Supporting Information

Highly Sensitive Dual-Sensing of Blood Glucose and UV light Enabled by Complexing Biazopyridiniums with Quantum Dots

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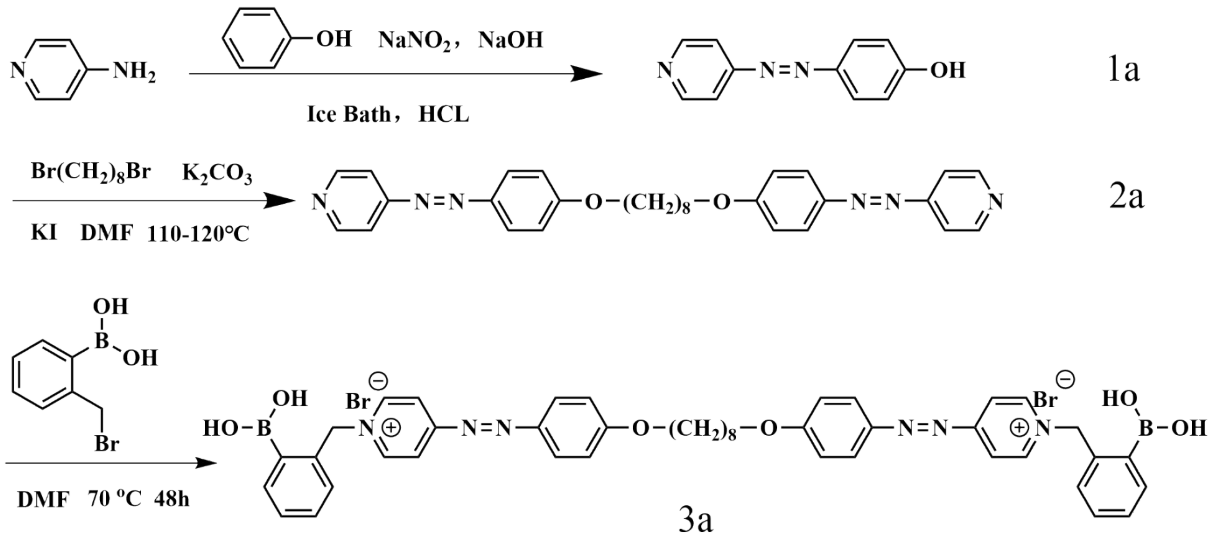
Keywords: Bisazopyridine borates, Fluorescent probes, Glucose detection, UV detection.

Contents

Preparation of the Bisazopyridine borates (8DAPB).

The synthesis route of the Bisazopyridine borates (8DAPB) is shown in Scheme S1.



Scheme S1. Synthesis of the Bisazopyridine borates (8DAPB).

Compound 1a. A 10 w/w% NaOH aqueous solution (20 mL) comprising sodium nitrite (4.00 g, 58 mmol) and phenol (5.00 g, 53 mmol) was prepared and cooled to 0 °C. Subsequently, It was then added dropwise to another aqueous solution of HCl 45 mL (25 mL 11 N HCl and 20 mL deionised water) and 4-aminopyridine (6.00 g, 64 mmol). The reaction mixture was stirred in an ice bath (0 °C). Subsequently, the pH of the reaction mixture was adjusted to pH 6-7 by the addition of a 10 w/w% NaOH aqueous solution. A yellow precipitate was collected by filtration. The crude product was washed with water. After drying under vacuum for 24 h, the resulting bright yellow solid was obtained: yield 3.77 g (35.74%)

Compound 2a (8DAP). 1,8-Dibromooctane (0.6800 g, 2.5 mmol), K_2CO_3 (0.7700 g, 5.57 mmol), KI (a catalytic amount) and 4-(4-hydroxyphenylazo) pyridine (0.9950 g, 5 mmol) were dissolved in N, N-dimethylformamide (DMF, 40 mL). The mixture was heated in an oil bath to 114–115 °C. After 5 hours, the mixture was poured into water (200 mL) and a purple precipitate was collected by filtration. The crude product was purified by silica gel column chromatography using a mixture of ethyl acetate and petroleum ether as the eluent. The solvent was removed using a rotary evaporator and the product was recrystallised from ethanol. The resulting bright yellow solid was obtained in 4.2% yield. The ^{1}H NMR spectrum of the compound was recorded for a 5% (w/v) solution in $CDCl_3$, as shown in Figure S1.

1H NMR (600 MHz, Chloroform-d) δ 8.77 (d, J = 6.2 Hz, 4H), 7.95 (d, J = 8.9 Hz, 4H), 7.67 (d, J = 6.3 Hz, 4H), 7.02 (d, J = 8.9 Hz, 4H), 4.07 (t, J = 6.5 Hz, 4H), 1.93-1.76 (m, 4H), 1.56-1.37 (m, 8H)

