

Supplementary Information

DNA mediated assembly of Quantum Dot-Protoporphyrin IX FRET Probe and Effect of FRET Efficiency on ROS Generation

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Dynamic Light Scattering (DLS) Measurement of QD and QD-DNA Conjugate:

Hydrodynamic size was taken from DLS measurement of QD and QD-DNA suspension in water. The sample solution of QD and QD-DNA was filtered and sonicated for few minutes for DLS measurement.

The hydrodynamic diameter of QD was measured as 12 nm while QD-DNA conjugate have hydrodynamic size of 21 nm (Figure S1). The increase in hydrodynamic size of QD after conjugation with DNA indicates its successful conjugation with DNA.

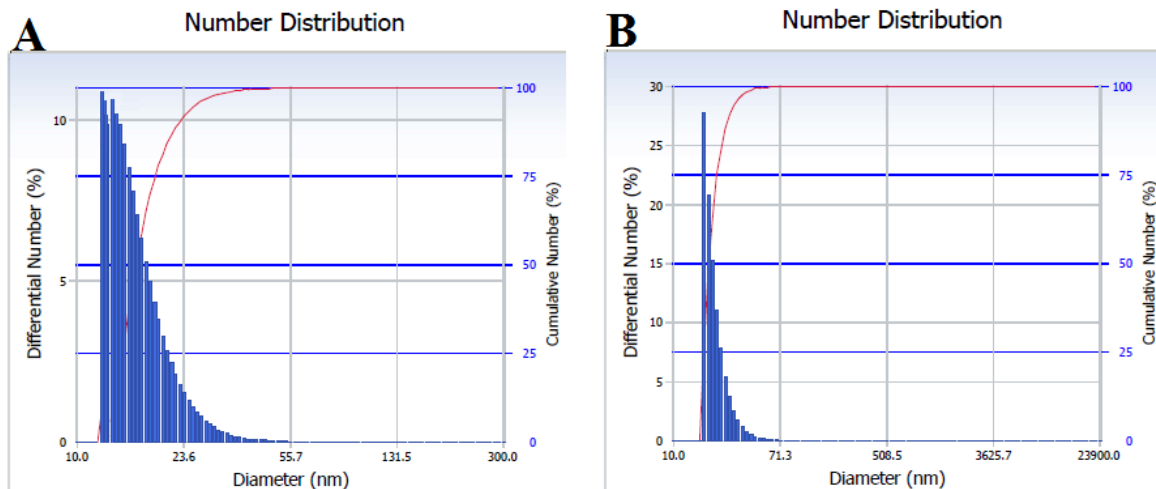


Figure S1: DLS studies showing number distribution **A.** QD and **B.** QD-DNA (S1) conjugate.

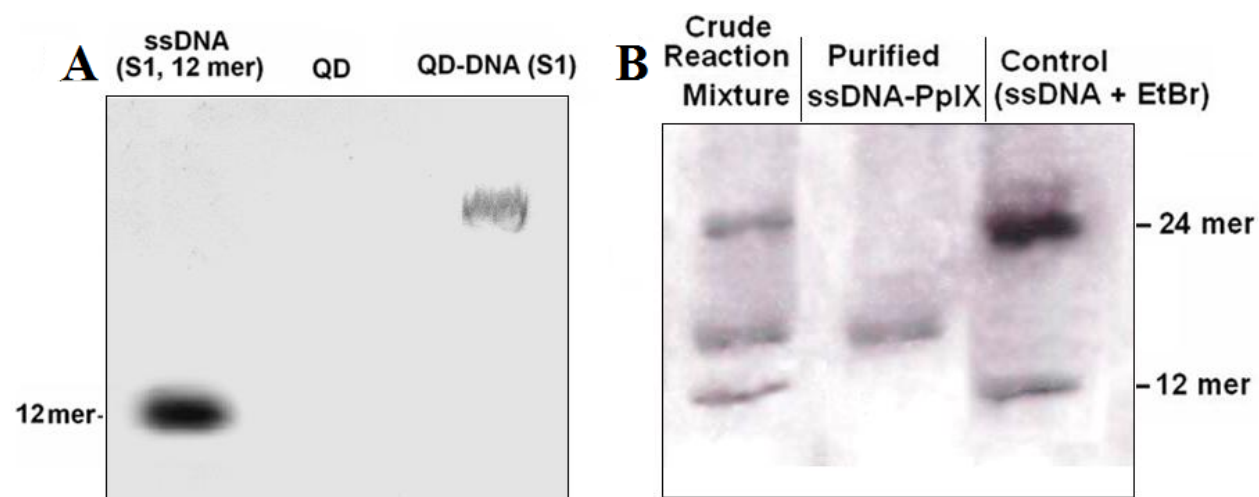


Figure S2: **A.** Agarose gel image showing formation of QD-DNA (S1) conjugate. **B.** PAGE analysis of Pp IX-DNA (S2) conjugate. Pictures were acquired by CCD camera of Gel documentation system.

MALDI-TOF Spectra of Pp IX-ssDNA Conjugate:

The purified Pp IX-ssDNA (S2) extracted from PAGE was subjected to molecular weight determination by MALDI-TOF. The calculated mass is 4549.44 and observed mass is 4546.09.

