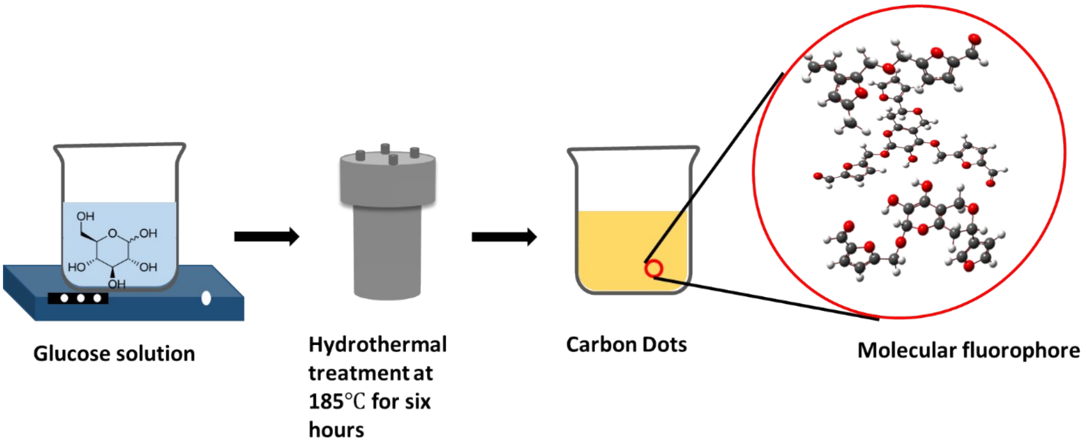
Electronic Supplementary Material (ESI) for Nanoscale.

SUPPORTING INFORMATION

White Light Emission from Helically Stacked Humin Mimics based H-aggregate in Heteroatom Free Carbon Dots

Synthesis of CDs:

Briefly, 150 mg of glucose powder (Merck) was dissolved in 200 ml of mili Q water and sonicate the mixture for 10 min to get the clear solution which was then transferred to Teflon sealed autoclave for 6 hours at 185 degrees Celsius. After naturally cooling down to room temperature and filtered using 1.5kDa dialysis tube to remove the unwanted product, then the clear was freeze dried to obtain a brown powder.



Scheme S1: Carbon dots synthesis

Instrumentations techniques for characterization of CDs

Particle distribution and the morphology of synthesized CDs were shown by transmission electron microscope (TEM) in a TECNAI G2 20S-TWIN (Japan) machine with an acceleration voltage of 200 kV. Alcoholic solution of CDs was prepared for TEM measurement, where the sample was well distributed and drop casted into a 300 mesh carbon-coated copper cast and the solvent was evaporated for overnight at room temperature. FT-IR spectrum was carried out within 4000–400 cm^{-1} range in a Perkin-Elmer Spectrum RX-II (Model no. 73713, USA) instrument to confirm the presence of different functional groups of CDs. The UV-Vis spectra and fluorescence emission spectra were taken by using a UV-vis spectrophotometer (SHIMADZU UV-2450, Japan) and fluorescence emission spectra were recorded in a Fluorescence spectrophotometer (HITACHI F-7000, Japan). The X-ray photoelectron spectrum (XPS) of CDs was recorded in a PHI 5000 Versa probe-II scanning microprobe (United States) outfitted with an Al-Kα X-ray monochromator (1486.7 eV). The binding energy scale of the spectrum has been calibrated by standard value of C 1s at 284.6 eV. The Raman spectra were recorded in a HORIBA Jobin Yvon T64000 Raman spectrometer (Japan) by using an Ar-Kr laser source of fixed wavelength ($\lambda = 514$ nm), equipped with a microscope (model BX41 Olympus, Japan).

TRES and TRANES:

TRES were constructed from the time-resolved fluorescence decays measured at a number of wavelengths (with a 10 nm interval) across the entire emission spectrum. The fluorescence decays were then fitted by using a multiexponential decay function to deconvolute the instrumental response, and the impulse response function at each wavelength was calculated through the procedure described by Lakowicz. To construct the TRES, the impulse response functions at different wavelength were normalized to make the intensity integrated at each wavelength equal to the steady-state intensity at that wavelength. A set of H(λ) was calculated as follows

$$I(t) = \Sigma\alpha_i \exp(-t/\tau_i),\ i = 1\text{–}4,$$

where α_i can be negative (excited-state kinetics), by the standard method of nonlinear least-squares and iterative reconvolution. TRES plotted as intensity vs wavenumber, were constructed using $\alpha_i(\nu)$ and $\tau_i(\nu)$, and steady-state emission spectrum that was corrected for the quantum efficiency of the photomultiplier. The equation used is-

$$I(\nu,t) = I_{ss}(\nu)\frac{\sum_j \alpha_j(\nu)e^{\frac{-t}{\tau_j(\nu)}}}{\sum_j \alpha_j(\nu)\tau_j(\nu)}$$

where $I_{ss}(\nu)$ is the steady-state fluorescence intensity at ν and $\alpha_j(\nu)$ and $\tau_j(\nu)$ are the values of the fit parameters.

