

Supporting Information

Photophysical studies of CdTe quantum dots in the presence of a Zinc cationic porphyrin

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Contents

- Fig. S1** HRTEM of CdTe
- Fig. S2** Zeta potential measurements of CdTe
- Fig. S3** Uncorrected absorption spectra of 4.4 μM ZnTMPyP4 in the presence of low and high CdTe equivalents
- Fig. S4** Observation of the emergence of QD emission in the presence of Porphyrin.
Comparison of CdTe emission in presence and absence (expected) of ZnTMPyP4
- Fig. S5** Fluorescence spectra of 4.4 μM ZnTMPyP4 in presence of increasing CdTe (0-2.64 μM). $\lambda_{\text{exc}} = 400 \text{ nm}$.
- Fig. S6** Absorption spectra of 2.5 μM CdTe in presence of ZnTMPyP4
- Fig. S7** SAXS measurements of CdTe and CdTe:ZnTMPyP (1:1) in water
- Fig. S8** Behaviour of CdTe bleach at different pump energies
- Fig. S9** Bleach recovery at 510 nm for 5 μM CdTe in Millipore water. Excitation at 400 nm, 25 nJ.
- Fig. S10** Kinetic fits to CdTe recovery and ZnTMPyP4 grow-in. [CdTe] = 5 μM , [ZnTMPyP4] = 2.5 μM , (2:1 CdTe:ZnTMPyP4). E = 10 nJ.
- Fig. S11** Ps-TA spectra of 25 μM ZnTMPyP4 in presence of 50 μM CdTe and kinetic fits to bleach recoveries. (E = 100 nJ)
- Fig. S12** Monoexponential fit to ZnTMPyP4 bleach grow-in. [ZnTMPyP4] = 25 μM , [CdTe] = 50 μM (2:1 CdTe:ZnTMPyP4). E = 100 nJ. Biexponential fit to CdTe bleach recovery. [ZnTMPyP4] = 25 μM , [CdTe] = 50 μM . E = 100 nJ
- Fig. S13** Ps-TA spectra of 50 μM CdTe and 12.5 μM ZnTMPyP4 (4:1 CdTe:ZnTMPyP4) and kinetic fits to bleach recoveries. E = 100 nJ
- Fig. S14** Ps-TA spectra of 5 μM CdTe and 1.25 μM ZnTMPyP4 (4:1 CdTe:ZnTMPyP4) and kinetic fits to bleach recoveries. E = 5 nJ
- Note S1** SAXS data treatment
- Note S2** Estimates of thermodynamic driving force for photo-induced electron transfer
- References**

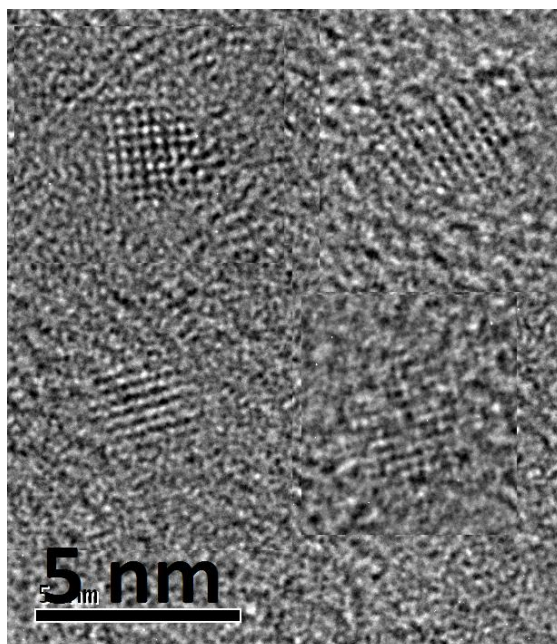


Fig. S1: HRTEM images of CdTeQDs

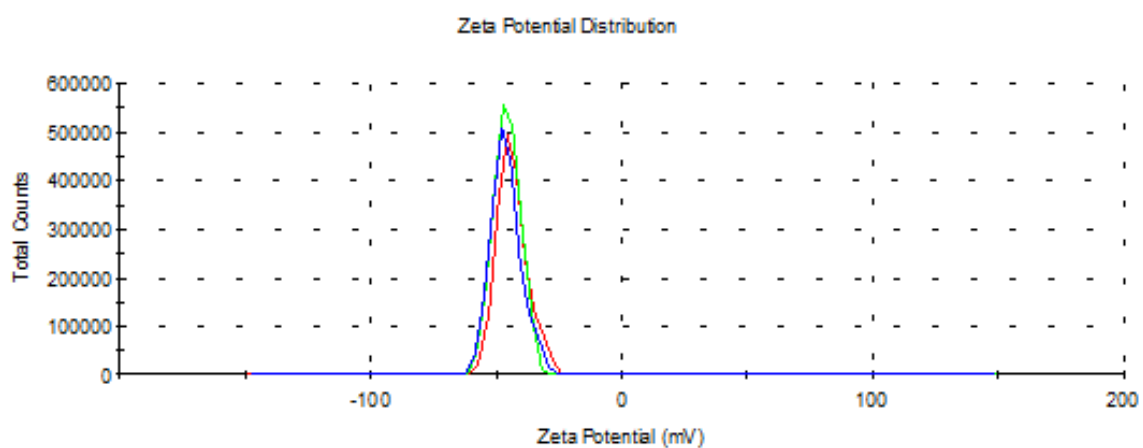


Fig. S2: Zeta potential measurements of CdTe QDs in aqueous solution at pH 7, ionic strength to a value of 0.010 M using NaCl.

