department of Physics, Hampton University, Hampton, VA 23668, US

6 School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China

* Corresponding author: wyu6000@gmail.com (W. W. Yu)

Experimental Section

Materials

Diphenyl ether, *p*-phenylenediamine, polystyrene (PS, MW=35,000), poly(methyl methacrylate) (PMMA, MW=350,000), poly(ethylene glycol) (PEG, MW=7,000–9,000) were purchased from Alfa Aesar. Poly(vinyl pyrrolidone) (PVP, MW=10,000) was obtained from Fluka. Benzyl alcohol, 1-hexanol, 1-octanol, poly(vinyl alcohol) (PVA, MW=89,000–98,000) was provided by Aldrich. The organic solvents of carbon tetrachloride, toluene, chloroform, acetone, *N,N*-dimethylformamide, methanol and ethanol were purchased from Pharmco and used directly.

Synthesis of carbon dots

In a three-neck, round bottomed flask with reflux condensation system, diphenyl ether (15 mL) was heated to 250°C. *p*-Phenylenediamine (0.20 g, 1.8 mmol) was dispersed in diphenyl ether (1 mL) and heated to 80°C to completely dissolve. Then the *p*-phenylenediamine solution was quickly injected into the flask. The mixture was kept at 250°C for 8h and then cooled down to room temperature. The mixture was poured into hexane (100 mL) to precipitate. Then the whole mixture was centrifuged at 4000 rpm for 20 min. After repeating the precipitation and centrifugation process for three times, 0.164 g of black powder was obtained. The yield was normally around 85—90%.

Preparation of CD/polymer films

CD/PS, CD/PMMA, CD/PVP, and CD/PEG films

For each CD/polymer film preparation, a selected polymer of 0.20 g was mixed with 1 mL CD solution (1.0 mg in dichloromethane) and treated by ultrasound to a complete dissolution. Then the obtained mixture was transferred into a clean glass vial and dried overnight under ambient circumstances to get a composite film. The polymers used were PS, PMMA, PVP and PEG for dark green, green, yellow and dark yellow emissions, respectively.

CD/PVA film

0.50 g PVA was mixed with 1 mL CD solution (1.0 mg in water) and heated to 80°C to be completely dissolved. The obtained mixture was transferred into a clean glass vial and dried overnight under ambient circumstances to get the composite film for red emission.

Characterizations

The fluorescence spectra were collected using a Horiba Jobin Yvon Fluorolog-3 Spectrofluorometer. The UV-vis absorption spectra were measured on a PerkinElmer Lambda 25 UV-vis spectrometer. Transmission electron microscope (TEM) images were recorded on TECNAI F20. Atomic force microscopy (AFM) images were obtained with Veeco DI-3100 instrument. The FTIR spectra were measured on a Thermo Scientific SMART FTIR spectrometer. X-ray photoelectron spectroscopy (XPS) was conducted on an ESCALAB250 spectrometer. The fluorescence lifetimes of the CDs in different solvents were measured on Edinburgh Analytical Instrument FLS 920 time-resolved spectrofluorometer (UK).

Quantum yield (QY) measurement

QYs of the CDs in different solvents were determined based on reference dyes with known QYs according to a published method¹⁻². Specifically, Rhodamine 6G with QY 95% in ethanol was used for the measurements of the emission range of 500–560 nm (for CDs in CCl₄, toluene, CHCl₃, acetone, and DMF). Rhodamine B with QY 56% in ethanol was used for the emission range of 580-615 nm (for CDs in methanol, ethanol, benzyl alcohol, 1-hexanol, 1-octanol, and H₂O).

