Supporting Information

Gram-Scale Synthesis and Kinetic Study of Bright Carbon Dots from Citric Acid and *Citrus japonica via* a Microwave-Assisted Method

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General procedure for CD preparation

Varying power, time and volume. A stock solution of 0.1 g/mL CA in DI water was prepared by dissolving citric acid monohydrate ($CA \cdot H_2O$) (1.1 g) in 10 mL DI water and stirred. For aminated samples, a 1:1 CA:amine molar was prepared by adding 348 µL EDA to every 10 mL CA stock solution. A selected sample volume (1, 2 or 3 mL) was transferred to a pre-weighed scintillation vial and the mixture was heated in a domestic microwave oven (900W GE Microwave oven JE12560SPSS) using a determined microwave power (50% equivalent to 430 W and 70% to 630 W) and heating time pattern (2 or 5 min). The heating was stopped when the colorless samples turned into a red-brown solid. Unless indicated, pyrolyzed samples were dried in a vacuum oven (constance vacuum oven set at 0.0845 MPa) at ambient temperature to ensure complete removal of water. Three trials were prepared for each sample. The UV absorption and the photoluminescence emission of the samples were carried out using 1.21×10^{-5} g CD/mL DI water and 1.2 mg CD/mL DI water, respectively. Samples were labeled as 70P_5min_1mL where, 70P-70% power, 5min- 5-minutes repetitive heating, 1 mL-initial sample volume.

Varying Amine. For samples utilizing passivating agents other than EDA, the solutions were prepared using amines such as diethylamine (DEA) (CA_DEA with 538 uL DEA), triethylamine (TEA) (CA_TEA with 729 uL TEA) and quinine (CA_Quinine with 1.695 g quinine) per 10 mL CA stock solution. CA-amine stock solution (3 mL) was dispensed in scintillation vials and heated using 70% (630 W) power at 2-min repetitive heating pattern. Amine samples containing no CA were also pyrolyzed using the same conditions and these were labeled as the amine (i.e., DEA for diethylamine).

Varying CA content. CA stock solutions were prepared with and without EDA by varying CA concentrations (0.5 g, 1 g, 1.5 g, 3 g and 5 g CA per 10 mL DI water) while keeping EDA concentration constant. Pyrolysis was carried out using 3 mL sample volume, 70% power (630W) at 2 min repetitive heating until red-brown product was obtained. Samples were labeled as: CA-1g (CA-1G) for CA solution with 1 g of citric acid or CAEDA-1G for 1 g CA with 348 µL EDA to every 10 mL CA stock solution.

Varying EDA content. Using 0.1 g/mL CA in DI water or 100% CJ as the carbon source, various EDA concentrations were utilized to check the effect of amine. The stock solutions were prepared by adding desired amine concentration to 10 mL of 0.1 g/mL CA in DI water or to 10 mL pure CJ. Different CA:EDA combinations were obtained: 1:0.25 (10 mL of 0.1 g/mL CA in DI water:86.9 µL EDA), 1:0.5 (10 mL of 0.1 g/mL CA in DI water:173.37 µL EDA), 1:1 (10 mL of 0.1 g/mL CA in DI water:348 µL EDA), 1:1.5 (10 mL of 0.1 g/mL CA in DI water:521 µL EDA) and 1:2 (10 mL of 0.1 g/mL CA in DI water:695 µL EDA). For calamansi-based CDs, calamansi fruit was cut and the juice was extracted. A strainer was used to remove the seeds and pulp. Pure CJ was stirred using a magnetic stirrer to ensure homogeneous solution. Different CJ:EDA combinations were obtained: 1:0.25 (10 mL CJ:86.9 µL EDA), 1:0.5 (10 mL:173.37 µL), 1:1 (10 mL:348 µL), 1:1.5 (10 mL:521 µL) and 1:2 (10 mL:695 µL). A 3 mL solution was dispensed to pre-weighed scintillation vial and the sample was heated in a microwave oven using a 70% power (630W) at 2-min repetitive heating. The heating was stopped when red-brown product is obtained.

Table S1 Establishing CA and CJ CD synthesis parameters. *Power and time.* Product yield and total heating time of the samples prepared using: 0.1 g/mL CA in DI water, at 50% or 70% microwave power, 5 or 2 min repetitive heating, at 1, 2, or 3 mL-initial sample volume. Sample codes were shown as 70P_5min_1mL, where 70P is 70% microwave power, 5-min repetitive heating, 1 mL. *Varying Amine* (Effect of varying amine in CD passivation). Synthesis parameters: 1:1 CA:amine molar ratio/10 mL DI water, 70P, 2-min repetitive heating. Sample code: CA-citric acid, EDA- ethylenediamine, DEA-diethylamine, TEA-triethylamine. *Varying CA content with and without EDA.* Synthesis parameters: CA with and without 348 µL EDA in DI solution, 70P, 2-min repetitive heating. Sample code: CA-citric acid; CAEDA-citric acid with EDA; Xg-amount of citric acid. *Varying EDA content.* Synthesis parameters: 0.1 g/mL CA in DI water, 70P, 2-min repetitive heating. Sample code: CAEDA-citric acid with EDA; 0.25-molar concentration of EDA. For CJ samples, the conditions are similar to CA except that pure 100% calamansi juice was used. All samples were run in triplicates, the average emission intensity at 462 nm are reported together with the standard deviations.

Sample Code	Average product yield based from gram solution (%)	Average product yield based from CA used (%)	Total heating Time (min)	Average emission intensity at 462.49 nm	Standard deviation of emission
Power and Time					
70P_5min_1mL	6.9	73	24	31.7	13
70P_5min_2mL	7.3	52	20	82.4	21
70P_5min_3mL	3.84	33	20	85.9	38
50P_5min_1mL	7.05	87	30	25.9	25
50P_5min_2mL	7.82	65	20	36.0	19
50P_5min_3mL	6.25	54	20	41.5	12
70P_2min_1mL	5.5	61	24	217.5	36
70P_2min_2mL	3.53	37	20	175.3	59
70P_2min_3mL	3.10	32	20	282.1	108
50P_2min_1mL	5.87	61	30	166.7	36
50P_2min_2mL	3.40	35	20	128.6	11
50P_2min_3mL	3.06	32	20	214.3	71
Varying amine					
CA_EDA	8.14	87	10	2129.6	1476.76
CA_Quinine	13.2	77	10	1338.3	1525.72
CA_DEA	7.19	75	4	17.1	10.64
CA_TEA	7.64	41	4	38.6	24.04
CA_no amine				12.9	6.86
EDA				5.4	
Quinine				14.3	
DEA				7.4	
TEA				4.6	
Varying CA content					
CA-0.5G	1.66	16	22	20.4	5.95
CA-1G (CA)	2.17	22	32	24.5	3.96
CA-1.5G	3.98	39	26	32.9	13.60
CA-3G	6.43	72	18	27.9	8.97
CA-5G	6.32	73	22	36.0	8.47

