Dual-Emission Ratiometric Fluorescent Sensor Based on Tannic Acid Carbon Dots and Eosin for Selective Detection of Paraquat in Water and Food Samples

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2.2. Instrumentation and characterization

The optical properties of the CDs were investigated using fluorescence and ultraviolet-visible (UV-Vis) spectroscopy. Fluorescence emission spectra were recorded using a Shimadzu RF-5301PC spectrofluorometer, with samples excited at 335 nm and 5 nm slit widths. Absorption spectra were recorded on a Shimadzu 1601 PC UV-Vis spectrophotometer. To elucidate the structural and morphological characteristics of the TA-CDs, several analytical techniques were employed. Transmission electron microscopy (TEM) was performed using a JEOL 2100F instrument at 200 kV accelerating voltage, providing insights into the size and shape of the nanoparticles. X-ray diffraction (XRD) patterns were collected using a Philips PW 1700 diffractometer to assess the crystalline structure. Fourier transform infrared (FTIR) spectroscopy was conducted on KBr pellets using a Nicolet 6700 spectrometer, revealing information about functional groups present on the CDs' surface. Surface chemical composition and bonding states were analyzed through X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific ESCALAB250 spectrometer. This comprehensive suite of characterization techniques provided a detailed understanding of the optical, structural, and chemical properties of the CDs, enabling a thorough evaluation of their potential for sensing applications.

2.4. Quantum yield of the prepared TA-CDs

The quantum yield (QY) of the CDs was determined using quinine sulfate (QS) as a reference standard. The calculation was performed according to the following methodology: quinine sulfate, dissolved in 0.1 M H_2SO_4, served as the reference fluorophore with a known quantum yield of 54%. Both the CDs and QS solutions were prepared at concentrations that yielded absorbance values below 0.05 to minimize inner filter effects and ensure linearity of the fluorescence response. The absorbance and emission spectra of the CDs and QS were measured at an excitation

wavelength of 360 nm. The integrated fluorescence intensities and absorbance values were then used in the following equation to calculate the quantum yield of the CDs:

$$\phi_{CDs} = \phi_{QS} \times \frac{F_{CDs}}{F_{QS}} \times \frac{A_{QS}}{A_{CDs}} \times \frac{\eta_{CDs}}{\eta_{QS}}$$

In this context, Φ_{CDs} denotes the quantum yield of the CDs, while ϕ_{QS} represents the quantum yield of quinine sulfate (QS). F_{CDs} and F_{QS} correspond to the fluorescence intensities of the CDs and quinine sulfate, respectively. The term A refers to the absorbance value and η indicates the refractive index of the solvent. For this experiment, the CDs were dissolved in distilled water with a refractive index of η = 1.33, and quinine sulfate was dissolved in 0.1 M H_2SO_4, also with a refractive index of η = 1.33.

