Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Quantum Confinement-Tunable Intersystem Crossing and Triplet State Lifetime of Cationic Porphyrin-CdTe Quantum Dot Nano-assemblies

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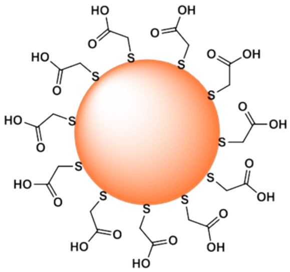
Experimental Section

Sample preparation. TGA-capped CdTe QDs (Structure given in Scheme S1) with diameters ranging from 1.2 to 6.3 nm, 5,10,15,20-Tetrakis(1-methyl-4-pyridinio)porphyrin tetra(*p*-toluenesulfonate) (TMPyP), and 5,10,15,20-tetra(4-pyridyl)-porphyrin (TPyP) were purchased from Sigma and were used as received. These reagents were dissolved in deionized water. TPyP measurements were carried out in a mixture of methanol and deionized water for solubility issues. The porphyrin-CdTe QDs nanocomposites were prepared through successive additions of 0–24.05 μM CdTe into solutions of the porphyrin in water. The resulting mixtures were used for steady state characterizations and laser flash photolysis measurements.



Scheme S1. Structure of TGA-capped CdTe QDs

Steady-State Measurements. Steady state absorption, fluorescence, and Raman spectroscopies were used to characterize the optical properties and the formation of charge-transfer complexes in the porphyrin–CdTe QDs nanocomposites. A Cary5000 UV-visible spectrometer (Agilent Technologies) was used for absorption measurements from 300 to 800 nm. A Fluoromax-4 spectrofluorometer (Horiba Scientific; slit width of 5 nm and scan rate of 500 nm/min) was used to record fluorescence spectra from 600 to 850 nm after excitation at 580 nm. A LabRam Aramis Raman spectrometer (Horiba Jobin Yvon) equipped with a 477-nm Argon ion laser excitation source was employed to acquire vibrational Raman spectra. The Raman signal was acquired using an integration time of 60 s. Raman bands were observed in the fingerprint region from 300 to 1700 cm^{-1} at a spectral resolution of 1.1 cm^{-1}.

Transient Measurements: Femtosecond transient absorption was collected using an ultrafast Systems Helios UV-NIR femtosecond transient absorption spectroscopy system. Nanosecond transient absorption recorded using EOS-sub-nanosecond transient absorption spectrometer from Ultrafast systems. Samples were measured in aqueous solutions at room temperature. The probe beam white-light-continuum probe pulse generated in a 2-mm-thick Calcium Floride (CaF_2) plate in an Ultrafast System LLC spectrometer using a few μJ pulse energy of the fundamental output of a Ti:Sapphire femtosecond regenerative amplifier operating at 800 nm with 35 fs pulses and a repetition rate of 1 kHz. For both Helios and EOS a two-channel probe (probe-reference) method is used. In this method the probe beam is split into two before passing through the sample. While one arm travels through the sample, the other is sent directly to the reference spectrometer that monitors the fluctuations in the probe beam intensity. The main advantage of this technique is that it allows the user to achieve the specified signal-to-noise ratio with a lower number of averaged laser pulses. The pump pulses at 650 nm were created from spectrally tunable (240-2600 nm) femtosecond pulses generated in the Optical Parametric Amplifier (Newport Spectra-Physics). The pump and probe beams were focused on the sample solution, and the transmitted probe light from the samples was collected and focused on the broadband UV-Vis detector to record the time-resolved transient absorption spectra.

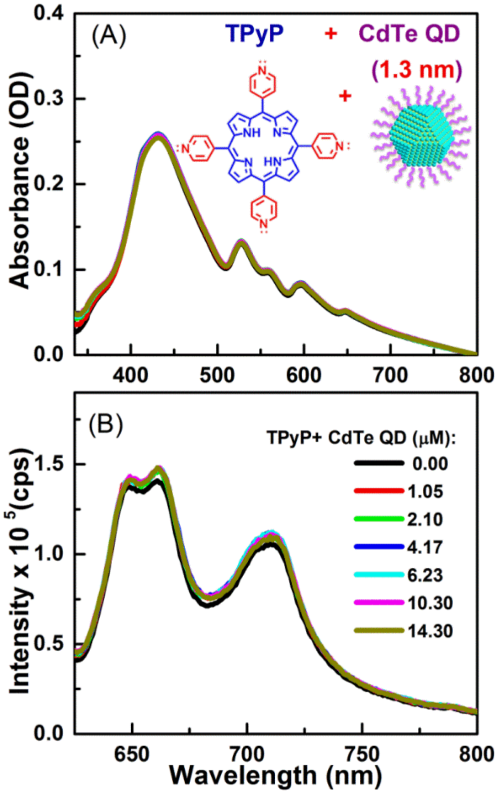


Figure S1. *(A) Absorption and (B) emission after excitation at 580 nm of TPyP with successive additions of CdTe QD (1.3 nm).*