Sample Code	Average product yield based from gram solution (%)	Average product yield based from CA used (%)	Total heating Time (min)	Average emission intensity at 462.49 nm	Standard deviation of emission
CAEDA-0.5G	5.81	60	16	3608.7	156.42
CAEDA-1G (CAEDA)	9.94	100	22	3685.9	240.19
CAEDA-1.5G	11.80	100	16	2496.4	1291.76
CAEDA-3G	18.93	100	12	163.2	12.99
CAEDA-5G	21.37	100	12	131.8	9.46
Varying EDA content					
CAEDA-0.25	9.13	83	20	368.7	283.70
CAEDA-0.50	14.26	100	20	250.4	207.28
CAEDA-1.00 (CAEDA)	9.94	100	22	3685.9	240.19
CAEDA-1.50	10.45	100	4	2417.5	318.77
CAEDA-2.00	10.57	100	4	2944.8	221.22
CJEDA-0.25	8.34	80	6	41.4	10.12
CJEDA-0.50	9.40	91	6	494.5	414.93
CJEDA-1.00	9.94	100	6	2118.1	1711.41
CJEDA-1.50	10.09	100	6	2284.5	188.11
CJEDA-2.00	12.37	100	6	1923.2	547.21

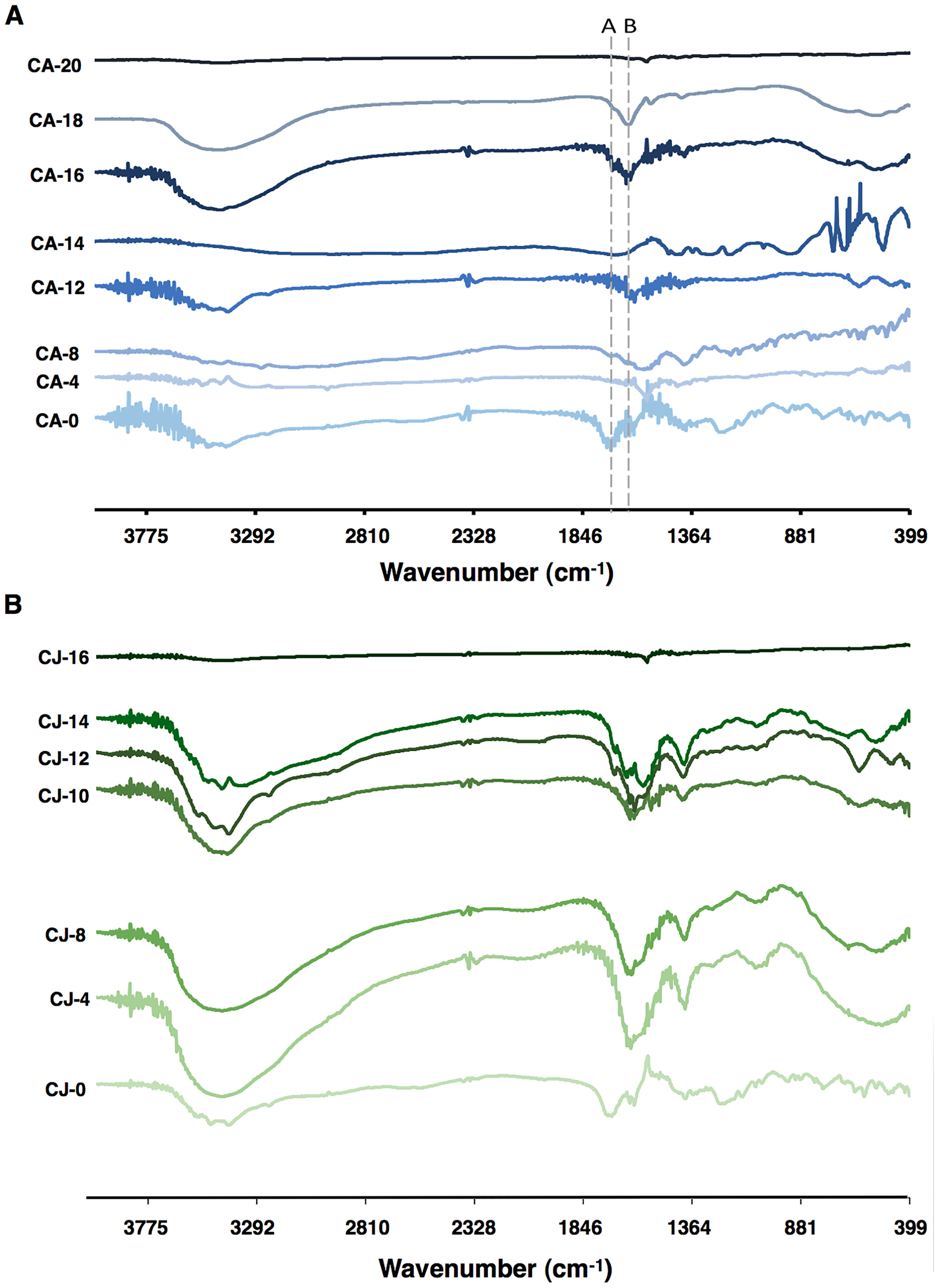

Figure S1 FTIR (KBr pellet) spectra of dried CA and CJ samples after subjecting to time study (pyrolysis) and then freeze drying. The CA samples (100 mL of 0.1 g/mL of CA in DI water and 3480 μL EDA) were pyrolized at 4, 8, 12, 14, 16, 18, 20 min; and CJ samples (100 mL of CJ and 3480 μL EDA) were pyrolized at 4, 8, 10, 12, 14, 16 min using 70% microwave power (630W) at 2 min repetitive heating. A.) FTIR spectrum for each samples were plotted as CA-0 (sample with no heating) to CA-4, 8, 12, 14, 16, 18, 20 min total heating time. B.) FTIR spectrum for each samples were plotted as CJ-0 (sample with no heating) to CJ-4, 8, 10, 12, 14, 16 min total heating time.

