Supplementary Information

Molecularly Engineered Nitrogen-Enriched and Solid-State Emissive Carbon Dots for Visual Zeptomole Explosive Tracing

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Preparation of stock solutions:

Stock solutions of aromatic compounds, anions, metal ions, and biomolecules were prepared by dissolving the required amounts in deionized water to obtain a concentration of 0.1 M. These stock solutions were further diluted to prepare sensing solutions with a concentration of 1 mM. The stock solution of N-Cdots was prepared separately in DMF at a concentration of 10 mg/mL (w/v).

Fluorescence and absorbance studies of N-Cdots:

50 µL of the Cdot stock solution (10 mg/mL) was added to 1.95 mL of DMF to obtain a total volume of 2 mL in a cuvette. The fluorescence of N-Cdots was then recorded. Subsequently, different analyte solutions were introduced (final analyte concentration: 0.183 mM), and the corresponding changes in fluorescence intensity were monitored at room temperature. The excitation wavelength was set at 365 nm. Similarly, absorbance spectra of N-Cdots

(0.25 mg/mL) were recorded, and solutions of PA were separately introduced to observe the changes in absorbance induced by PA.

Preparation of artificial seawater:

Artificial seawater was prepared by weighing 0.325 g of magnesium sulfate ($MgSO_4$), 0.226 g of magnesium chloride ($MgCl_2$), 0.112 g of calcium chloride ($CaCl_2$), and 2.673 g of sodium chloride (NaCl). These salts were sequentially added to 100 mL of deionized water using a volumetric flask. The mixture was stirred continuously until complete dissolution of all components was achieved. The prepared artificial seawater was stored at room temperature for further use.

Calibration Curve

For the calibration experiment, 2 mL of 0.5 mg/mL N-Cdots solution was taken in a cuvette, and picric acid was added incrementally in volumes of 10 µL, 20 µL, 30 µL, 40 µL, and 50 µL. After each addition, PL intensity was recorded. The obtained changes in intensity were plotted against the corresponding picric acid concentrations to construct a calibration curve.

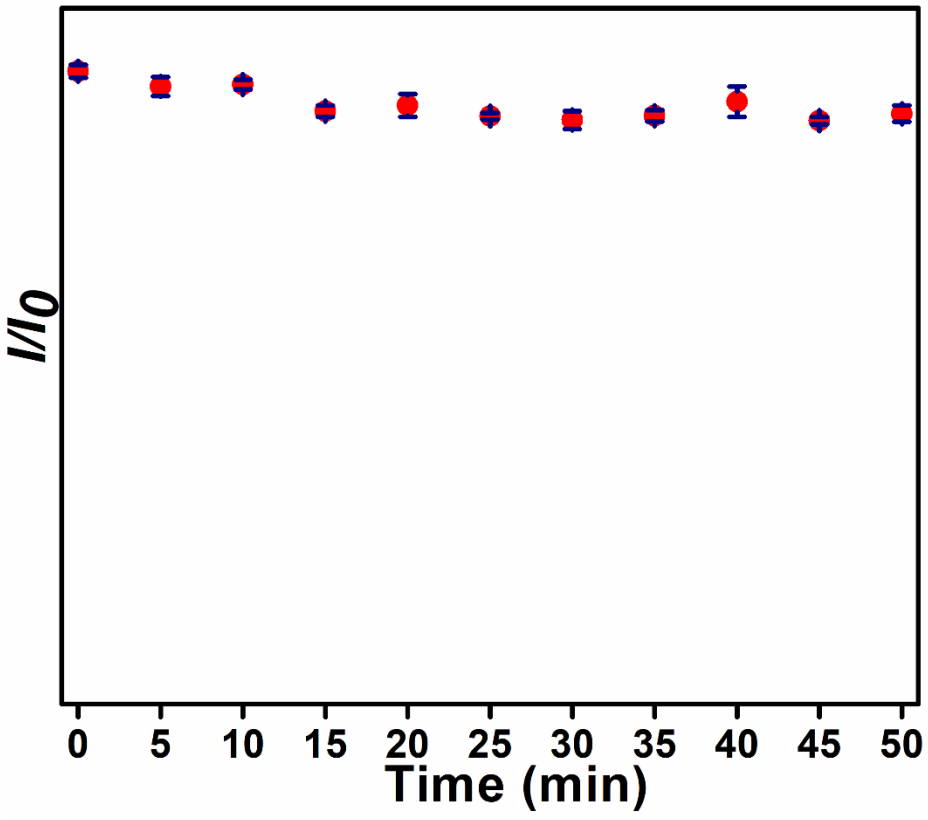

Figure S1: Photostability plot of N-Cdots in DMF.