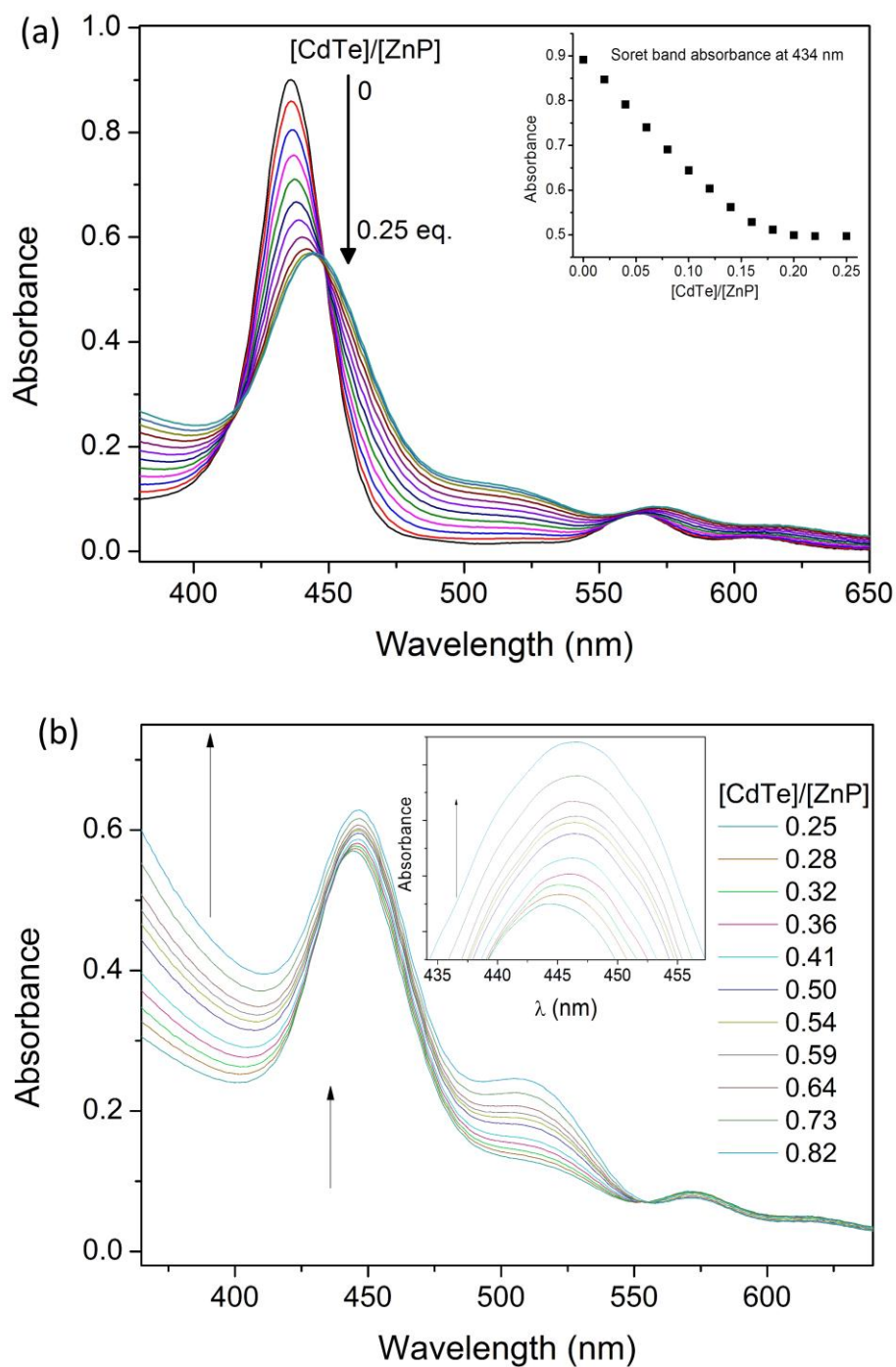


Fig. S3: Uncorrected absorption spectra of 4.4 μM ZnTMPyP4 in the presence of CdTe at (a) 0-0.25 equivalents and (b) larger equivalents ($[\text{CdTe}]/[\text{ZnTMPyP4}] > 0.25$). Inset: shift in porphyrin Soret band.

