Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Excited-State and Charge-Carrier Dynamics in Binary Conjugated Polymer Dots towards Photocatalytic Hydrogen Evolution

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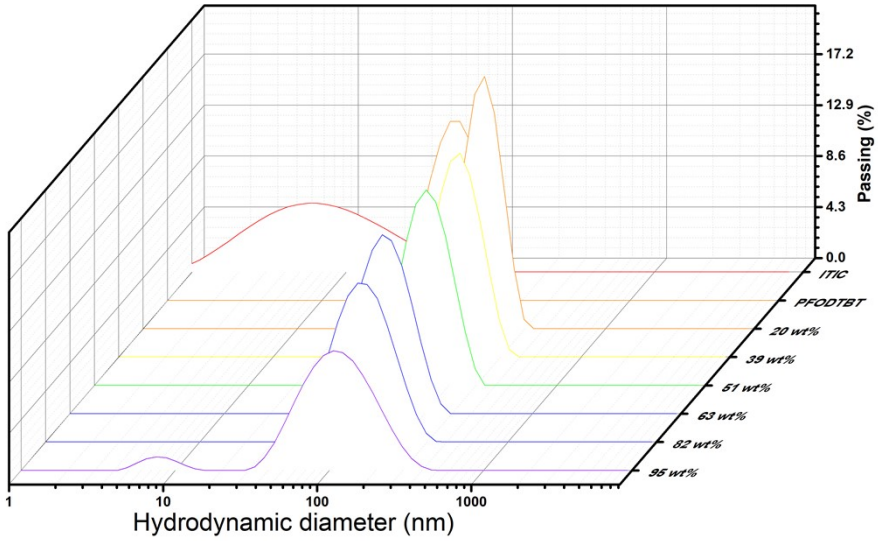

Figure S1. Dynamic Light Scattering (DLS) analysis of ITIC dots, PFODTBT Pdots and D/A binary Pdots with various amount of ITIC wt%.

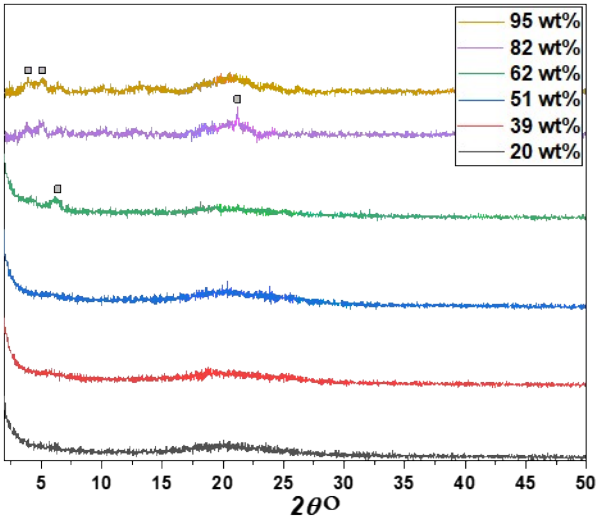

Figure S2. Powder X-ray diffraction (PXRD) patterns of D/A Pdots with mass ratio of ITIC 20wt%, 39wt%, 51wt%, 62 wt%, 82 wt% and 95 wt%. gray square: the characteristic peaks of ITIC. The characteristic peaks of D Pdots and A dots we refer to reference of [1].[1]