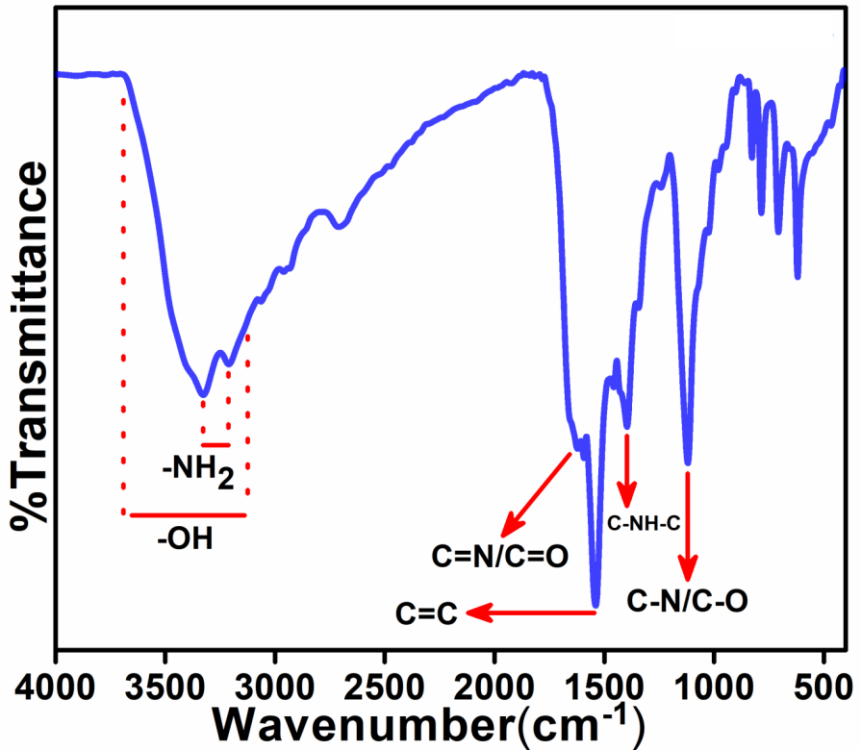

Figure S2: FTIR spectrum of N-Cdots.

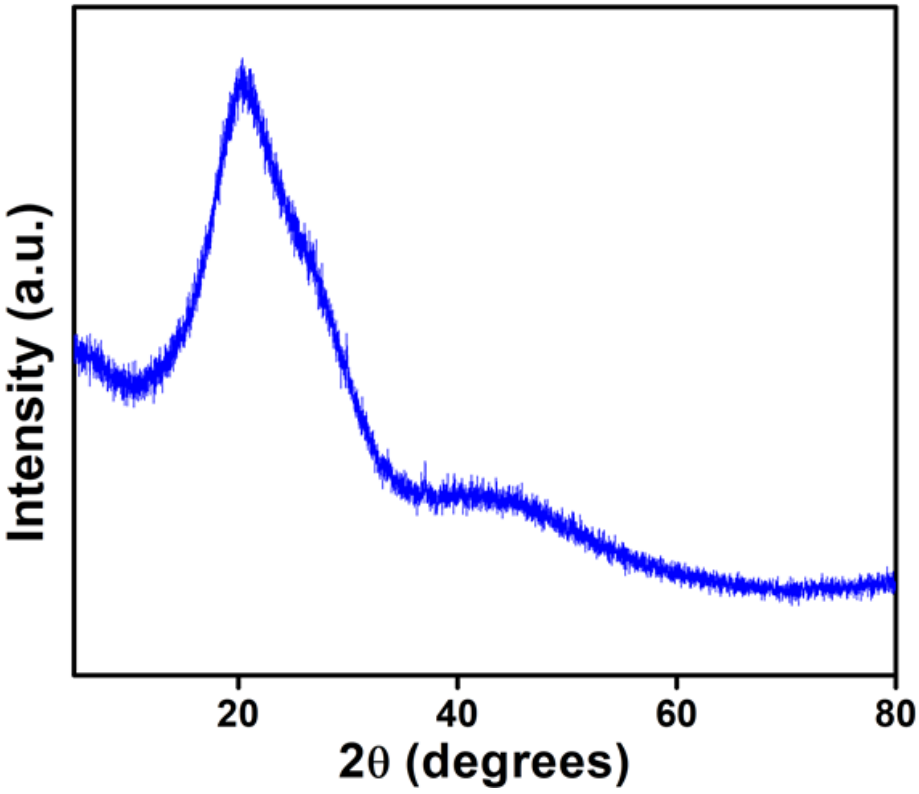

Figure S3: PXRD spectrum of N-Cdots.