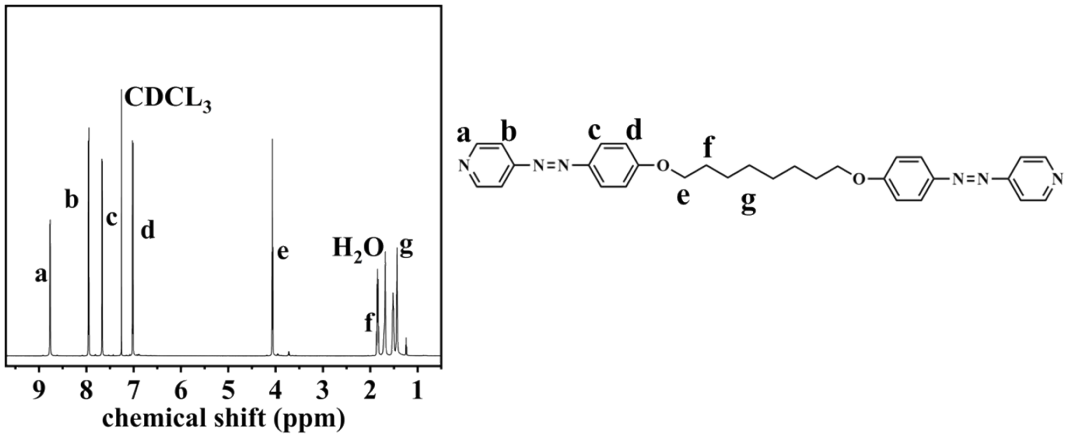


Figure S1. The ^{1}H NMR spectrum of compound 2a (8DAP) recorded in $CDCl_3$.

Bisazopyridine borates (8DAPB). The target compound 8DAPB was synthesised according to the following procedure: diazopyridine compound 2a (8DAP) (1.6 mmol) and 2-(bromomethyl) phenylboronic acid (4.1 mmol) were dissolved in N, N-dimethylformamide (DMF, 20 mL). The reaction mixture was heated in an oil bath at 70 °C for 48 h. Water was then added to precipitate the product, yielding an auburn solid. The ^{1}H NMR spectrum of the product (3a) was recorded for a 5 % (w/v) solution in $CDCl_3$, as shown in Figure S2.

Yield: 30.5%. The 1H NMR spectrum of 8DAPB was obtained by using a 5 % (w/v) $CDCl_3$ solution of the compound. 1H NMR (500 MHz, $CDCl_3$) δ 9.16-9.05 (m, 4H), 8.98 (d, J = 6.7 Hz, 4H), 8.16-8.09 (m, 4H), 8.06-7.97 (m, 4H), 7.53-7.43 (m, 4H), 7.09-7.01 (m, 4H), 6.10 (s, 4H), 4.11 (t, J = 6.4 Hz, 4H), 1.85 (m, 4H), 1.38 (m, 8H).

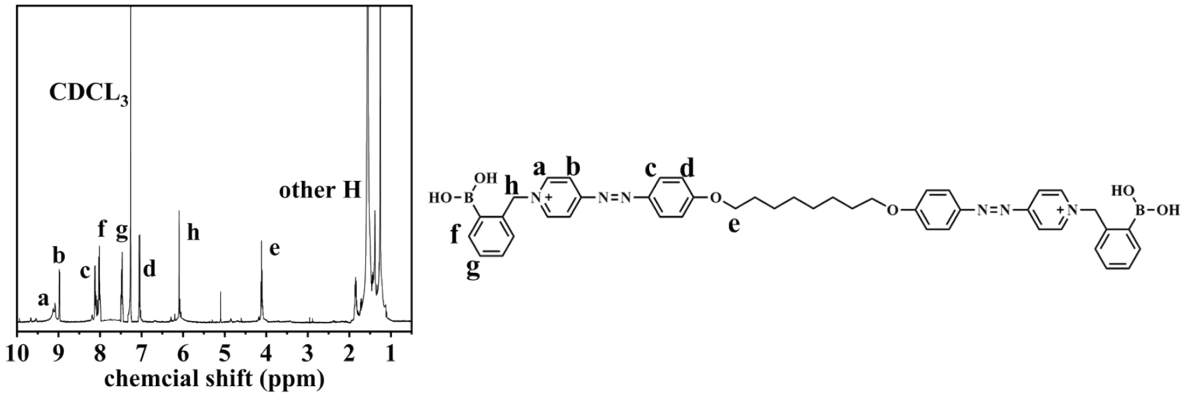


Figure S2. The 1H NMR spectrum of compound 3a (8DAPB) recorded in $CDCl_3$..

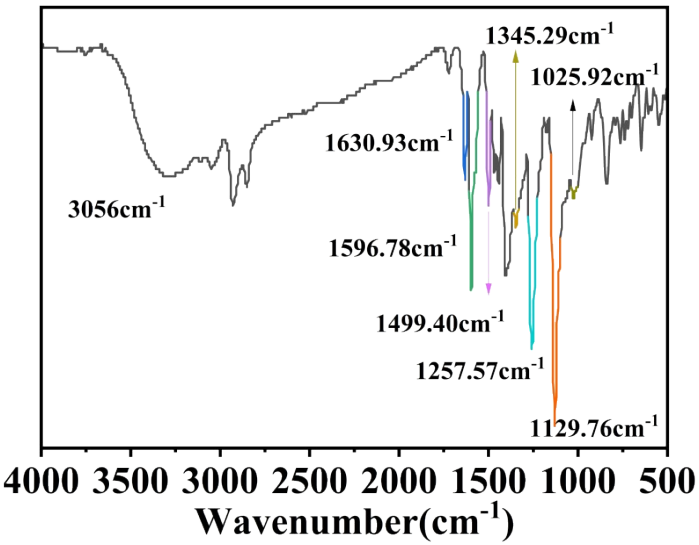


Figure S3. FTIR spectra of 8DAPB measured in KBr pellets.

