Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Information

Recognition and Ratiometric Visual Sensing of Unsaturated Fatty Acids by White Light Emitting-Quantum Dot Complex

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Experimental Section:

Materials: Zinc acetate dihydrate (Merck, assay = 99.5–101.0 %), manganese acetate tetrahydrate (Merck, assay ≥ 99.0 %), sodium sulphide flakes purified (Merck, assay > 50.0 %), 8-hydroxyquinoline (HQ: Merck, assay ≥ 99.0 %), sodium carbonate (Merck, assay ≥ 99.9 %), sodium hydroxide (Merck, assay ≥ 99.0 %), sodium fluoride (Merck, assay ≥ 99.5 %), di-sodium oxalate (Merck, assay ≥ 99.8 %), tri-sodium citrate dihydrate (Merck, assay = 99.0-101.0 %), di-sodium tartrate dihydrate (Merck, assay ≥ 99.5 %), calcium chloride (Merck, assay ≥ 98.0 %), potassium chloride (Merck, assay ≥ 99.5 %), magnesium chloride (Merck, assay ≥ 98.0 %), sodium chloride (Merck, assay ≥ 99.5 %), methanol (Merck, assay ≥ 99.9 %), sodium oleate (Merck, assay ≥ 82.0 %), sodium stearate (Merck, assay ≥ 99.0 %), linoleic acid (Merck, assay ≥ 99.0 %), palmitic acid (Merck, assay ≥ 99.0 %), geranic acid (Merck, assay = 85.0 %), erucic acid (Merck, assay ≥ 99.0 %), sunflower oil (Fortune company), soybean oil (Fortune company), edible oil (Saffola company) were purchased and directly used without further purification. Water of Milli-Q grade was used for all experiments.

Fabrication of white light emitting quantum dot complex (WLE-QDC):

(i) Synthesis of Mn^{2+}-doped ZnS quantum dots (Qdots): Mn^{2+}-doped ZnS Qdots were synthesized using a previously reported procedure.[S1] In short, an aqueous solution of sodium sulfide was added to an aqueous mixture of zinc acetate dihydrate and manganese acetate tetrahydrate in such a way that the concentrations of S^{2-}, Zn^{2+} and Mn^{2+} ions in the reaction mixture were 5.0 mM, 5.0 mM and 0.75 mM, respectively. The reaction mixture was heated at 100 °C and refluxed for 4 h with continuous stirring. To separate synthesized colloidal particles from aqueous phase, (i) at first, the milky white reaction mixture was centrifuged for 10 min with speed of 20,000 rpm and (ii) then, the separated colloidal particles (i.e., pellet after centrifugation) were redispersed

into same amount of water and centrifuged with same experimental condition in order to remove the unreacted reactants. The separation process was repeated again and finally the solid pellet was dispersed into 200.0 mL of water using sonication. The colloidal dispersion was used as stock for all other experiments. **(ii) Preparation of 8-hydroxyquinoline (HQ) solution:** 7.3 mg of solid HQ was dissolved in 10.0 mL of methanol by sonication at room temperature to prepare 5.0 mM methanolic solution of HQ. **(iii) Fabrication of WLE-QDC:** The WLE-QDC was prepared by adding 15.0 µL of 5.0 mM methanolic solution of HQ into 3.0 mL of as-prepared aqueous dispersion of Qdots (with absorbance of 0.04 at 357 nm). Then, the aforementioned mixture of HQ and Qdots was centrifuged at 20,000 rpm for 10 min. The pellet obtained from centrifugation was redispersed into same volume of water and centrifuged under same condition and then the pellet was washed as before. Finally, the pellet was dispersed into same volume of water, which was then used for further experiments. For the preparation of WLE-QDC, the optimum concentration of HQ used was calculated to be 25.0 µM.

Sensing of LCUFAs: The sensing of LCUFA was performed by adding 2.5 mM aqueous solution of sodium oleate sequentially to 3.0 mL of aqueous dispersion of WLE QDC (with absorbance of 0.06 at 357 nm) followed by recording of their photoluminescence spectra and other optical properties. The experiment was carried out in triplicate. The intensity ratio (I_{480}/I_{590}) of WLE QDC against concentration of oleate was plotted to find out the linear range and to calculate the limit of detection (LOD). Equation $3\sigma/k$ was used for the calculation of LOD. Similarly, the sensing of other LCUFAs (like linoleate and erucate) by WLE-QDC was also carried out.

Recognition of long chain unsaturated fatty acid (LCUFA) from their saturated form: The different responses of WLE-QDC towards LCUFA (e.g., oleic acid) and their corresponding saturated form (i.e., stearic acid) were examined by adding mixture of sodium salt of oleic acid and stearic acid with different ratio of concentrations (with keeping total concentration of fatty acids to a fixed amount) into the solution of WLE-QDC. Accordingly, five different ratiometric mixtures were prepared with oleate and stearate ratio of 0:1, 1:3, 1:1, 3:1 and 1:0 (keeping the total fatty acid concentration equal to 2.5 mM). The highest amount of oleate added to WLE-QDC (with absorbance of 0.06 at 357 nm) for this experiment was 80.6 µM and the photoluminescence properties of oleate added WLE-QDC were monitored. Similar experiment was performed for stearate (of 80.6 µM). The experiments were performed in triplicate.

Selectivity of Sensing by WLE-QDC towards LCUFAs: Selectivity of sensing by WLE-QDC towards LCUFAs was examined by adding sodium salt of different saturated and unsaturated fatty acids (like oleic acid, linoleic acid, erucic acid, palmitic acid, lauric acid, geranic acid and stearic acid), anions (like citrate tartrate, oxalate and fluoride) and metal ions (like Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}). The mentioned interfering substances were added to 3.0 mL of aqueous dispersion of WLE QDC (with absorbance of 0.06 at 357 nm) separately such that their concentration became 80.6 µM (same as the highest concentration used in sensing experiment as in Fig. 2 of the manuscript). The experiments were carried out executed in triplicate. The change in intensity ratio ($\Delta (I_{480}/I_{590}) = (I_{480}/I_{590})_{\text{after addition}} - (I_{480}/I_{590})_{\text{before addition}}$) of WLE-QDC after addition of each substance was

plotted in bar diagram for comparative study. It is to be noted here that linoleic acid, erucic acid, palmitic acid, lauric acid and geranic acid were converted to their corresponding sodium salts by following a previously reported method.[S2] In short, excess amount of solid sodium carbonate was added to 5.0 mL of 100 mM methanolic solution of above mentioned fatty acids separately and stirred for 20 min at 40 °C. The reaction mixtures were then filtered to remove unreacted Na_2CO_3 and were dried in vacuum to get sodium salt of corresponding fatty acids.[S2]