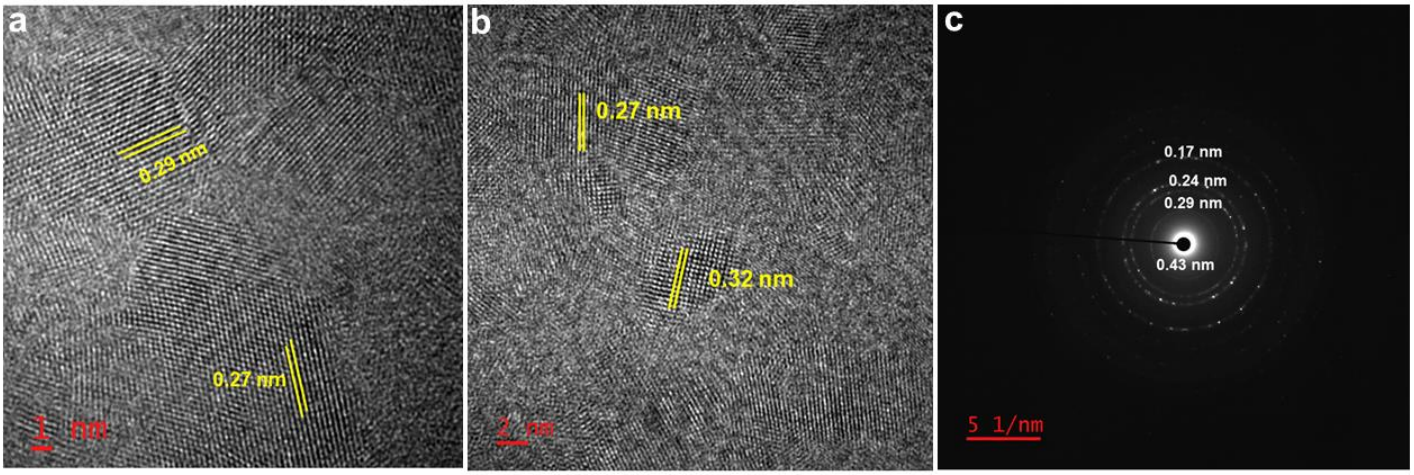

Figure S4: (a & b) HRTEM analysis of N-Cdots. (c) SAED pattern of N-Cdots.

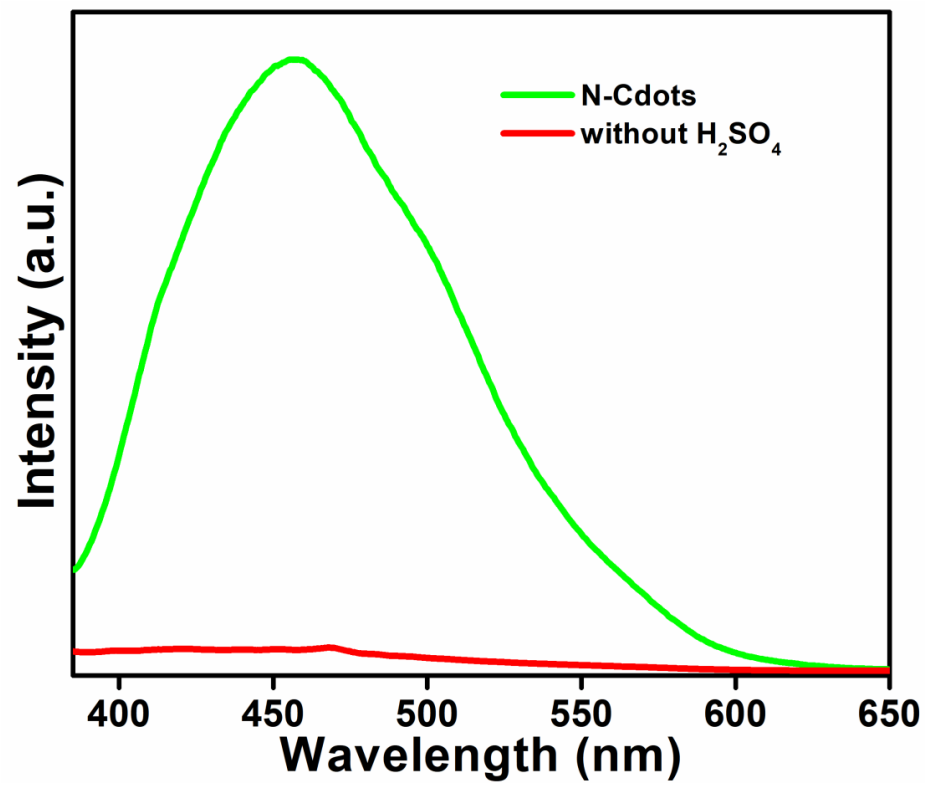

Figure S5: PL spectra of the control experiment for N-Cdots synthesized in the absence of H_2SO_4.