Table S2 Gram-scale synthesis of CA and CJ CDs. Synthesis parameters: 0.1 g/mL CA in DI water and 3480 µL EDA/100 mL solution, 70% power at 2-min repetitive heating. Sample code: CAEDA-citric acid with EDA, XmL-amount of solution pyrolyzed. (See Figure 2)

Sample Code	Average product yield based from gram solution (%)	Average product yield based from CA used (%)	Total heating Time (min)	Average emission intensity at 462.49 nm
CAEDA-100 mL	9.93	99	18	3758.6
CAEDA-50 mL	4.88	98	12	3460.5
CAEDA-3 mL (CAEDA)	10.53	100	22	3578.2

Table S3 Tabulated reproducibility data for bulk (100 mL) CA-18 and CJ-14 CD synthesis with total heating time. Photoluminescence emission intensity of the samples at 462 nm were taken using 1.2 mg CD/mL DI water. The standard deviation of the six emission intensity readings were obtained. Samples were excited using a 355 nm laser. Sample code: Gram-scale (bulk or 100 mL sample volume of 0.1 g/mL CA in DI water pyrolyzed)_CAEDA (0.1 g/mL CA in DI water with 3480 µL ethylenediamine)_Trial number. (See Figure 3)

Sample	Average product yield based from gram solution (%)	Average product yield based from CA (%)	Total heating time (min)	Emission intensity at 462 nm	Standard deviation of emission
Gram-scale_CAEDA_Trial 1	9.5	95.0	18	3546	
Gram-scale_CAEDA_Trial 2	9.4	94.0	18	3761	
Gram-scale_CAEDA_Trial 3	10.4	100.0	18	3800	
Gram-scale_CAEDA_Trial 4	9.4	94.0	18	3505	
Gram-scale_CAEDA_Trial 5	10.7	100.0	18	3933	
Gram-scale_CAEDA_Trial 6	8.9	100.0	18	3796	
AVERAGE	9.7	97		3724	165
Gram-scale_CJEDA_Trial 1	7.1		14	3793	
Gram-scale_CJEDA_Trial 2	7.1		14	3933	
Gram-scale_CJEDA_Trial 3	6.8		14	3516	
Gram-scale_CJEDA_Trial 4	6.7		14	3931	
Gram-scale_CJEDA_Trial 5	7.4		14	3782	
Gram-scale_CJEDA_Trial 6	6.7		14	3943	
AVERAGE	7.0			3816	164

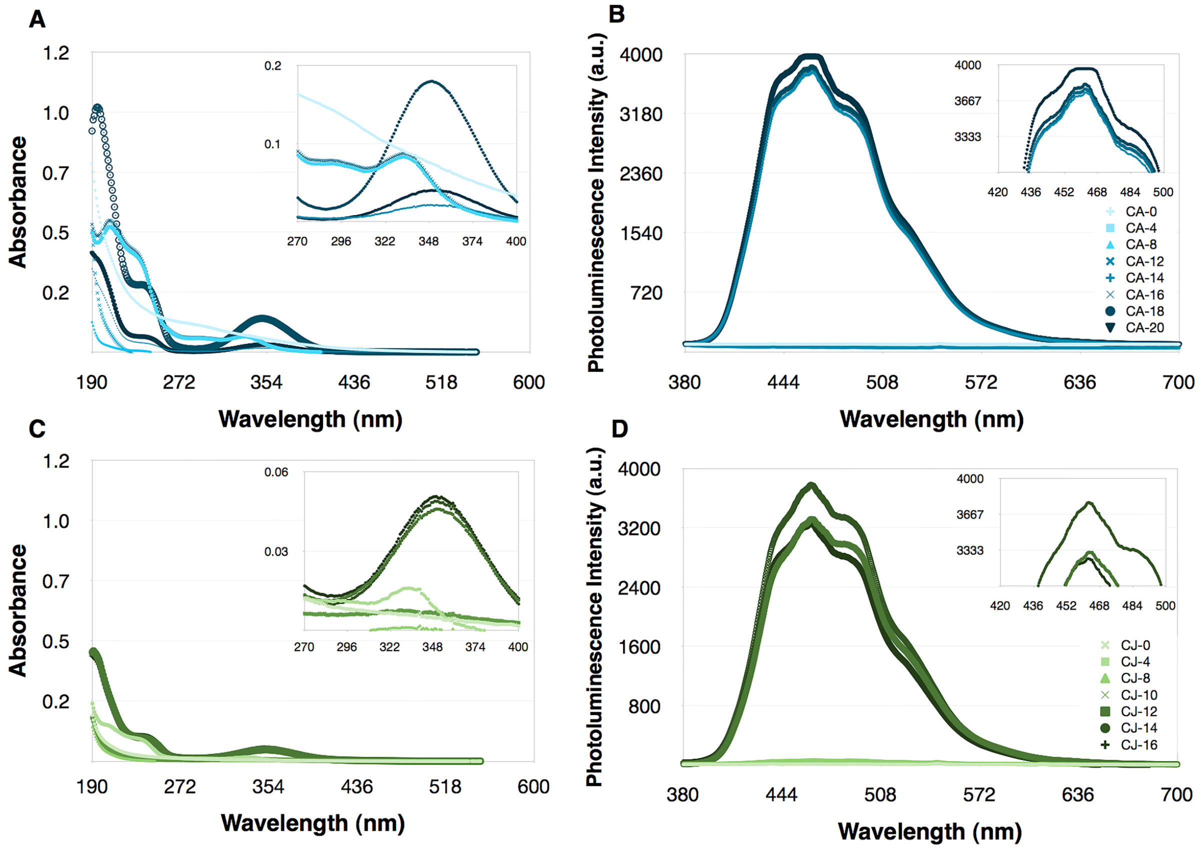

Figure S2 Photoluminescence emission and UV-Vis absorption spectra of CA and CJ CD solutions after subjecting to time study. The CA samples (100 mL of 0.1 g/mL CA in DI water and 3480 μL EDA) were pyrolized at 4, 8, 12, 14, 16, 18, 20 min total heating time; and CJ samples (100 mL of CJ and 3480 μL EDA) were pyrolized at 4, 8, 10, 12, 14, 16 min total heating time using 70% microwave power (630W) at 2 min-repetitive heating. CA samples: A.) UV absorption of 1x10^{-5} g CA sample/mL DI water. Inset shows the expanded region along 350 nm region. (B) fluorescence emission spectra of 1.2 mg CA sample/mL DI water. Inset shows the expanded region along 462 nm. CJ samples: C.) UV absorption of 1x10^{-5} g CJ sample/mL DI water. D.) fluorescence emission spectra of 1.2 mg CJ sample/mL DI water. The samples were excited using 355 nm laser.