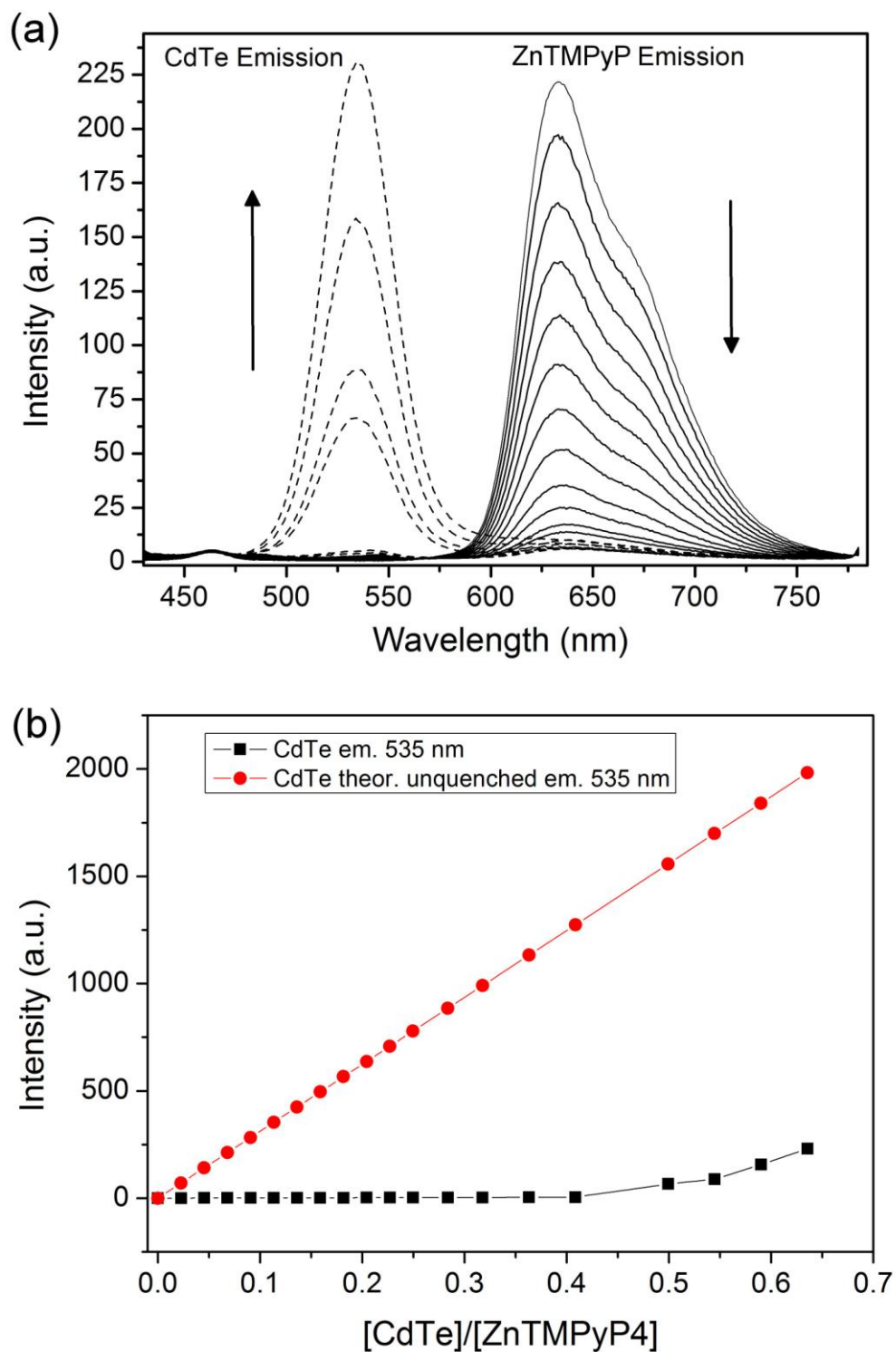


Fig. S4: (a) Fluorescence spectra of 4.4 μM ZnTMPyP4 in presence of increasing CdTe (0-2.64 μM) highlighting the re-emergence of QD emission after the addition of 0.4 equivalents of QD. (b) Comparison of observed CdTe (0-2.64 μM) emission at 535 nm in the presence of 4.4 μM ZnTMPyP4 (■) with that expected in the absence of ZnTMPyP4 (●)

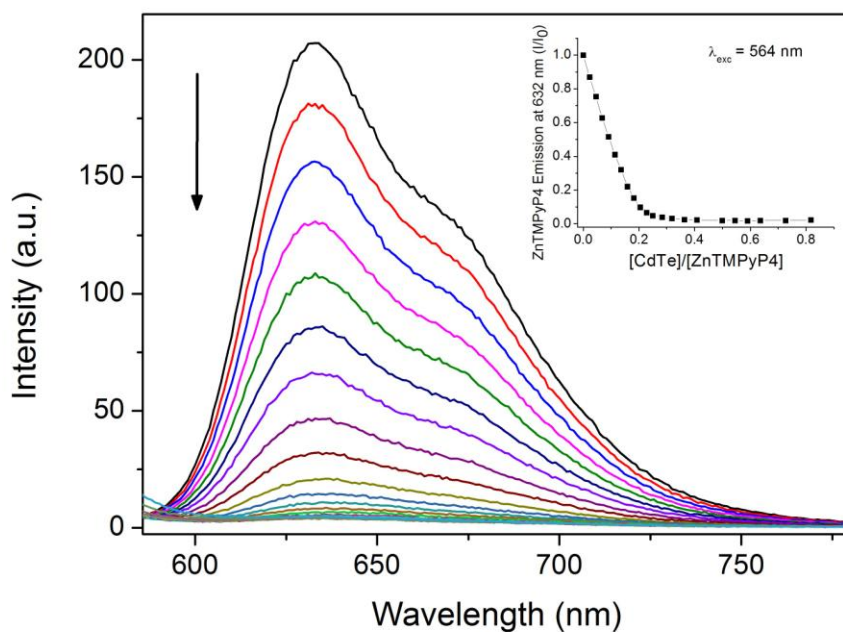


Fig. S5: Fluorescence spectra of 4.4 μM ZnTMPyP4 in presence of increasing CdTe (0-2.64 μM). λ_{exc} = 564 nm.

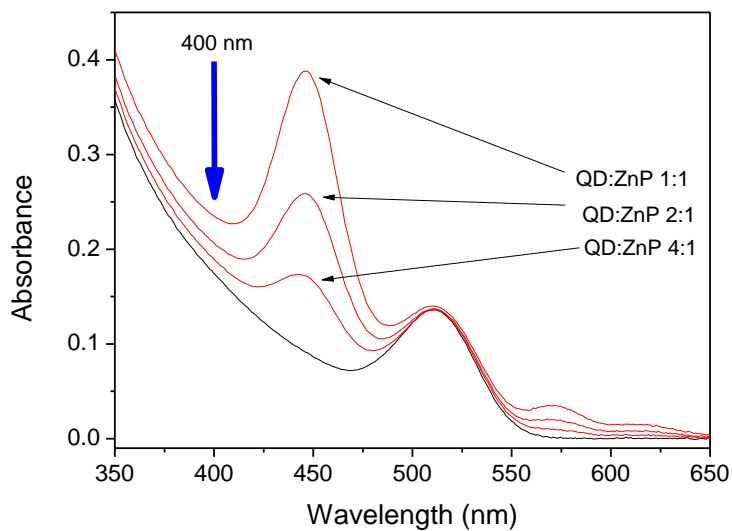


Fig. S6: Absorption spectra of 2.5 μM CdTe in presence of ZnTMPyP4 highlighting the overlap in absorbance and the absorbance at the laser excitation wavelength of 400 nm