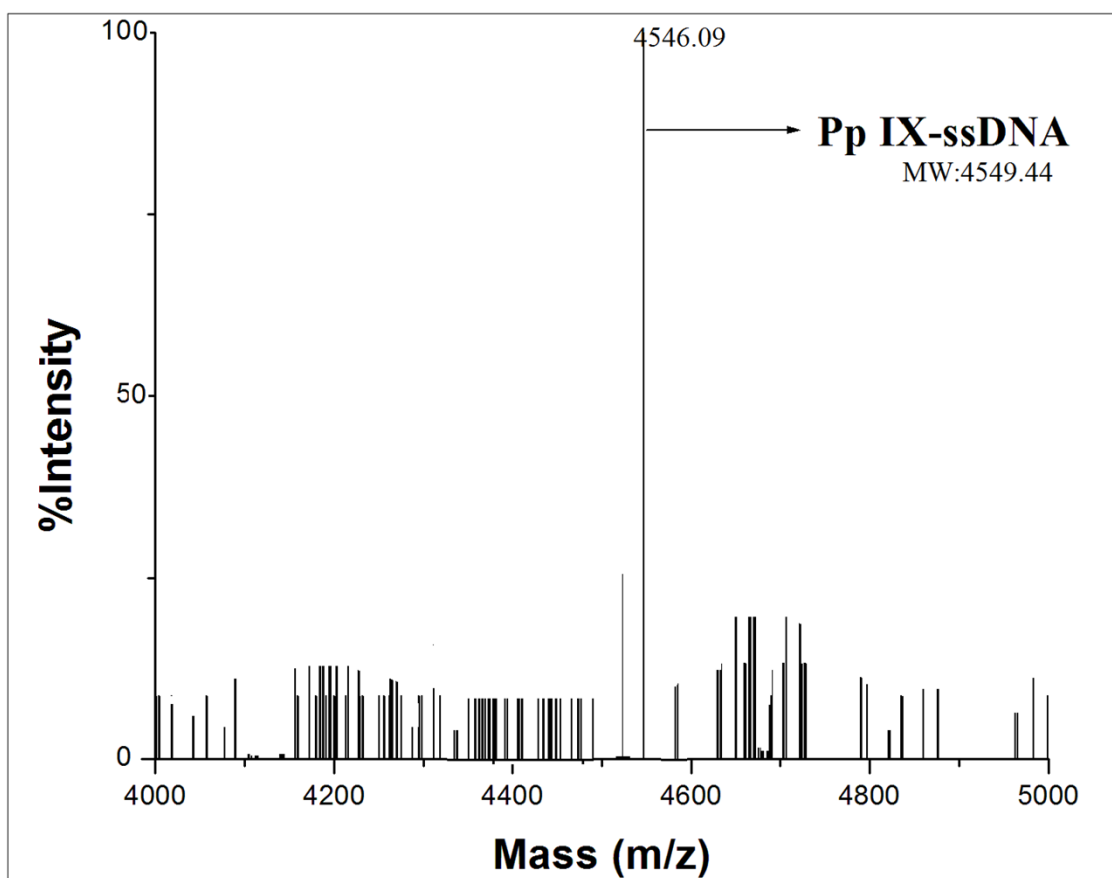


Figure S3: MALDI-TOF spectra of Pp IX-ssDNA (S2) conjugate.

