

Electronic Supplementary Information (ESI)

Influence of thermal treatment conditions (solvothermal versus microwave) and solvent polarity on morphology and emission of phloroglucinol-based nitrogen-doped carbon dots

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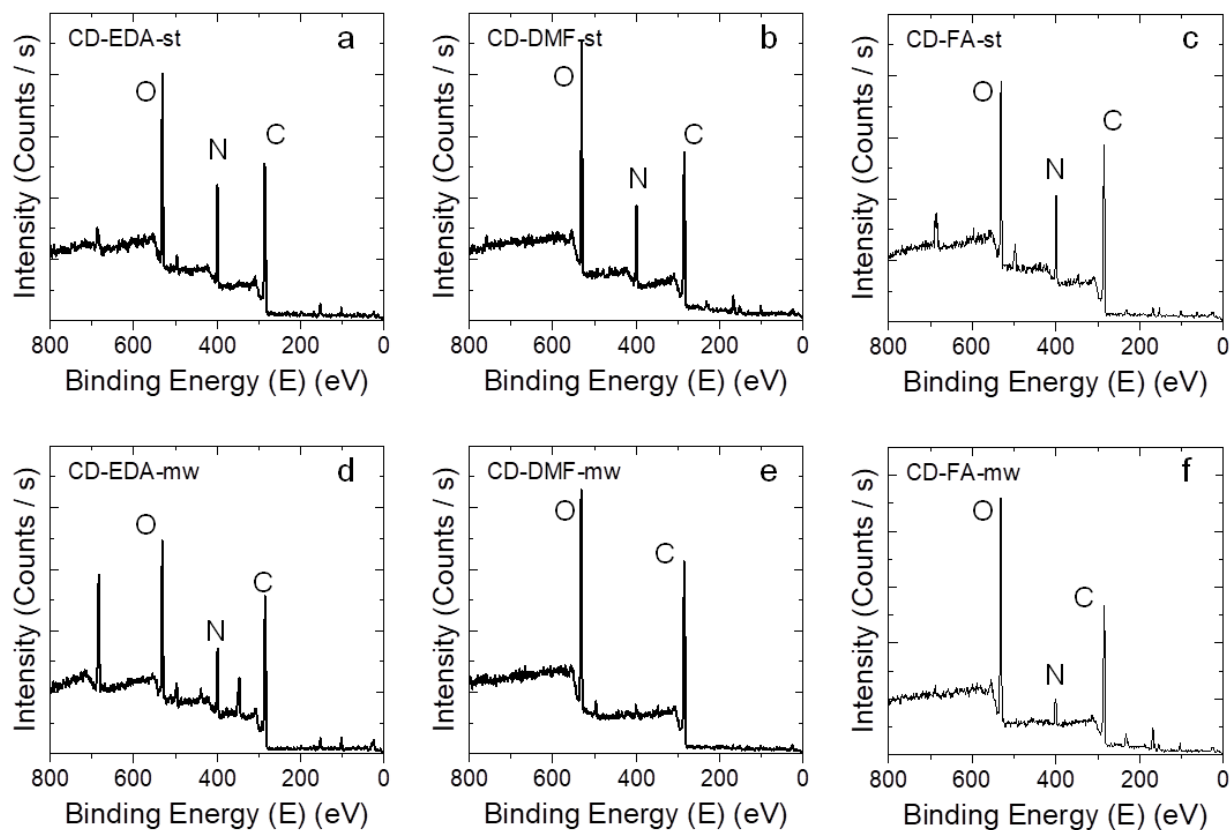


Figure S1. XPS survey of CD samples: (a) CD-EDA-st, (b) CD-DMF-st, (c) CD-FA-st, (d) CD-EDA-mw, (e) CD-DMF-mw, and (f) CD-FA-mw.