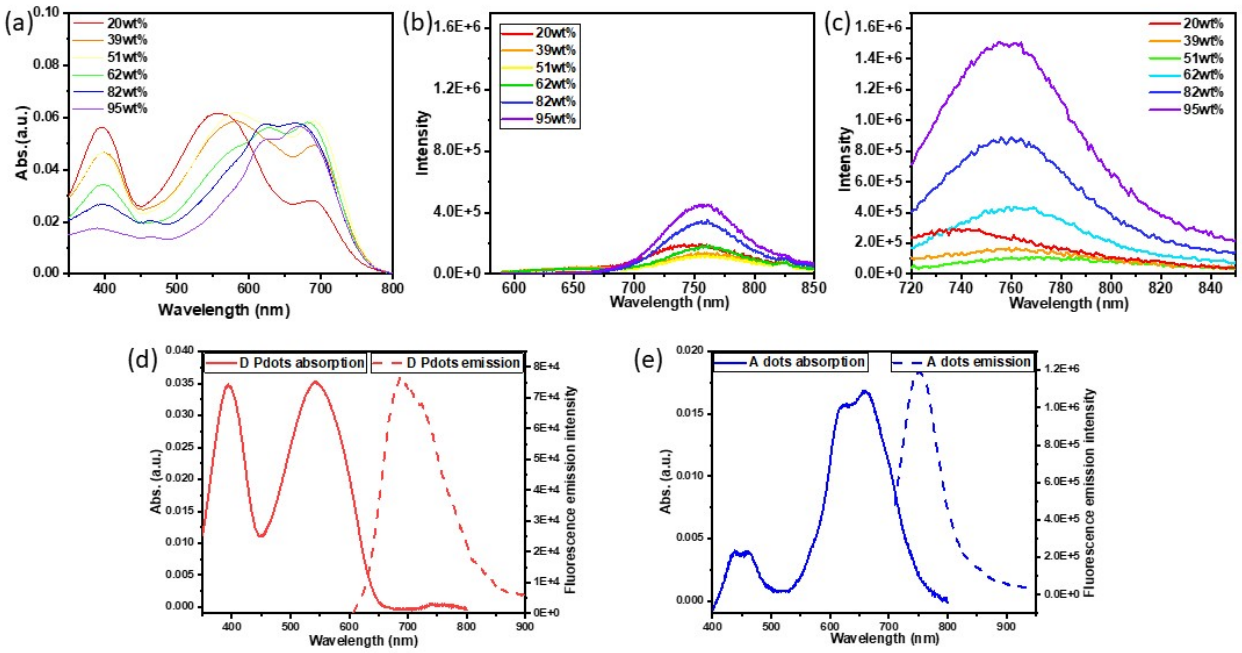

Figure S3. (a) UV-Vis absorption spectrum of D/A Pdots for fluorescence emission study; Steady-state fluorescence emission of binary Pdots under excitation of (b) λ_{ex}=550 nm and (c) λ_{ex}=680 nm. UV-vis absorption and Fluorescence emission of (d) PFODTBT Pdots and (e) ITIC dots.

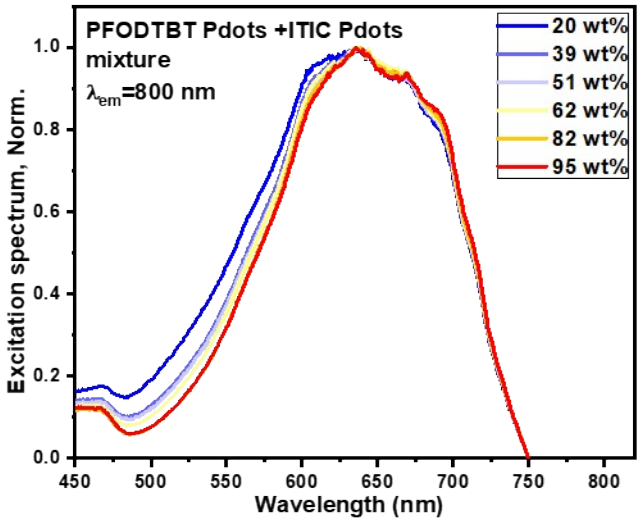

Figure S4. Excitation spectrum of a mixture of D (PFODTBT) Pdots and A (ITIC) dots with various mass ratio under the emission wavelength of 800. Different from the binary Pdots, for mixture of pure A- and pure D-Pdots, only ITIC characteristic feature was observed.

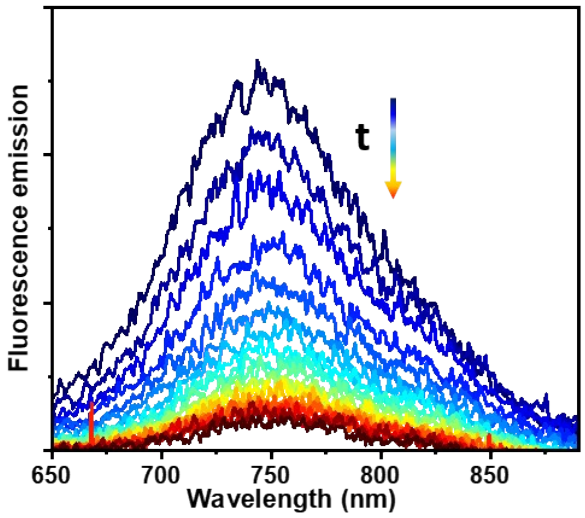

Figure S5. Time-resolved photoluminescence spectra of A (ITIC) dots under the excitation of 550 nm.