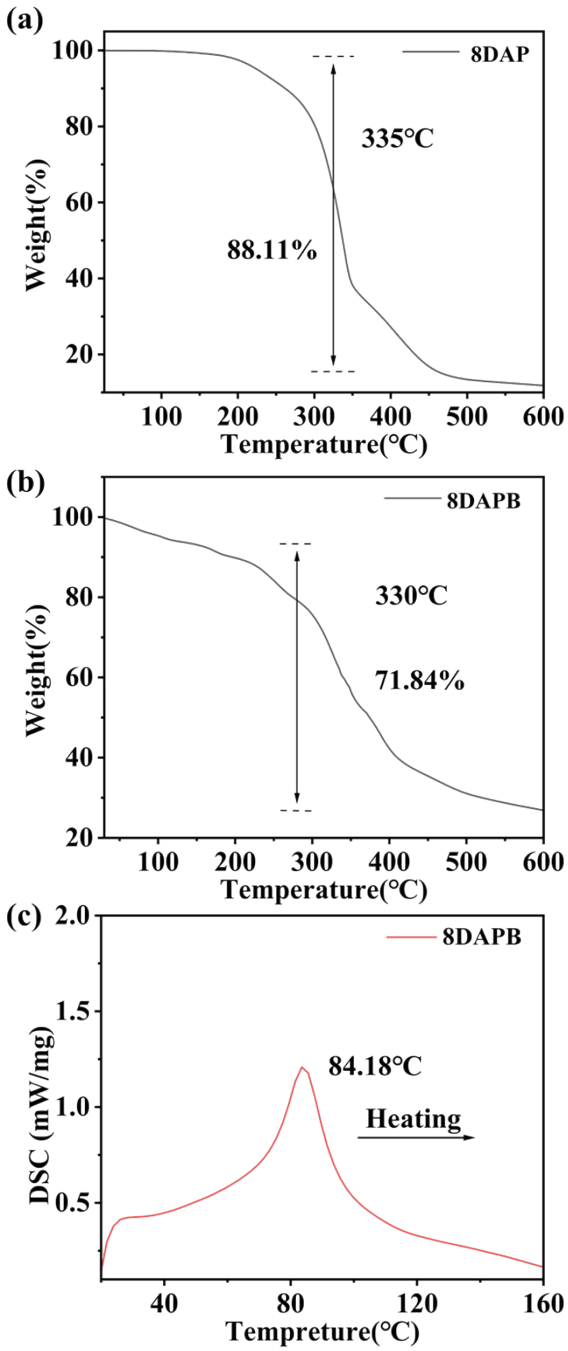


Figure S4. Thermal properties of 8DAPB & 8DAP. (a) Thermogravimetric analysis (TGA) of 8DAP. (b) Thermogravimetric analysis (TGA) of 8DAPB. (c) Differential scanning calorimetry (DSC) traces of 8DAPB. The experiment was conducted with heating and rates of 10 °C/min under N^2 atmosphere.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to determine the thermal properties of 8DAP and 8DAPB. The TGA of the 8DAPB shows a 75% weight loss at 330°C, the TGA of the 8DAP shows as 88% weight loss at 335°C, the decomposition rapidly accelerated above this temperature (Fig. S4(a) or (b)). The DSC heating

trace of 8DAPB shows a weak endothermic transition at 84.11°C (Fig. S4(c)), which was associated with the glass transition of the compound.

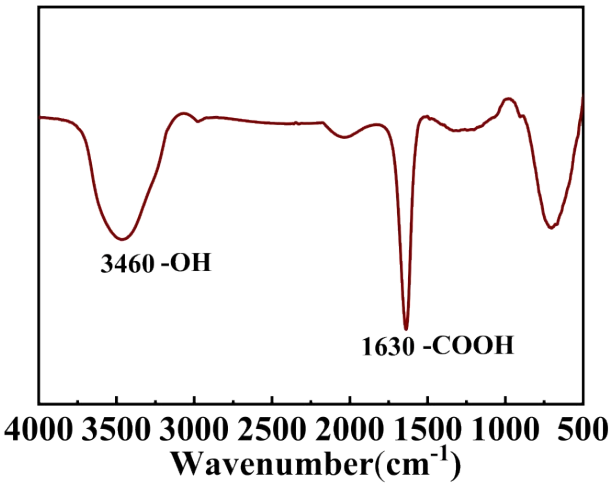


Figure S5. FTIR spectra of CdSe/ZnS QDs.

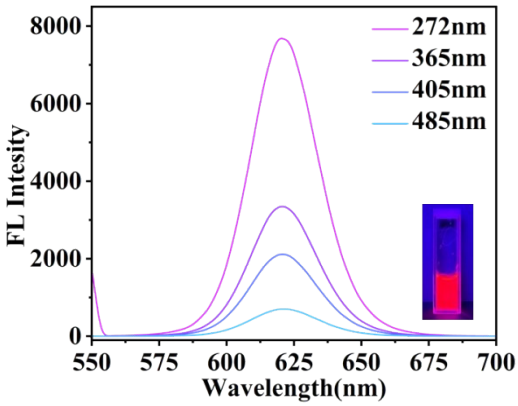


Figure S6. Emission spectra of CdSe/ZnS QDs with excitation at different wavelengths.