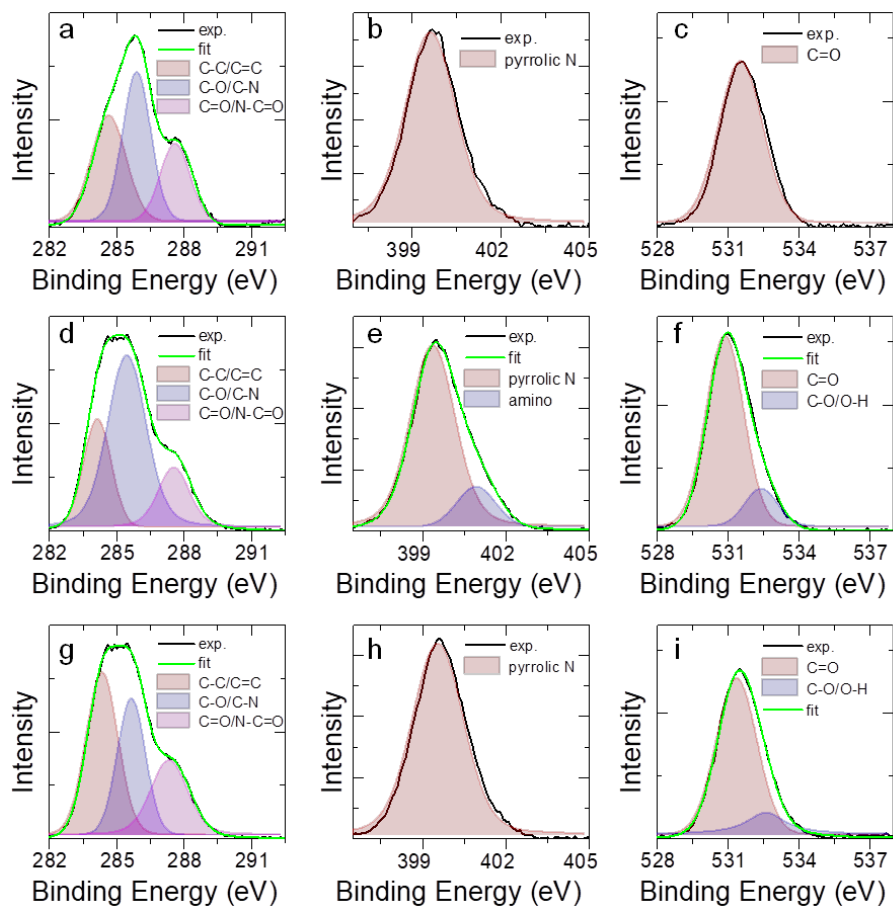


Figure S2. High resolution XPS spectra of C 1S (a, d, g), N 1S (b, e, h), and O 1S (c, f, i) of the solvothermally synthesized CD samples: CD-EDA-st (a-c), CD-DMF-st (d-f), and CD-FA-st (g-i). Experimental data (exp.) are shown by black lines, and the overall fitting curves (fit) – by green lines. Differently colored individual deconvoluted peaks are assigned to different bonds as explained on the frames.