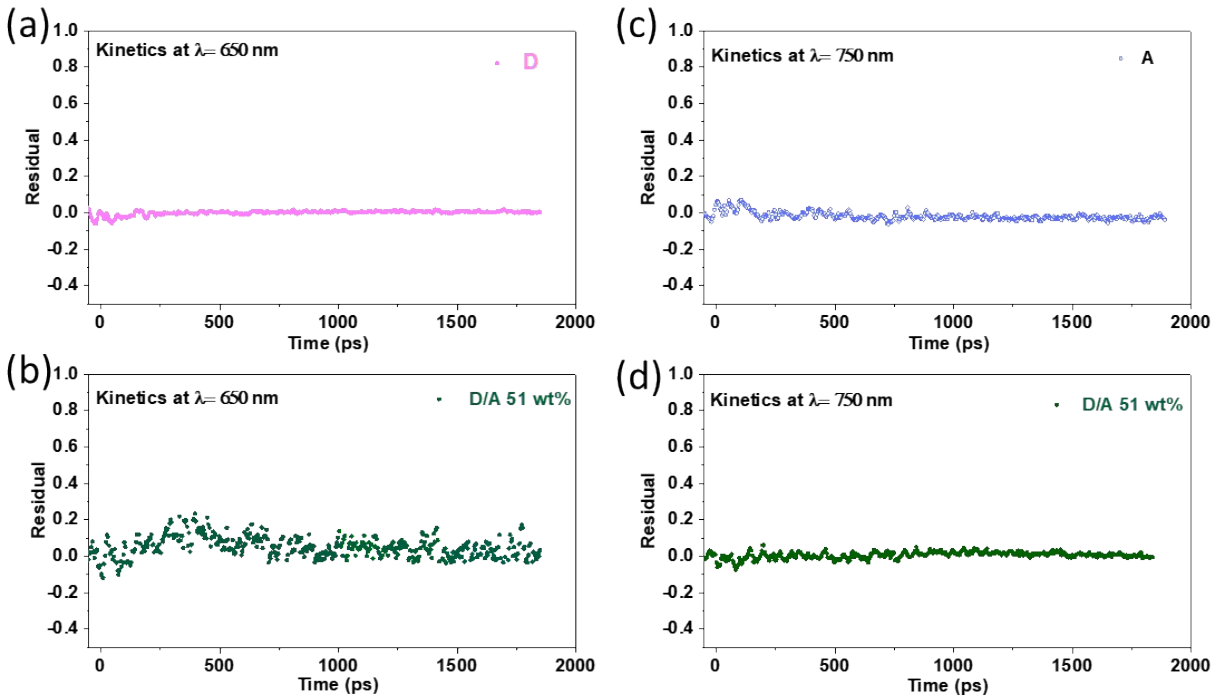

Figure S6. Residual plots of time-resolved photoluminescence (TRPL) results fittings in the main text, Figure 4: (a) D dots and (b) D/A Pdots for Figure 4d in the main text, (c) A dots and (d) D/A Pdots for Figure 4e in the main text.