Commercial Vegetable Oil Analysis. For real sample analysis commercial sunflower, edible and soybean oils were purchased from local market and saponified with 20% aqueous NaOH solution following a well-known procedure.[S2] In short, 5.0 mL of 20% aqueous NaOH was added to 5.0 mL of each of above-mentioned oils separately and stirred for 30 min at 80 °C. The formed sodium salts of fatty acids were precipitated out by cooling the reaction mixture in an ice cold condition. Then the precipitate was filtered and washed with ice cold water followed by drying in vacuum. Dried solid salt of sunflower, edible and soybean oil were dissolved in water to make 0.2, 0.5 and 0.3 mg/mL solutions, respectively. LCUFAs in those solutions were determined following above-mentioned sensing procedure by adding 20.0 µL of each solution to 3.0 mL of WLE QDC (with absorbance of 0.06 at 357 nm) separately and monitoring the photoluminescence properties. Notably, a linear relationship between I_{480}/I_{590} of WLE-QDC and concentrations of equivalent mixture of (i) oleate, (ii) linoleate and (ii) erucate was measured (Fig. S15, ESI) and used for the quantification of LCUFAs in commercial vegetable oils such as sunflower, edible and soybean oils (Table 1 of Manuscript).

Instruments: To characterize the samples and to probe the recognition and sensing phenomena, HORIBA Jobin Yvon FluoroMax-4 spectrofluorimeter was mainly used to record photoluminescence. Digital photographs were taken using Realme Mobile (Realme 5) under spectrofluorimeter excitation source. OSRAM color calculator (CIE-1931) software was used to calculate chromaticity coordinates from photoluminescence spectra and Image-J software was used to calculate hue from digital photograph. PerkinElmer Lambda 35 UV–vis spectrophotometer was used to record the absorption spectra of the samples. Transmission electron microscopy (TEM; Model: JEOL JEM 2100F, maximum accelerating voltage: 200 kV) was used to analyze the size and lattice parameters of the nanoparticles. Gatan Digital Micrograph software was used to analyze TEM image, High resolution TEM image and corresponding inverse fast Fourier transformation. X-ray diffraction patterns of the samples were recorded by using Rigaku TTRAX-III X-ray diffractometer.

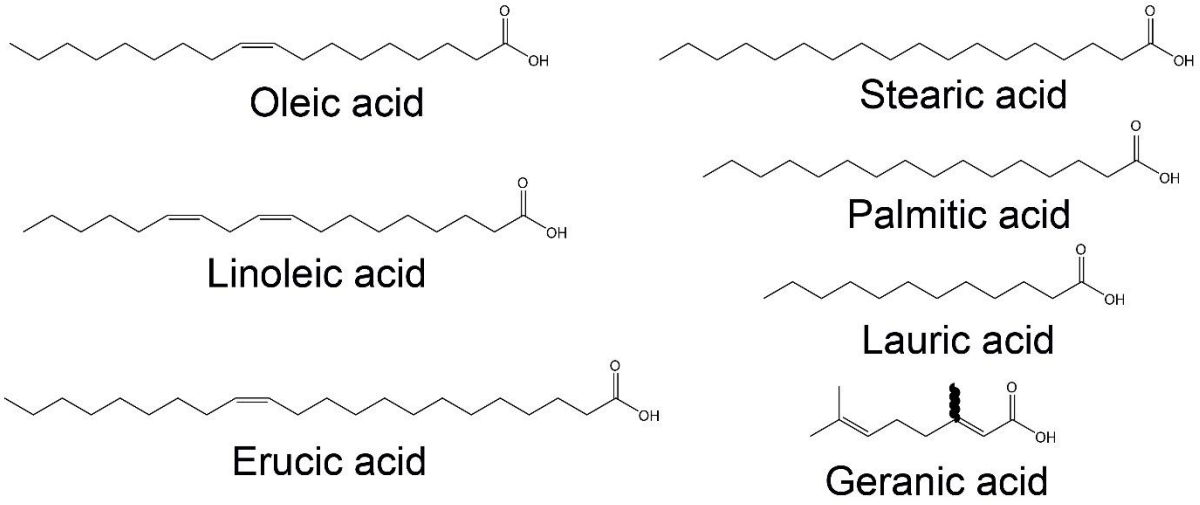

Fig. S1. The molecular structures of the unsaturated and saturated fatty acids that have been used for experiments reported in this work.

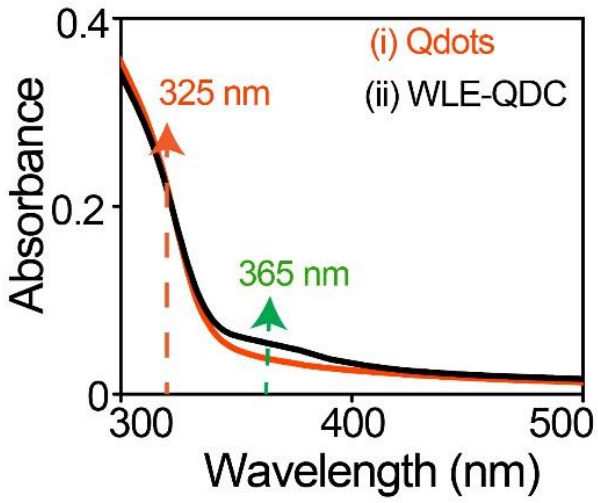

Fig. S2. UV-vis spectra of (i) Qdots and (ii) WLE-QDC.