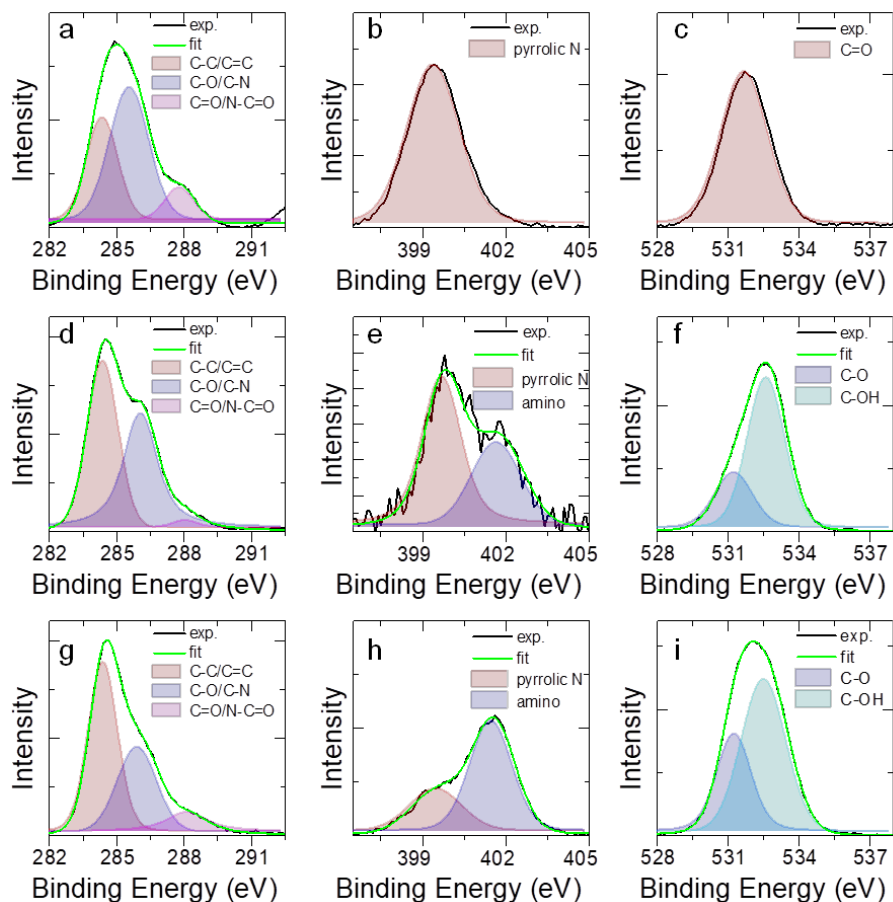


Figure S3. High resolution XPS spectra of C 1S (a, d, g), N 1S (b, e, h), and O 1S (c, f, i) of the CD samples synthesized by microwave-assisted method: CD-EDA-mw (a-c), CD-DMF-mw (d-f), and CD-FA-mw (g-i). Experimental data (exp.) are shown by black lines, and the overall fitting curves (fit) – by green lines. Differently colored individual deconvoluted peaks are assigned to different bonds as explained on the frames.

High-resolution XPS spectra show the presence of the following bonds in the CD samples: C=C/C-C (284.4 eV), C-O (286.1 eV), and C=O/COO⁻ (288.5 eV) in C 1S; pyrrolic N (399.6 eV) and amino N (401 eV); and C=O (530.9 eV), C-O/O-H (531.9 – 532.7 eV). Note that for CDs synthesized by the solvothermal method the N atoms are mostly observed in pyrrolic form, while for CDs synthesized by the microwave-assisted method an increased number of C-O/O-H bonds as compared to C=O bonds are observed.

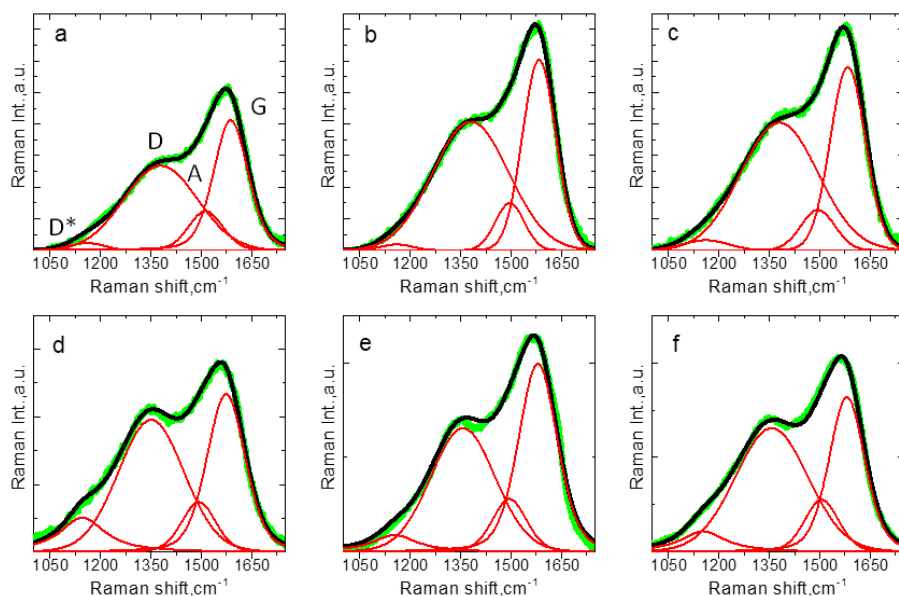


Figure S4. Raman spectra of CD samples: CD-EDA-st (a), CD-DMF-st (b), CD-FA-st (c), CD-EDA-mw (d), CD-DMF-mw (e), and CD-FA-mw (f). Experimental data are shown in green, deconvoluted peaks corresponding to D*, D, A, and G bands – in red, and the overall fitting curves – in black. The background originated from CD's luminescence signal was subtracted by using Renishaw software.