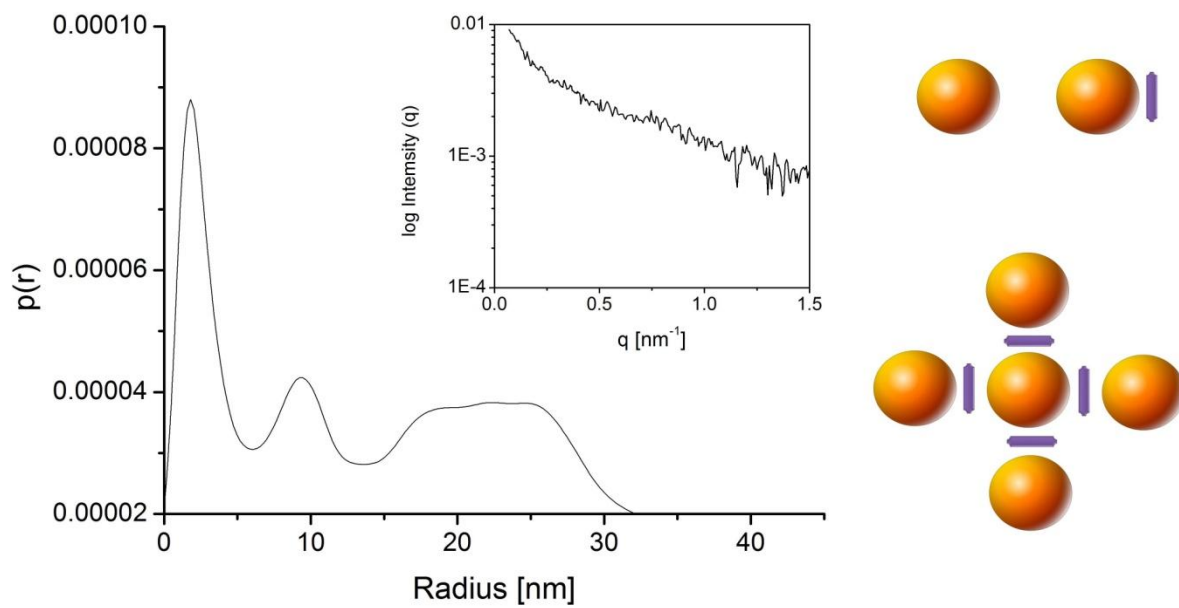


Fig. S7: SAXS measurements of CdTe:ZnTMPyP (1:1) in water. [CdTe] = 3.5 μ M. Inset SAXS experimental scattering curves.

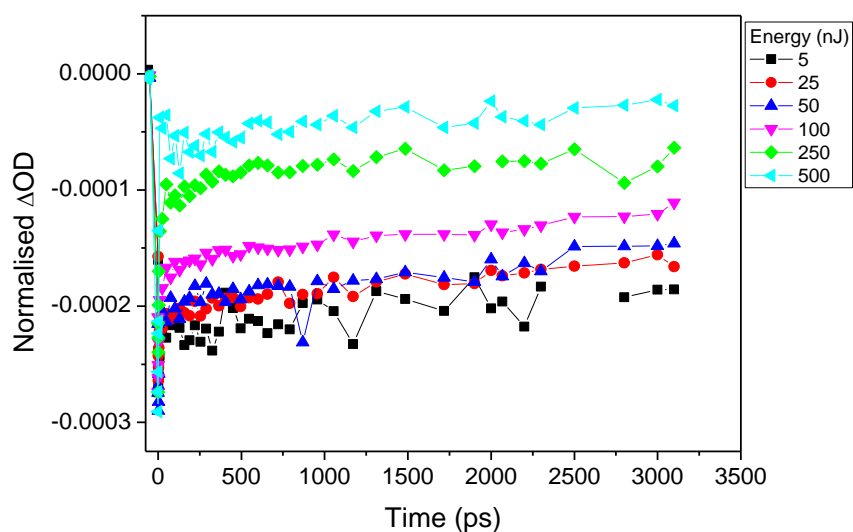


Fig. S8: Behaviour of exciton bleach of 5 μM CdTe as a function of laser pump energy. (Note multiphoton events typically result in faster recovery kinetics. However, the kinetics for the recovery of the bleached band-edge were found to be invariant between 5-50 nJ)