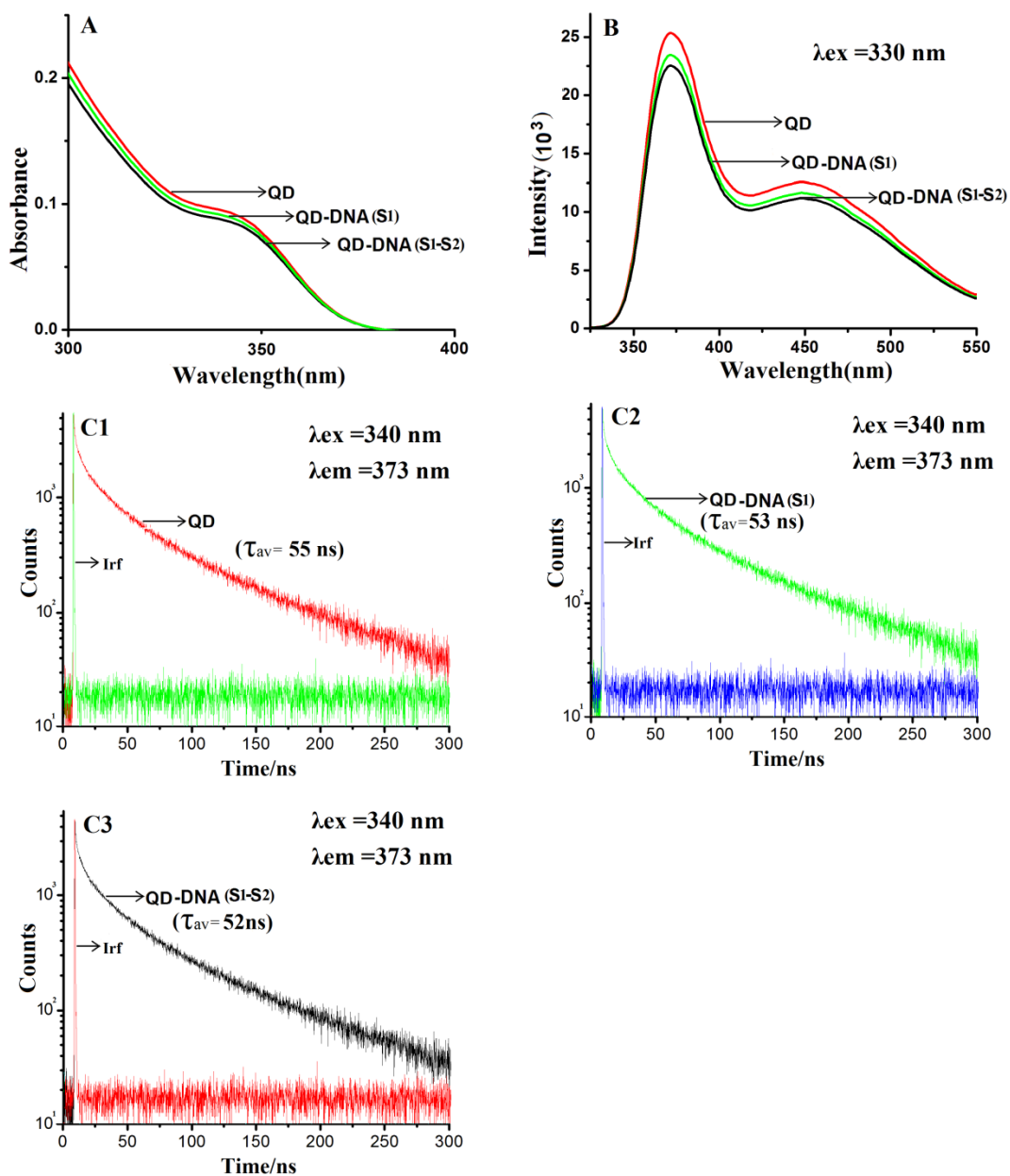


Figure S4: A. UV-Visible spectra B. Steady-State fluorescence spectra and C1, C2, C3. Time resolved fluorescence decay of QD, QD-DNA (S1) and QD-DNA (S1-S2) respectively.

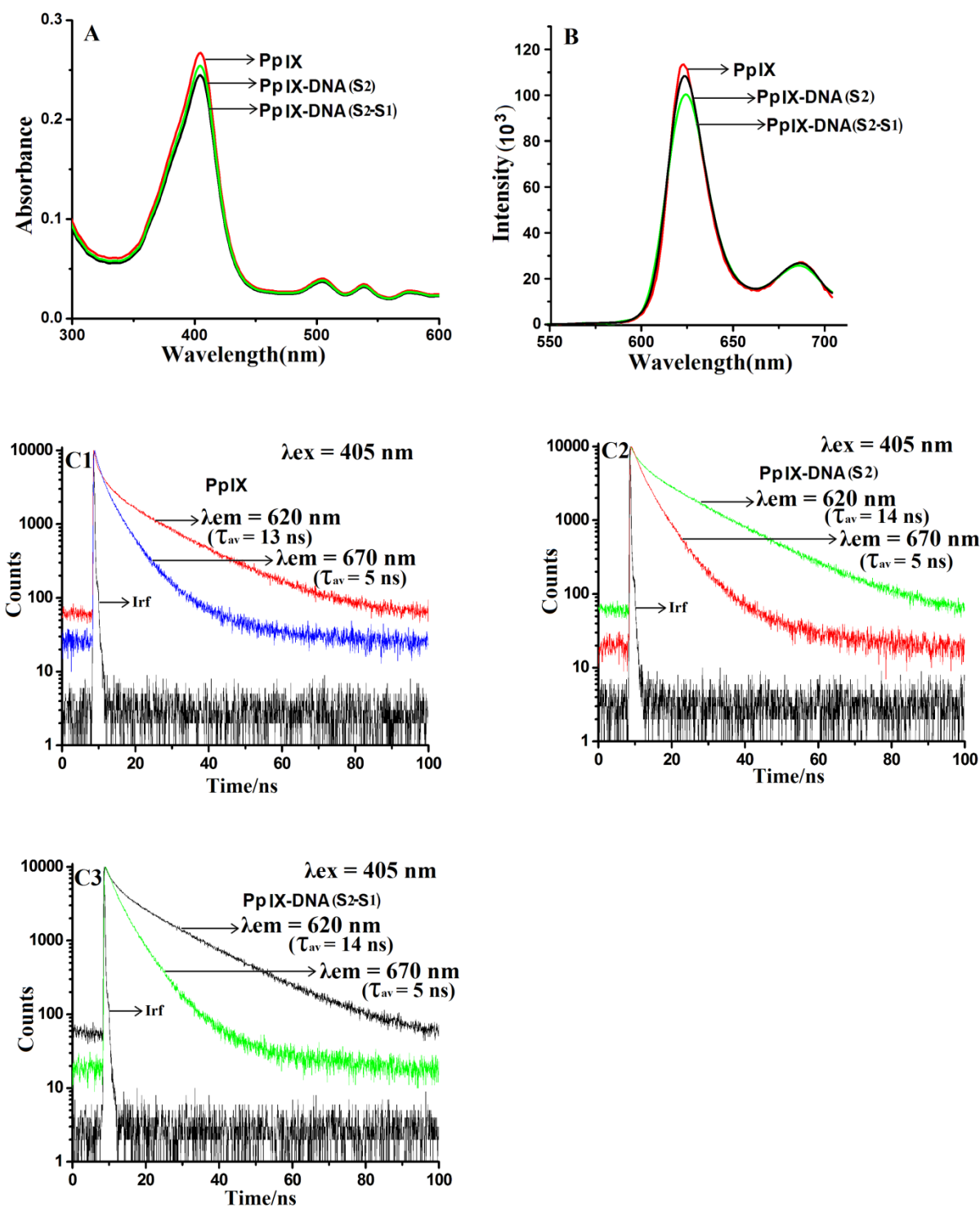


Figure S5: A. UV-Visible spectra B. Steady-State fluorescence spectra and C1, C2, C3. Time resolved fluorescence decay of Pp IX, Pp IX-DNA (S2) and Pp IX-DNA (S1-S2) respectively.