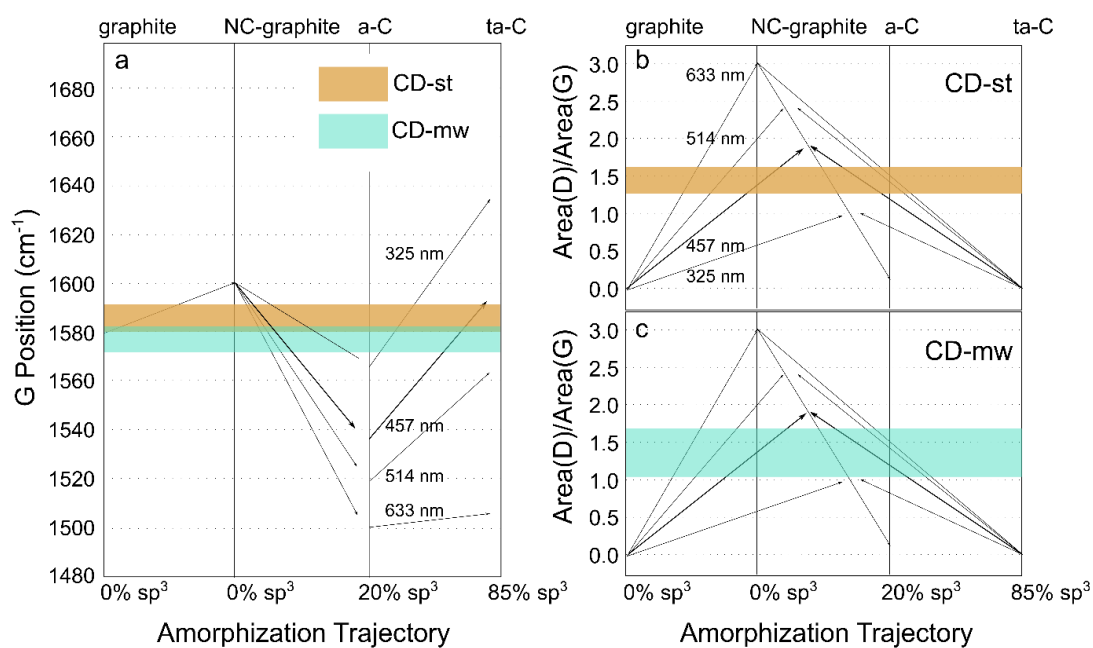


Figure S5. Comparison of the experimental data from this work for the CD-st set (orange) and the CD-mw set (green) with amorphization trajectories redrawn from the work: A. C. Ferrari and J. Robertson, Phys. Rev. B, 2001, 64, 075414.