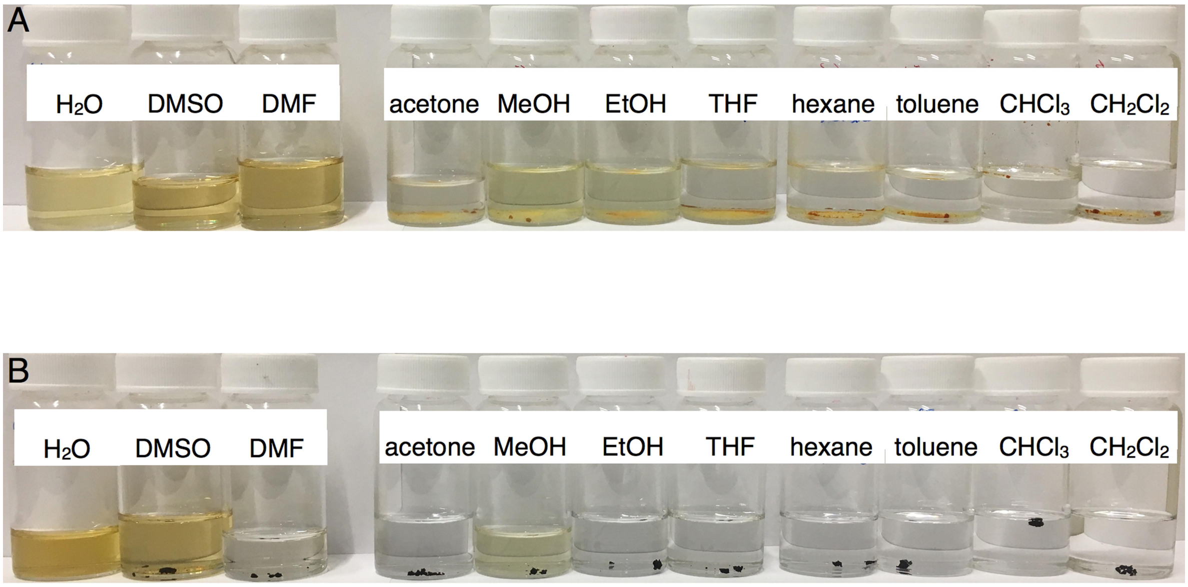

Figure S3. Dispersity test of CA-18 and CJ-14 CDs in different solvents at a concentration of 1 mg/mL. CA-18 CDs can be dispersed in water, DMSO and DMF, while CJ-14 CDs can be dispersed only in water.

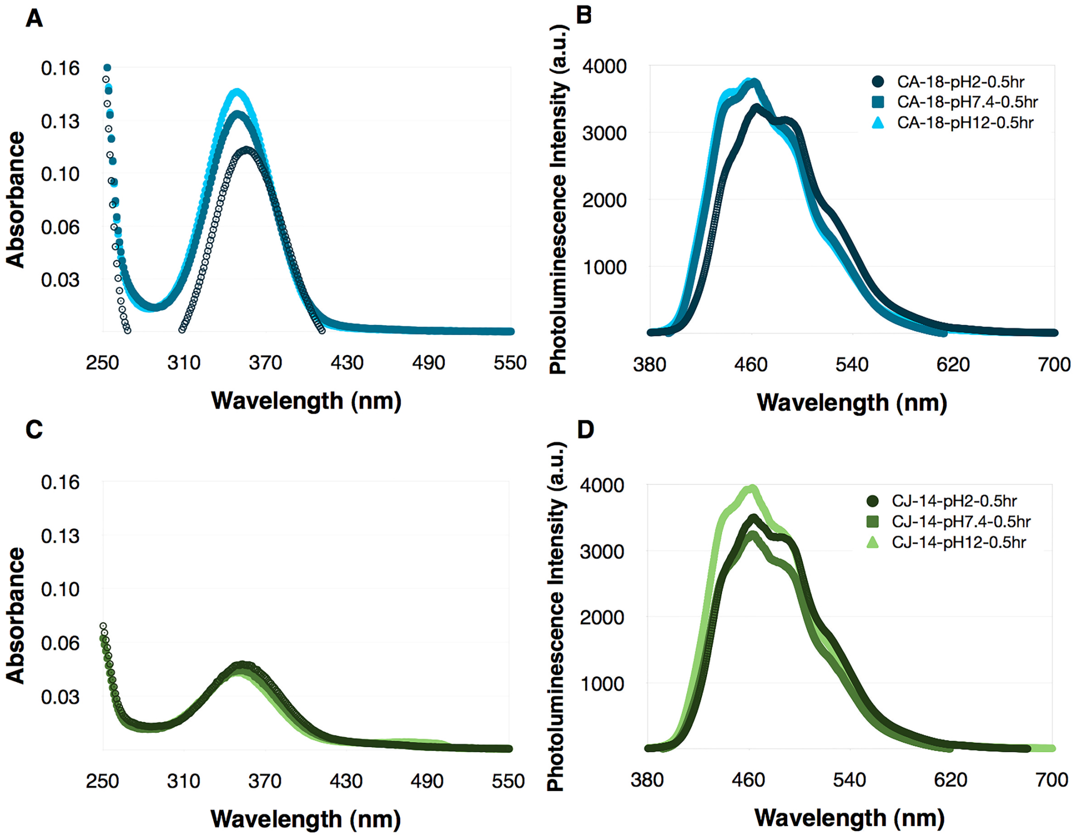

Figure S4 Absorption and emission spectra of CA-18 and CJ-14 CDs after 0.5 hr dispersion in pH 2, 7.4 and 12 solutions, separately. The CA-18 sample (100 mL of 0.1 g/mL CA in DI water and 3480 μL EDA) was pyrolized for 18 min total heating time and CJ-14 sample (100 mL of CJ and 3480 μL EDA) was pyrolized for 14 min total heating time using 2 minute-repetitive heating under 70% microwave power (630W). A.) UV absorbance of $1\text{x}10^{-5}$ g CA-18 CD/mL DI water. B.) fluorescence emission spectra of 1.2 mg CA-18 CD/mL DI water. C.) UV absorbance of $1\text{x}10^{-5}$ g CJ-14 CD/mL DI water. D.) fluorescence emission spectra of 1.2 mg CJ-14 CD/mL DI water, the samples were excited using 355 nm laser. (See Figure S5)