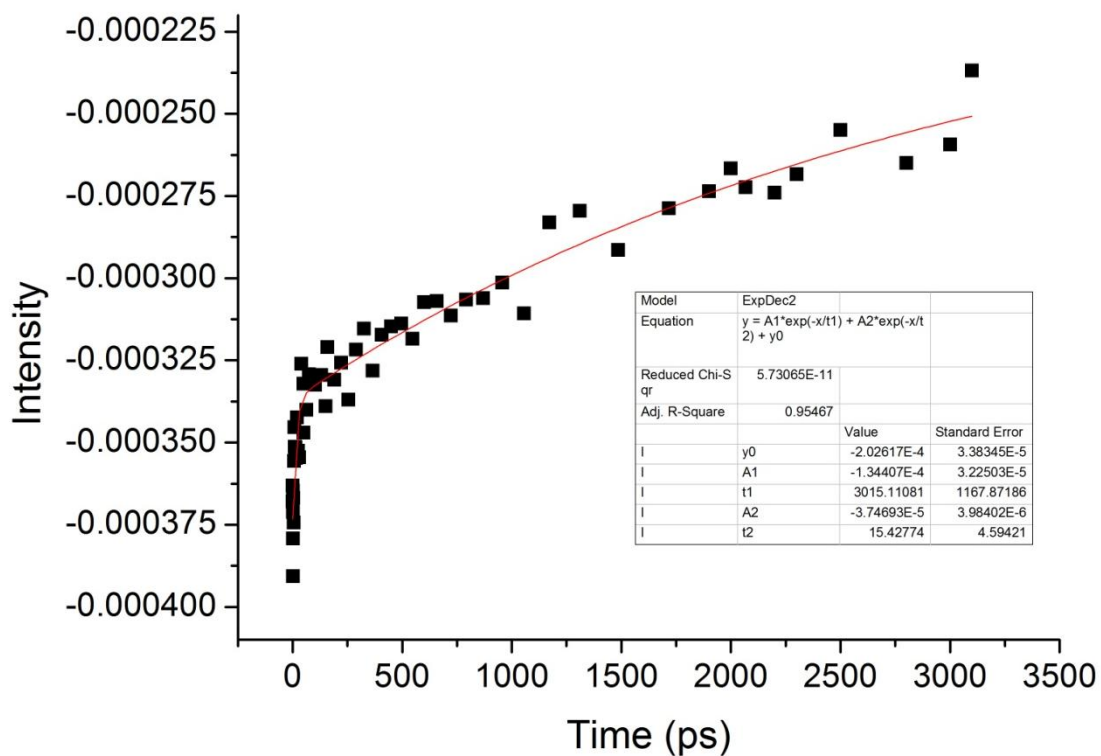


Fig. S9: Bleach recovery at 510 nm for 5 μM CdTe in Millipore water. Excitation at 400 nm, 25 nJ.

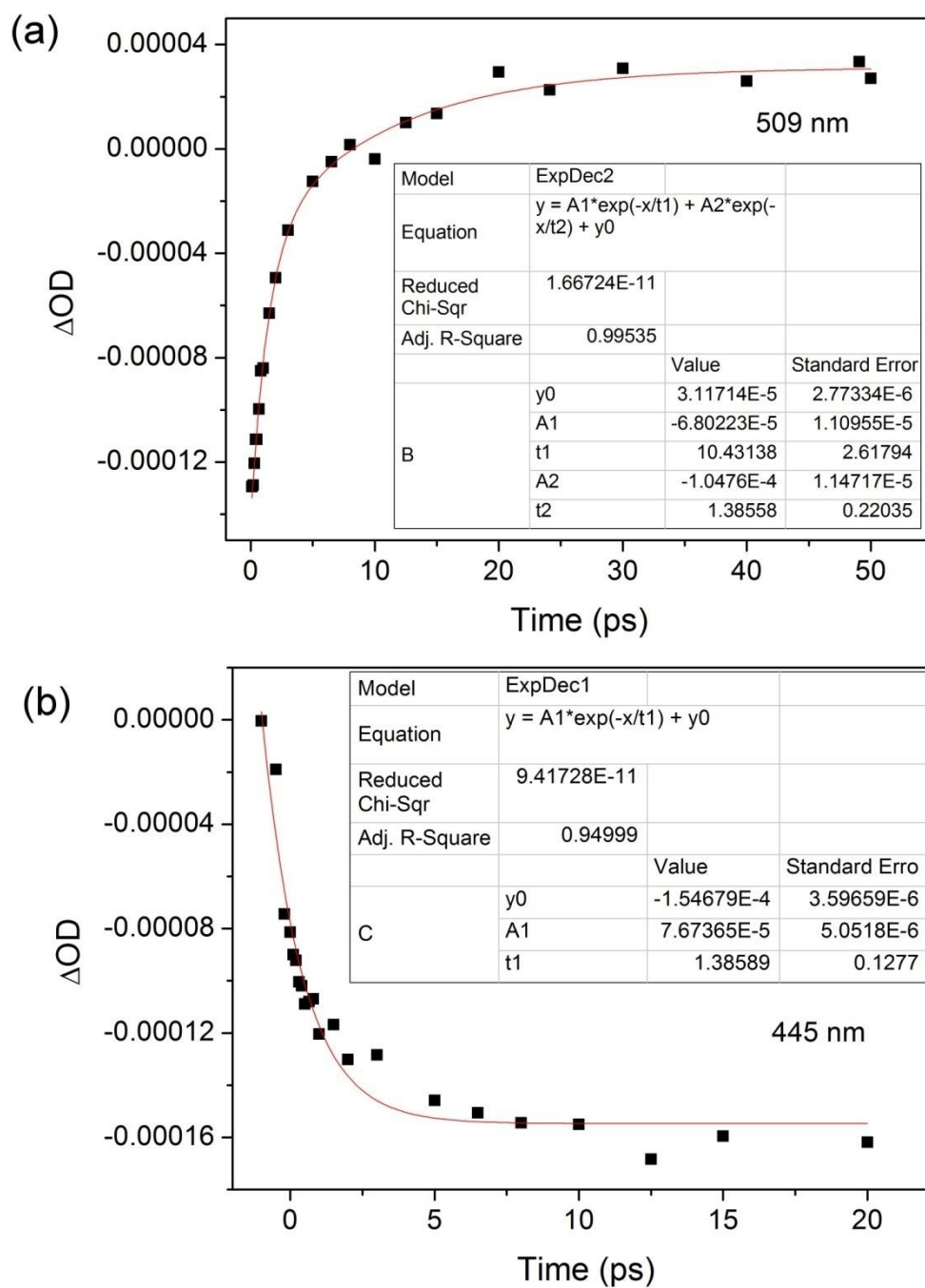


Fig. S10: (a) Biexponential fit to CdTe recovery at 510 nm (b) monoexponential fit to ZnTMPyP4 bleach grow-in at 445 nm. [CdTe] = 5 μ M, [ZnTMPyP4] = 2.5 μ M, (2:1 CdTe:ZnTMPyP4). Excitation at 400 nm, 10 nJ.