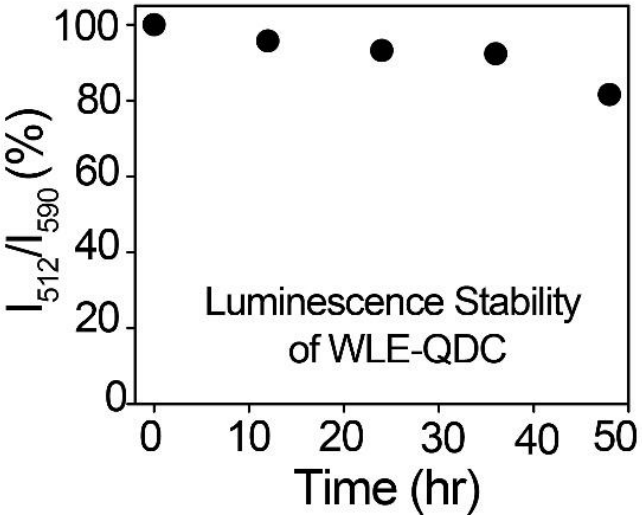

Fig. S3. Time dependent luminescence stability of WLE-QDC (in water). The stability of WLE−QDC in terms of the emission intensity ratio (I_{512}/I_{590}) at different time intervals (upto 48 h) in a water medium was monitored at an excitation wavelength of 357 nm.

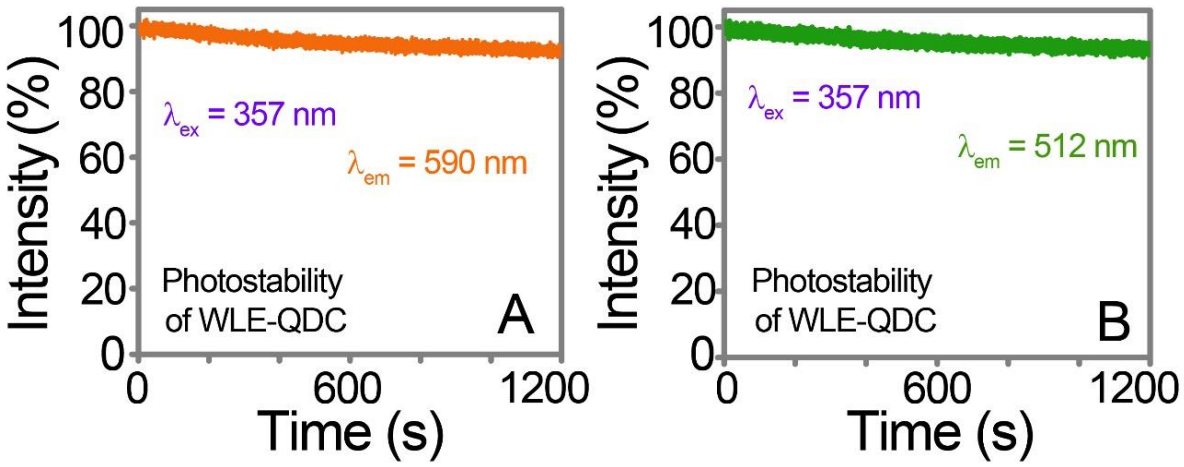

Fig. S4. Photostability of WLE-QDC (in water) with regard to λ_{em} at (A) 590 and (B) 512 nm. The photostability of WLE-QDC was monitored under a continuous irradiation of 357 nm light for 20 minutes and with respect to emission maxima of Qdots (590 nm) and surface ZnQ_2 complex (512 nm).

Table S1. Tabulated form of the photoluminescence intensity ratios and chromaticity values of WLE-QDC following the addition of different amount of oleate. The data were extracted from Fig. 2 (Manuscript).

Conc. of Oleate (μM)	I_{480}/I_{590}	Chromaticity	
		CIE-X	CIE-Y
a) 0	0.93	0.33	0.43
b) 4.2	1.74	0.28	0.40
c) 8.3	2.32	0.26	0.38
d) 12.4	2.73	0.25	0.37
e) 16.6	3.07	0.24	0.36
f) 20.7	3.29	0.23	0.35
g) 24.8	3.52	0.23	0.35
h) 32.9	3.75	0.22	0.34
i) 41.0	3.94	0.22	0.33
j) 49.0	4.06	0.22	0.33
k) 57.0	4.20	0.21	0.33
l) 64.9	4.32	0.21	0.32
m) 80.6	4.39	0.21	0.32

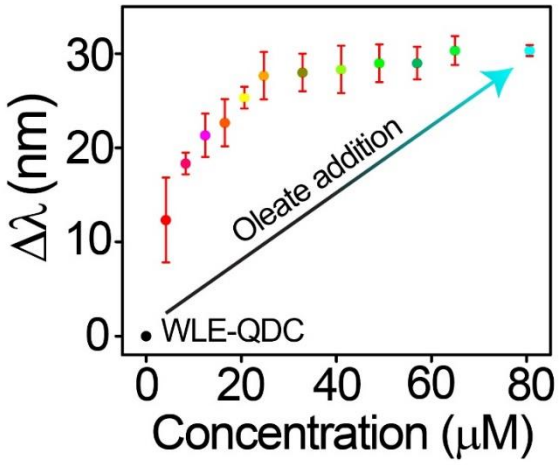

Fig. S5. Change in λ_{max} (at 512 nm) of WLE-QDC with increasing concentration of oleate in the range of 0.0-80.6 μM.

Table S2. Tabulated form of the comparison of (A) recognition systems and (B) optical sensors for recognition and ratiometric visual sensing of long chain unsaturated fatty acids.

(A) References for Recognition	Used Recognition Probes	Selective Recognition Ability	Analytical Method Used
This work	White light emitting quantum dot complex (WLE-QDC)	Long chain unsaturated fatty acids (LCUFAs; e.g. Na-salt of oleic acid) from their corresponding saturated forms (Na-salt of stearic acid)	Fluorescence
Ref. S3a	Polyaromatic receptor	Oleic acid over stearic acid	NMR + Mass
Ref. S3b	Cavitand receptor	Unsaturated ω-3, -6, and -9 fatty acids	NMR
Ref. S3c	Polyaromatic molecular tube	Oleic acid methyl ester (cis-5c)	NMR
Ref. S3d	Supramolecular nano-capsule	Molecular protection of C18 fatty acid methyl esters	NMR
Ref. S3e	Ubxd8 membrane protein	Long chain unsaturated fatty acids (Oleate)	Circular dichroism
(B) References for Ratiometric Sensing	Used Optical Probes	Optical Sensing Ability	Analytical Method Used
This work	White light emitting quantum dot complex (WLE-QDC)	Ratiometric visual detection, with a detection limit of 0.127 μM in the linear range of 4.2-16.6 μM and its practical utilization in quantification of LCUFAs in commercial vegetable oils (such as sunflower, edible and soybean oils)	Fluorescence
Ref. S4a	Polymerized liposome	Colorimetric sensing of oleic acid and linoleic acid in μM scale	Colorimetric response
Ref. S4b	A multichannel Au nanosensor	Colorimetric sensing of in the oleic acid concentration range of 0.0–10.0 μM	Colorimetric response
Ref. S4c	Calix-naphthalene based molecular tubes	Cis-fatty acids Octanoic acid (1-10 *m*M)	Fluorescence
Ref. S4d	Fluorescent fatty acid binding protein (FABP)	Ratiometric fluorescence sensing of oleic acid in the concentration range of 0.02–4.7 μM	Fluorescence
Ref. S4e	Duplex-pyrene-cyclodextrin based fluorescent sensors	Ratiometric fluorescence sensing of oleic acid in the concentration range of (0–7.0 equiv.)	Fluorescence
Ref. S4f	CdSe/ZnSMPA-BSARhod complex	Ratiometric fluorescence sensing of oleic acid in 10–1000 nM scale	Fluorescence