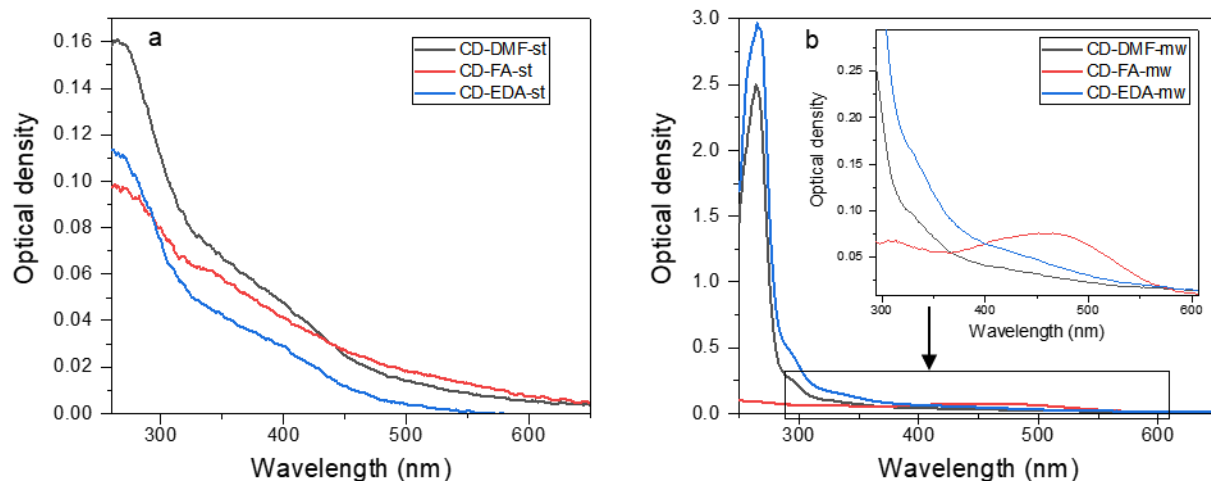


Figure S6. Absorption spectra of CD samples synthesized by (a) solvothermal and (b) microwave-assisted methods. Concentration of CDs was 6, 25, 1, 20, 13, 3 $\mu\text{g/mL}$ for CD-EDA-st, CD-DMF-st, CD-FA-st, CD-EDA-mw, CD-DMF-mw, CD-FA-mw, respectively.

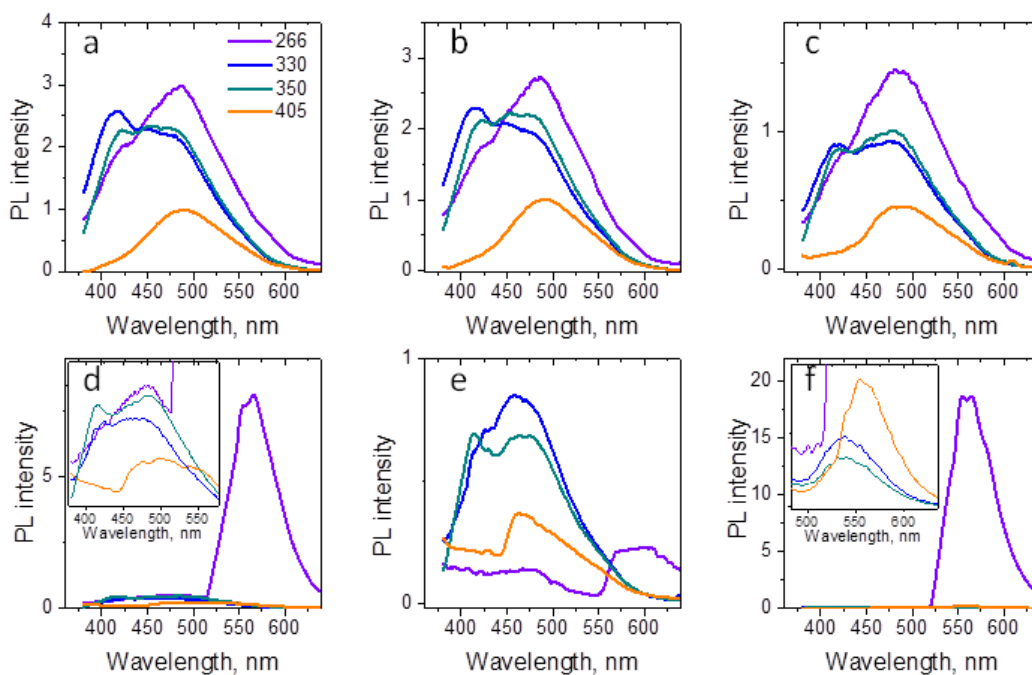


Figure S7. PL spectra of CDs samples: CD-EDA-st (a), CD-DMF-st (b), CD-FA-st (c), CD-EDA-mw (d), CD-DMF-mw (e), CD-FA-mw (f). Color coding for spectra obtained using different excitation wavelengths is provided in the legend of the frame (a). Insets in (d) and (f) show zoom-ins into some particular spectral windows.