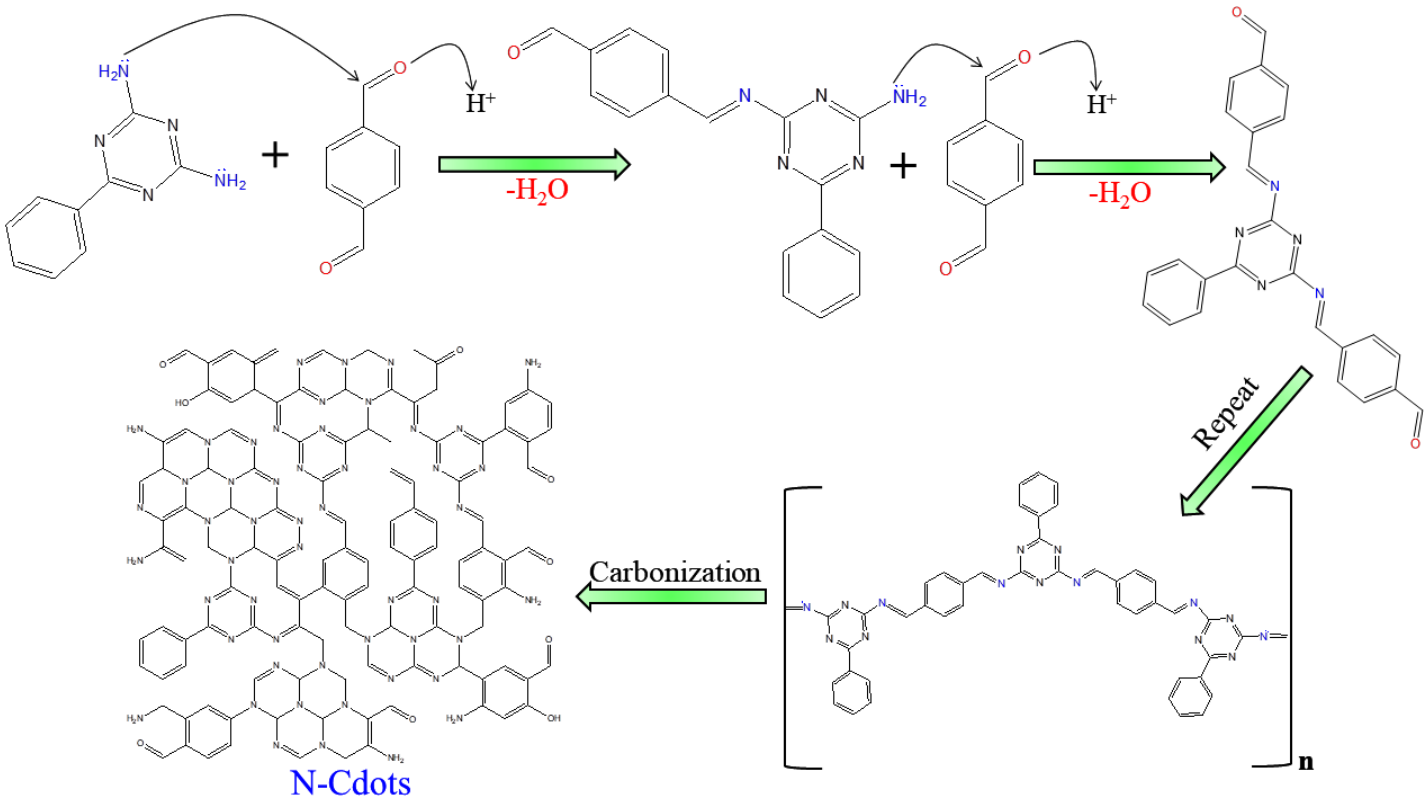

Figure S6: Proposed mechanism illustrating the plausible formation pathway of N-Cdots.