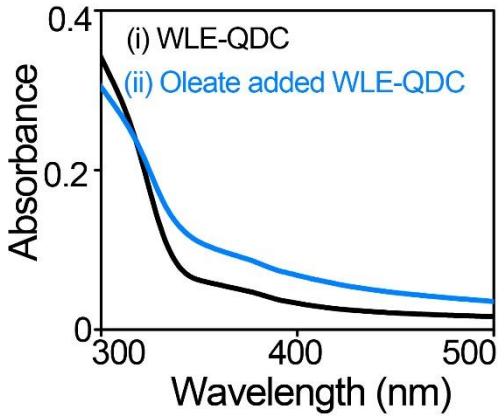

Fig. S6. UV-vis spectra of (i) WLE-QDC and (ii) oleate added WLE-QDC.

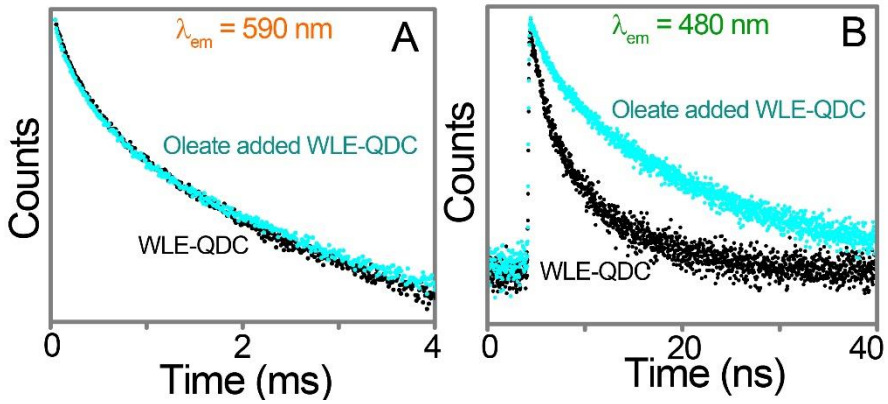

Fig. S7. (A) Time-resolved photoluminescence spectra (λ_{ex} = 330 nm) of WLE-QDC monitored at 590 nm (i) before and (ii) after addition of oleate. (B) Time-resolved photoluminescence spectra (λ_{ex} = 375 nm laser) of WLE-QDC monitored at 480 nm (i) before and (ii) after addition of oleate. The decay curves were fitted with tri-exponential function.

Table S3. Tabulated form of the average life times monitored at **(A)** 590 and **(B)** 480 nm of (i) WLE-QDC and (ii) oleate added WLE-QDC. The data were extracted from Fig. S7, ESI.

(A) Samples at λ_{em} = 590 nm	α_1 (%)	τ_1 (ms)	α_2 (%)	τ_2 (ms)	α_3 (%)	τ_3 (ms)	τ_{av} (ms)	χ^2
(i) WLE QDC	44.12	0.31	16.74	1.38	39.15	0.09	**0.91**	0.99
(ii) WLE QDC + oleate	56.37	0.26	72.14	0.04	19.93	1.33	**0.90**	0.99
(B) Samples at λ_{em} = 480 nm	α_1 (%)	τ_1 (ns)	α_2 (%)	τ_2 (ns)	α_3 (%)	τ_3 (ns)	τ_{av} (ns)	χ^2
(i) WLE QDC	8.10	0.57	36.74	2.93	55.16	9.47	**8.30**	1.00
(ii) WLE QDC + oleate	10.00	1.30	34.44	5.43	55.56	14.90	**13.00**	1.01

The decay curves were fitted to a multi-exponential model using following equations

$$I(t) = \sum_i \alpha_i \exp\left(-t/\tau_i\right) \qquad (1)$$

The tri exponential functions were applied to fit respective decay curve to acquire χ^2 close to 1.0. The averaged life times (τ_{av}) were determined from the results of three exponential model using

$$\tau_{av} = \frac{\sum_i \alpha_i \tau_i^2}{\sum_i \alpha_i \tau_i} \qquad (2)$$

Where, α_i = pre-exponential factors and τ_i = excited-state luminescence decay time associated with the *i*-th component.

Table S4. Tabulated form of the photoluminescence intensity ratios and chromaticity values of WLE-QDC following the addition of the mixture of stearate and oleate. The data were extracted from Fig. 3 (Manuscript).

Stearate : Oleate	I_{480}/I_{590}	Chromaticity	
		CIE-X	CIE-Y
0:0	0.93	0.33	0.43
1:0	2.19	0.26	0.37
3:1	2.74	0.25	0.36
1:1	3.26	0.23	0.34
1:3	3.50	0.23	0.33
0:1	4.39	0.21	0.32

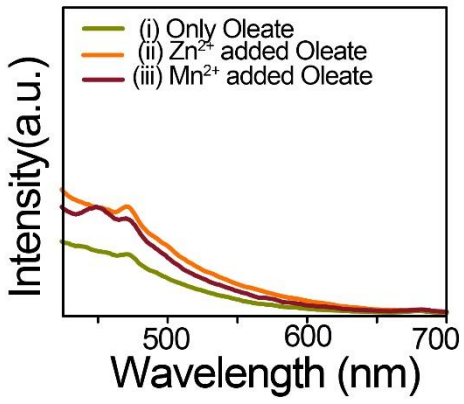

Fig. S8. Emission spectra (λ_{ex}= 357 nm) of (i) oleate (80.6 µM; in water), (ii) Zn^{2+} ions added oleate (iii) Mn^{2+} ions added oleate.