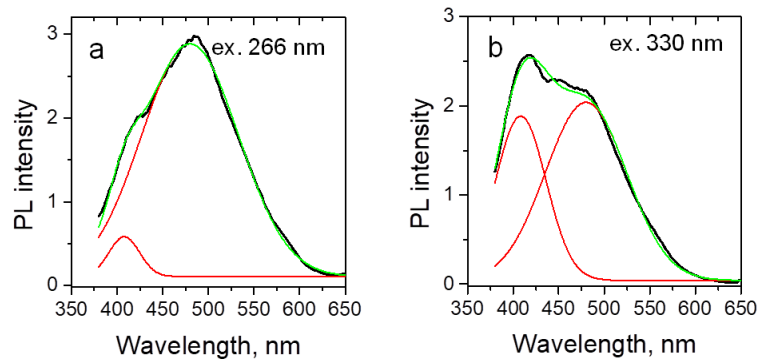


Figure S8. PL spectra of the CD-EDA-st sample excited at 266 nm (a) and 330 (b) nm. Experimentally measured PL bands (in black) were fitted by two Gaussian peaks (red curves) centered at 408 and 480 nm, whose sum is represented by green lines.

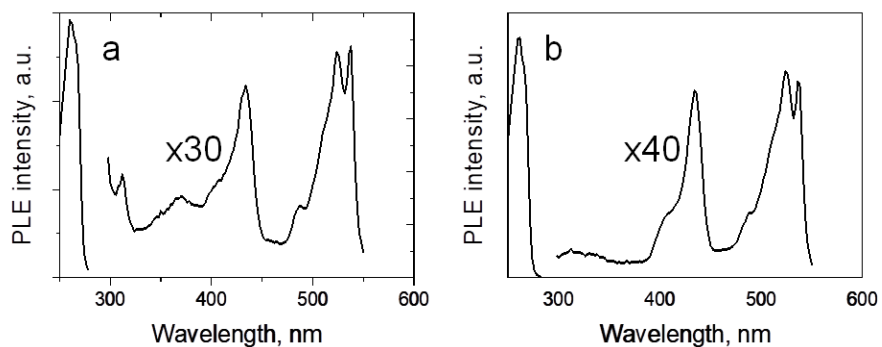


Figure S9. PLE spectra of (a) CD-EDA-mw and (b) CD-FA-mw samples monitored at 580 nm.

