Electronic Supplementary Information

An insight into the molecular and surface state photoluminescence of carbon dots revealed through solvent induced modulations in their excitation wavelength dependent emission properties

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Note S1: Synthesis of the Carbon dots (LD1 and LD2)

The two kinds of carbon dots used in the present study were synthesized directly from freshly squeezed lemon juice, a natural bioresource, by simple one-step thermolysis reaction at two different temperature conditions.¹ Based on the raw material used (*Citrus limon*), the obtained carbon dots are referred as LD1 and LD2.

For LD1, 25 ml of filtered lemon juice was taken in a glass beaker and heated at 100°C for 90 minutes, till the colour of the sample changed to orange brown. The liquid was then centrifuged for 30 minutes at 10000 rpm. The resulting supernatant was further filtered using Whatman filter paper and the filtrate containing LD1 suspension was stored in a refrigerator for further use.

For LD2, 25 ml of filtered lemon juice was taken in a glass beaker and heated at 120°C for 120 minutes, till the solvent evaporated and the sample transformed to an orange brown gel. This was dissolved in 25 ml water and then centrifuged for 30 minutes at 10000 rpm. The resulting supernatant was further filtered using Whatman filter paper. The carbon dot samples dispersed in the filtrate were stored in a refrigerator for further use.

Based on previous studies on the formation of carbon dots from different carbohydrate precursors, in this case too, we believe that LD1 and LD2 are formed due to the decomposition of the ingredients present in lemon juice, by hydrolysis and dehydration, followed by polycondensation and aromatization.²⁻⁴ The presence of weak acids (ascorbic, citric, malic) assists the reactions to proceed in an effective and controlled manner. The higher temperatures used in the synthesis of LD2 compared to LD1, is expected to lead to a higher degree of carbonization for the former carbon dot.



Fig. S1. FTIR spectra of LD1 (black) and (B) LD2 (red).



Fig. S2. Absorption spectra (enlarged view) of LD1 (black) and LD2 (green) in aqueous dispersions.



Fig. S3. Photographs of aqueous dispersions of LD1 (A) and LD2 (B) under daylight (I) and upon illumination with UV light (II).

λ_{ex} (nm)	LD1	LD2
300	0.019	0.003
320	0.023	0.008
340	0.030	0.014
360	0.024	0.023
380	0.005	0.030
400	0.002	0.031
430	-	0.030

Table S1. Quantum yields of LD1 and LD2 in water at different excitation wavelengths.

System	λ_{em} (nm)	A ₁ (%)	$\tau_1 (ns)^b$	$A_{2}(\%)$	τ_2 (ns)	A ₃ (%)	τ_3 (ns)
LD1	400	31	0.04	23	1.3	46	4.9
	420	15	0.04	22	1.4	63	5.3
	450	7	0.04	20	1.6	73	5.5
	500	7	0.04	16	1.2	77	5.4
	560	23	0.04	18	0.74	59	4.9
	580	24	0.04	20	0.64	56	4.7
LD2	400	14	0.04	33	1.4	53	5.8
	420	16	0.04	32	1.3	52	5.8
	450	11	0.04	33	1.3	56	5.9
	500	16	0.04	32	1.1	52	5.3
	560	19	0.04	35	0.92	46	4.6
	580	22	0.04	37	0.81	41	4.1

Table S2. PL decay parameters^a for LD1 and LD2 aqueous dispersions at different monitoring wavelengths. Excitation wavelength: 374 nm.

^{*a*}The PL decays are fitted as, $I(t) = \sum_{i} a_{i} \exp(\frac{-t}{\tau_{i}})$, and the relative contributions for each of the decay time constants, τ_{i} , are calculated as, $A_{i} = a_{i}\tau_{i} / \sum_{i} a_{i}\tau_{i}$. Here a_{i} is the absolute pre-exponential

factor for the i^{th} decay component.⁵

^bThe shortest decay component has been fixed as 40 ps, which is the time resolution of the present TCSPC setup.



Fig. S4. Absorption spectra of LD1 and LD2 in different solvents: EA (black), ACN (blue), MeOH (green) and water (red). Absorption spectra of the carbon dots could not be recorded below 250 nm in EA due to solvent interference.



Fig. S5. Intensity decay traces of LD1 (A) and LB2 (B) dispersions in EA (1, black), ACN (2, green) and MeOH (3, red) monitored at 450 nm. Excitation wavelength: 374 nm.

Solvent	LD1	LD2
Water	0.024	0.023
EA	0.020	0.020
ACN	0.019	0.021
MeOH	0.025	0.024

Table S3. Quantum yields of LD1 and LD2 in different solvent media (λ_{ex} 360 nm).

Table S4. PL decay parameters^a for LD1 and LD2 dispersed in different solvents. Excitation wavelength: 374 nm and emission wavelength: 450 nm.

System	Solvent	A ₁ (%)	τ_1 (ns)	A ₂ (%)	τ_2 (ns)	A ₃ (%)	τ_3 (ns)	$<\tau>_{avg}$ (ns)
LD1	EA	18	0.15	43	1.6	39	6.5	3.25
	ACN	12	0.19	52	1.5	36	7.0	3.32
	MeOH	9	0.10	41	1.8	50	6.8	4.15
LD2	EA	20	0.19	45	1.8	35	6.8	3.23
	ACN	14	0.17	38	1.8	48	7.1	4.12
	MeOH	10	0.10	38	2.0	52	7.7	4.77

^{*a*}The PL decays are fitted as, $I(t) = \sum_{i} a_{i} \exp(-t/\tau_{i})$, and the relative contributions for each of the decay time constants, τ_{i} , are calculated as, $A_{i} = a_{i}\tau_{i} / \sum_{i} a_{i}\tau_{i}$. Here a_{i} is the absolute pre-exponential factor for the ith decay component.⁵



Fig. S6. Excitation spectra of LD1 in (A) EA and (B) MeOH solvents monitored for the emission at 450 nm (black) and 470 nm (red).



Fig. S7. TRANES of LD1 in EA solvent.at 0.8, 1, 1.2, 1.5, 2, 2.5, 3, 4, 5, and 6.5 ns (1-10). Excitation wavelength is 374 nm.

References

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