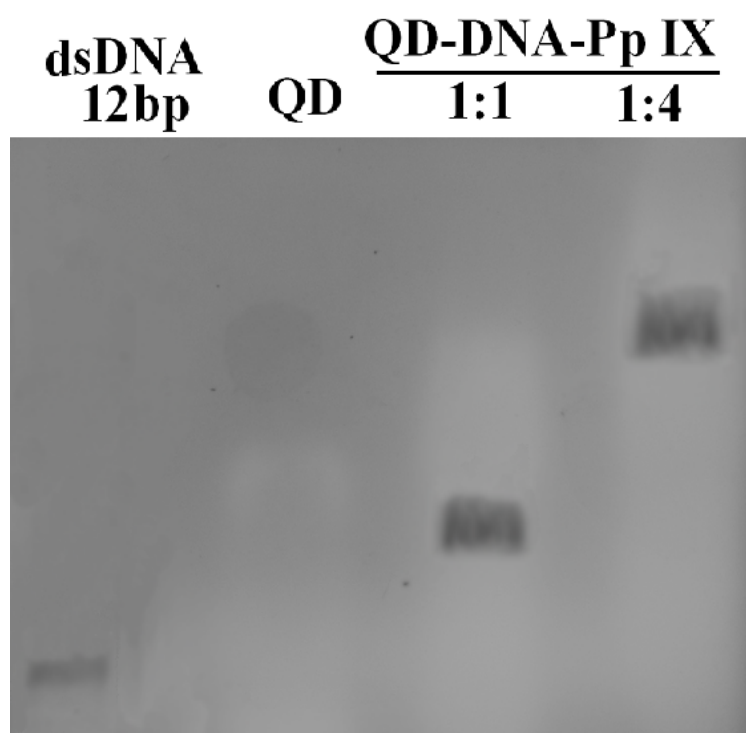


Figure S6: Agarose Gel electrophoresis of QD-DNA-Pp IX assembly. Pictures were acquired by CCD camera of Gel documentation system.

Forster distance measurement between QD (donor) and Pp IX (acceptor):

The QD fluorescence spectra and Pp IX absorption spectra was normalised to unity to calculate the spectral overlap of donor and acceptor (Figure S5). The molar absorptivity of Pp IX acceptor was taken as 241,000 M⁻¹cm⁻¹. The spectral overlap integral was calculated from equation (1).

$$J = \int_0^{\infty} F_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda \quad (1)$$

Where F_D is fluorescence emission spectrum of QD, ϵ_A is the molar absorptivity of Pp IX at wavelength λ . The Forster distance R_0 at which FRET efficiency is 50% was calculated using spectral overlap integral from equation (2).

$$R_0 = 0.02108 [\kappa^2 \phi_0 \eta^{-4} J]^{1/6} \quad (2)$$

Where κ^2 is dipole orientation factor taken as 2/3, ϕ_0 is quantum yield of donor (0.32 for ZnSe/ZnS QD) and η is refractive index of medium. The Forster radius, R_0 was found to be 4.85 nm.

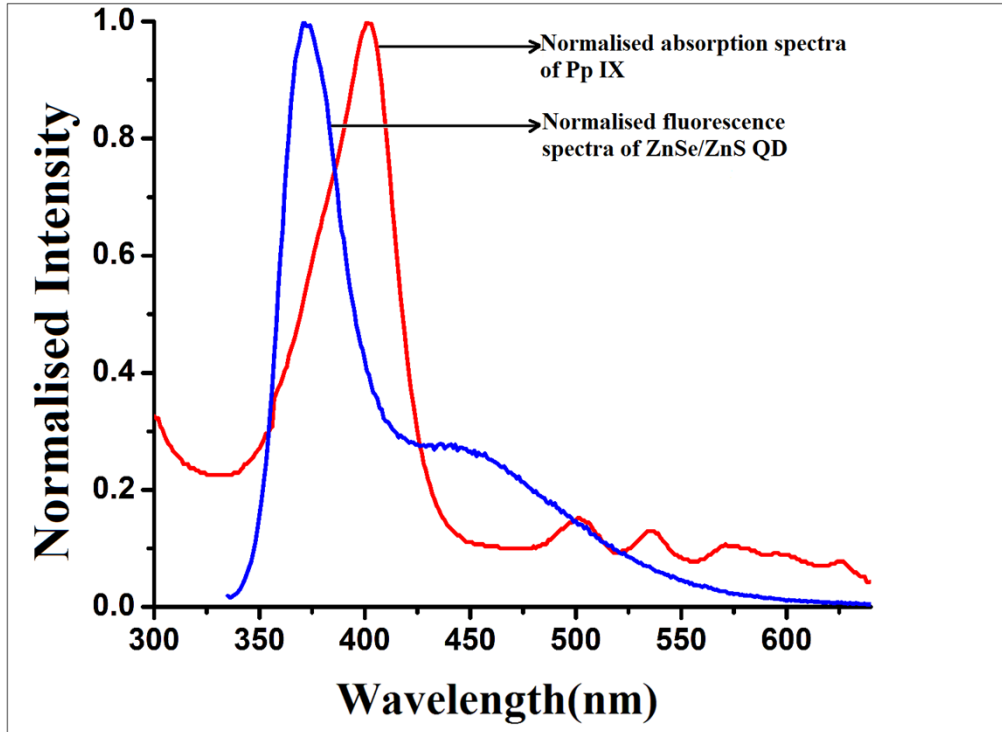


Figure S7: Normalised Pp IX (acceptor) absorption spectra and QD (donor) fluorescence spectra.