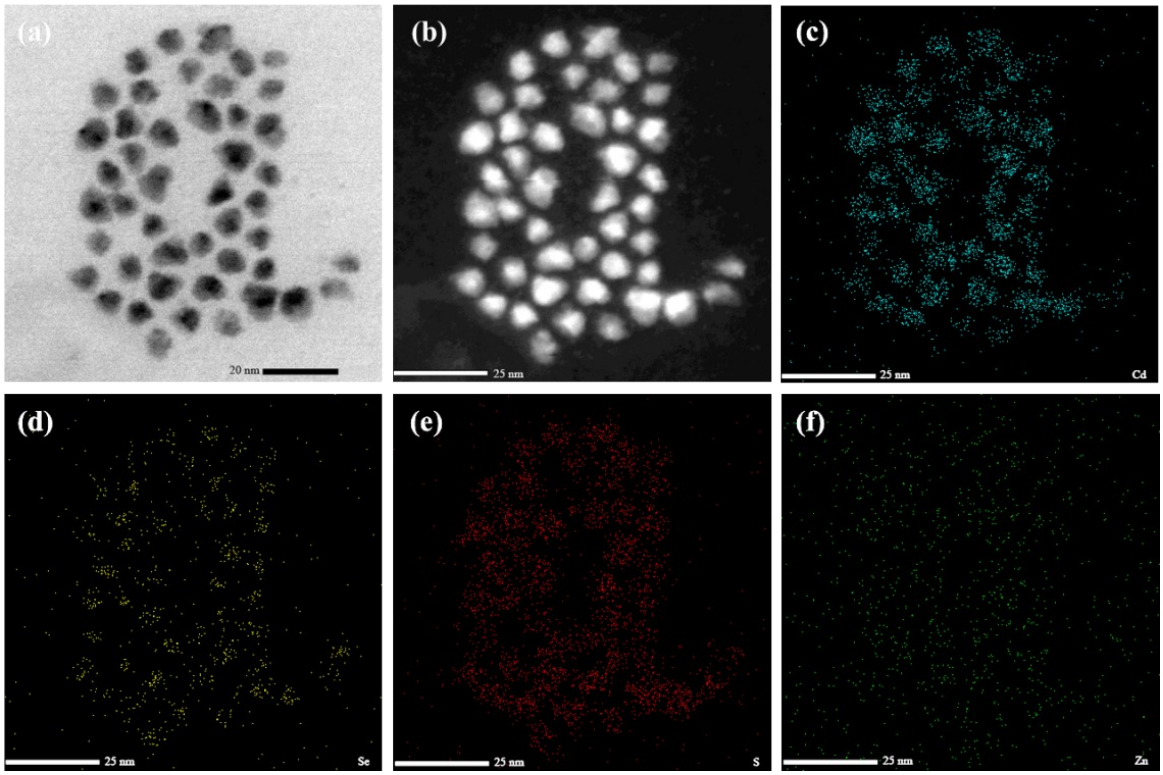


Figure S7. Characterisation of the QDs. (a)STEM image of the QDs. (c–f) STEM image of the elements contained in CdSe/ZnS QDs; (c)Cd cyan; (d)Se yellow; (e)S red; (f)Zn green.

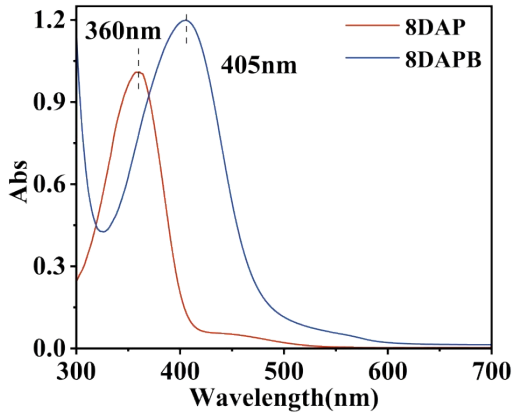


Figure S8. UV-vis absorption spectra of 8DAP and 8DAPB in Ethyl alcohol.