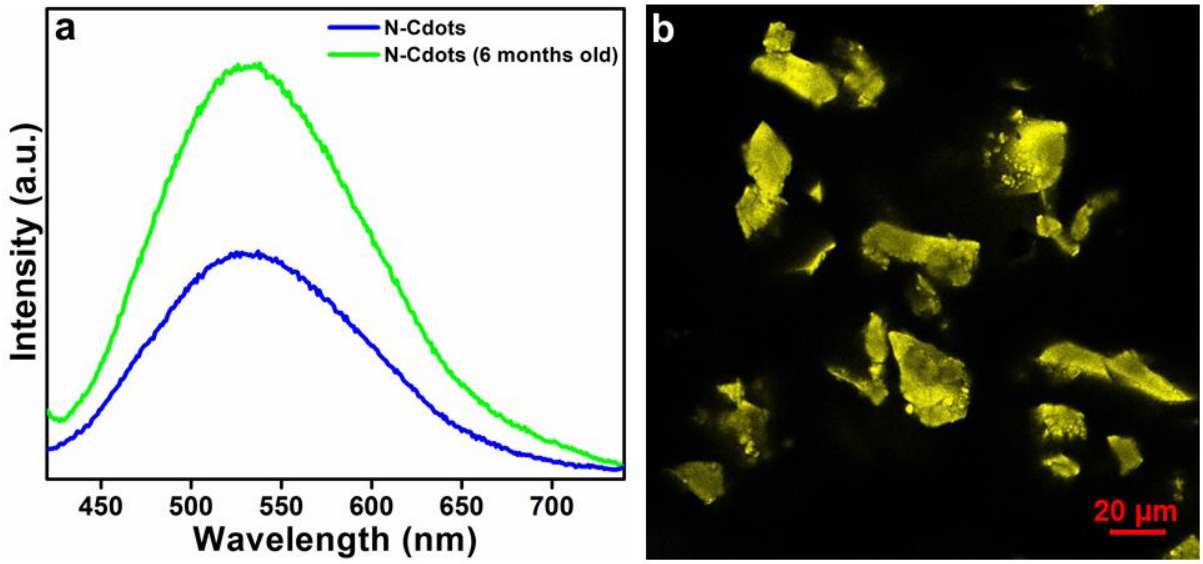

Figure S7: Assessment of long-term stability of six-month-old powdered N-Cdots stored under ambient laboratory conditions. (a) Represent solid-state fluorescence and (b) solid-state confocal PL images of six-month-old powdered N-Cdots.

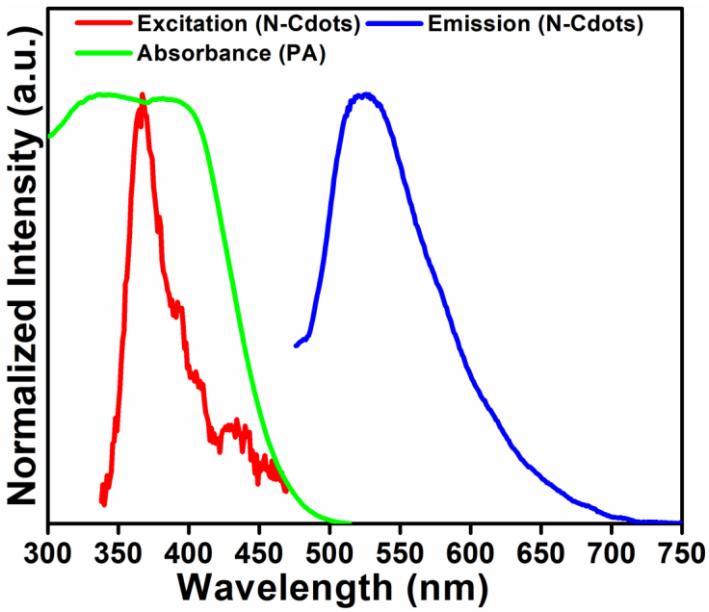

Figure S8: Combined UV-Vis absorption spectrum of PA and solid-state excitation and emission spectra of N-Cdots.