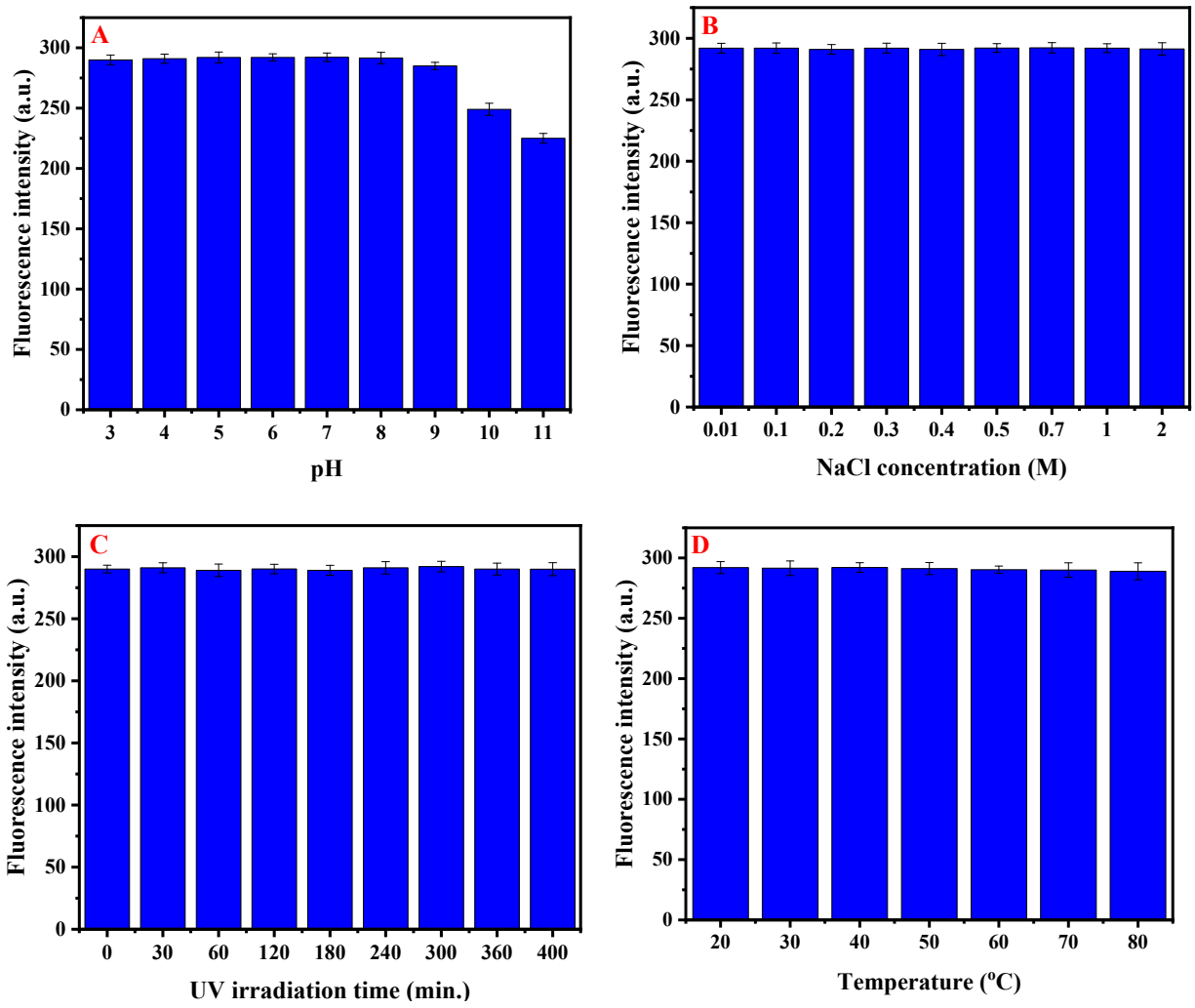

Fig. S1. Stability of the fluorescence response of the prepared TA-CDs under various conditions: (A) effect of pH (3–11), (B) effect of NaCl concentration (0.01–2.0 M), (C) effect of UV irradiation time (0–400.0 min.) and (D) effect of different temperatures (20 – 80 °C).