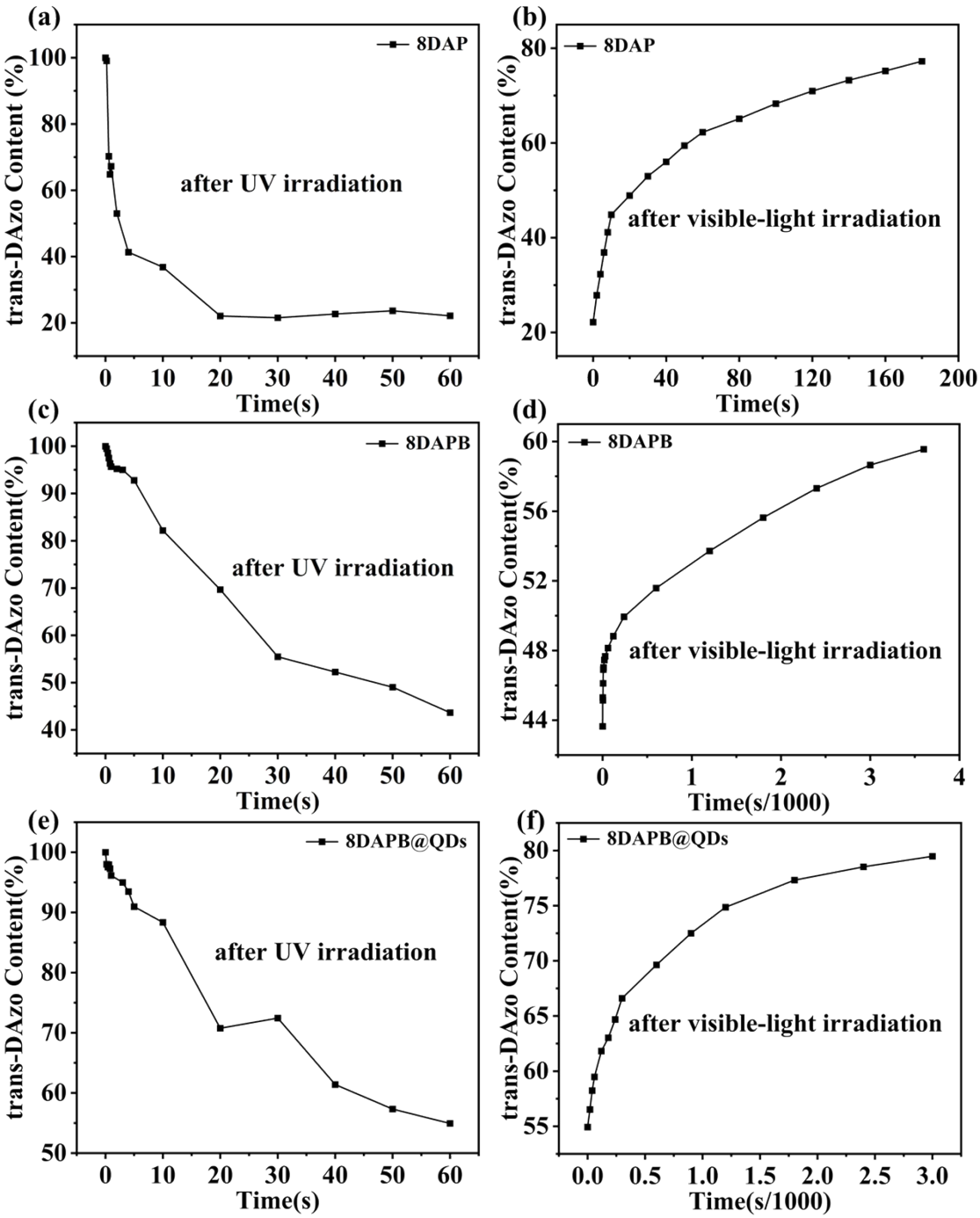


Figure S9. The plots of trans-DAzo content versus time of the 8DAP/8DAPB dissolved in Ethyl alcohol, (a,c) after UV irradiation; (b,d) after visible-light irradiation; the plots of trans-DAzo content versus time of the 8DAPB@QDs dissolved in aqueous ethanol solution, (e) after UV irradiation; (f) after visible-light irradiation; The trans-DAzo content is defined as the ratio of absorption intensity over the pristine absorption intensity at 405 nm.

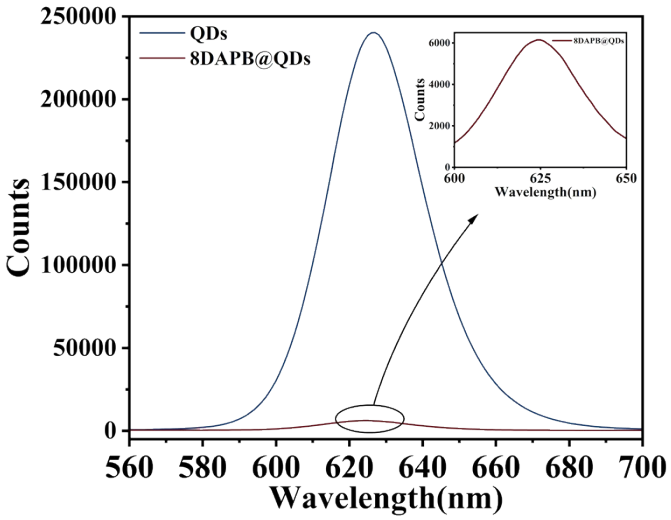


Figure S10. Fluorescence efficiency plots for the QDs and 8DAPB@QDs.

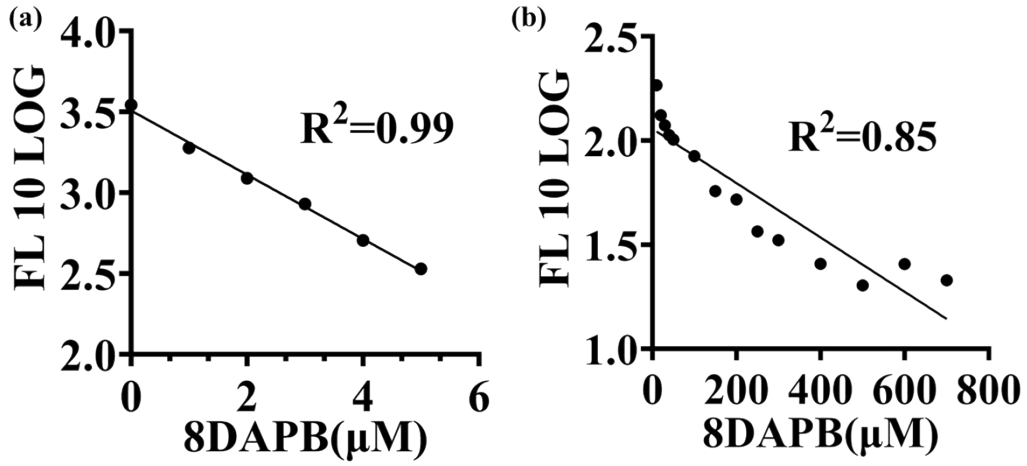


Figure S11. Plots of the QDs quenched by various amounts of 8DAPB in ethanol/water mixtures (65% v/v); (a) The concentrations of 8DAPB were (μM): 0,1, 2, 3, 4, 5; (b) The concentrations of 8DAPB were (μM): 6.10..100...750.