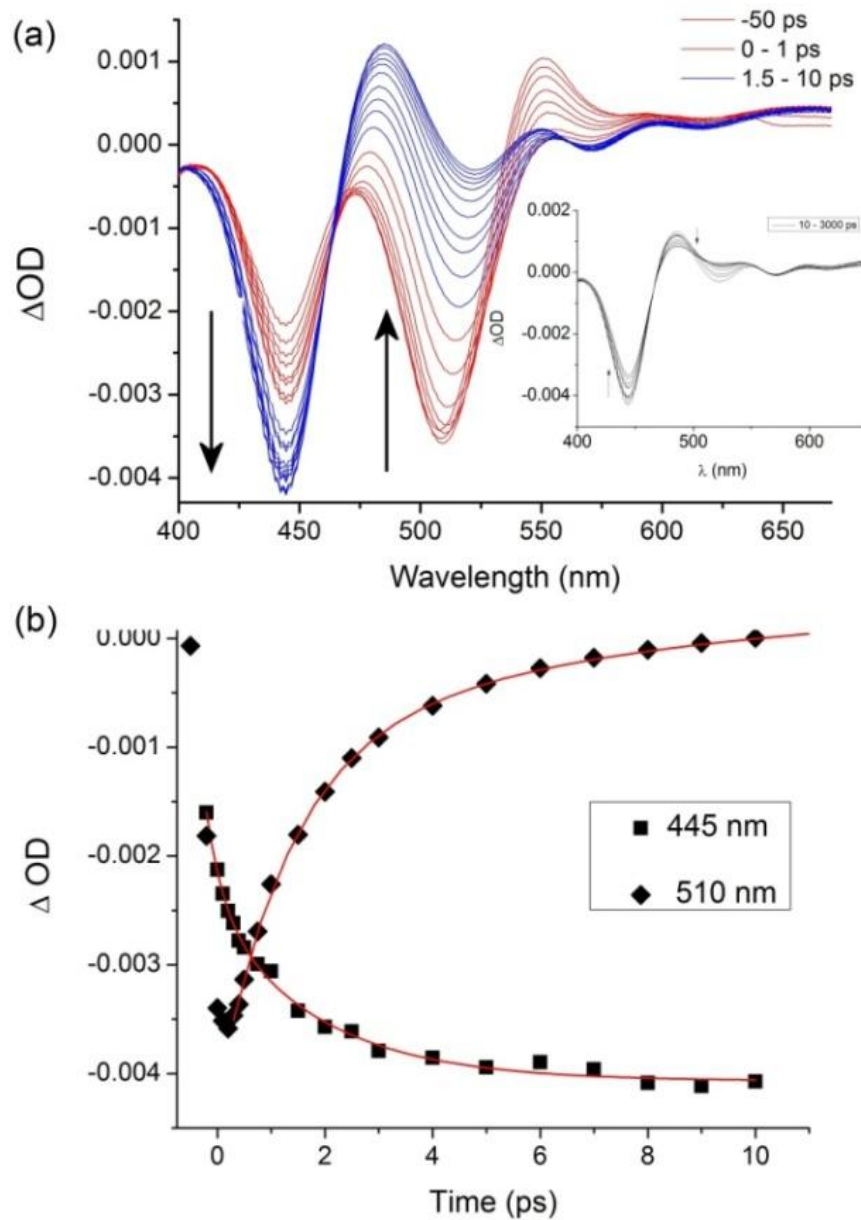


Fig. 11 (a) Ps-TA spectra of 25 μM ZnTMPyP in presence of 50 μM CdTe (b) Recovery of CdTe bleach at 510 nm and grow-in of ZnTMPyP4 bleach at 445 nm Excitation at 400nm, 100 nJ