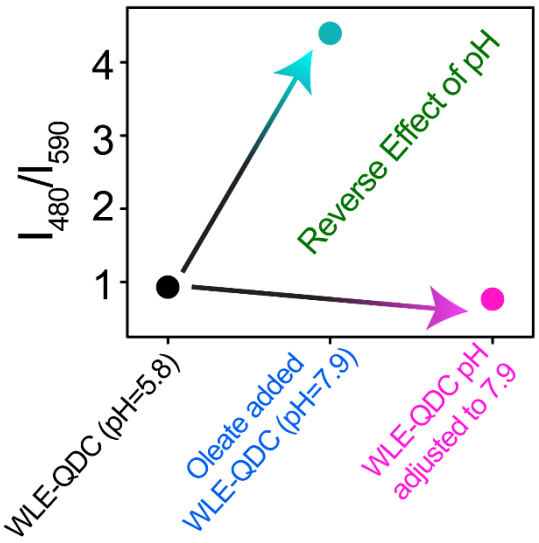

Fig. S9. Change in emission intensity ratio (I_{480}/I_{590}) of (i) WLE QDC (pH= 5.8) (ii) 80.6 µM oleate added WLE-QDC (pH-7.9) and (iii) WLE-QDC adjusted to pH = 7.9 (i.e., the same pH of oleate added WLE-QDC).

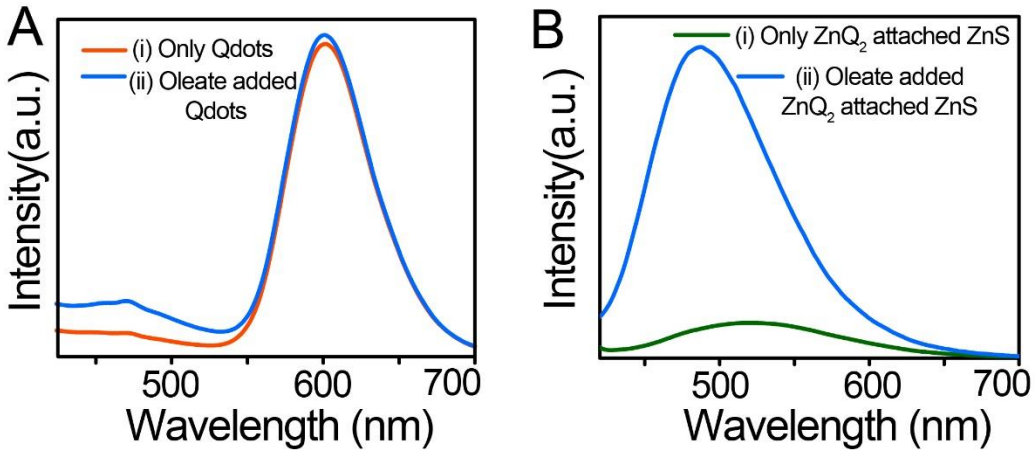

Fig. S10. (A) Emission spectra (λ_{ex}= 357 nm) of the aqueous dispersion of (i) Qdots and (ii) Qdots following addition of 80.6 µM oleate. (B) Emission spectra (λ_{ex}= 357 nm) of (i) ZnQ_2 attached ZnS Qdots and (ii) ZnQ_2 attached ZnS Qdots following addition of 80.6 µM oleate.

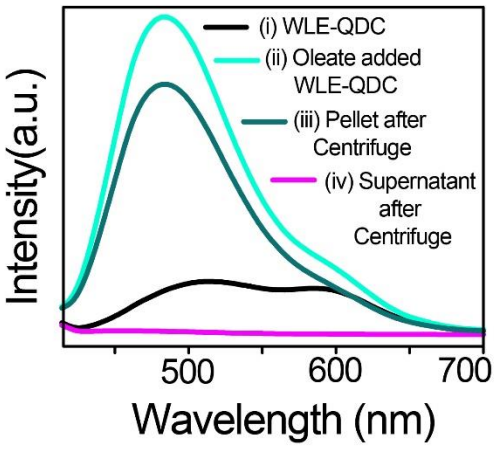

Fig. S11. Emission spectra (λ_{ex} = 357 nm) of (i) WLE-QDC, (ii) 80.6 µM oleate added WLE-QDC before centrifugation, (iii) the pellet obtained following centrifugation and redispersion into same amount of water and (iv) of the supernatant following centrifugation.

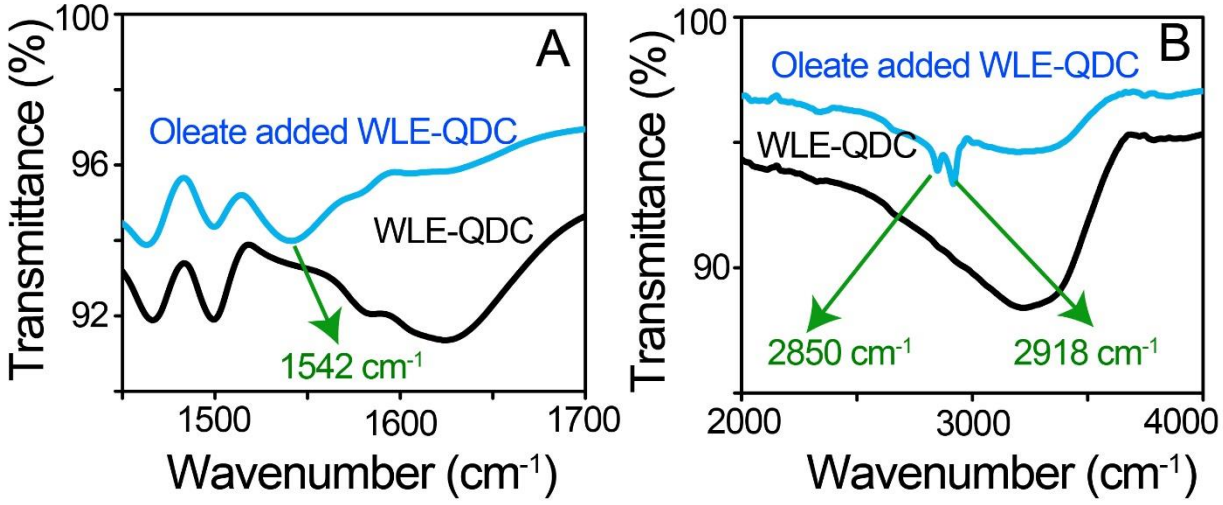

Fig. S12. FTIR spectra of (i) WLE-QDC and (ii) 80.6 µM oleate added WLE-QDC (following centrifugation) in the range of (A) 1450-1700 cm^{-1} and (B) 2000-4000 cm^{-1}.