Raman spectroscopy. The Raman shifts in the 300–500 cm^{-1} region provide clear evidence for strong interactions between TMPyP and CdTe QDs, as indicated by the disappearance of the band at 332 cm^{-1} of free-base TMPyP and the appearance of a new vibrational band at 374 cm^{-1} of TMPyP in the presence of the CdTe QDs. The band at 332 cm^{-1} has been assigned to the in-plane bending mode of the macrocycle moiety of free-base TMPyP,[1, 2] and the band at 403 cm^{-1} has been attributed to the in-plane bending modes of the macrocycle and pyridinium groups of TMPyP bound to metal atoms.[1] Therefore, the Raman shifts shown in Figure SI 2 indicate that TMPyP binds to the CdTe QDs through strong electrostatic interactions between the porphyrin macrocycle and the surface of the QDs, similar to other metalation-like nanocomposites or the SAT configuration of porphyrin–nanoparticles.[2-7]

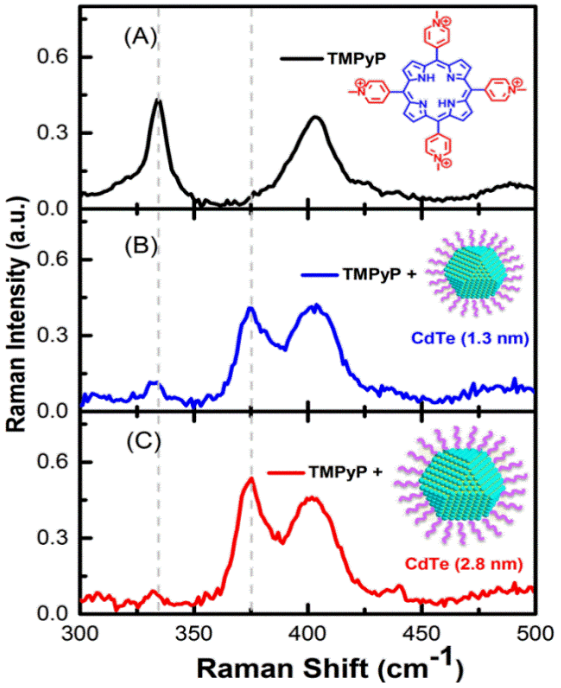


Figure S2. *Raman spectra of TMPyP (A) and of TMPyP in the presence of CdTe QDs (1.3 nm) (B), and CdTe QDs (2.8 nm) (C).*

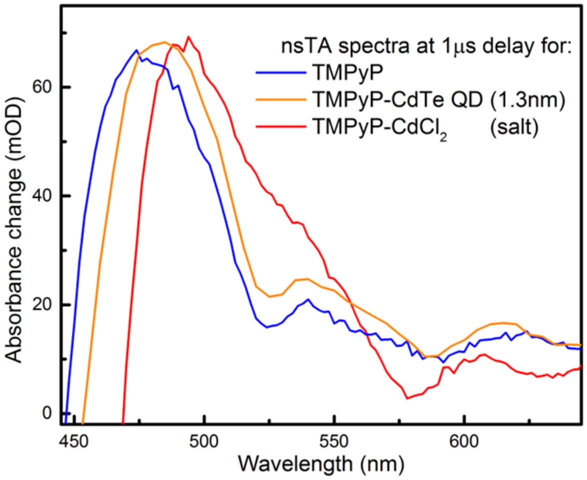


Figure S3. *Nanosecond transient absorption spectra of TMPyP (blue), TMPyP-CdTe (1.3 nm) QD (red), and TMPyP after interaction with CdCl$_2$ (orange).*