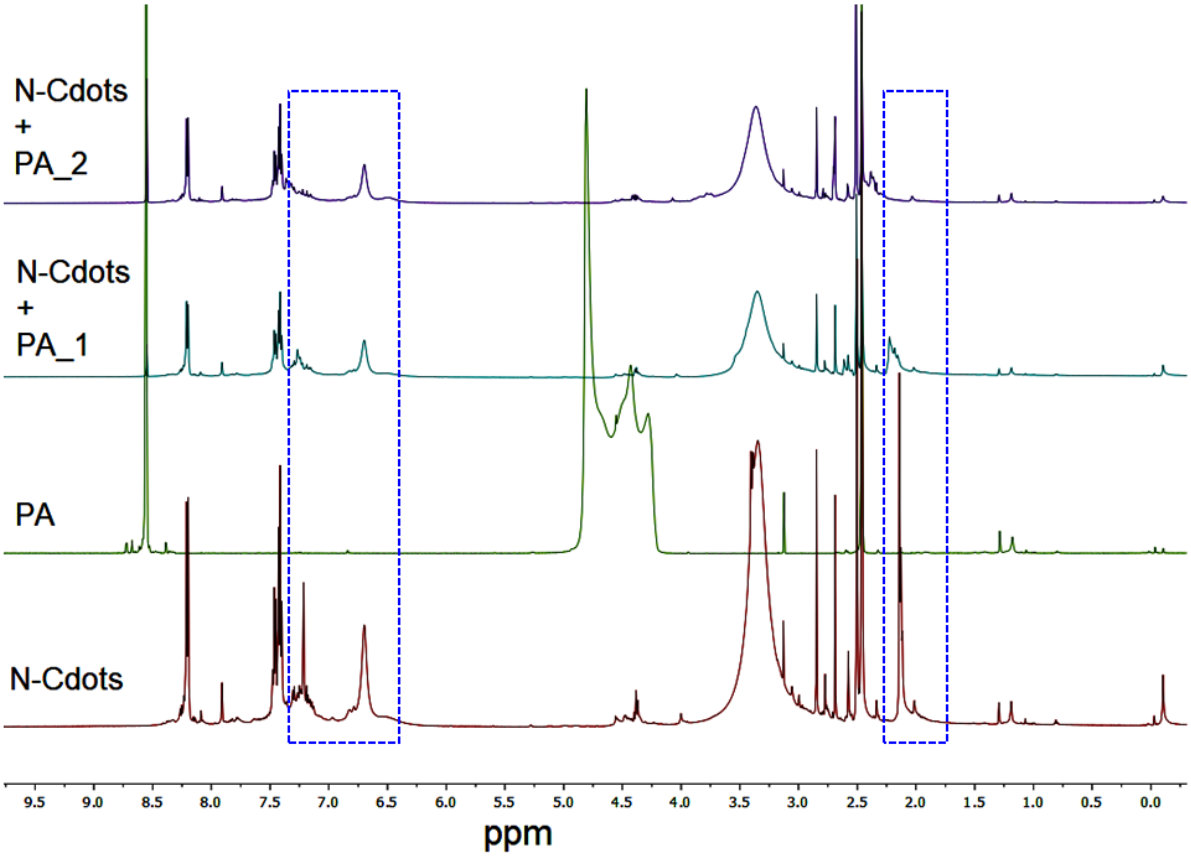

Figure S9: ^{1}H NMR spectra of N-Cdots and PA, along with N-Cdots upon the gradual addition of increasing concentrations of PA (N-Cdots + PA_1 and N-Cdots + PA_2). The solvent used for recording 1H NMR was DMSO-d6.

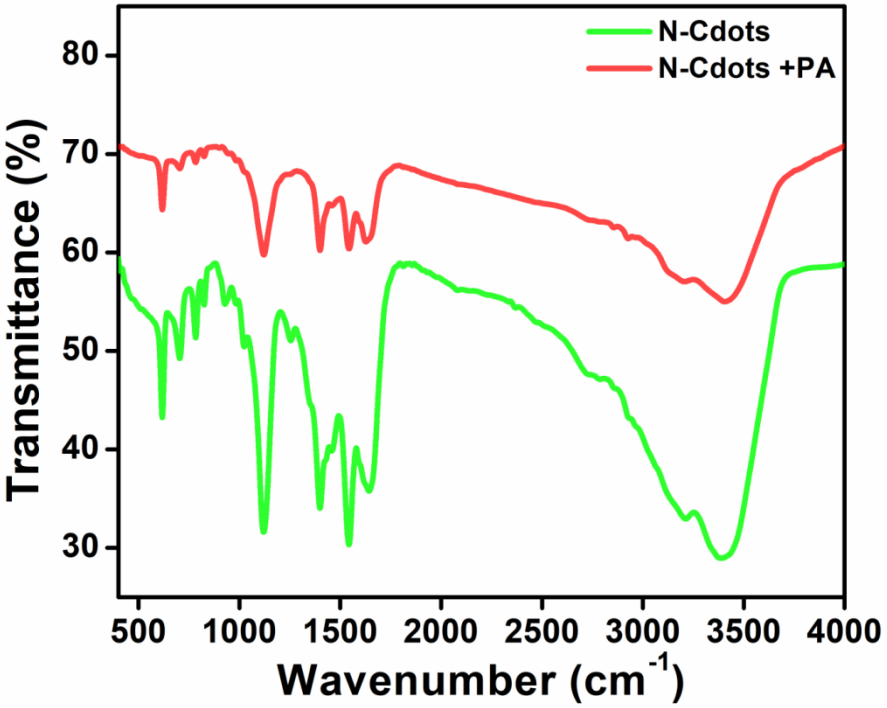

Figure S10: FTIR spectra of N-Cdots before and after the addition of PA.