Table S5. Tabulated form of FTIR peaks of (i) WLE-QDC and (ii) 80.6 µM oleate added WLE-QDC (following centrifugation). The data were extracted from Fig. S12, ESI.

Wave number (cm^{-1})	Functional Groups	Ref.
2850 & 2918	symmetric & asymmetric stretching of $-CH_2$	S6
1542	asymmetric stretching of COO^-	

The incorporation of oleate on the surface of WLE-QDC was further confirmed by observing their main functional group's characteristic symmetric and asymmetric stretching peaks of $-CH_2$ (at 2850 and 2918 cm^{-1}) and that of COO^- (at 1542 cm^{-1}) – along with the main functional groups of ZnQ_2 - in the FTIR spectra of oleate treated WLE-QDC (Fig. S12, Table S5, ESI**)**.[S5] This clearly confirmed the incorporation of oleate on the surface of WLE-QDC.

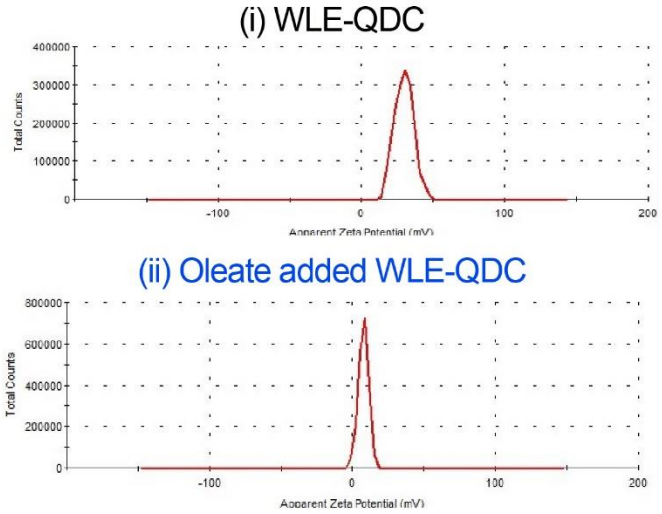

Fig. S13. Zeta potential curves of (i) WLE-QDC and (ii) 80.6 µM oleate added WLE-QDC (following centrifugation).

Table S6. Tabulated form of zeta potentials of (i) WLE-QDC and (ii) 80.6 µM oleate added WLE-QDC (following centrifugation). The data were extracted from Fig. S13, ESI.

	Samples	Zeta potential (mV)
(i)	WLE QDC	28.53
(ii)	Oleate added WLE QDC	7.42

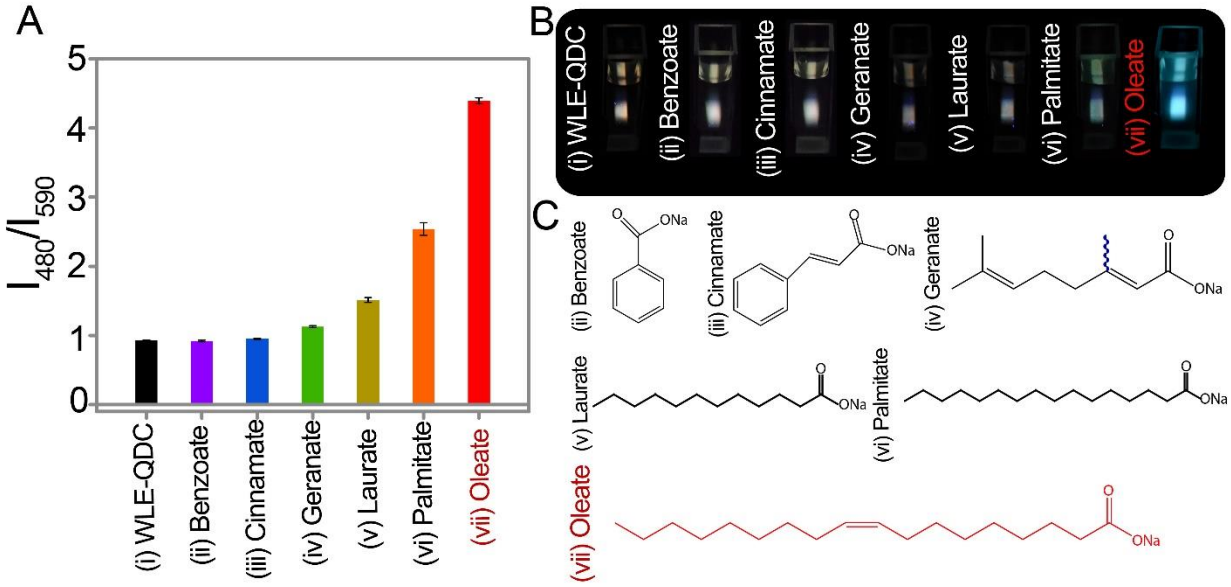

Fig. S14. (A) Bar diagram of the comparison of emission intensity ratio (I_{480}/I_{590}) and **(B)** corresponding photographs (λ_{ex}= 357 nm) of (i) WLE-QDC obtained following addition of (ii) benzoate (80.6 μM, aromatic compound that favours π–π interaction), (iii) cinnamate (80.6 μM; aromatic compound that favours π–π interaction), (iv) geranate (80.6 μM; short chain unsaturated fatty acid that favours π–π interaction), (v) laurate (80.6 μM; medium chain saturated fatty acid that favours hydrophobic interaction), (vi) palmitate (80.6 μM; long chain saturated fatty acid that favours hydrophobic interaction) and (vii) oleate (80.6 μM; long chain unsaturated fatty acid that favours hydrophobic and π–π interaction). Each experiment was performed in triplicate. **(C)** The molecular structures of the Na-salts of benzoate, cinnamate, geranate, laurate, palmitate and oleate that have been used for experiments reported in this work.