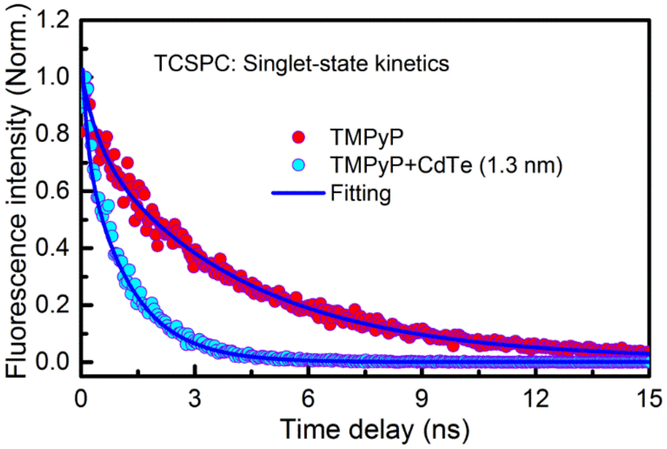


Figure S4. *Time-correlated single photon counting decay of TMPyP and TMPyP in the presence of CdTe QDs (1.3 nm) collected after excitation at 450 nm.*

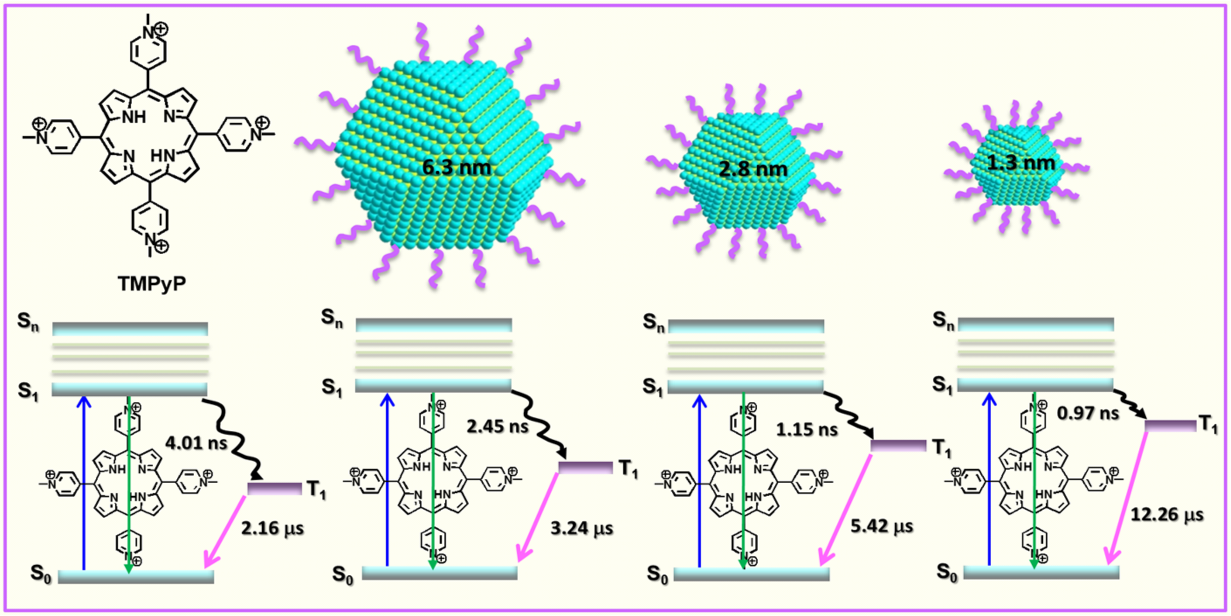


Figure S5. Schematic illustration comparing free TMPyP and its assemblies with the different CdTe QDs used in terms of energy levels (as deduced from spectral changes), fluorescence lifetime extracted from (TCSPC measurements), and triplet state lifetime (from nsTA).

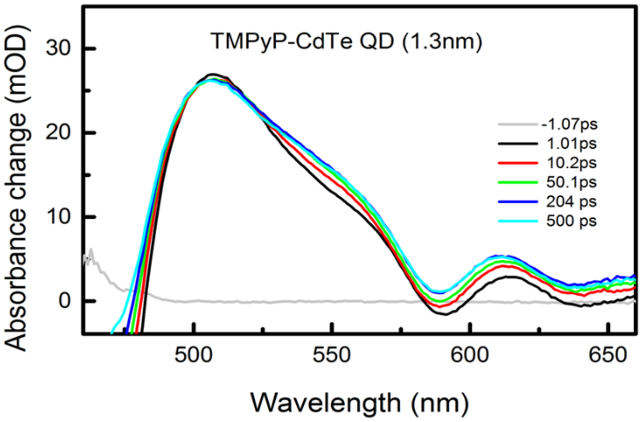


Figure S6. *Femtosecond transient absorption spectra of TMPyP-CdTe QDs (1.3 nm) nanoassembly collected after excitation at 460 nm.*

References

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