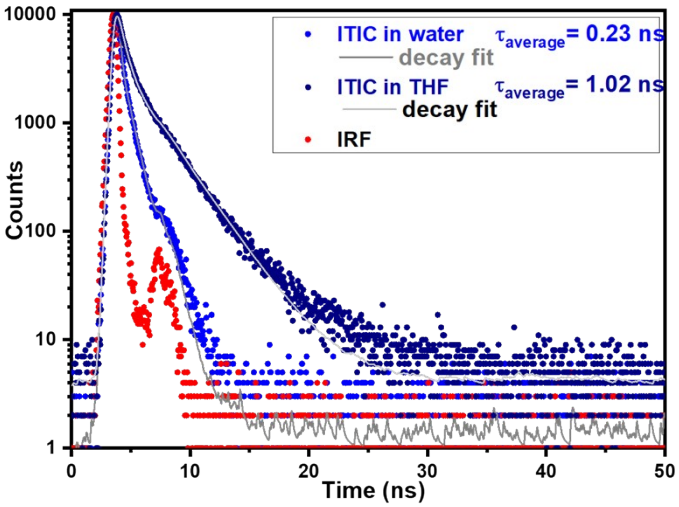

Figure S7. Time-Correlated Single Photon Counting (TCSPC) analysis of ITIC in water (A dots) and THF. The lifetime of ITIC dots in water with a bi-exponential fit ((τ_1=13 ps (87%), τ_2=88 ps (13%)) and the lifetime of ITIC in THF with a bi-exponential fit (τ_1=554 ps (79%), τ_2=2.74ns (21%)).

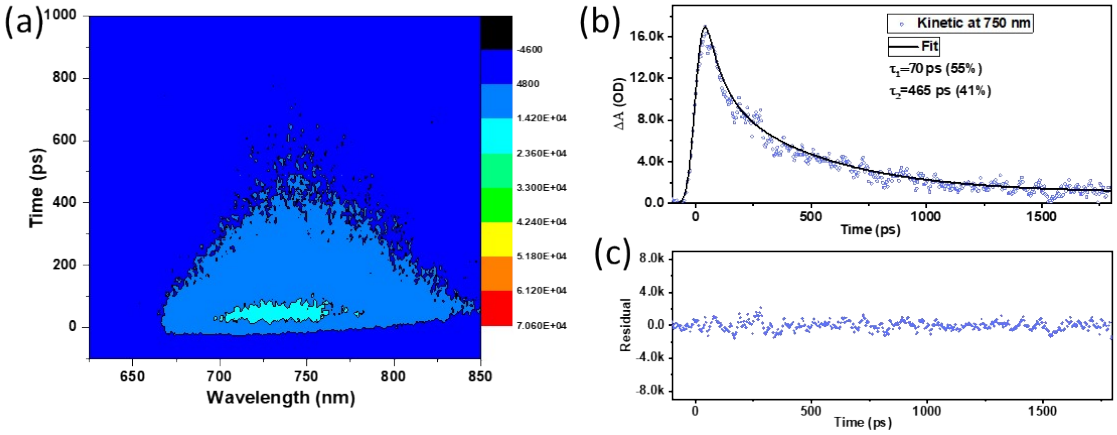

Figure S8. Binary Pdots with ITIC 82 wt%, (a) time-resolved photoluminescence spectra under excitation of 550 nm, (b) kinetic traces at 750 nm with a bi-exponential fit (τ_1=70 ps (55%), τ_2=465 ps (41%) and (c) residual plot of the fit in panel (b).

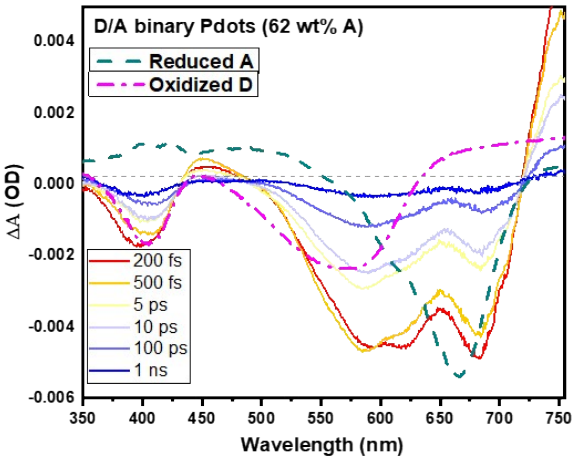

Figure S9. Time resolved absorption (TA) spectroscopy data for D/A binary Pdots (62 wt% A) under excitation of 550 nm, 140 uW, with dashed lines from spectroelectrochemical difference spectra of reduced ITIC and oxidized PFODTBT. The TA spectra are in good agreement with the sum of difference spectra for the oxidized donor and reduced acceptor. The two species of the charge separated state result is a weak net positive absorption around 475 nm due to $A^{\bullet-}$,[1] which is a wavelength where the excited *D Pdots show an isosbestic point (see also Figure S13).