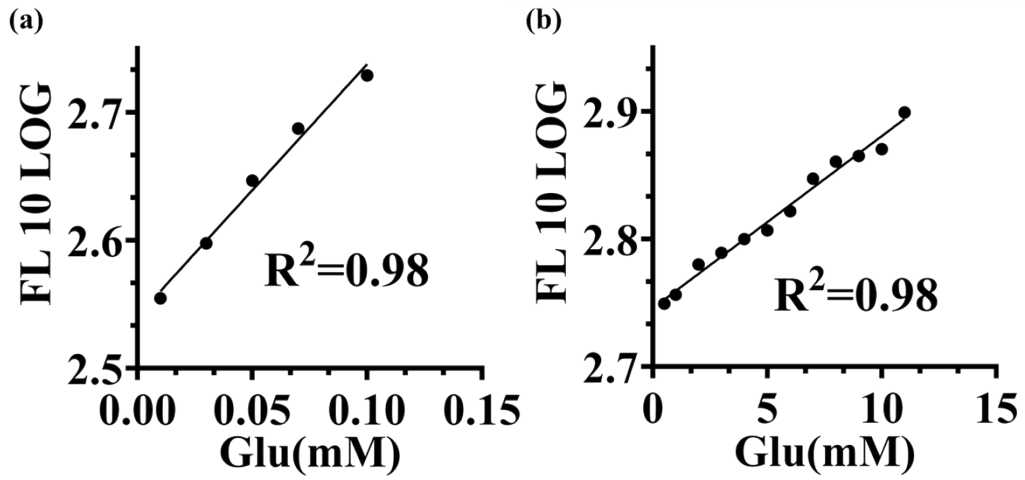


Figure S12. Plots of the 8DAPB@QDs recovery by various amounts of glucose in ethanol/water mixtures (65% v/v); (a) The concentrations of glucose were (mM): 0.01, 0.03, 0.05, 0.07, 0.1; (b) The concentrations of glucose were (mM): 0.5, 1, 2...11.

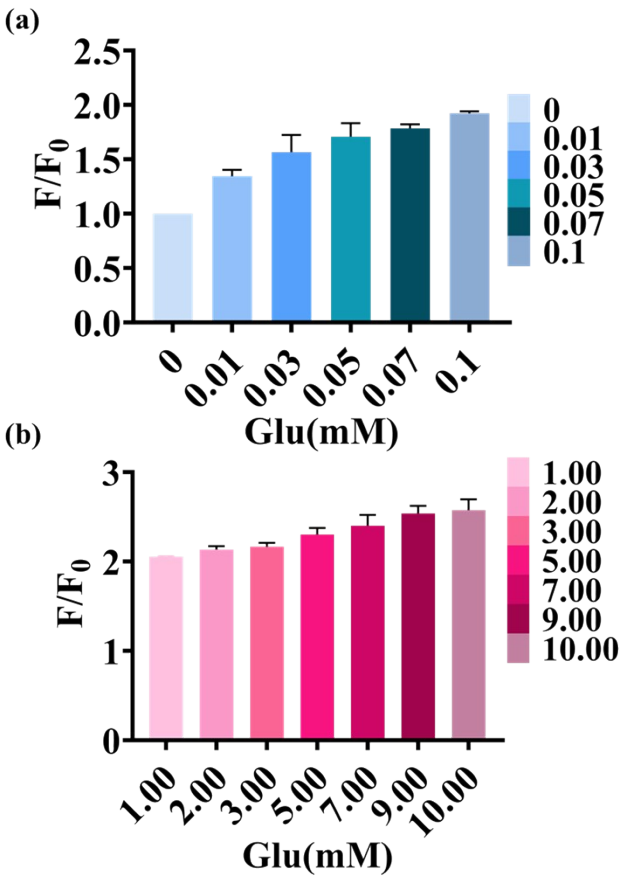


Figure S13. ANOVA plot of relative fluorescence recovery (F/F_0) of 8DAPB@QDs at different glucose concentrations. (a) The concentrations of glucose were (mM): 0.01, 0.03, 0.05, 0.07, 0.1; (b) The concentrations of glucose were (mM): 1, 2...10.

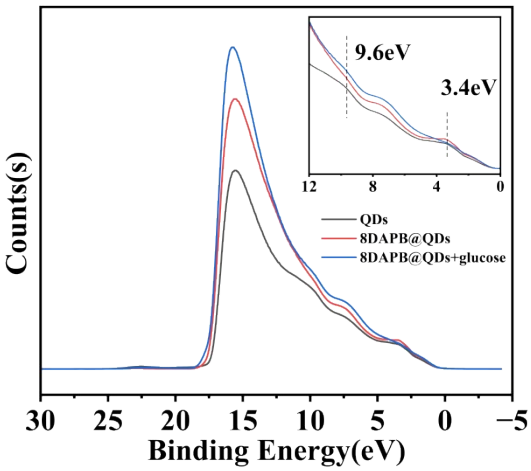


Figure S14. Ultraviolet photoelectron spectroscopy of QDs alone, 8DAPB@QDs, and 8DAPB@QDs +glucose, respectively.

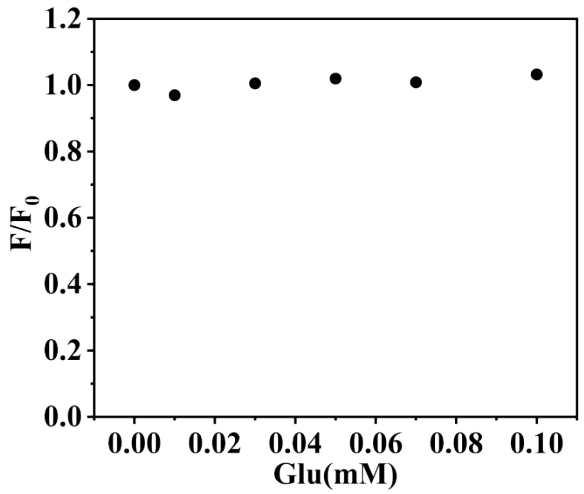


Figure S15. Effect of different concentrations of glucose on the FL(F/F_0) of QDs without 8DAPB. The concentrations of glucose were 0.01, 0.03, 0.05, 0.07, 0.1, mM.