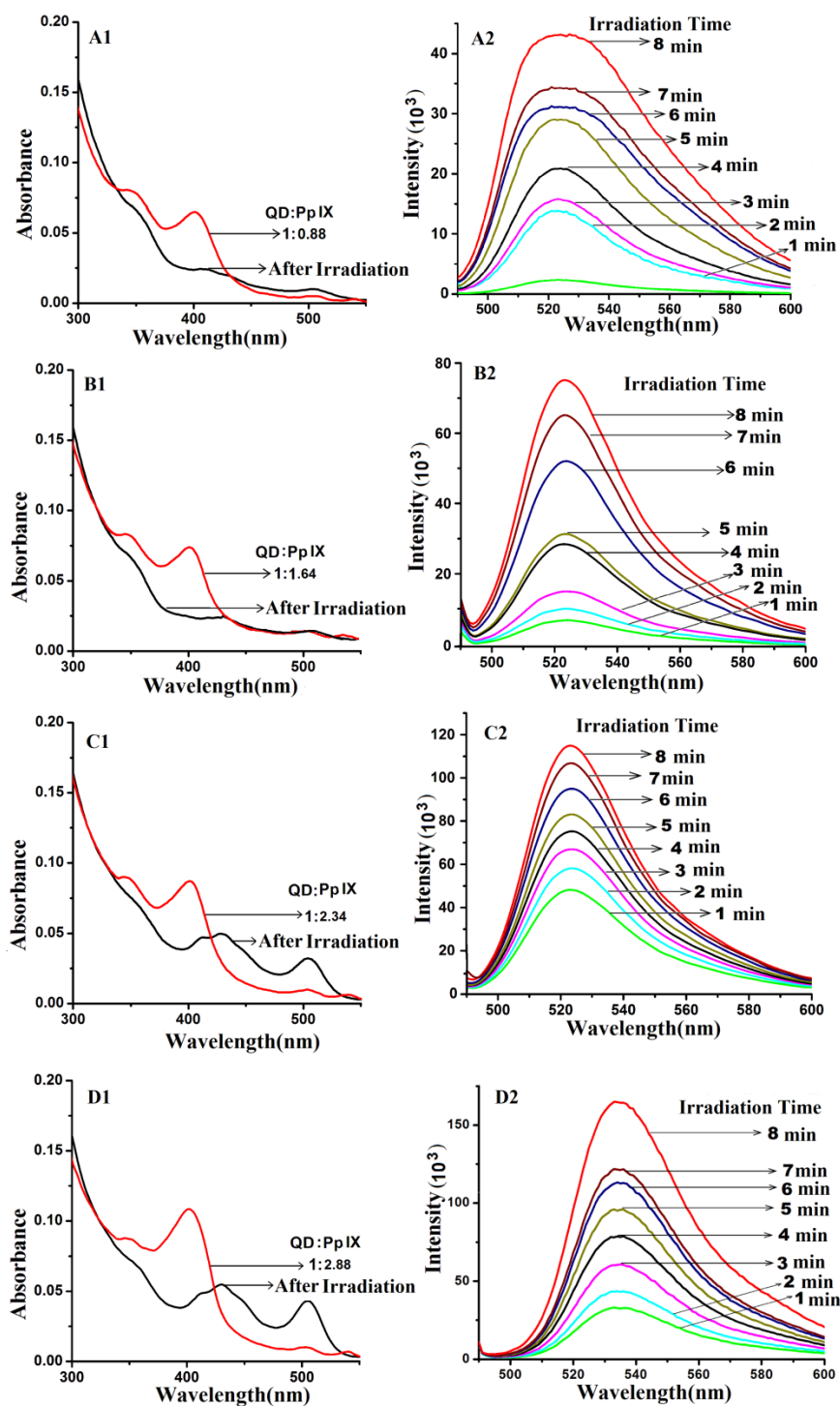


Figure S8: A1, B1, C1, D1. UV-Visible spectra of QD-Pp IX direct conjugates in ratio of 1:0.88 to 1:2.88 with DHR 123 before and after irradiation

A2, B2, C2, D2. Fluorescence spectra of Rhodamine 123 at $\lambda_{ex} = 485$ nm in QD-Pp IX direct conjugates on ROS generation.