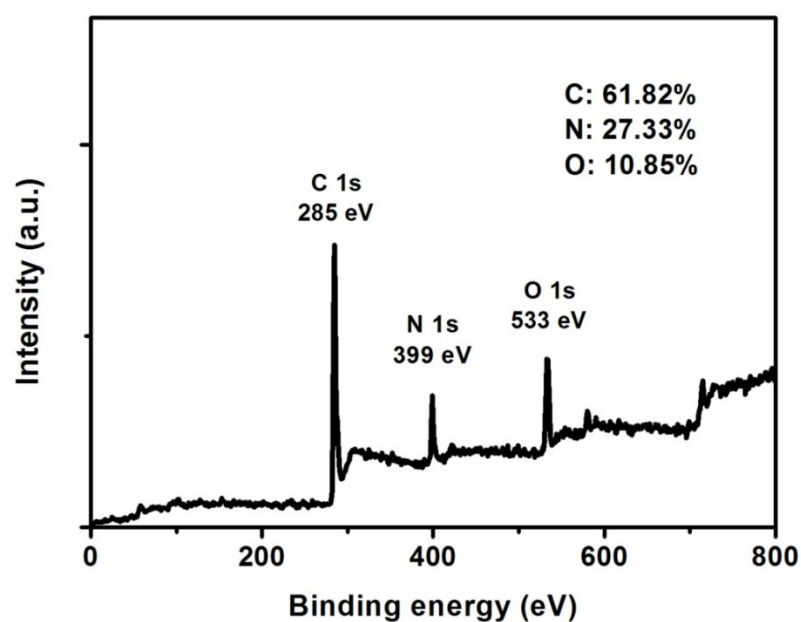


Figure S1. The XPS survey spectrum of the CDs

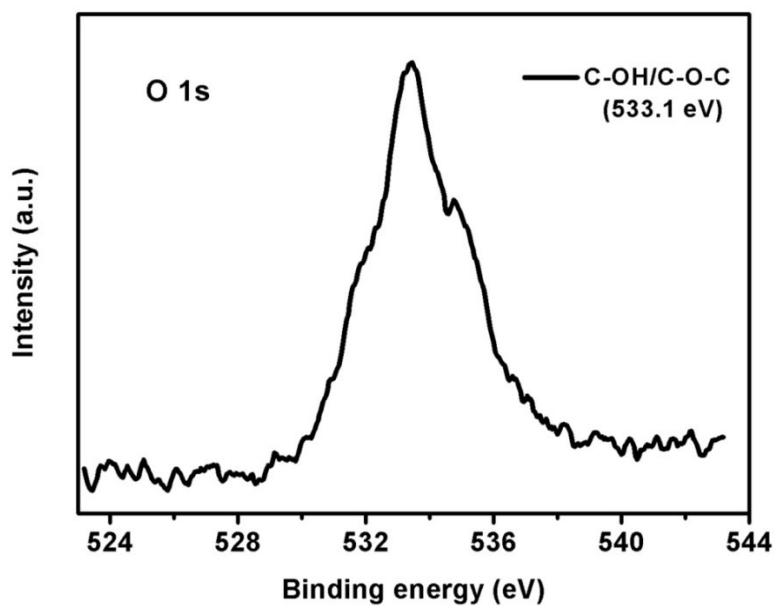


Figure S2. The high-resolution XPS spectrum of O 1s.