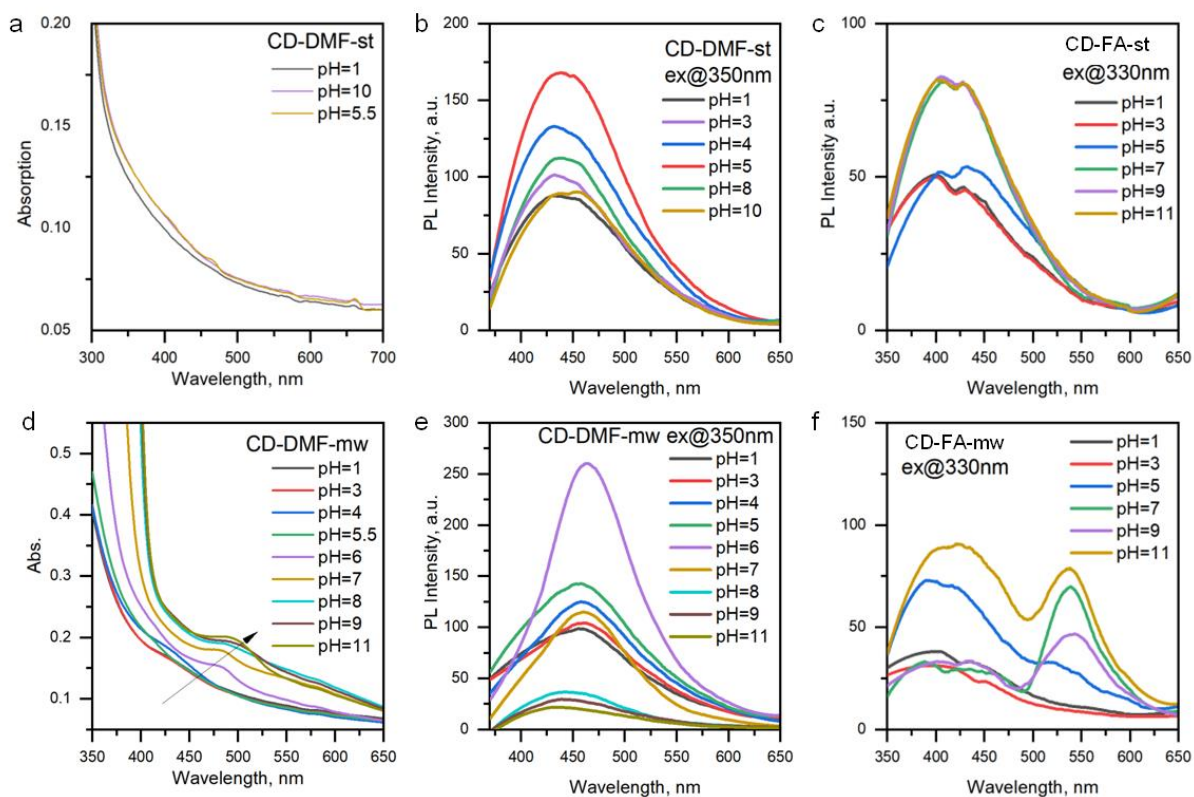


Figure S10. Absorption (a, d) and PL (b, c, e, f) spectra of different CD samples as a function of changing pH. Sample names and PL excitation wavelengths are provided on individual frames. pH measurements were performed on samples possessing the same optical density at initial pH. The pH value was further adjusted by adding 0.1 M NaOH or 0.1 M HCl solutions.

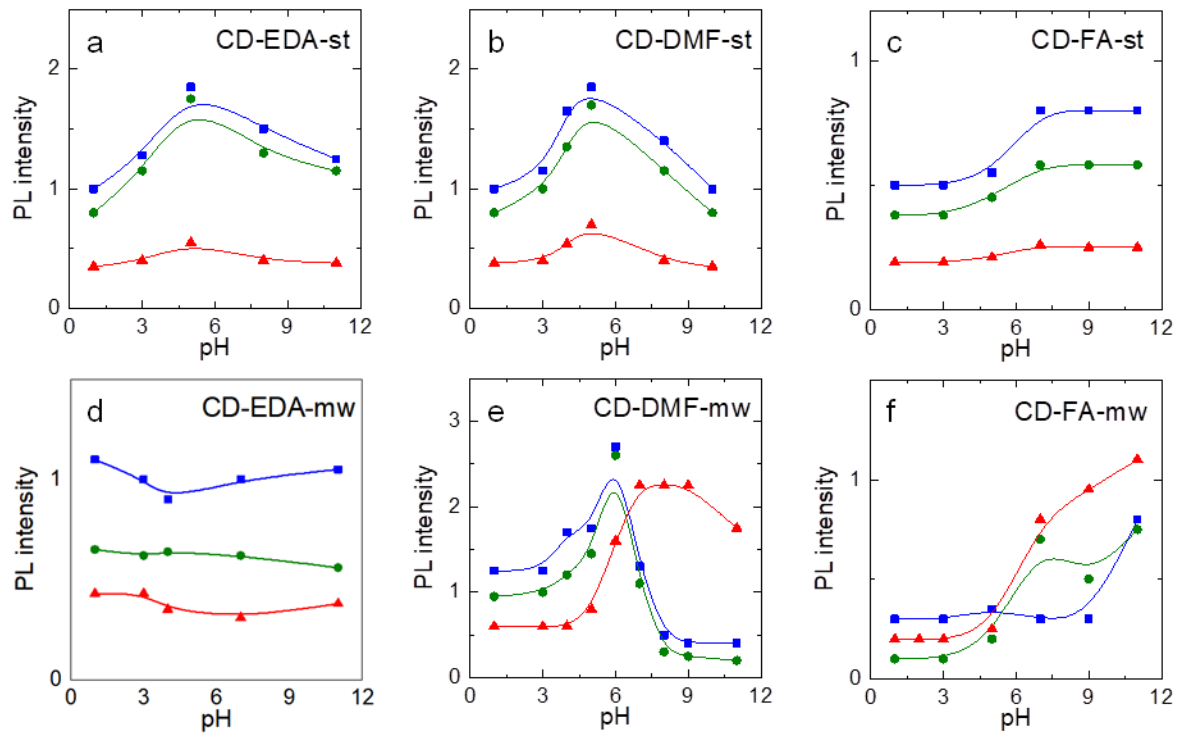


Figure S11. pH dependence of the relative PL peak intensity (normalized and shifted vertically for the sake of better visibility) of CDs samples excited at 330 nm (blue), 350 nm (green), and 405 nm (red). Sample names are provided on each frame.