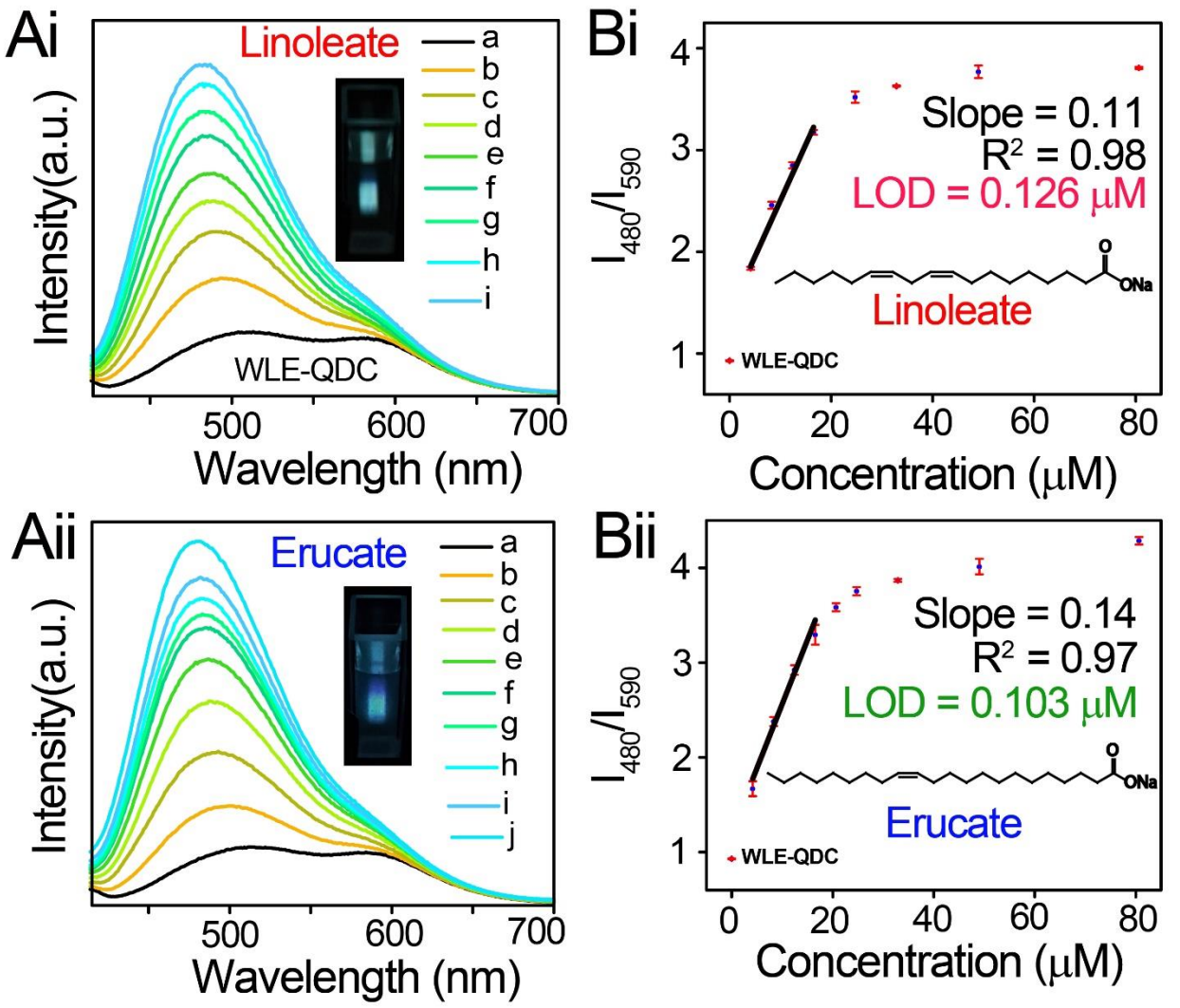

Fig. S15. (A) Emission spectra (λ_{ex}= 357 nm), **(B)** changes in emission intensity ratio (I_{480}/I_{590}) of WLE-QDC noted following addition of different concentrations of (i) linoleate: ((a) 0.0, (b) 4.2, (c) 8.3, (d) 12.4, (e) 16.6, (f) 24.8, (g) 32.9, (h) 49.0 and (i) 80.6 μM) and (ii) erucate ((a) 0.0, (b) 4.2, (c) 8.3, (d) 12.4, (e) 16.6, (f) 20.7, (g) 24.8, (h) 32.9, (i) 49.0 and (j) 80.6 μM). The experiments were carried out in triplicate. A linear relationship between I_{480}/I_{590} of WLE-QDC and concentrations of (i) linoleate or (ii) erucate was used to estimate limit of detection (LOD). The digital photographs of WLE-QDC following addition of linoleate and erucate, which are LCUFAs and has capability of concurrent hydrophobic and π–π interactions similar to oleate. (inset; Fig. S15A, ESI).