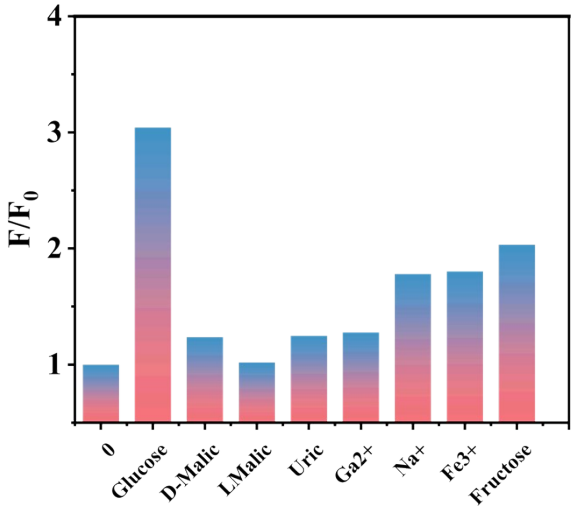


Figure S16. Effect of common species (e.g., Glucose, D-Malic acid, L-Malic acid, Uric acid, Ga^{2+}, Na^{+}, Fe^{3+}, Fructose) on the Fluorescence Intensity (F/F_0) of 8DAPB@QDs.

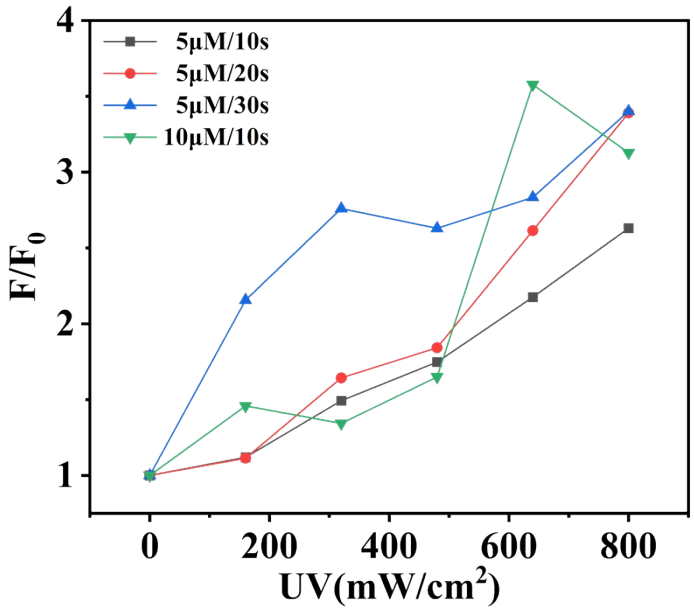


Figure S17. UV response curves obtained from the 8DAPB@QDs (5,10 μm) system under different UV irradiation durations.

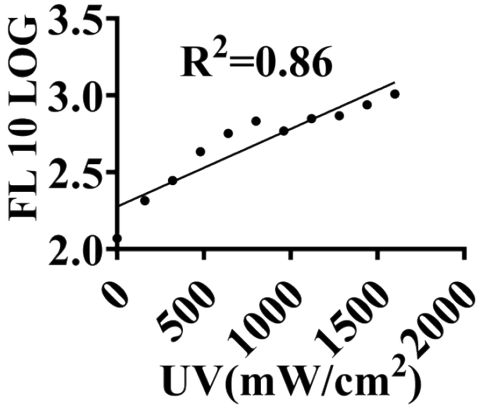


Figure S18. Plots of the 8DAPB@QDs recovery by various irradiance of UV in ethanol/water mixtures (65% v/v), The irradiance of UV were 160, 320, 480... 1600, mW/cm^2.

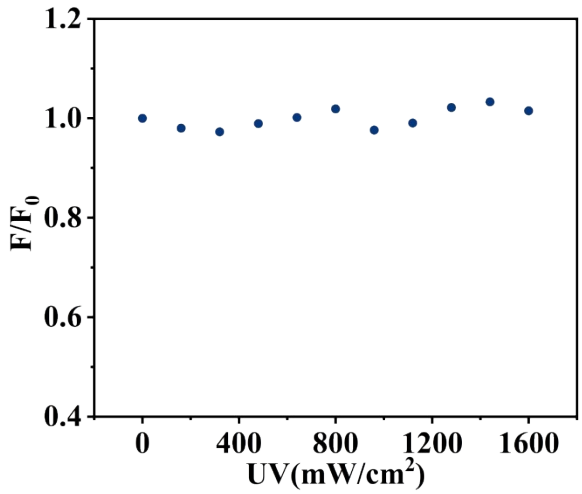


Figure S19. Effect of different irradiance of UV on the FL(F/F_0) of QDs without 8DAPB. The irradiance of UV were 160, 320, 480... 1600, mW/cm^2.

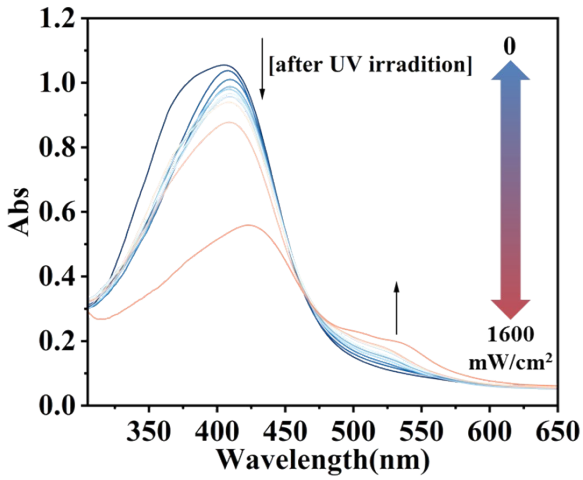


Figure S20. Changes in the absorption spectrum of 8DAPB upon irradiation with 365 nm light in Ethyl alcohol, The irradiance of UV were 160, 320, 480... 1600, mW/cm^2.