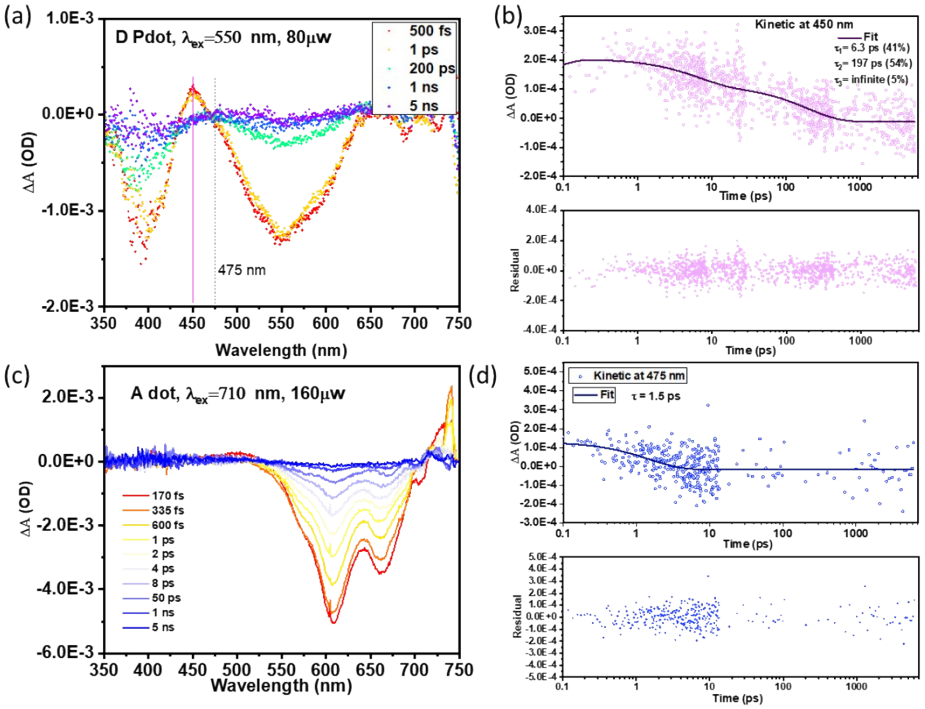

Figure S10. (a) D Pdots under the excitation of λ_{ex}=550 nm, pump power 80 μW purged with Ar before the measurement, and (b) kinetic traces at 450 nm with a bi-exponential fit + offset (τ_1 = 6.3 ps (41%), τ_2 = 197 ps (54%), offset 5%; upper panel), with residual plot (lower plot). (c) A Pdots under the excitation of 710 nm, pump power 160 μw. and (d) kinetic traces at 475 nm with a single-exponential fit (τ = 1.5 ps; upper panel), with residual plot (lower plot).