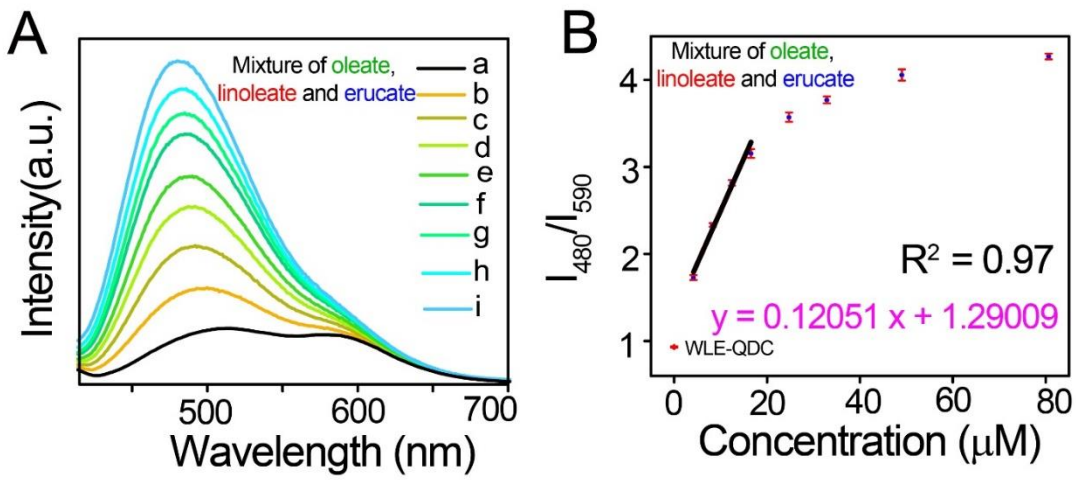

Fig. S16. (A) Emission spectra (λ_{ex}= 357 nm), **(B)** changes in emission intensity ratio (I_{480}/I_{590}) of WLE-QDC noted following addition of different concentrations of equivalent mixture of (i) oleate, (ii) linoleate and (ii) erucate ((a) 0.0, (b) 4.2, (c) 8.3, (d) 12.4, (e) 16.6, (f) 24.8, (g) 32.9, (h) 49.0, (i) 80.6 μM). The experiments were carried out in triplicate. A linear relationship between I_{480}/I_{590} of WLE-QDC and concentrations of equivalent mixture of (i) oleate, (ii) linoleate and (iii) erucate was obtained and used for the quantification of LCUFAs in commercial vegetable oils such as sunflower, edible and soybean oils (Table 1 of Manuscript).

Table S7. Tabulated form of the change in intensity ratio of WLE-QDC following addition of the mentioned interfering substances in Fig. 4 (Manuscript). The data were extracted from Fig. 4 (Manuscript). The Δ (I_{480}/I_{590}) was considered as 100% for oleate added WLE-QDC.

Interfering Substances	Δ (I_{480}/I_{590}) (%)
Oleate	100.00
Linoleate	83.03
Erucate	96.85
Equivalent mixture oleate, linoleate and erucate	96.34
Tartrate	1.12
Geranate	4.13
Laurate	15.29
Fluoride	-0.52
Oxalate	1.57
Palmitate	46.80
Citrate	2.57
Stearate	37.73
Na^+	-0.68
K^+	-0.59
Ca^{2+}	-0.32
Mg^{2+}	-0.33

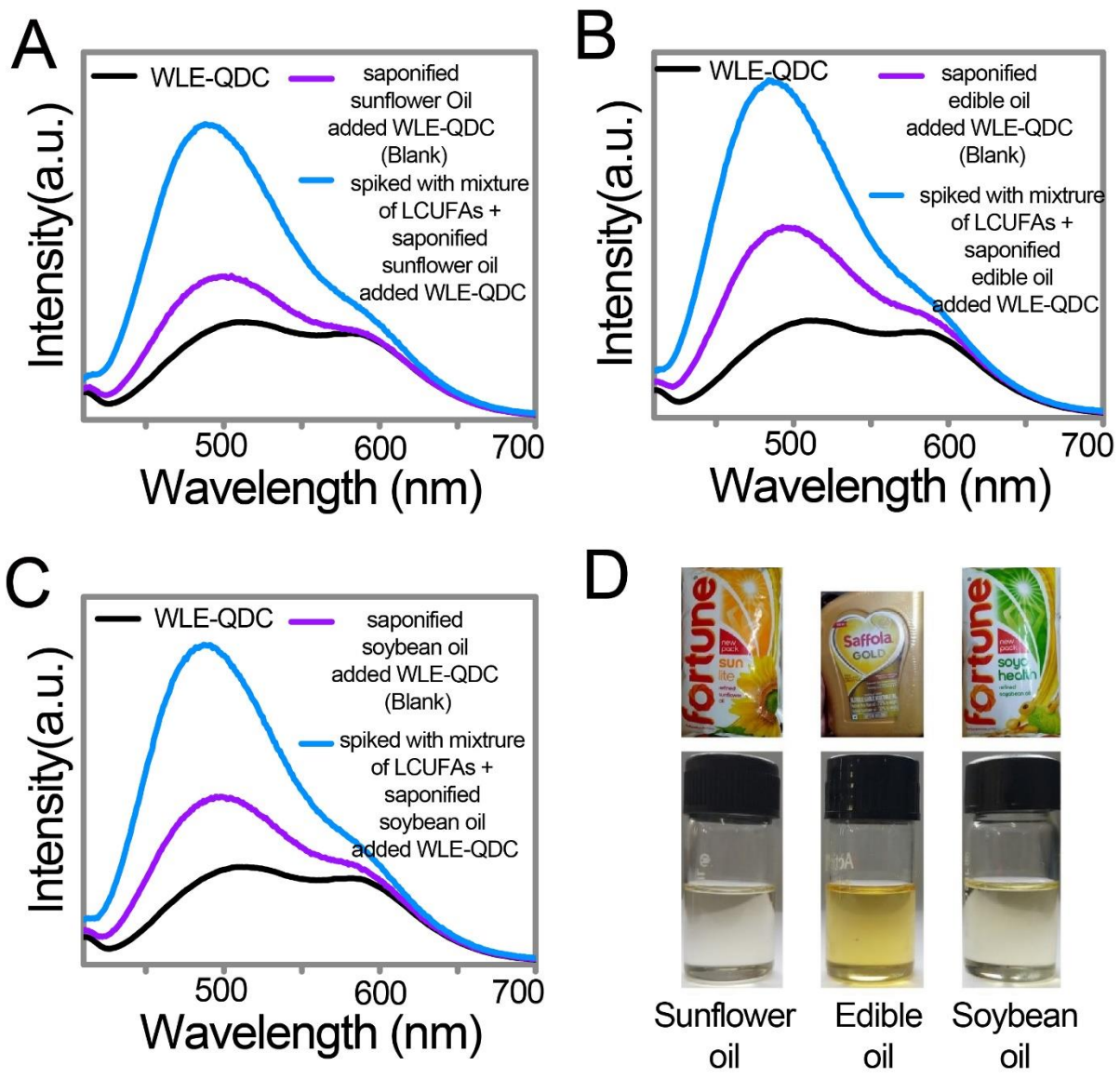

Fig. S17. (A, B & C) Representative emission spectra (λ_{ex}= 357 nm) of WLE-QDC recorded following addition of different concentrations of saponified commercial sunflower, edible and soybean oils, respectively. The extracted concentrations aganist the data from Fig. S17 (A-C) are clearly described and tabulated in Table 1 (manuscript). **(D)** The digital photographs of the commercial vegetable oils such as sunflower, edible and soybean oils that were used for experiments in this work.

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