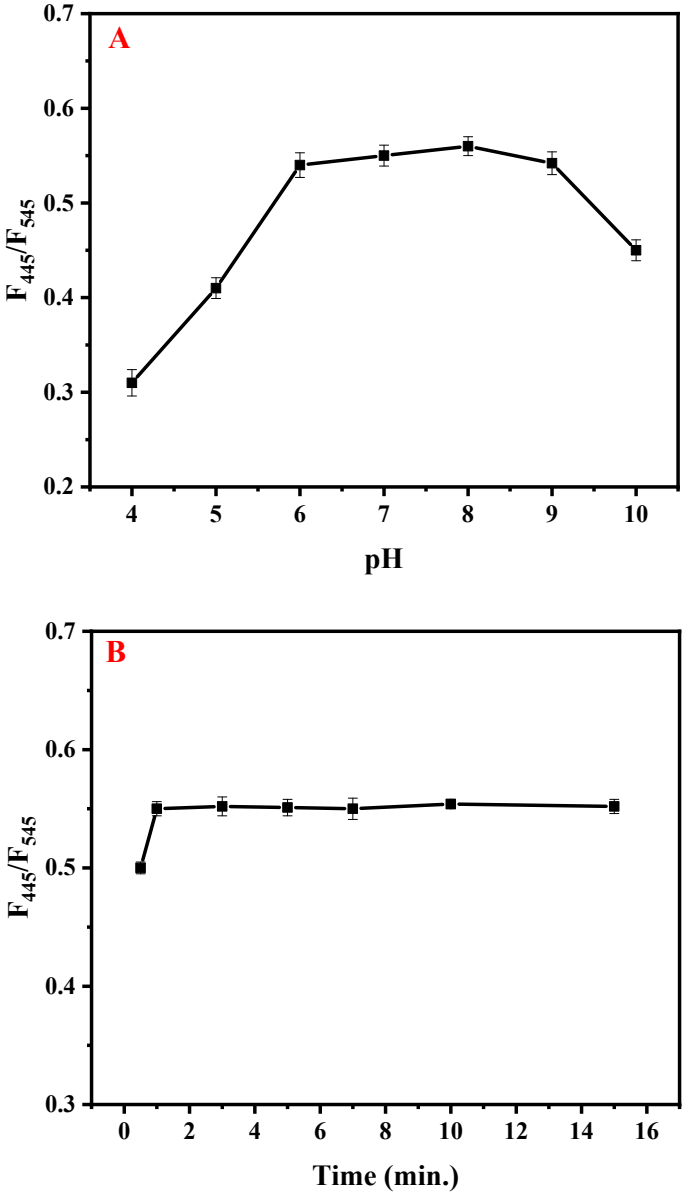

Fig. S2. (A) The effect of pH (4.0 to 10.0), (B) different reaction time (0.5 to 15.0 min.) on F_{445}/F_{545} of TA-CDs after addition of paraquat.

Table S1: Comparison of the reported methods for paraquat detection with proposed method.

Probe	Linearity range (µM)	LOD (nM)	Matrix	Ref.
BPNSs	0.0039 – 389	0.70	Green tea, black tea, and matcha powder	[1]
Squaraines	0.017 – 0.15	372	Chinese cabbage	[2]
Polymeric probe	0 – 6,000	11,000	Water sources, soil, apples, and lettuce	[3]
Pyranine	1.0 – 20.0	200	Tap water	[4]
CdS QDs	0.1–5.8	38.9	Environmental and agricultural	[5]
TGA CdTe/CdS NCs	0.01 – 0.1	3.5	Natural water	[6]
GSH/β-CDs-AuNCs	0.019–0.389	4.7	Chinese cabbage	[7]
Calix[6]arene	0.0039–0.070	0.12	Drinking water	[8]
Q[7]@PAL sensor	0–12.0	340	…….	[9]
Cucurbit[8]uril	0.00024 – 250	0.24	…….	[10]
$[Fluo][P_{66614}]_2$	0.3–7.0	64.0	Vegetables and environmental samples	[11]
SiO_2@CdTe QDs@MIP	0.0389 – 3.89	1.94	Water and corn	[12]
N-CQDs@CuNCs	5 – 100	3.03	…….	[13]
G/R–AuNCs	19–1935	6.5	Agricultural products, local lake water and tap water	[14]
Eosin/TA-CDs	0.005 – 0.15	2.11	Water and cabbage	**This work**

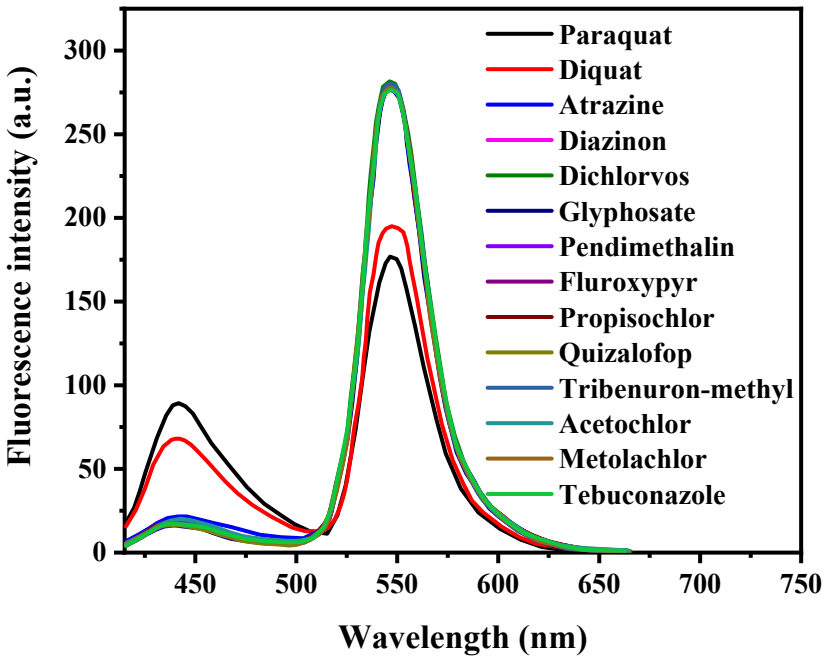

Fig. S3. Fluorescence spectra of the eosin/TA-CDs system upon addition of various herbicides.