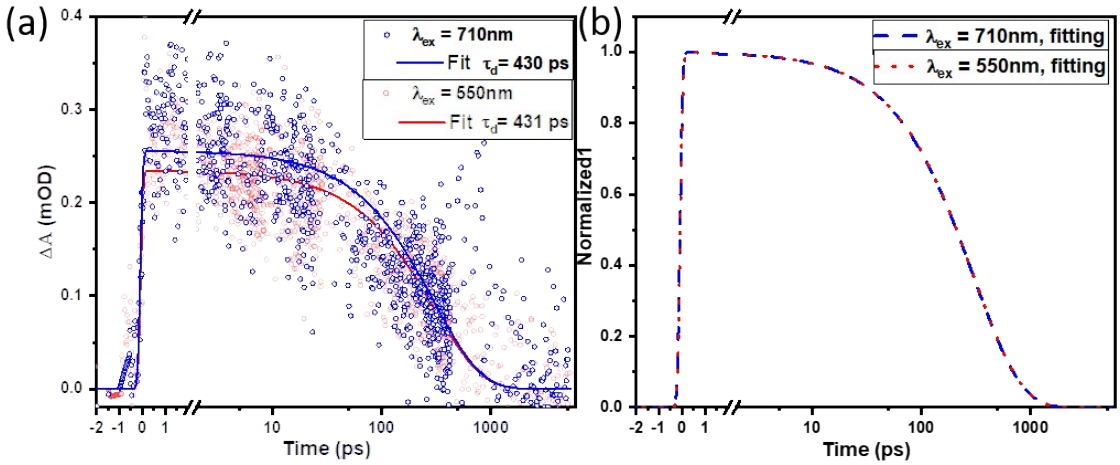

Figure S11. Raw data of TAS decay for D/A binary Pdots with 39 wt% A. Kinetic traces at λ=475 nm under the pump excitation of 550 nm and 710 nm with pump intensity of 80 μW, (a) raw data and their fittings, single-exponential fitting was used for both kinetic traces, (b) normalized fitting under excitation of 710 nm and 550 nm, respectively. Note, their charge generation processes were described in detail in our precious study.[1] It is now presented here for the purpose of charge recombination discussion.

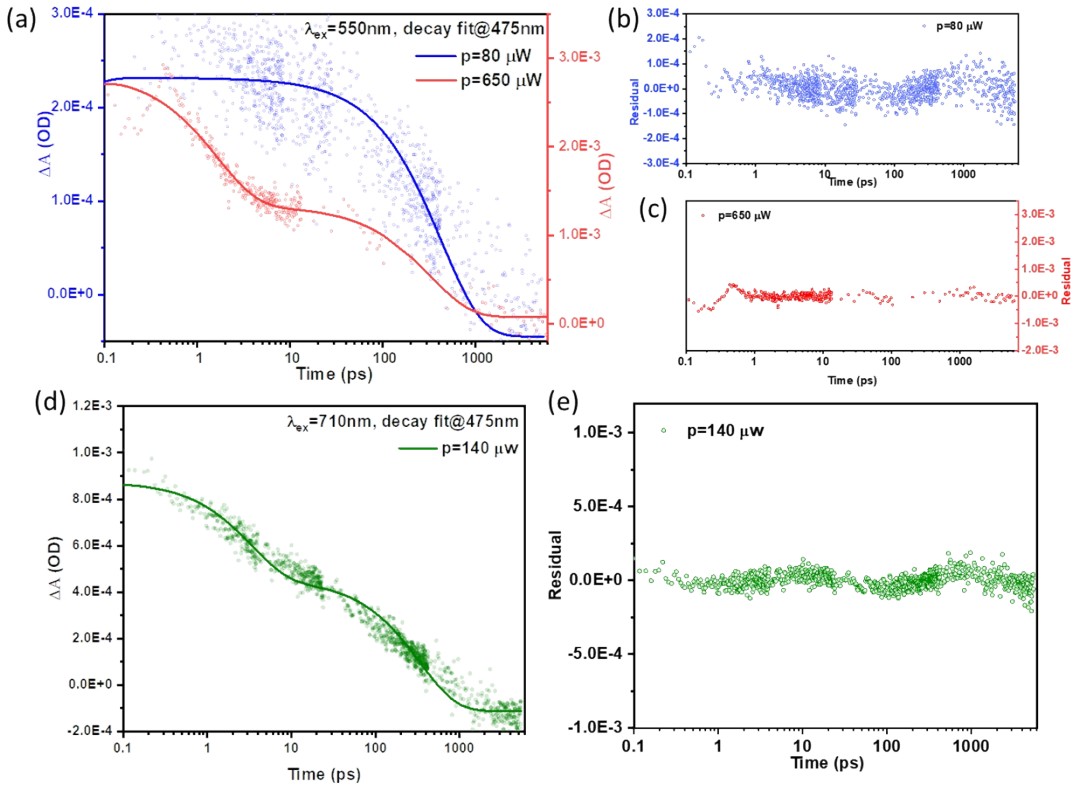

Figure S12. Raw data of TAS decay kinetics at 475 nm of D/A binary Pdots with 39 wt% A, (a) under the excitation wavelength of 550 nm, pump intensity of 80 μW (single-exponential fitting was used for kinetic traces at 475 nm, τ=431 ps) and 650 μW (bi-exponential fitting was used for kinetic traces at 475 nm,

τ_1=1.6 ps (55.8%), τ_2=326.6 ps (45.2%)); (b) and (c) are residual plots for (a). (d) Excitation wavelength at 710 nm with intensity of 140 μW (bi-exponential fitting was used for kinetic traces at 475 nm, τ_1=3.4 ps (43.9%), τ_2=341.4 ps (56.1%)), and (e) residual plot of (d).