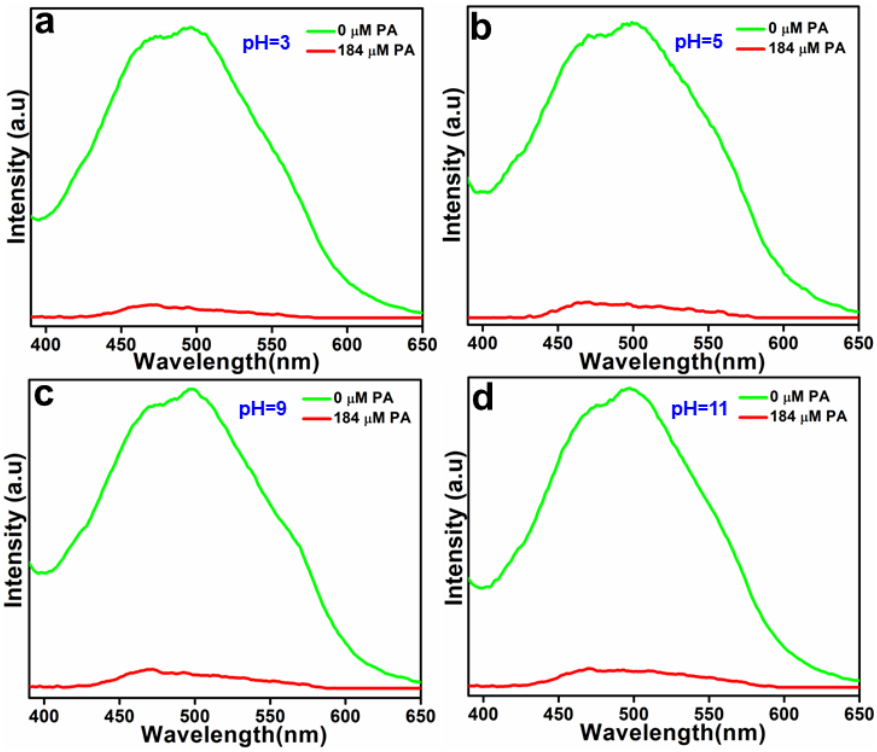

Figure S11: Behaviour of PL spectra of N-Cdots in different pH on adding 450 uL of PA. (a) pH-3 (b) pH-5 (c) pH-9 (d) pH-11

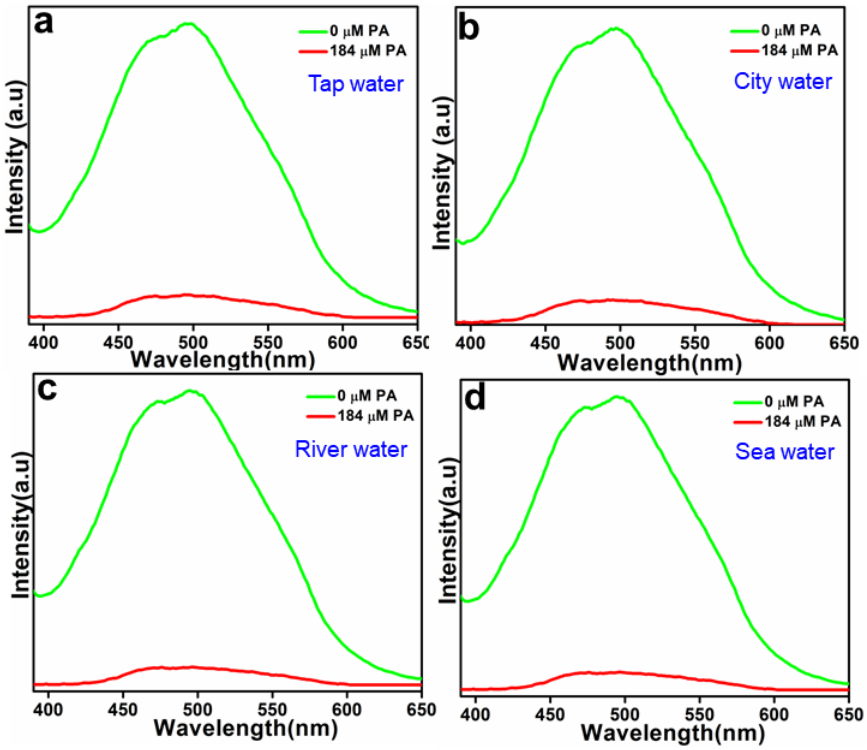

Figure S12: Behaviour of PL spectra of N-Cdots in real samples. (a) Tap water (b) sea water (c) river water (d) city water.