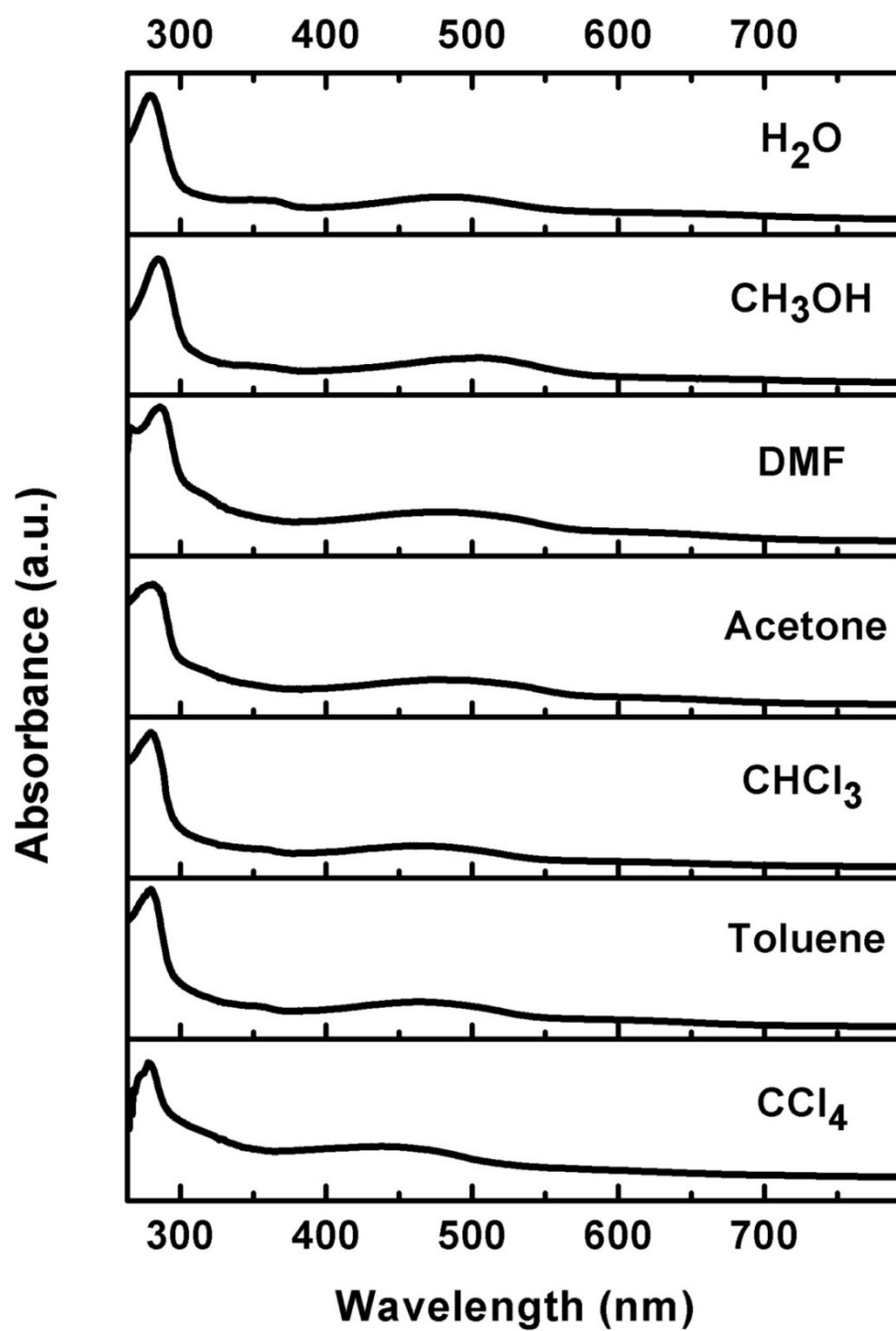


Figure S3. The complete UV-vis absorption spectra of CDs in different solvents.

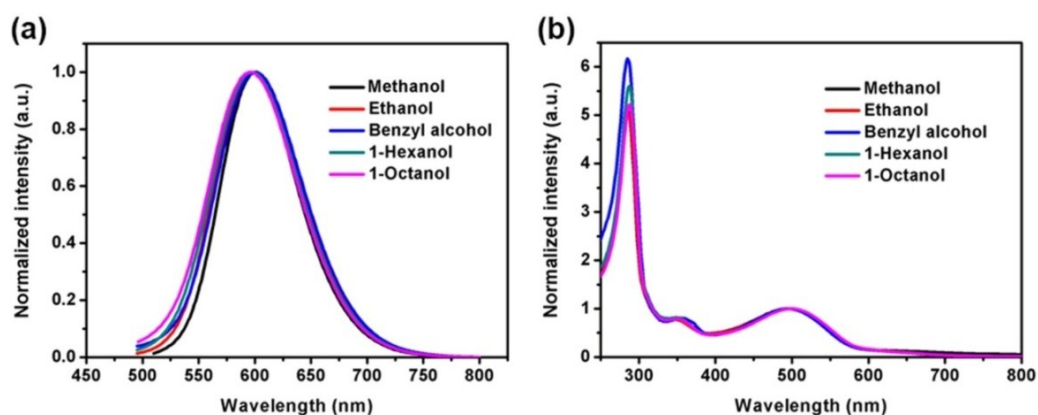


Figure S4. The photoluminescence (excited by 460 nm light) (a) and the corresponding absorption (b) spectra of the CDs in methanol, ethanol, benzyl alcohol, 1-hexanol, and 1-octanol.