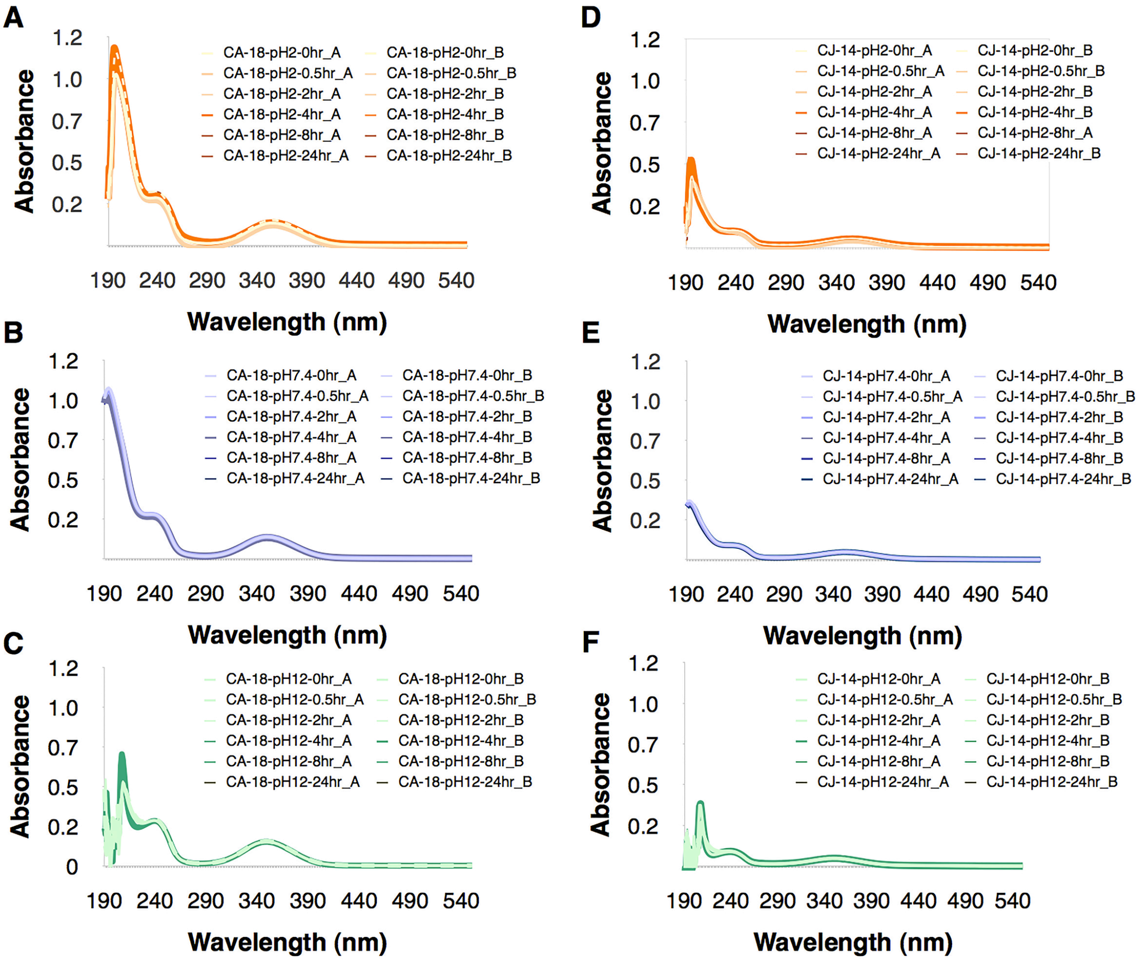

Figure S5 Absorption spectra of CA-18 and CJ-14 CDs at different pHs suspended at 0, 0.5, 2, 4, 8, 24 hrs. UV absorption spectra of $1.21\text{x}10^{-5}$ g CA-18 CD/mL DI water at A.) pH 2, B.) pH 7.4, C.) pH 12. UV absorption spectra of $1.21\text{x}10^{-5}$ g CJ-14 CD/mL DI water at D.) pH 2, E.) pH 7.4, F.) pH 12. (See Figure S4)