Instrumentation of TAS:

The ultrafast transient absorption experiment setup utilizing a regenerative amplified Ti: sapphire laser system from Coherent (808 nm, 80 fs, 3 mJ/pulse, and 1 kHz repetition rate). The 30/70 beam splitter splits the 808 nm laser beam into two parts; the reflected part is used as pump beam for TOPAS Optical parametric Amplifier. It generates the pump beam for the TAS experiment within 290-1300 nm band. For the present work, the pump beam of wavelength 470 nm is attenuated by variable neutral density filter set at different fluences focused on the sample. The transmitted part of 808 nm laser pulse again splits into two beams, one part with less than 10% is first transmitted through retro reflector stage to generate time delay between pump and probe followed by a neutral density filter and focused into CaF2 crystal to generate a white light continuum

(WLC) from 350 nm to 950 nm used as probe beam. It is then focused on the sample by curved mirror. The transmitted/ reflected probe from the sample is then focused and collected by fiber coupled spectrometer. The synchronized optical chopper is used to chop the pump at the frequency of 500 Hz. The induced absorption change (ΔA) is calculated by difference in absorption of two adjacent probe.

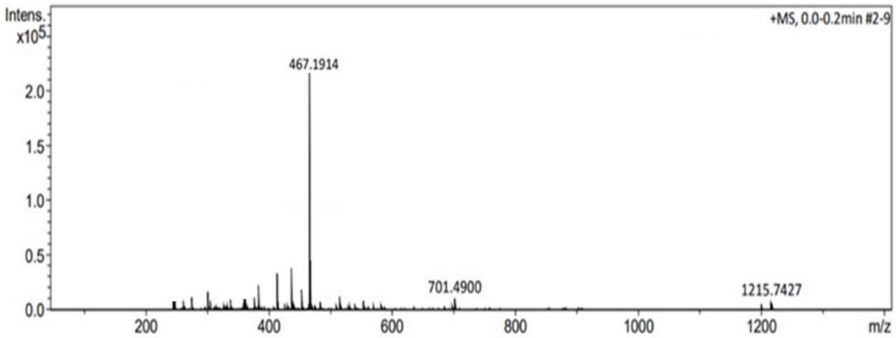


Fig S1: HRMS of CDs

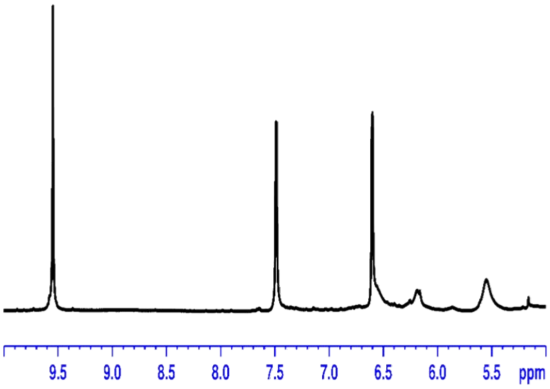


Fig S2: 1H-NMR of CDs

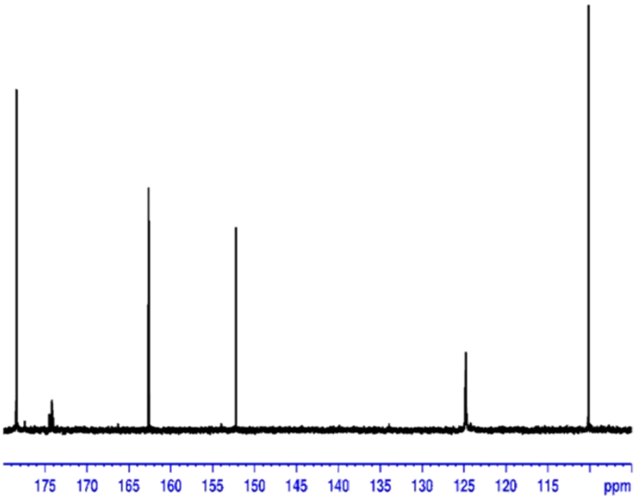


Fig S3: ^{13}C-NMR of CDs

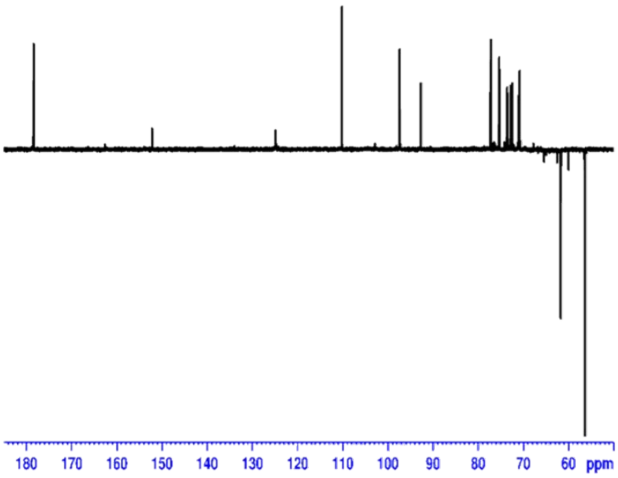


Fig S4: ^{13}C-DEPT-135 NMR of CDs

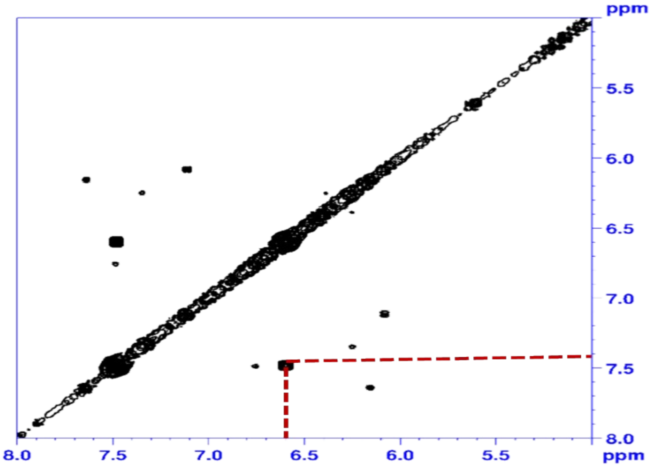


Fig S5: COSY NMR of CDs

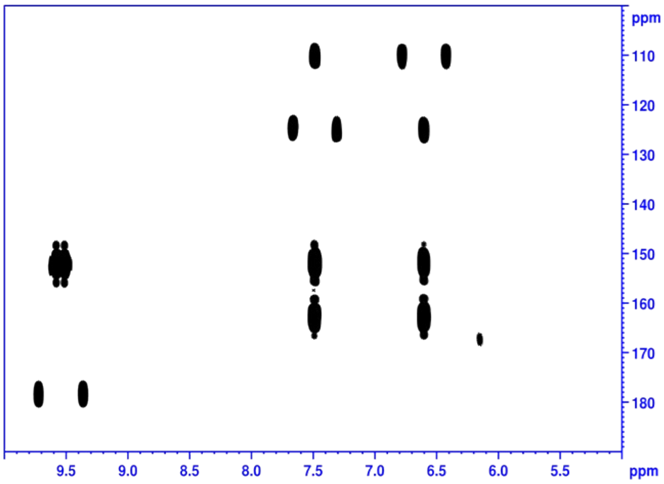


Fig S6: HMBC NMR of CDs

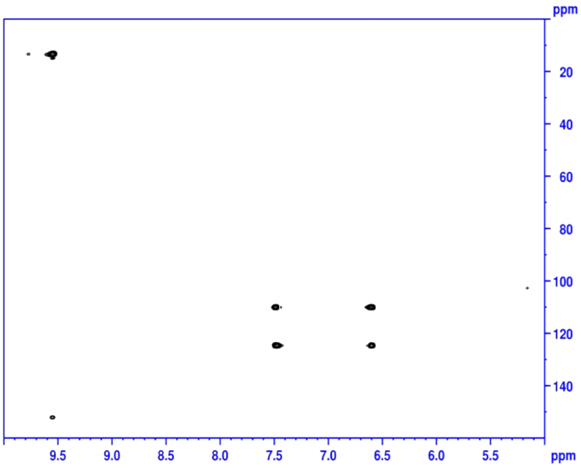


Fig S7: HSQC NMR of CDs

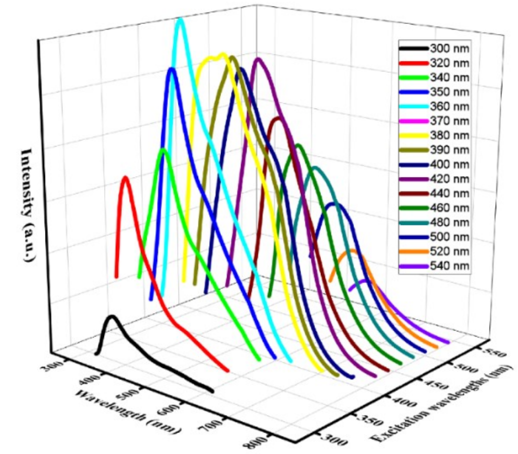


Figure S8: A) 3D-plot of Un-Normalized Excitation-dependent emission spectra of CDs from 300-540 nm wavelength