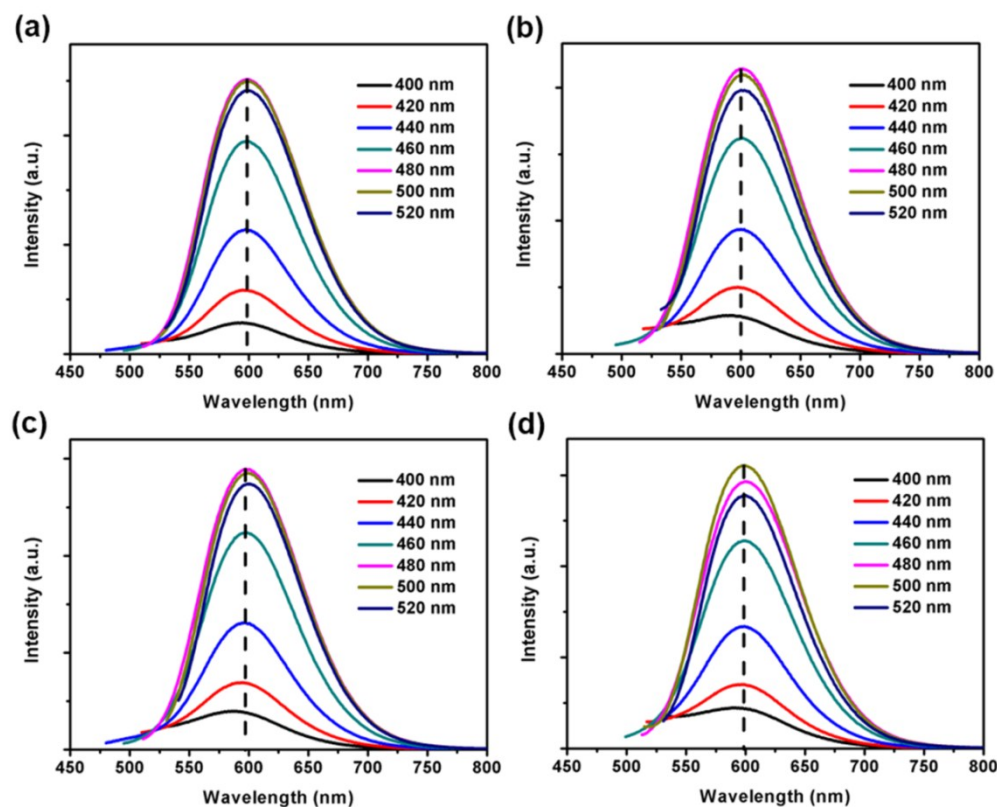


Figure S5. The fluorescence spectra of CDs in ethanol (a), benzyl alcohol (b), 1-hexanol (c) and 1-octanol (d) under various excitation wavelengths.