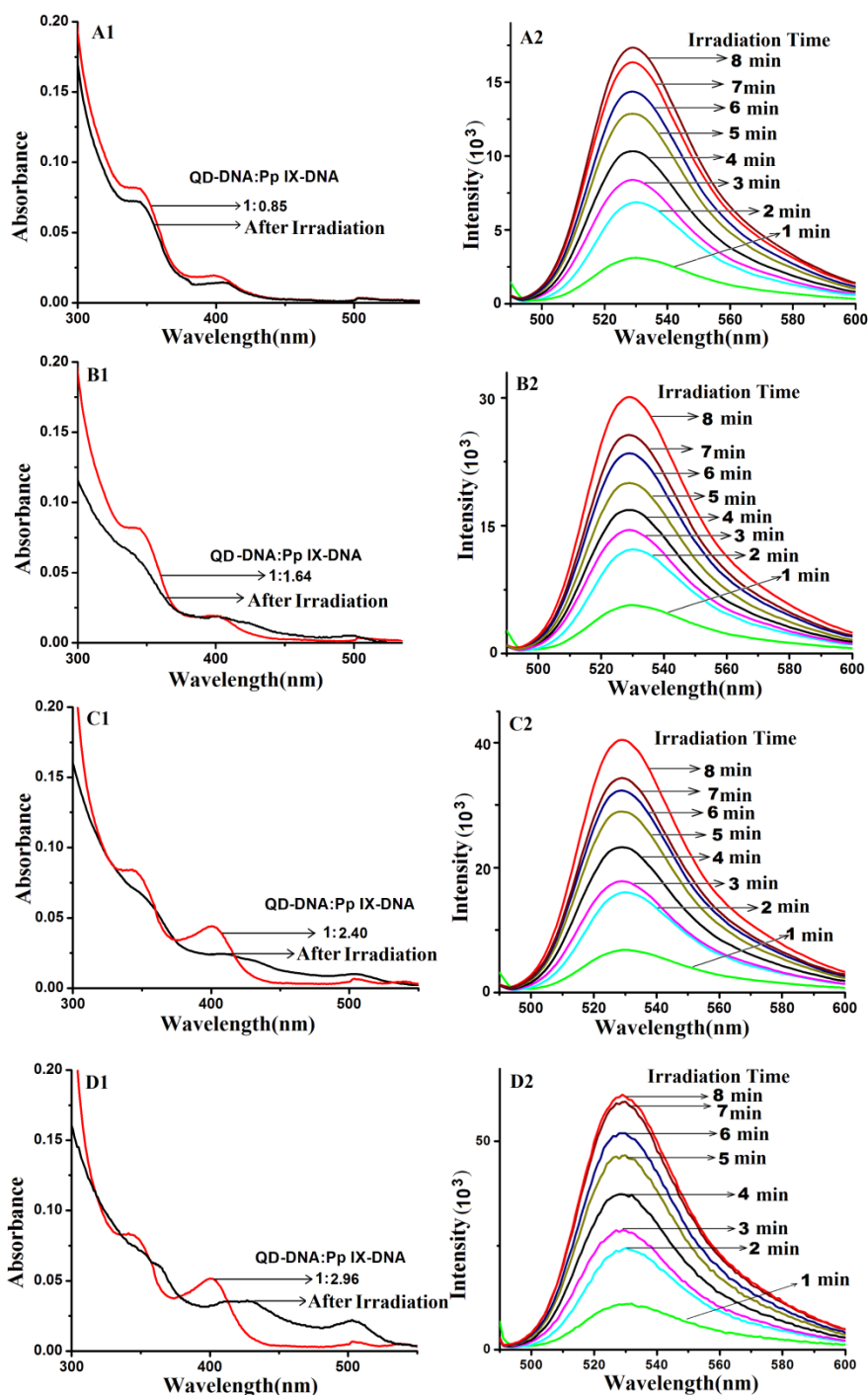


Figure S9: A1, B1, C1, D1. UV-Visible spectra of QD-DNA-Pp IX assembly in ratio of QD-DNA: Pp IX-DNA as 1:0.85 to 1:2.96 with DHR 123 before and after irradiation. **A2, B2, C2, D2.** The corresponding fluorescence spectra of Rhodamine 123 at $\lambda_{ex} =$

485nm in QD-DNA-Pp IX assembly on ROS generation in the same ratio of QD-DNA: Pp IX-DNA as A1, B1, C1 and D1.