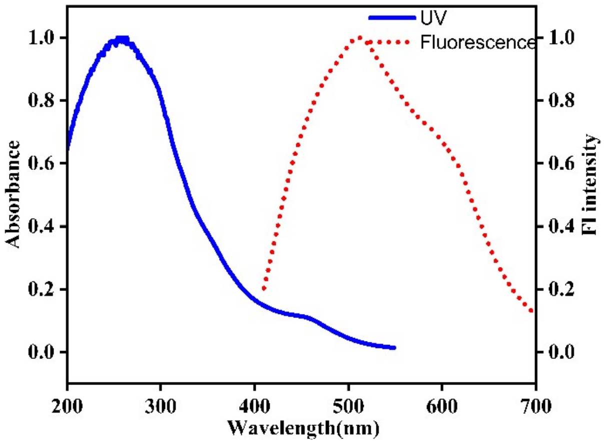


Figure S9: Normalized absorption and emission spectra of CDs showing absence of mirror image relationship between them

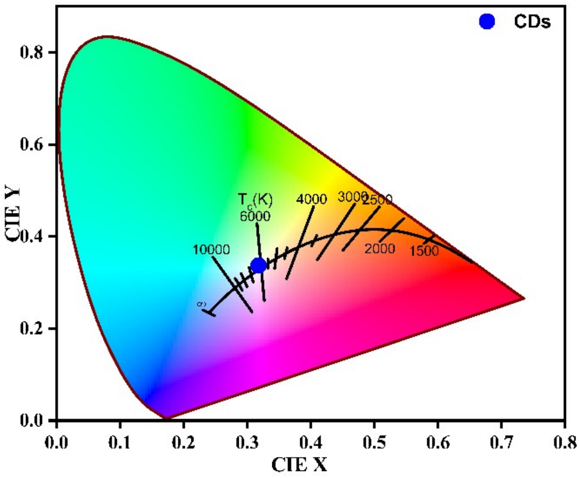


Figure S10: CIE diagram of CDs at 390 nm source showing colour temperature ~6000k

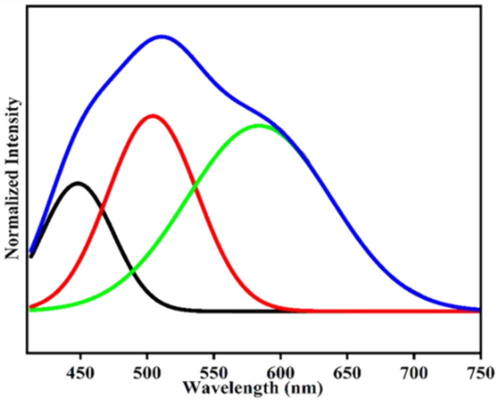


Fig S11: Deconvulated emission spectrum of CDs at 390 nm excitation wavelength

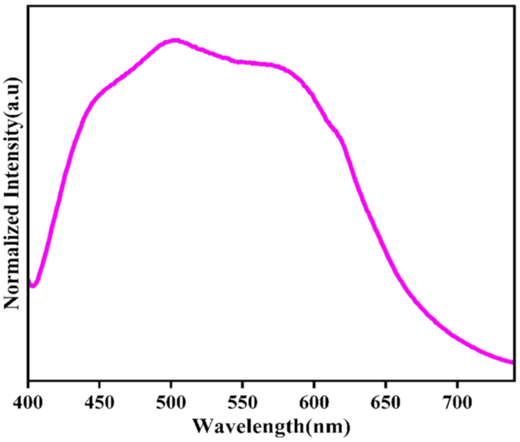


Figure S12: Broad emission spectra of CDs at 765 nm excitation wavelength.

Computational details: The molecular structure was designed using GAUSSIAN VIEW 6.0, and all computational studies were performed with the GAUSSIAN 09W program, the calculations were carried out using the density functional theory (DFT) method implemented in the series of programs within the computational package [1]. For this computational study, we employed the B3LYP DFT functionals. The geometry optimization of the ground state of A, B, and C was calculated step wise using the basis sets, 6–31 ++ G(d,p). The energy calculation of the first six vertical excited states was carried out using TD-DFT/IEFPCM 1model, with basis sets 6–31 ++ G(d,p), in a water solvent, we calculated the absorption spectra, circular dichroism spectra, and fluorescence spectra as well given in Fig S14, S19, and S20 respectively.