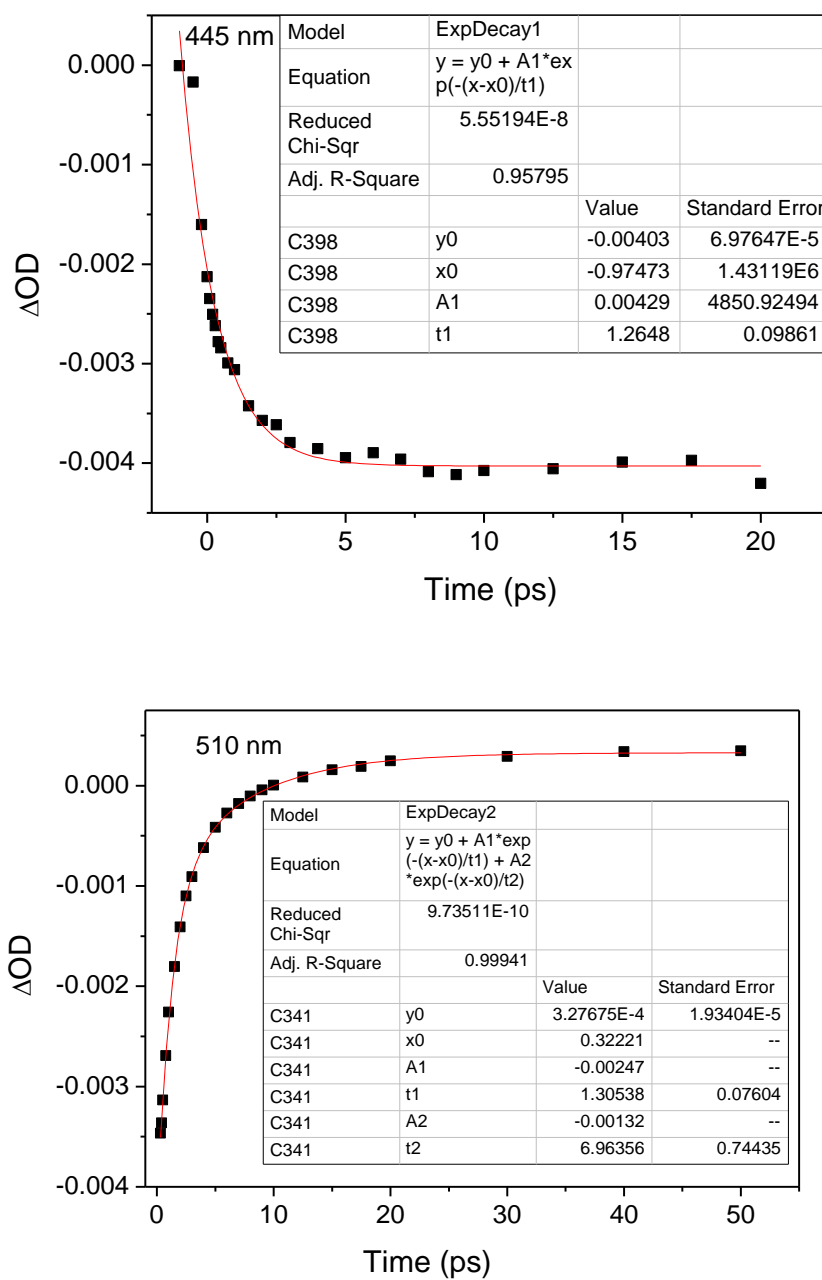


Fig S12: (upper) Grow-in of ZnTMPyP4 bleach at 445 nm fitted to monoexponential function. [ZnTMPyP4] = 25 μ M, [CdTe] = 50 μ M (2:1 CdTe:ZnTMPyP4). Excitation at 400 nm, 100 nJ. (lower) Recovery of CdTe bleach at 510 nm fitted to a biexponential function. [ZnTMPyP4] = 25 μ M, [CdTe] = 50 μ M. Excitation at 400 nm, 100 nm

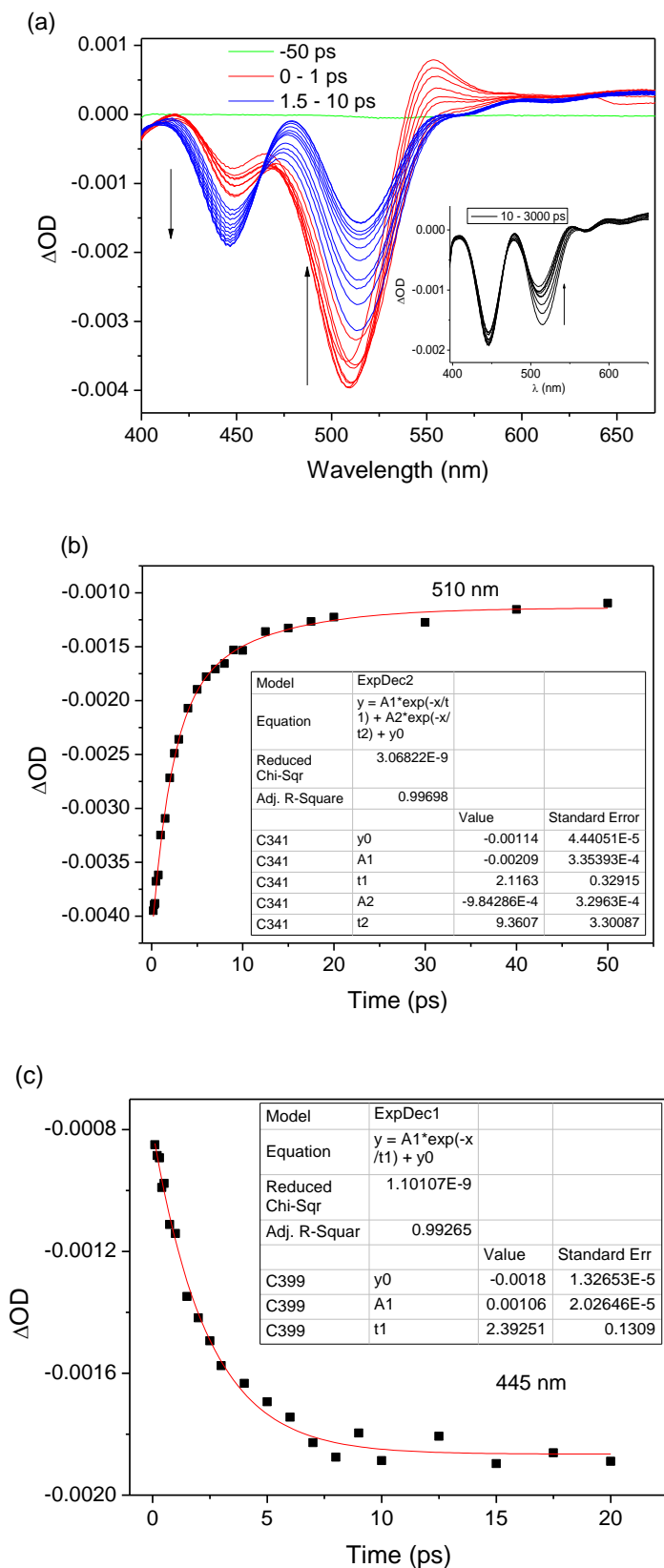


Fig. S13: (a) ps-TA spectra for 50 μM CdTe and 12.5 μM ZnTMPyP4 (4:1 CdTe:ZnTMPyP4) (b) biexponential fit to CdTe bleach recovery at 510 nm (c) monoexponential fit to ZnTMPyP4 bleach grow-in at 445 nm. Excitation = 400 nm, 100 nJ