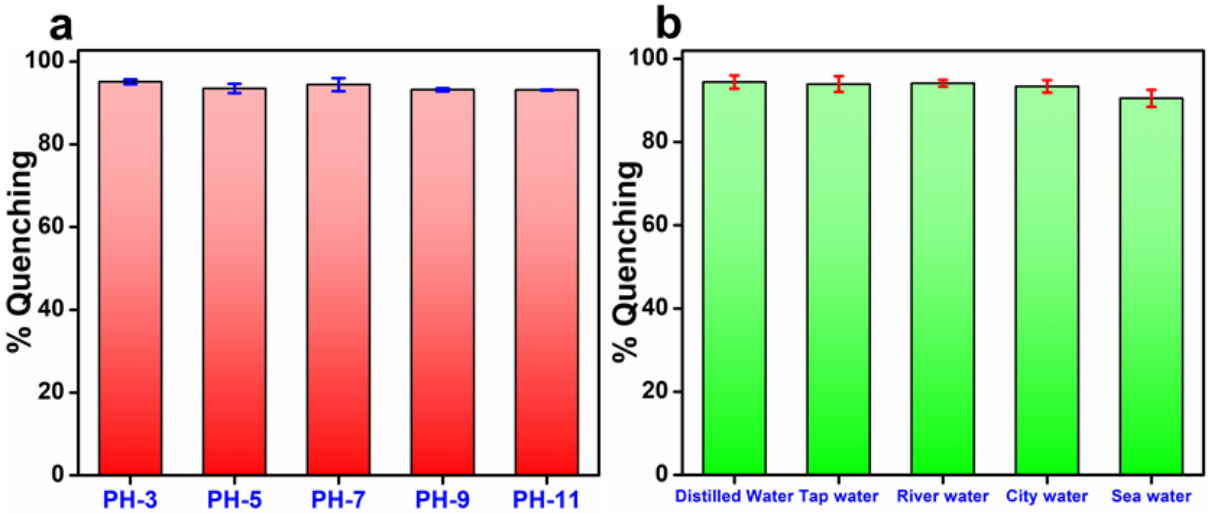

Figure S13: (a) % quenching in different pH. (b) % quenching in real sample.

Table S1: Comparative assessment of the structural characteristics and solid-state emissive properties of materials based on the choice of appropriate reactants.

Precursor	Method	Structural Type	Solid-State Fluorescence	Remarks	Reference
DPT	Solvothermal (180 °C)	Mesoporous and hydrophobic carbon dot aggregates	No	Nitrogen-rich mesoporous Cdots aggregates designed for adsorption applications	*Small*, 2025, **21**, e08118.
DPT	Heating at 310 °C in inert atmosphere	Aromatic carbon nitride (PhCN)	No	Provide information about the correlation between structural and optical properties of PhCN and intermediates.	*Inorg. Chem. Front.*, 2024, **11**, 2346–2354.
DPT	Heating at 350 °C in inert atmosphere	Carbon nitride oligomer *i.e.* polymeric carbon nitride	Yes	Emission arises from restricted intramolecular motion in the aggregated state and solid state.	*Spectrochim. Acta, Part A*, 2022, **276**, 121238.
DPT or DPT with trithiocyanuric acid (TTCA)	Heating at 400 °C in inert atmosphere	Phenyl-modified and sulfur doped g-C_3N_4 (PhCNS)	Yes	Introduction of phenyl groups into g-C_3N_4 induces green emission, while increasing tri-s-triazine (TTCA) content enhances electron delocalization, leading to a red-shift in PL.	*ACS Appl. Nano Mater.*, 2020, **3**, 6798–6805.
Melamine & Citric Acid	Hydrothermal (220 °C to 260 °C)	Nitrogen-rich Cdots	No	Strong blue emission in solution; N-doping enhances quantum yield	*RSC Adv.*, 2016, **6**, 31884–31888.
Citric Acid & Melamine	Solid state synthesis without any additives at 180 °C	N-doped carbon dots	No	Solvent-free synthesis; strong aqueous PL; excellent as optical sensor in aqueous solution.	*Sens. Actuators, B*, 2018, **255**, 1130–1138.
Melamine, Formaldehyde & Citric Acid	Hydrothermal (220 °C)	N-doped Cdots with binary dopants	No	Multi-dopant strategy; improved PL intensity in solution with potential sensing application	*Sens. Actuators, B*, 2018, **268**, 84–92.

Table S2 Fluorescence lifetime parameters of N-Cdots and N-Cdots + PA systems.

Sample	Fraction of the first component (α_1)	First component lifetime (τ_1) (ns)	Fraction of the second component (α_2)	Second component lifetime (τ_2) (ns)	Fraction of the third component (α_3)	Third component lifetime (τ_3) (ns)	Average lifetime (τ_{av}) (ns)
N-Cdots	0.8199359	1.212415	0.17164994	2.983825	0.00841415	9.151032	2.17
N-Cdots + PA (91μM)	0.8708807	1.012407	0.12258916	2.846876	0.00653013	8.579211	1.84
N-Cdots + PA (184 μM)	0.9054413	1.110652	0.0902629	3.22263	0.0042957	10.34993	1.87

Table S3: Determination of PA concentration in real water samples.

Water Sample	**Amount of PA added (fM)**	**% Recovery**	**% Standard Deviation**
Tap water from the laboratory	50	95.4	2.0
	100	94.9	1.9
	150	100.4	1.5
River water	50	95.9	2.0
	100	103.9	1.6
	150	97.9	0.5