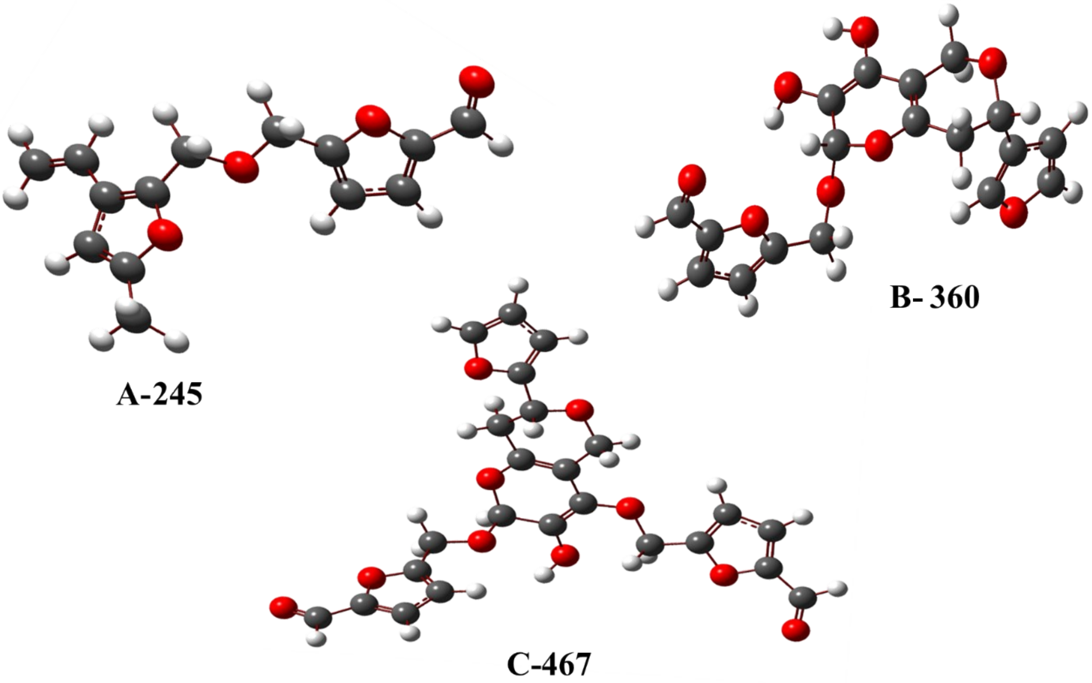


Fig S13: Proposed structure of three molecular fluorophores (A, B, and C) obtained from DFT (Grey-Carbon, White- Hydrogen, Red-Oxygen)