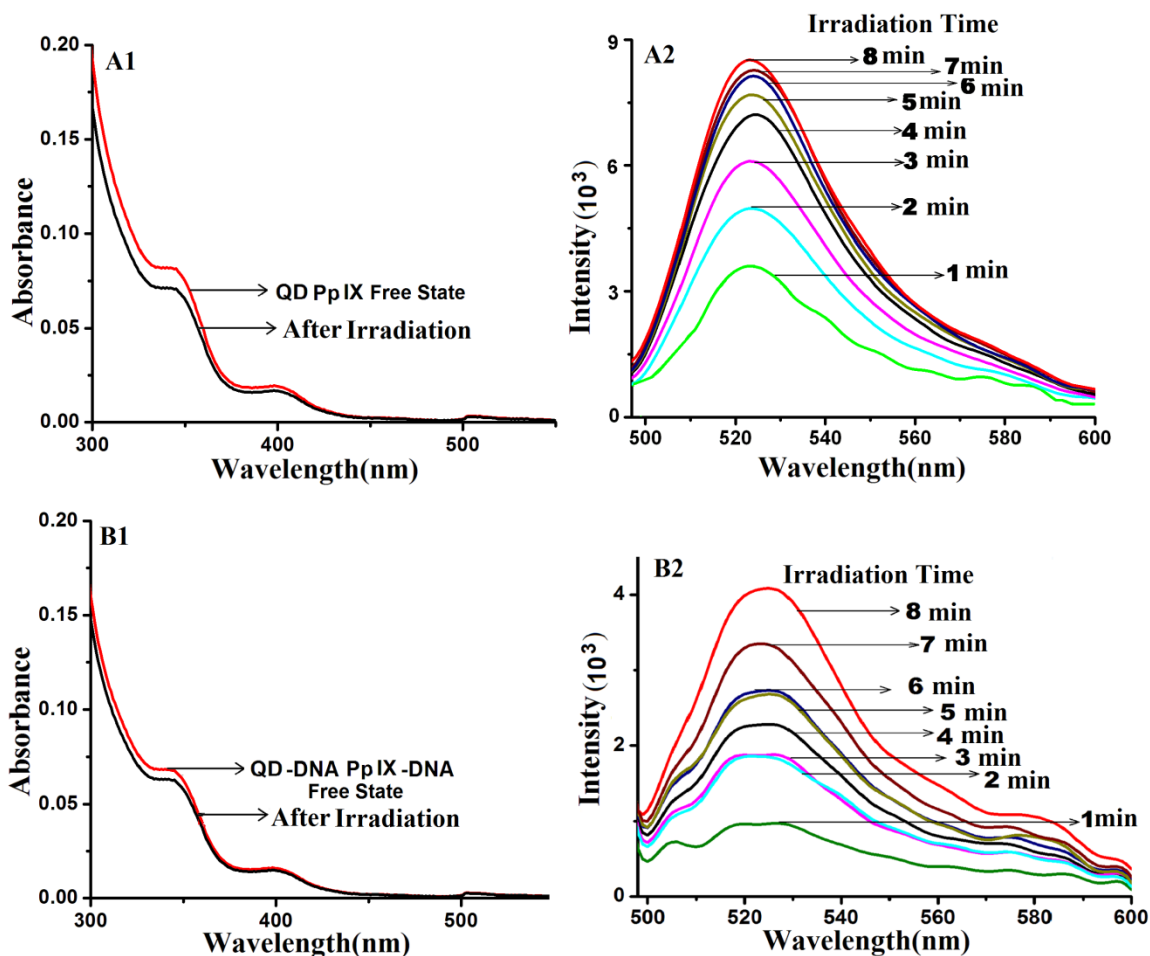


Figure S10: A1, B1. UV-Visible spectra of mixture of QD and Pp IX in free states and mixture of QD-DNA and Pp IX-DNA without hybridization with DHR 123 before (red) and after irradiation (black).

A2, B2. The corresponding fluorescence spectra of Rhodamine 123 at $\lambda_{ex} = 485$ nm for ROS generation from a mixture of QD and Pp IX in free state and mixture of QD-DNA and Pp IX-DNA without hybridization.