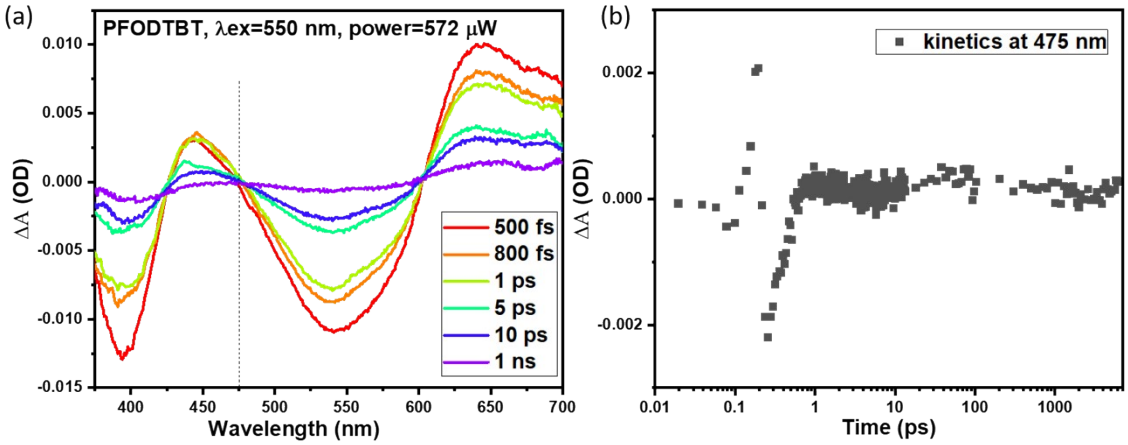

Figure S13. (a) TA spectra of PFODTBT Pdots under the excitation of λ_{ex}=550 nm, power 572 μW and (b) kinetic traces at 475 nm.