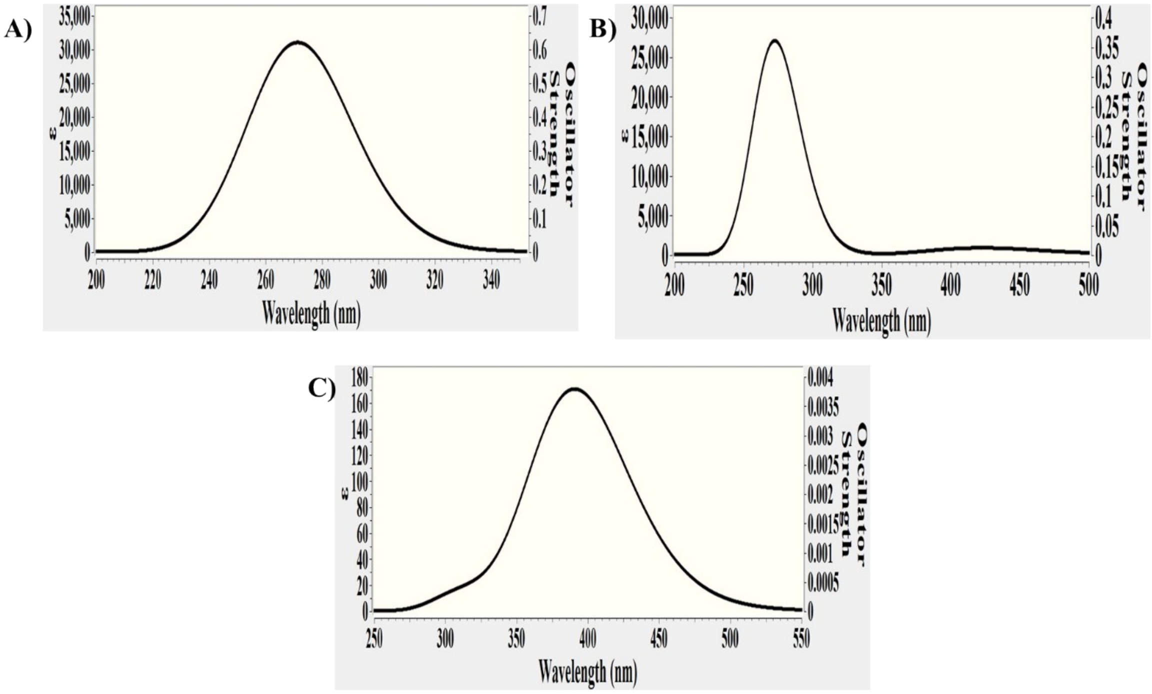


Fig S14: Simulated absorption spectra of three proposed molecular fluorophores (A-245, B-360, and C-467) obtained from time-dependent-density functional theory (TD-DFT) studies

Quantum Yield measurement:

The quantum yield of NSCDs was determined with respect to quinine sulphate (Sigma-Aldrich, Germany, 99%) dissolving 0.1 M H2SO4 (quantum yield 54%) as standard [39]. The absorbances of various NSCDs solutions and quinine sulphate solutions were measured in UV-Visible spectrophotometer (SHIMADZU UV-2450, Japan). The quantum yield of NSCDs was calculated by using the following equation:

$$\frac{\emptyset}{\emptyset_{std}} = \frac{A_{std}}{A} \times \frac{I}{I_{std}} \times \frac{n^2}{n_{std}^2}$$

Where Ø stands for quantum yield, "I" stands for measured integrated fluorescence intensity, n is the refractive index and A is the absorbance. "Std" refers to the standard fluorophore (quinine sulphate). The absorbance of all the solutions was kept less than 0.1 to avoid inner filter effects.

To find out the QY we have plotted integrated fluorescence intensities versus absorbance of various NSCDs and standard solutions and the following equation was used:

$$\emptyset = \emptyset_{std} \times \frac{slope}{slope_{std}} \times \frac{n^2}{n_{std}^2}$$

where "Slope" represents the slope of the plot of absorbance versus integrated intensity.