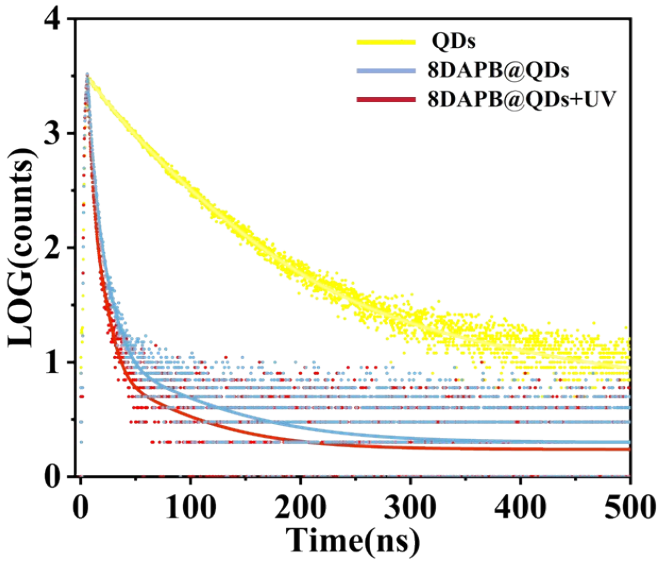


Figure S21. Time-resolved fluorescence decay curves for the pure QDs, 8DAPB@QDs, and UV-treated 8DAPB@QDs.

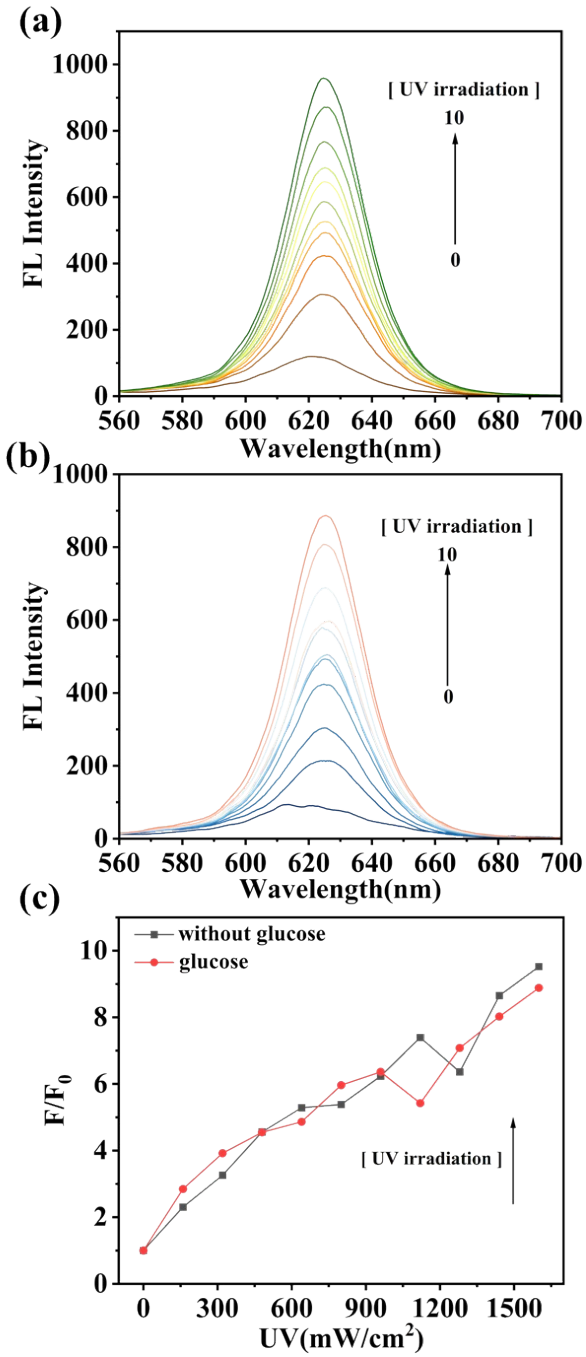


Figure S22 (a) FL spectra and curves of 8DAPB@QDs with glucose (100μM) recovery by various irradiance of UV in ethanol/water mixtures (65% v/v); (b) FL spectra and curves of 8DAPB@QDs recovery by various irradiance of UV in ethanol/water mixtures (65% v/v); (c) Fitting curve of the relative intensity of FL (F/F_0) vs UV irradiance,The irradiance of UV were 160, 320, 480... 1600, mW/cm^2.

Table S1. Fluorescence quantum yield of QD and 8DAPB@QDs.

Sample	Fluorescence quantum yield
QDs	84.87%
8DAPB@QDs	3.54%

Table S2 Fluorescence lifetimes obtained with three-exponential fit of the fluorescence decay curves of the QDs alone, 8DAPB@QDs, and 8DAPB@QDs+glucose, respectively.

Sample	τ_1 /ns	τ_2 /ns
QDs	25.84	64.55
8DAPB@QDs	16.48	44.33
8DAPB@QDs+glucose	18.02	47.39

Formula S1 Standard deviation

$$RSD = \frac{SD}{x(average)} \times 100\%$$