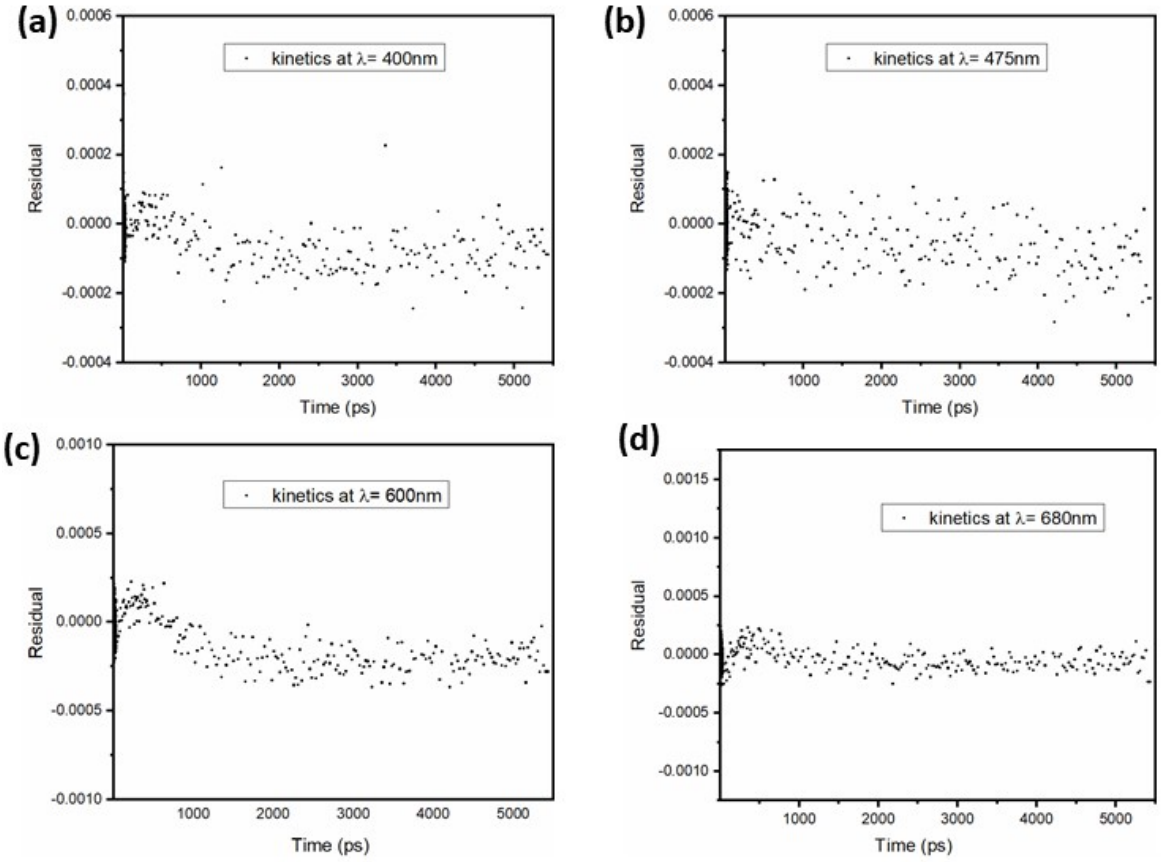

Figure S14. Residual plots of kinetic traces at 400, 475, 600 and 680 nm from global fitting analysis at Figure 5, for binary Pdots with 62wt% A under pump of 550 nm, intensity of 140 μW.

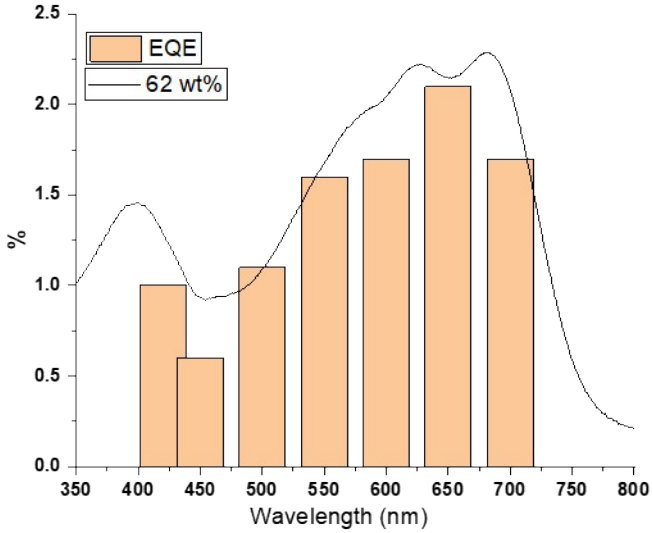

Figure S15. External quantum efficiency of binary Pdots with 62wt% of A.

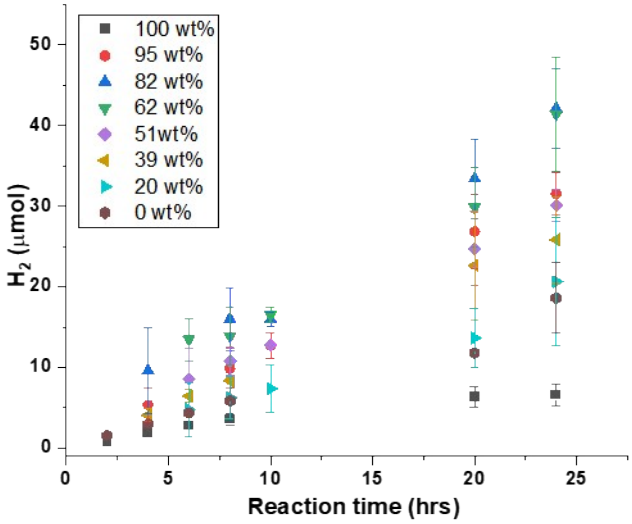

Figure S16. Hydrogen evolution versus time of D Pdots (0 wt%), A dots (100 wt%) and binary Pdots with varies D/A ratios.

References:

(1) Liu, A.; Gedda, L.; Axelsson, M.; Pavliuk, M.; Edwards, K.; Hammarström, L.; Tian, H. Panchromatic Ternary Polymer Dots Involving Sub-Picosecond Energy and Charge Transfer for Efficient and Stable Photocatalytic Hydrogen Evolution. *J. Am. Chem. Soc.* **2021**, 143, 7, 2875-2885.