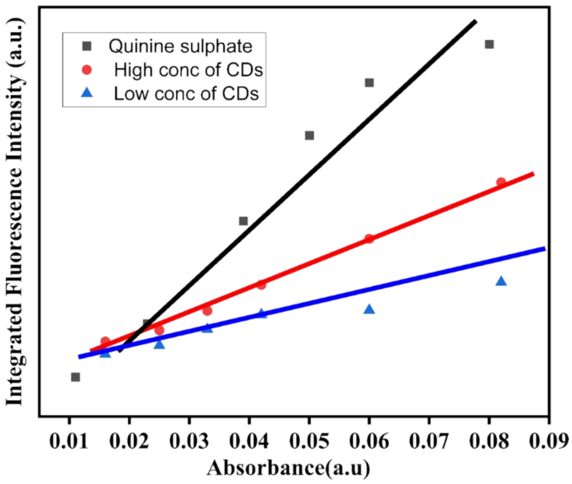


Fig S15: Quantum yield of CDs at high and low concentration

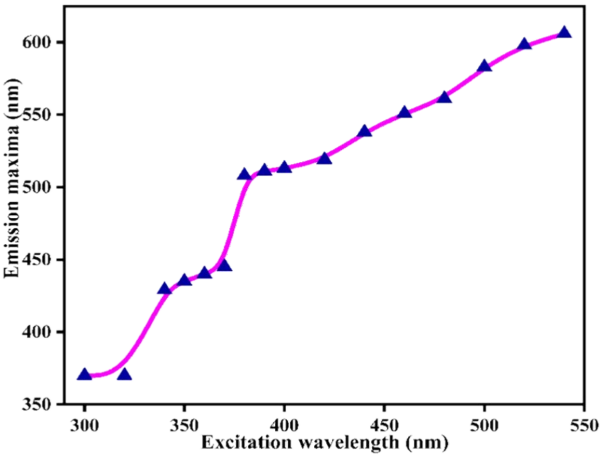


Fig S16: Summarization of Excitation-wavelength dependent emission peak

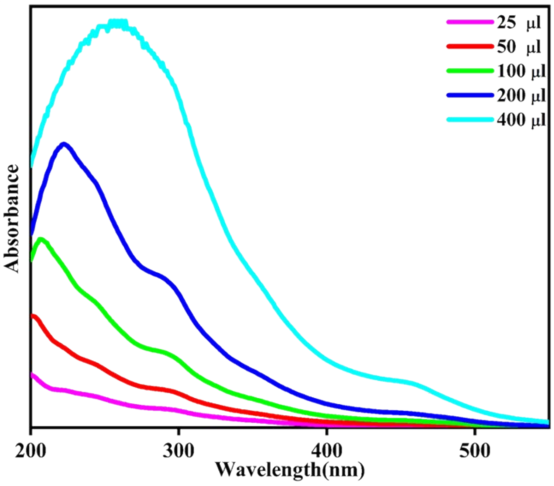


Fig S17: Concentration-dependent UV-Vis spectra of CDs

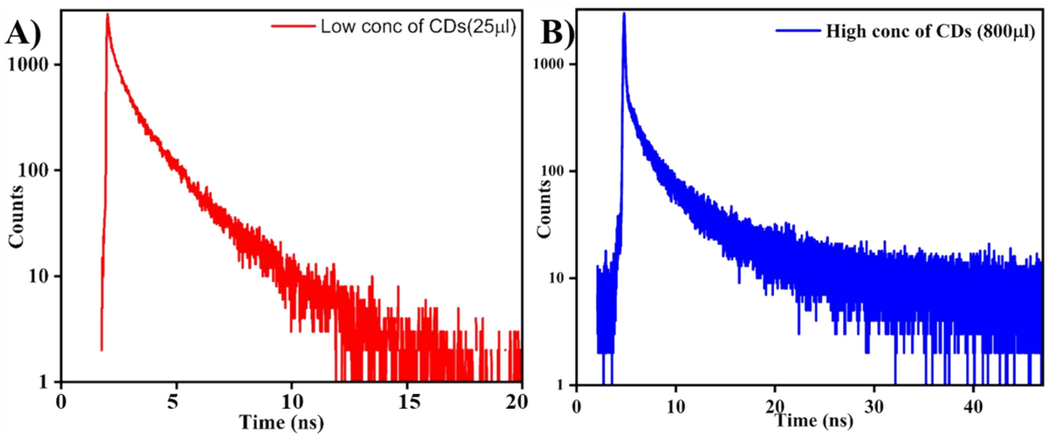


Fig S18: TCSPC spectra of CDs at A) very low concentration (25µl) B) Very high concentration (800 µl)

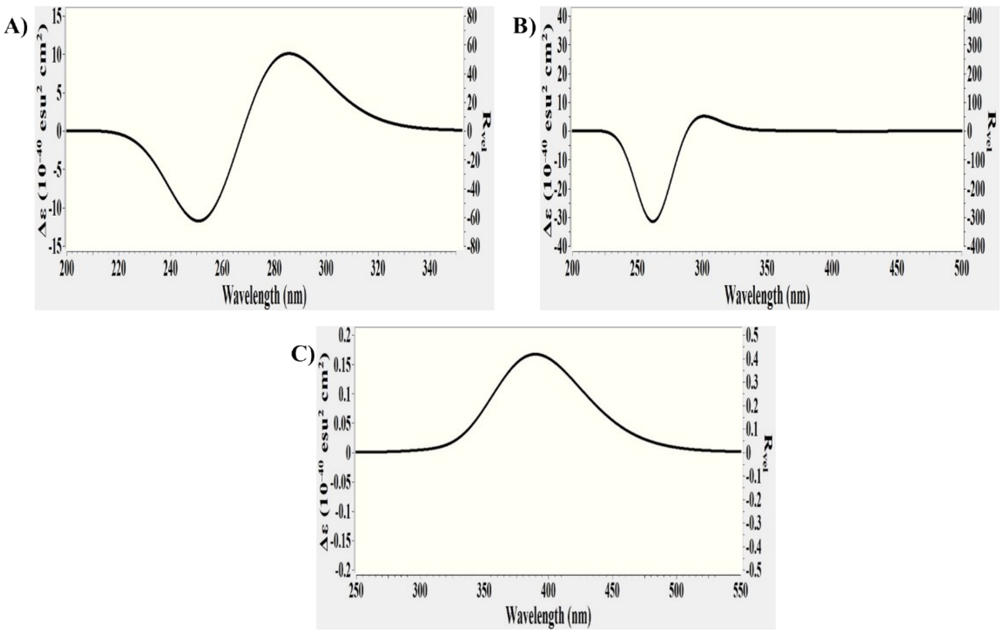


Fig S19: Simulated circular dichroism spectra of three proposed molecular fluorophores (A-245, B-360, and C-467) obtained from time-dependent-density functional theory (TD-DFT) studies