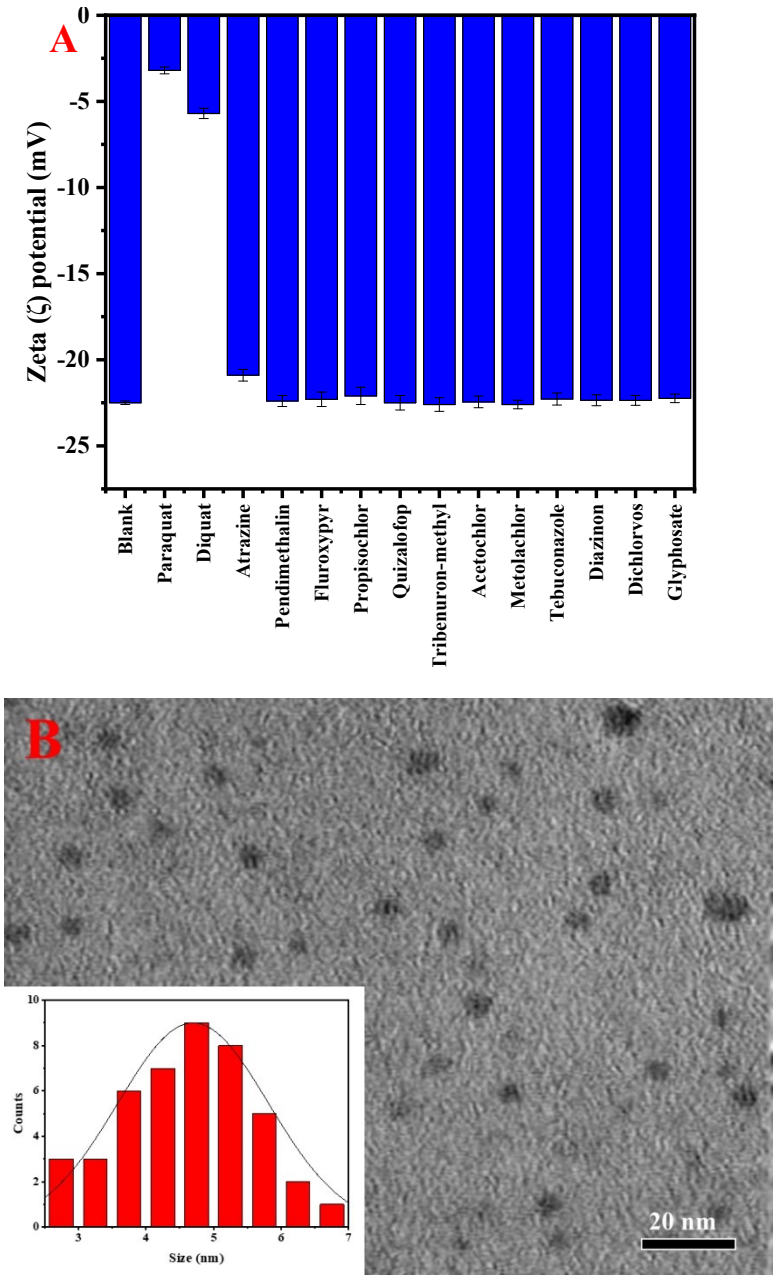

Fig. S4. (A) Fluorescence spectra of the eosin/TA-CDs system upon addition of various herbicides, (B) TEM image of the eosin/TA-CDs system upon addition of diazinon.

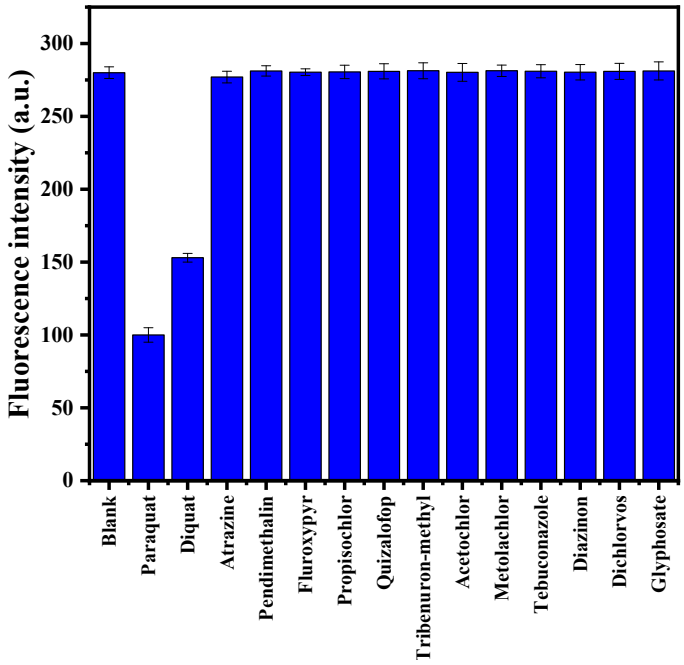

Fig. S5. Fluorescence spectra of the eosin upon addition of various herbicides.

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