Table S1. Summary of the morphology and optical properties of CD samples produced in this study

Synthesis	Solvent	PY, mg/mL	Average size, nm	Shape	FTIR bands	Abs peaks,* nm	PLE peaks,* nm	PL peaks,* nm	PLQY, %	Average PL lifetime, ns	
st	EDA	1.25	2.4	spherical	Amide; C-N; -CH ₃ ; -OH	270; 370	270; 330- 350	400; 480	7.6	3.4	
	DMF	1	2.8	spherical		275; 345; 515	270; 340- 360		9.8	10.5	3.4
	FA	0.23	12.5	onion-like		265, 295; 335; 440	270; 360; 430, 530		400; 480; 560	6.5	2.7
mw	EDA	4	3.6	spherical	C-N; -CH ₃ ; -NH ₂	265; 295; 335; 440	270; 360; 430, 530	400; 480; 560	6.5	2.7	
	DMF	2.6	2.3	spherical	C _{arom} ; C-N; -OH	265; 310; 460	290- 360	480	9.5	2.8	
	FA	0.6	9.0	onion-like		265; 310; 460	430, 530	560	0.8	0.5	

* PY - production yield after dialysis; PLQY – PL quantum yield measured relative to Rhodamine 6G with an excitation wavelength $\lambda = 350$ nm.

Optical transitions attributed to core states ($\pi-\pi^*$ and $n-\pi^*$ transitions) are highlighted in blue and green, and those attributed to the surface states of CDs are highlighted by orange color, respectively.

Table S2. PLQY dependence on the excitation wavelength for the CD-FA-mw sample

PLQY values estimated related to Rhodamine 6G (PLQY = 95%)			
Excitation wavelength, nm	250	350	530
PLQY, %	22.5	0.8	2.2
PLQY values estimated related to Fluoresceine (PLQY = 92%)			
Excitation wavelength, nm	250	470	514
PLQY, %	15.2	0.8	3.7

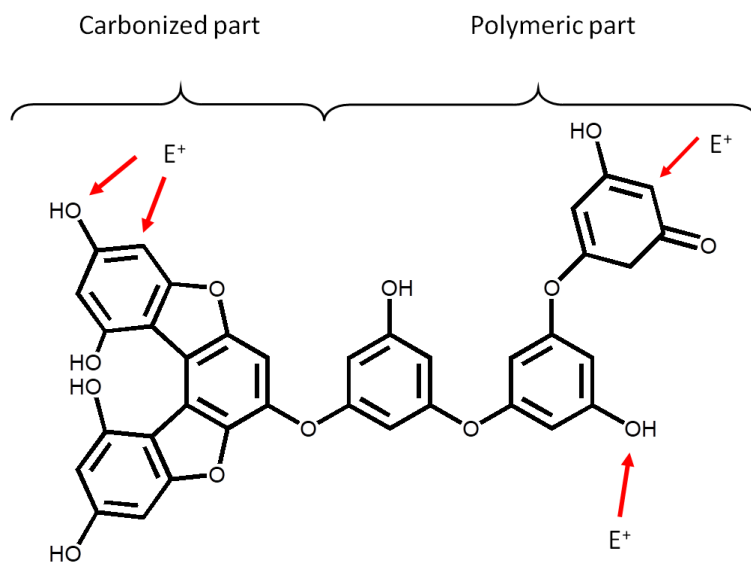


Figure S12. Illustration of dendrite-like polyphenolic structure formed by the phloroglucinol molecules. Red arrows show the sites where electrophilic attack can occur.