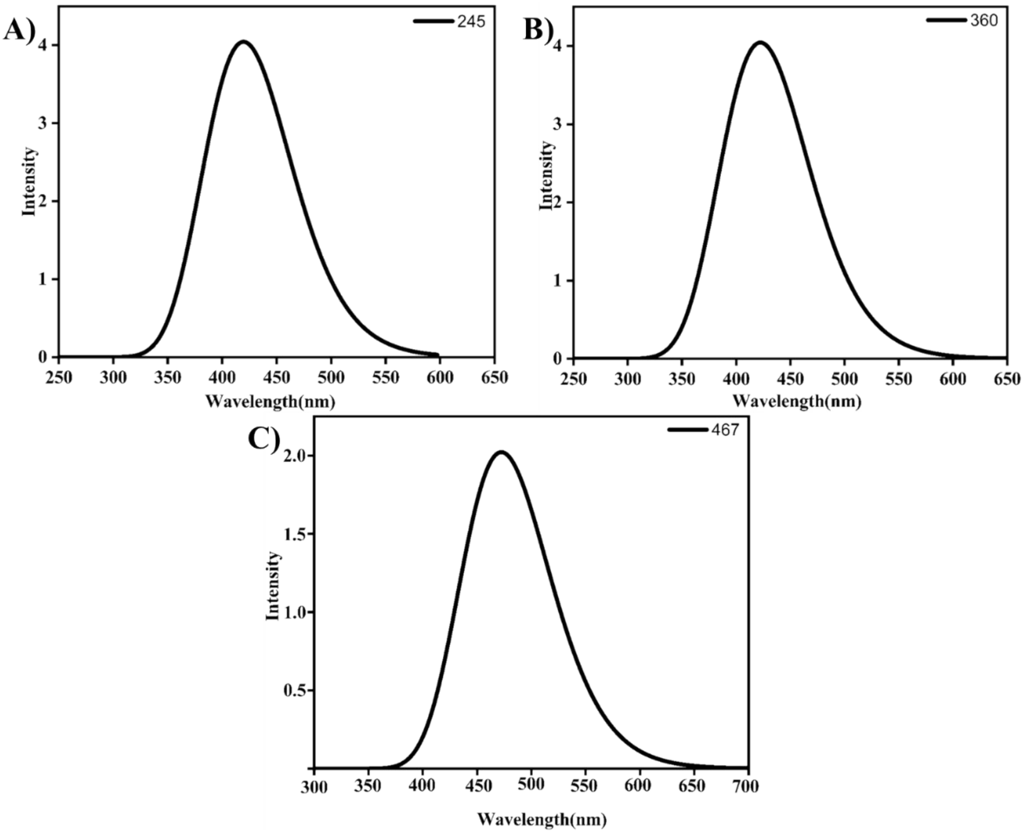


Fig S20: Simulated PL spectra of three proposed molecular fluorophores (A-245, B-360, and C-467) obtained from time-dependent-density functional theory (TD-DFT) studies

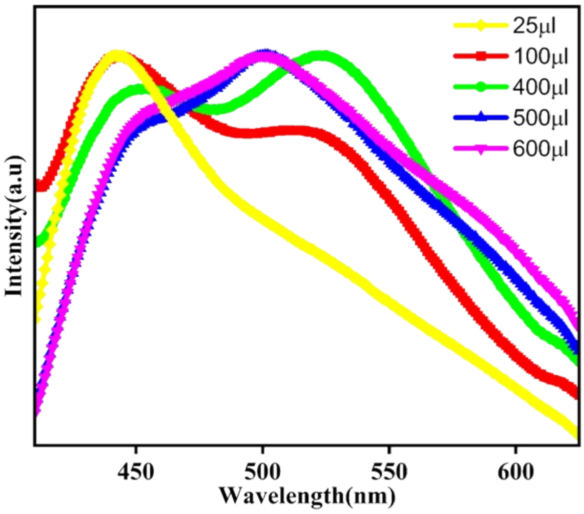


Fig S21: Concentration-dependent emission spectra of CDs

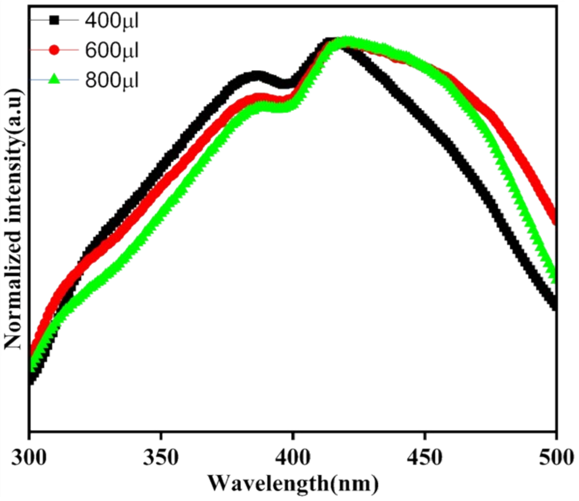


Fig S22: Concentration-dependent excitation spectra of CDs corresponding to 550 nm emission