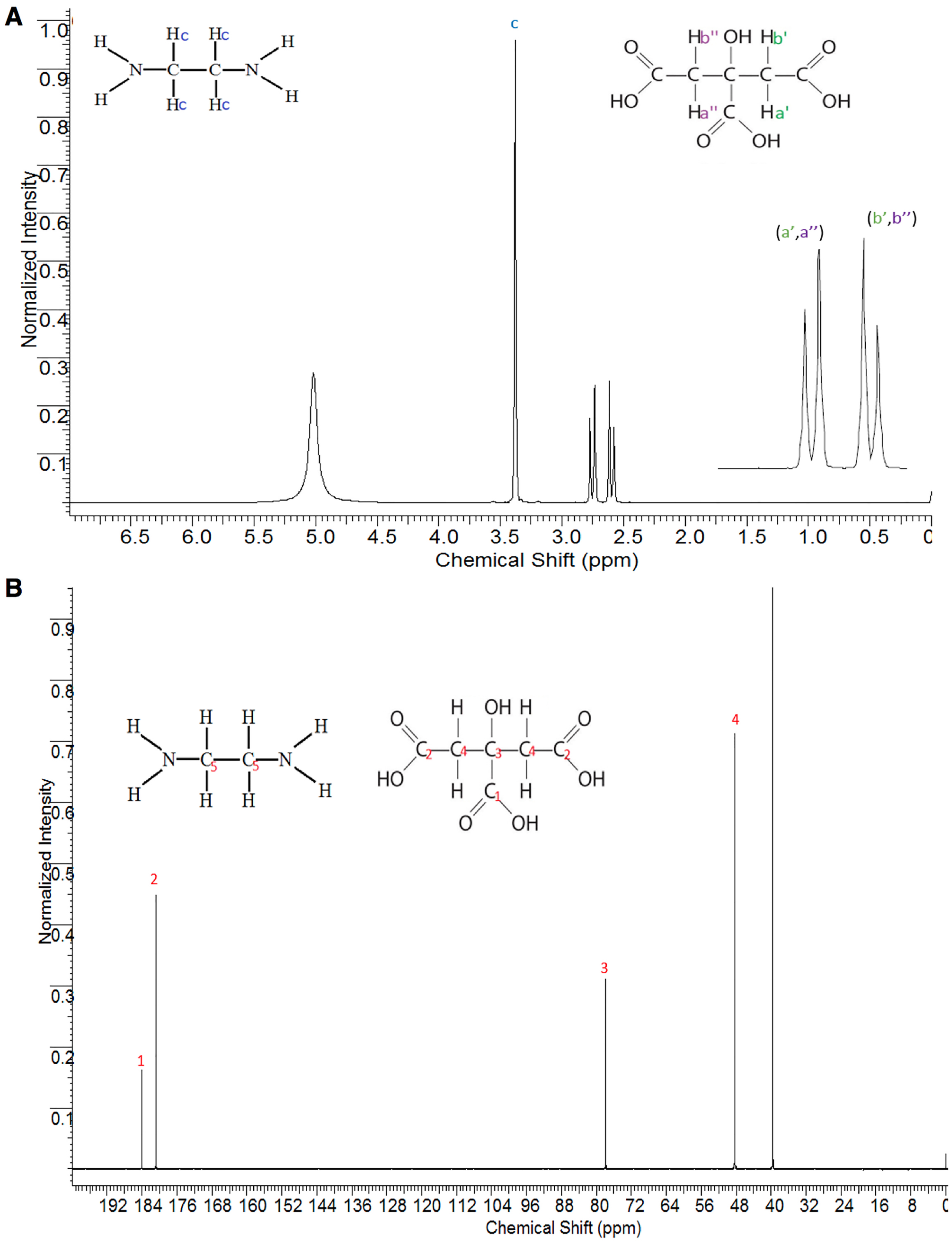

Figure S6 A.) ^{1}H NMR spectrum before microwave pyrolysis of 1:1 molar ratio CA:EDA suspended in D_2O. Inset: Upperleft: EDA chemical structure with proton labeled c; upper right: CA chemical structure with protons labeled as a' b',a'' and b''; bottom right: zoomed region from 2.5 to 3 ppm. B.) ^{13}C NMR spectrum before microwave heating of 1:1 molar ratio CA:EDA in D_2O.

^{1}H NMR spectrum of 1:1 CA and EDA before pyrolysis (0-minute heating time) shows that the mixture provided two doublets at 2.6 to 2.75 ppm (J=16 Hz), indicative of the α-methylene protons in CA (a', b', a'' and b'', Figure S6A). The singlet peak at 3.38 ppm corresponds to the methylene protons in EDA (c, Figure S6A). The exchangeable protons attached to the amines of EDA and the acid groups of CA are not observed. ^{13}C NMR spectrum shows 5 peaks (Figure S6B) where 184 ppm corresponded to the carbonyl carbon C1 in CA, 180 ppm to the two other carbonyl carbon assigned as C2, 78 ppm to the methine peak of CA assigned as C3, 48 ppm to the methylene peak of CA assigned as C4, and 40 ppm to the methylene peak of EDA assigned as C5.

Table S4. Tabulated NMR peak shifts of CA and CJ-samples after subjecting to time study in D_2O. A.)^{1}H NMR (ppm) of CA-samples, B.) ^{1}H NMR (in ppm) of CJ-samples, C.) ^{13}C NMR (in ppm) of CA-samples, B.) ^{13}C NMR (in ppm) of CJ-samples. Each sample was pyrolized using 100 mL of 0.1% CA in DI water and 3480 μL EDA or 100 mL CJ and 3480 μL EDA for a total time of 4, 8, 10 (CJ only), 12, 14, 16, 18 (CA only), 20 (CA only) min using 70% microwave power (630W) at 2 min-repetitive heating. (See Figure 5 and 6)

A. CA CDs H NMR Shifts (ppm)					
CA-0		2.6 (d, J=16)	2.75 (d, J=16)	3.38 (s)	
CA-4		2.62 (d, J=16)	2.75 (d, J=16)	3.38 (s)	
CA-8		2.65 (d, J=12)	2.8 (d, J=12)	3.38 (s)	
CA-12		2.64 (d, J=16)	2.79 (d, J=16)	3.38 (s)	
CA-14	2.5-4.2 (m)	2.65 (d, J=16)	2.79 (d, J=16)	3.38 (s)	
CA-16	2.5-4.2 (m)				5.5-9.0 (weak peaks)
CA-18	2.5-4.2 (m)				5.5-9.0 (weak peaks)
CA-20	2.5-4.2 (m)	2.6-2.8 (b)	2.8-2.9 (b)	3.4 (m)	5.0-9.0 (weak peaks)

B. CJ CDs H NMR Shifts (ppm)					
CJ-0		2.52 (d, *J*=16.8)	2.69 (d, *J*=12.8)	3.27 (s)	
CJ-4		2.58 (d, *J*=14.8)	2.73 (d, *J*=13.6)	3.39 (s)	
CJ-8		2.60 (d, *J*=16)	2.75 (d, *J*=16)	3.39 (s)	
CJ-10		2.58 (d, *J*=12)	2.72 (d, *J*=16)	3.38 (s)	
CJ-12	2.5-4.5 (m)	2.63 (d, *J*=16)	2.78 (d, *J*=12)	3.39 (s)	5.5-9.0 (weak peaks)
CJ-14	2.5-4.5 (m)	2.58 (d, *J*=20)	2.73 (d, *J*=20)	3.37 (s)	5.5-9.0 (weak peaks)
CJ-16	2.5-4.5 (m)	2.59 (d, *J*=16)	2.75 (d, *J*=16)	3.40 (s)	5.5-9.0 (weak peaks)

C. CA CDs C-13 NMR Shifts (ppm)									
CA-0		39.6		48.2		77.8		180.8	184
CA-4		39.6		47.8		77.6		180.0	184
CA-8		39.6		47.8		77.6		180.0	183.5
CA-12		39.6		47.8, 47.9		77.6		180.1	183.5
CA-14	39.0	39.6	40.5, 44.9, 47.4	47.8	75.8	77.6	179.6	180.0	183.4
CA-16	39-50	39.6		47.8	75	77.1	151, 154, 157, 165, 172, 174, 175, 178, 179	180.6, 180.7	182.4, 184
CA-18	39.1-42.1		44-46, 46.5	48	75.5	77 (very weak)	157.5, 165, 172, 172.5, 174, 175, 178.1, 178.2, 179	180.5, 180.5, 180.8, 182	183.3, 183.4
CA-20	39	39.6	40.5, 44.9, 47.2, 47.6, 47.8		75.7	77.4	155, 165.5, 172.5, 174.1, 179.5, 179.6	180.5	183.2

D. CJ CDs C-13 NMR Shifts (ppm)									
CJ-0	26	40.1	40-55	48.8	70-80	78.3		182.2	185.0
CJ-4		39.5	40-55	48.4	70-80	77.9		181.5	184.5
CJ-8		39.5	40-55	48.2	70-80	77.8		181	184.1
CJ-10		39.5	40-55	48.4	70-80	78		181.5	184.5