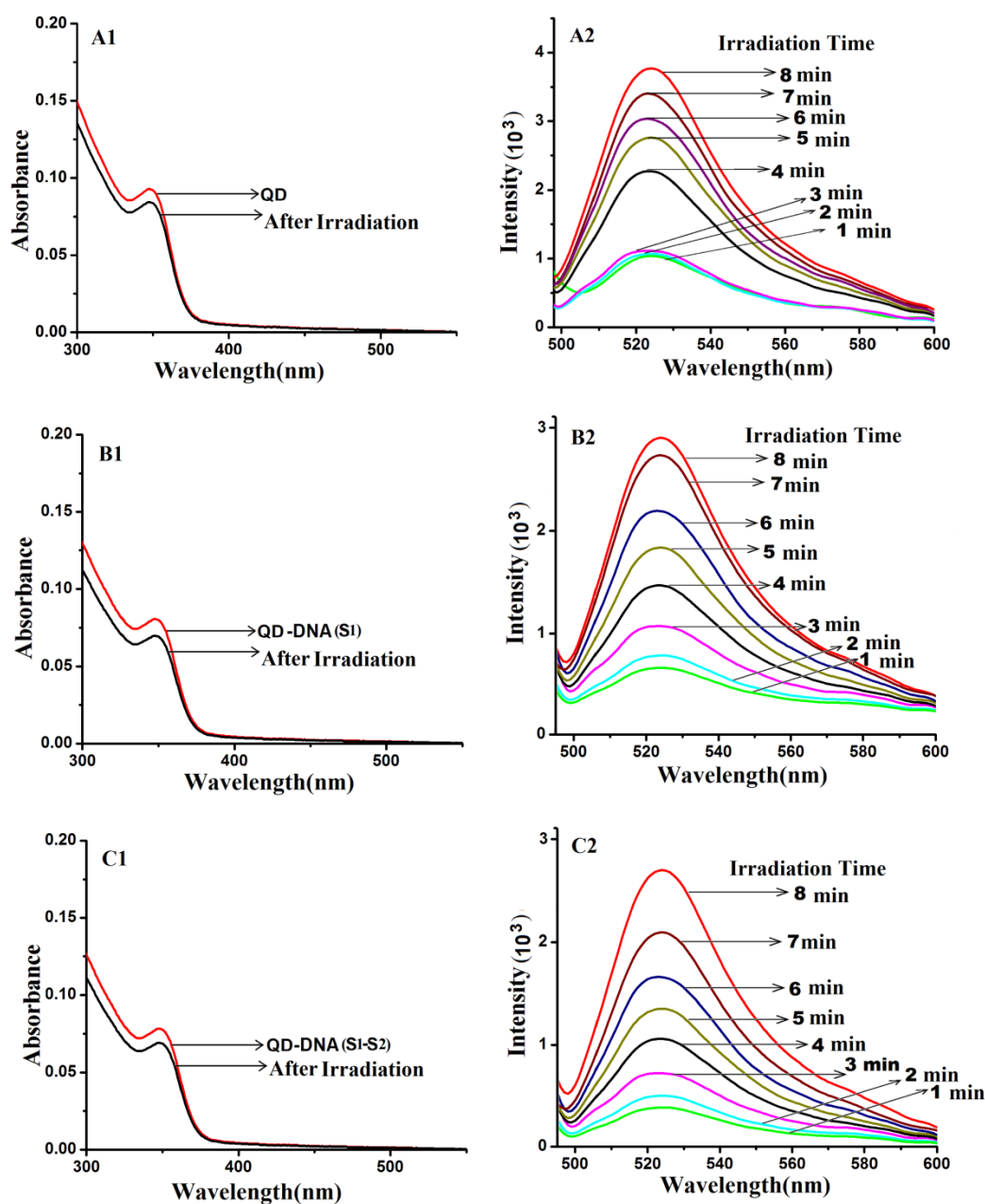


Figure S11: A1, B1, C1. UV-Visible spectra of QD, QD-DNA (S1), QD-DNA (S1-S2) respectively with DHR 123 before and after irradiation.

A2, B2, C2. The corresponding fluorescence spectra of Rhodamine 123 at $\lambda_{ex} = 485$ nm in QD, QD-DNA (QD-S1), QD-DNA (QD-S1-S2) respectively on ROS generation.

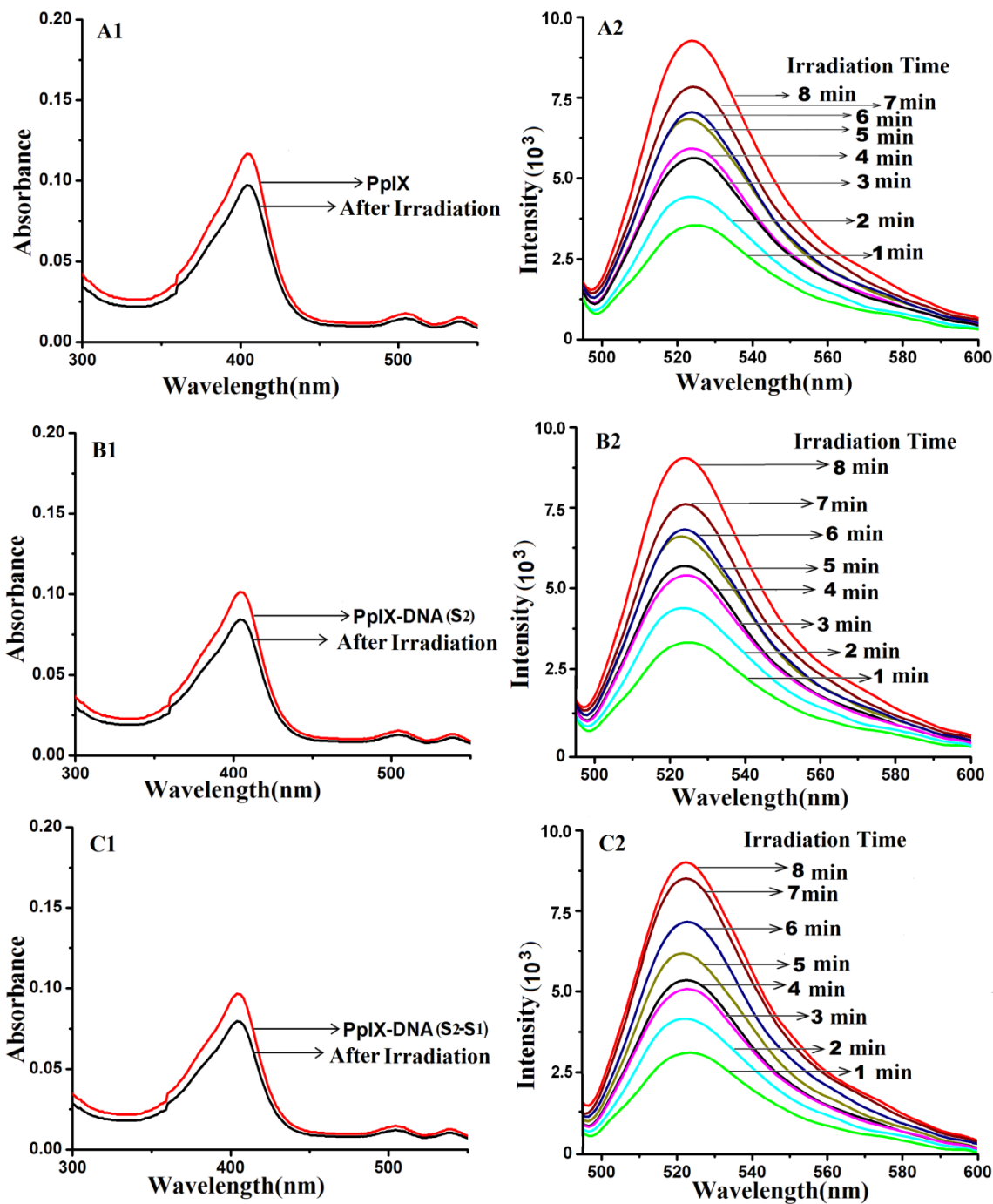


Figure S12: A1, B1, C1. UV-Visible spectra of Pp IX, Pp IX-DNA (S2), Pp IX-DNA (S2-S1) respectively with DHR 123 before and after irradiation.

A2, B2, C2. The corresponding fluorescence spectra of Rhodamine 123 at $\lambda_{ex} = 485$ nm in Pp IX, Pp IX-DNA (Pp IX-S2), Pp IX-DNA (Pp IX-S2-S1) respectively on ROS generation.