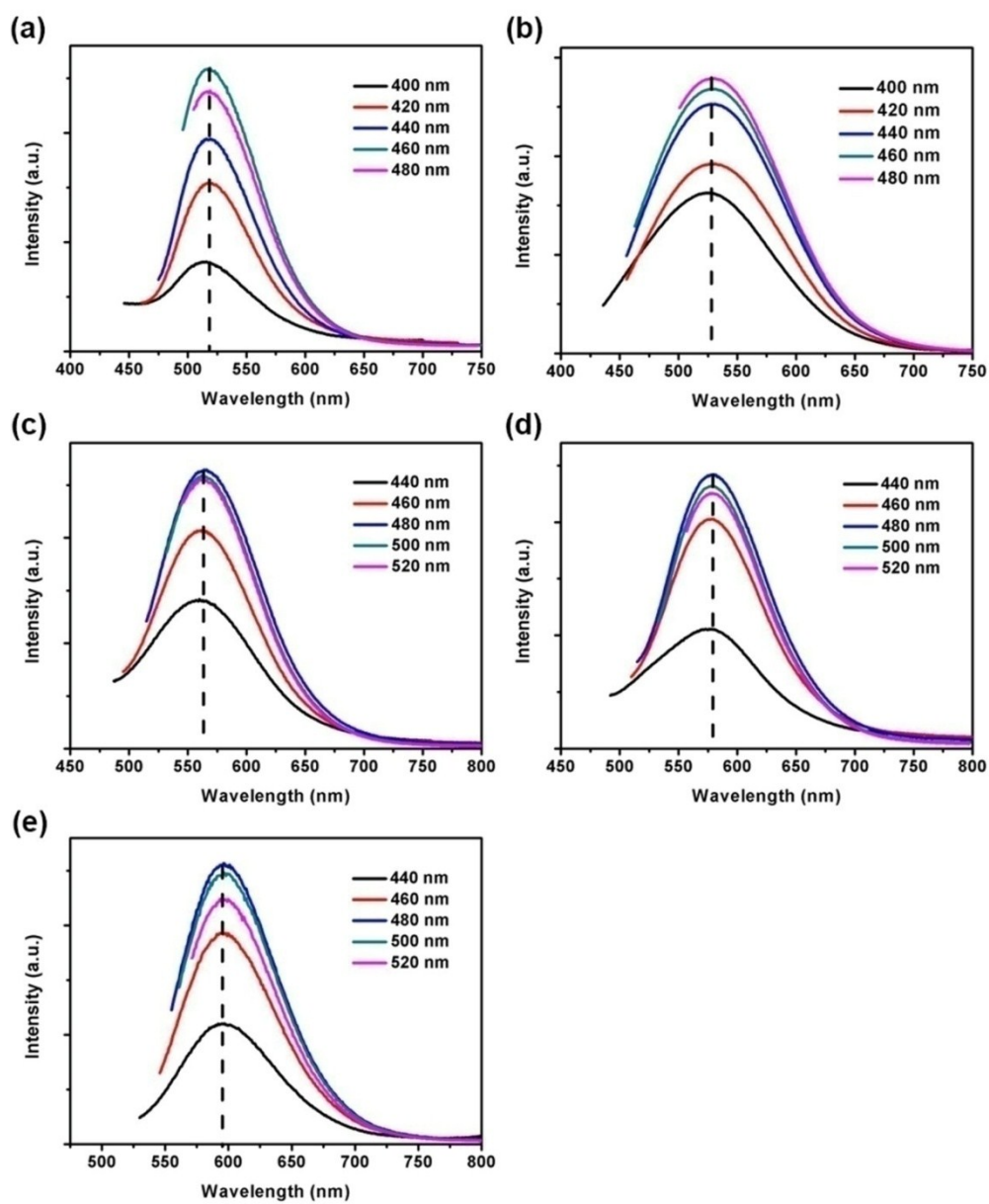


Figure S6. The fluorescence spectra of CD/PS (a), CD/PMMA (b), CD/PVP (c), CD/PEG (d) and CD/PVA (e) composite films under various excitation wavelengths.

Table S1. The photoluminescent properties of CDs in different solvents

Solvent	CCl ₄	Toluen e	CHCl ₃	Aceton e	DMF	CH ₃ OH	H ₂ O
Emission peak (nm)	511	525	545	554	568	602	615
FWHM (nm)	69	71	85	86	89	81	91
QY (%)	11.8	18.4	34.5	16.9	13.3	24.8	9.2

Table S2. The fluorescence lifetimes of CDs in different solvents (445 nm excitation)

	τ_1 (ns)	A ₁ (%)	τ_2 (ns)	A ₂ (%)	τ_{avg} (ns)	χ^2
CCl ₄	1.12	95.55	5.50	4.45	1.94	1.045
Toluene	2.38	67.87	9.97	32.13	7.43	0.985
CHCl ₃	2.41	41.76	12.66	58.24	11.43	1.037
Acetone	4.29	39.69	12.26	60.31	10.77	1.035
DMF	4.32	26.24	12.60	73.76	9.65	1.149

τ_n and A_n are the lifetime and amplitude of the nth component; τ_{avg} is the average lifetime.

Table S3. The QYs of CDs in five alcohol solvents

Solvent	Methanol	Ethanol	Benzyl alcohol	1-Hexanol	1-Octanol
Emission peak (nm)	602	598	601	598	599
FWHM (nm)	81	90	90	91	92
QY (%)	24.8	27.7	28.5	33.5	34.7

Table S4. The fluorescence lifetimes of CDs in different alcohol solvents (445 nm excitation)

	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_{avg} (ns)	χ^2
Methanol	0.87	24.33	8.14	75.67	7.90	0.950
Ethanol	2.60	34.70	9.25	65.30	8.39	1.001
Benzyl alcohol	2.06	34.34	9.19	65.66	8.44	0.971
1-Hexanol	3.86	36.06	9.55	63.94	8.49	1.004
1-Octanol	3.02	34.38	9.17	65.63	8.27	1.091

τ_n and A_n are the lifetime and amplitude of the n^{th} component; τ_{avg} is the average lifetime.

Table S5. The photoluminescent properties of CD/polymer

Polymer	PS	PMMA	PVP	PEG	PVA
Emission peak (nm)	518	531	564	580	594
FWHM (nm)	78	126	106	96	96

References

1. Cross, J. P.; Lauz, M.; Badger, P. D.; Petoud, S., Polymetallic lanthanide complexes with PAMAM-naphthalimide dendritic ligands: luminescent lanthanide complexes formed in solution. *J. Am. Chem. Soc.* **2004**, *126*, 16278-16279.
2. Jiang, K.; Sun, S.; Zhang, L.; Lu, Y.; Wu, A.; Cai, C.; Lin, H., Red, Green, and Blue Luminescence by Carbon Dots: Full-Color Emission Tuning and Multicolor Cellular Imaging. *Angew. Chem. Int. Ed.* **2015**, *54*, 5360-5363.