C. CA CDs C-13 NMR Shifts (ppm)									
CJ-12	33.5, 34, 39	39.5	40.3, 41.8, 41.9, 42.5, 44.5, 45, 45.2, 46-48	48.1	55-65, 70-80	75.7	151.5, 157.6, 165.5, 171, 171.8, 172, 175.5, 179.5, 180	181.5, 183	184
CJ-14		39.6	40.3-55	48.4	65, 70-80	78	151, 157.5, 165, 171, 172, 175, 179.5, 180.9	181.5	184.4
CJ-16	34, 39	39.5	40.2-55	48.5	57, 61.5, 63, 64.2, 65, 68, 70-80	78	151.2, 157.5, 165.5, 172.5, 175.0, 177.5, 179.5	181.5	184.5

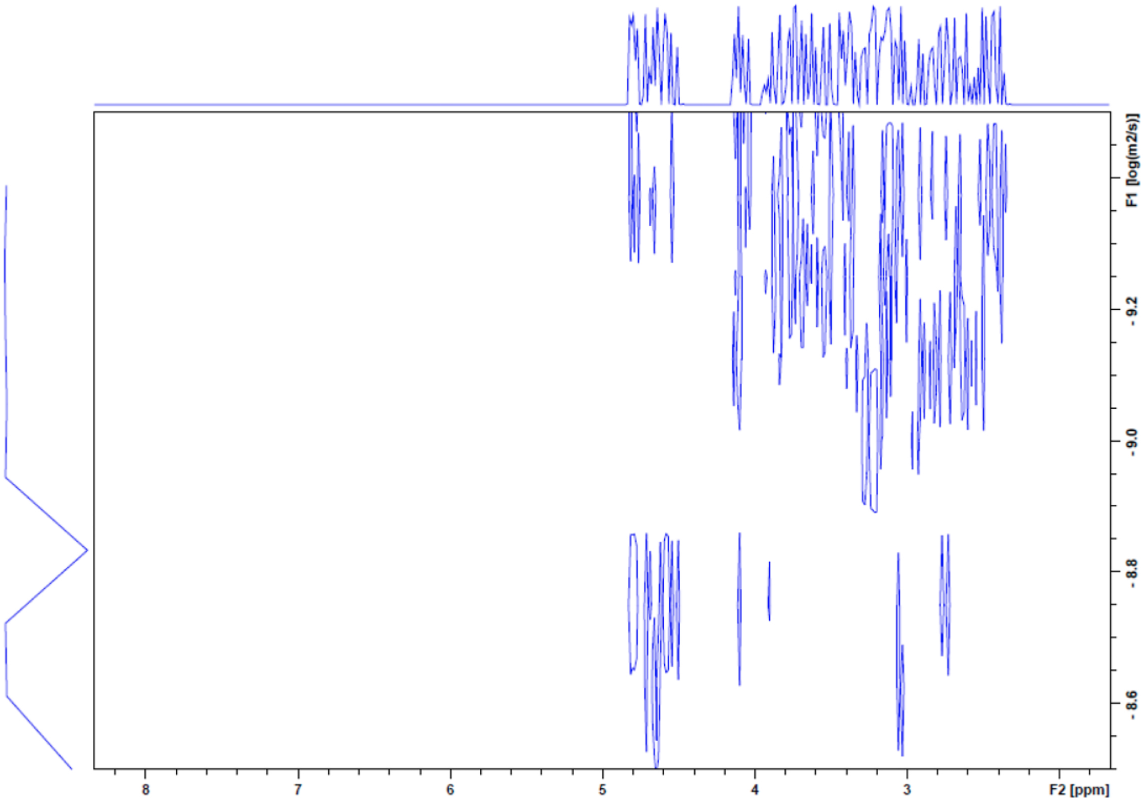

Figure S7 Diffusion-ordered spectrum of CA-20 in D_2O, obtained by suspending the sample to form a uniform solution with concentration of 10 mg/mL. The hydrodynamic radius was calculated based on equation (1), where $k=1.38x10^{-23}$ $m^2kg\ s^{-2}K^{-1}$, T=303 K, η is the viscosity of D_2O @300K=0.8509 kg $m^{-1}s^{-1}$; such that when logD=-8.7, R=0.13 nm; logD=-8.58, R=0.1 nm; logD=-9.4, R=0.65 nm. Therefore, the range of radius is 0.1 nm to 0.65 nm.

$$D = \frac{kT}{6\pi\eta R}$$ (Equation 1)