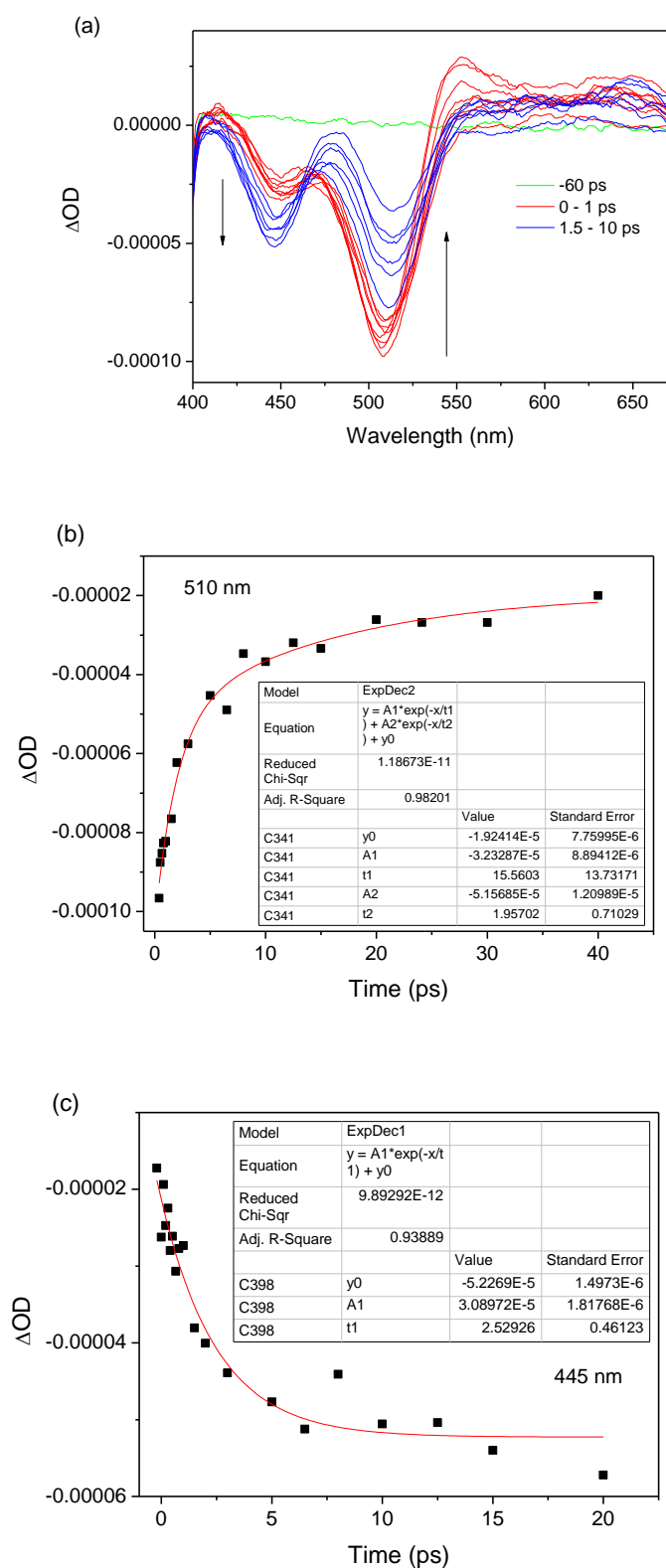


Fig. S14: (a) ps-TA spectra for 5 μM CdTe and 1.25 μM ZnTMPyP4 (4:1 CdTe:ZnTMPyP4) (b) biexponential fit to CdTe bleach recovery at 510 nm (c) monoexponential fit to ZnTMPyP4 bleach grow-in at 445 nm. Excitation = 400 nm, 5 nJ.

Note S1

The IFT technique transforms the scattering curve into real space resulting in a pair distance distribution function (PDDF) including corrections for instrumental broadening. This transformation is model free and there are no constraints except the maximum dimension of the particle. The model for the structure factor is assumed for use in the GIFT technique.¹ There are several ways to calculate the structure factors of charged particles that consist with using different closure relations of the Ornstein–Zernike equation.² The effect of the structure factor on scattering curves depends on the preferred ordering of the particles. In the case of monodisperse, homogeneous, globular particles, the total scattering intensity can be expressed by $I(q) = NS(q)P(q)$ where N is the number of particles. Here we used the rescaled mean spherical approximation RMSA model (charged spheres model)^{3, 4} Using this model requires tight restriction of one parameters and this was chosen as the radius of a single QD. This restriction resulted in a stable form factor and an accurate structure factor which resulted in a good fit and from our data appears to be an accurate model for the Porphyrin:QD complexes. Taken together the PDDF and the RMSA allow the best consideration of the structural nature of the colloidal assemblies. This is a known and accepted methodology for the treatment of scattering data and has been employed in the past for a number of related systems.⁵⁻⁷

Note S2

The Gibbs free energies for the possible excited-state redox processes were estimated from a form of the Rehm-Weller equation

$$\Delta G^0 = e\{E^0(D^+/D) - E^0(A/A^-)\} - hv$$

where E^0 are standard potentials, D is the electron donor, A the electron acceptor and hv is the excited state energy of the excited molecule.

	Oxidation (vs. SHE)	Reduction (vs. SHE)	Excited state energy
ZnTMPyP4	+1.18 V ⁸	-0.85 V ⁸	1.96 eV (632 nm)
CdTe	+0.95 V	-1.00 V	2.37 eV (535 nm)

Values for CdTe are estimates from linear extrapolation of previously published data⁹ to smaller particle sizes, and adjustment from Ag/AgCl reference to standard hydrogen electrode (+0.2V).

References

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