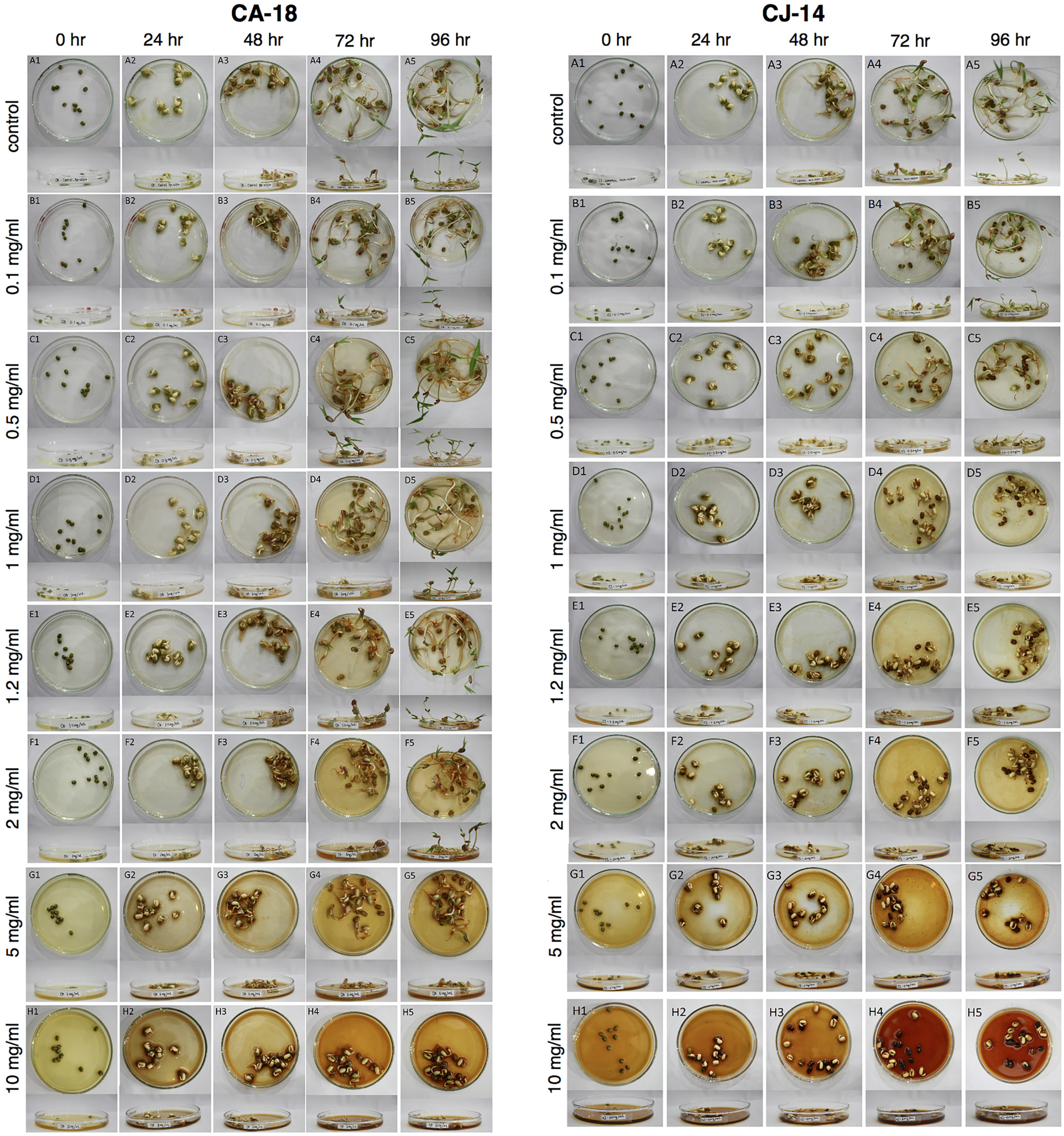

Figure S8 Photos of Mung beans cultivated using different CA-18 CD or CJ-14 CD concentrations, top (top view) and bottom (side view). Left: Ten mung seeds were grown in A.) control or deionized water, B.) 0.1 mg, C.) 0.5 mg, D.) 1 mg, E.) 1.2 mg, F.) 2 mg, G.) 5 mg and H.) 10 mg CA-18 CDs/ mL DI water. Right: Ten mung seeds were grown in A.) control or deionized water, B.) 0.1 mg, C.) 0.5 mg, D.) 1 mg, E.) 1.2 mg, F.) 2 mg, G.) 5 mg and H.) 10 mg CJ-14 CDs/mL DI. The results were observed at 0, 24, 48, 72, 96 hrs. (See Figure S9, Table S5)

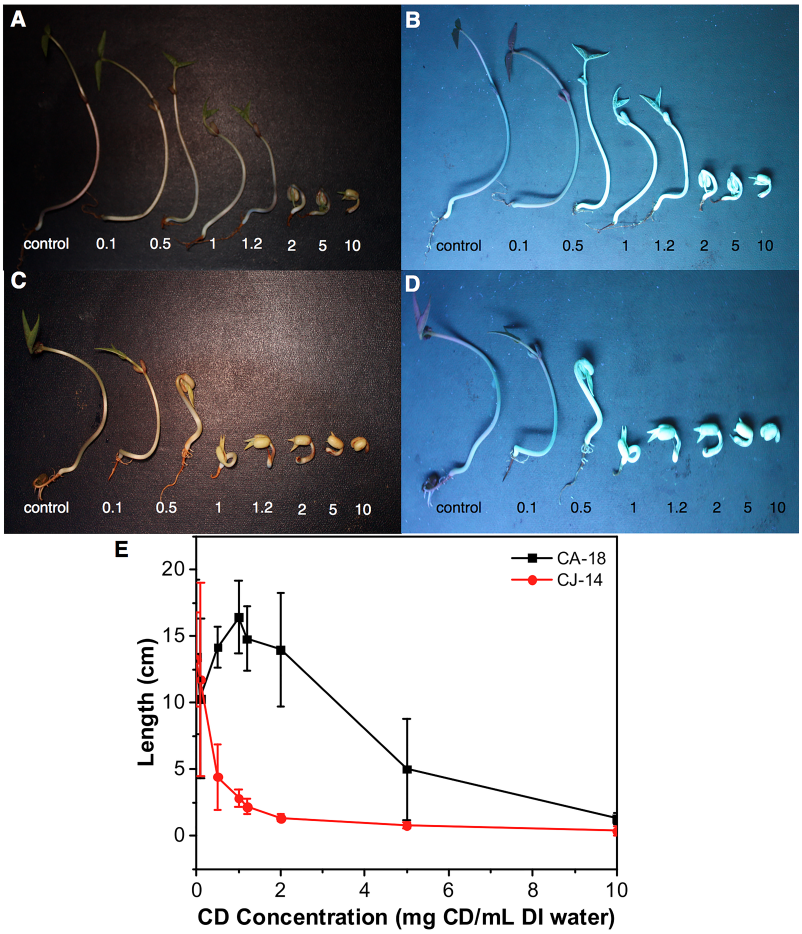

Figure S9 *Mung beans grown using different concentrations of CA-18 and CJ-14 CDs* (control-water only, 0.1, 0.5, 1, 1.2, 2, 5 and 10 mg/mL DI water) after 96 hr. Mung beans were grown at different CA-18 concentrations under A.) normal light and B.) UV light (365 nm). Mung beans grown at different CJ-14 concentrations under C.) normal light and D.) UV light (365 nm). E.) Average length of bean sprouts in different CD concentrations. The length (stem only) of the sprouts was measured after 144 hr of growth and plotted against increasing concentrations of CA-18 and CJ-14 CD concentrations. Sample size (n=9) beans were measured with each plotted data as the average. Beans which did not sprout were considered as 0 cm. (See Figure S8, Table S5)

Table S5 Length of mung bean sprouts grown in CA-18 and CJ-14 CDs. Sprouts (n=9)* were measured after 144 hrs. (See Figure S8 and S9)

CD concentration (mg/mL)	Average length of sprouts gown in CA-CDs (cm)*	Standard deviation of sprout length	Average length of sprouts grown in CJ-CDs (cm)*	Standard deviation of sprout length
0 (Control)	13.43	5.89	13.24	3.52
0.1	10.30	6.00	11.77	7.27
0.5	14.21	1.51	4.42	2.45
1	16.42	2.73	2.83	0.66
1.2	14.88	2.43	2.199	0.59
2	13.98	4.23	1.34	0.28
5	5.00	3.81	0.78	0.24
10	1.31	0.41	0.38	0.35