SUPPLEMENTARY INFORMATION FOR:

Mn(II)-doped CdS/ZnS core/shell quantum dot film photocatalyzes reductive organic transformations with a boost in efficiency from enhanced Auger processes

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EXPERIMENTAL

Materials

Cadmium oxide (CdO), oleic acid, octadecene technical grade (ODE), sulfur (S), oleylamine, manganese (II) acetate tetrahydrate ($Mn(OAc)_2 \cdot 4H_2O$), heptanediamine (HDA), 1,2-dibromo-1,2-diphenylethane (DDE), anhydrous methanol, heptyl viologen ($HV^{2+)}$, deuterated-dimethyl sulfoxide (d-DMSO), 1,1'-dimethyl-4-4'-bipyridinium ditriflate (MV^{2+}), 1,1'-diheptyl-4-4'-bipyridinium dibromide (HV^{2+}), mercaptopropyltrimethoxysilane (MPTMS) and ammonium formate, and nitrobenzene were obtained from Sigma Aldrich.

Synthesis of Manganese-doped Cadmium Sulfide Quantum Dots

In a typical synthesis of Mn:CdS QDs, three flasks separately containing 0.75 mmol of CdO in 7.9 g of ODE, 0.25 mmol of sulfur in 3.3 g of ODE, and 0.04 mmol of manganese (II) acetate tetrahydrate in 2.44 g of oleylamine were degassed for 30 minutes under nitrogen at 130 °C. The CdO solution was heated to 285°C, followed by the injection of the Mn oleylamine solution.[1–4] The temperature of the solution was quickly brought back up to 285 °C and the sulfur solution was rapidly injected to start the nucleation of the QDs. The reaction was kept at 265 °C for 3 minutes to allow for the growth of the particles. Then, the solution was cooled in a water bath to room temperature. The synthesis of undoped CdS QD was carried out similarly without Mn precursor in the oleylamine. The orange photoluminescence was observed for Mn:CdS and blue photoluminescence for undoped CdS QDs. The particles were washed via flocculation with ethanol and redispersing in toluene.

Growth of ZnS Shell via Successive Ionic Layer Adsorption and Reaction (SILAR)

Both doped and undoped quantum dots were passivated with a ZnS shell using previously established methods[5]. QDs were re-suspended in a 3:1 ODE/oleylamine mixture and degassed for 30 min at 130 °C. A 0.4 M zinc oleate solution was prepared by dissolving zinc oleate in octadecene at 200 °C. A sulfur precursor solution was prepared by dissolving sulfur in octadecene at 130 °C. The temperature of the QD solution was raised to 265-270 °C followed by the slow injection of aliquots of zinc oleate and sulfur solutions sequentially (~1 mL/minute) with 10 min reaction time between injections. The zinc oleate and sulfur solutions were injected while warm to prevent precipitation and each aliquot corresponded to the amount needed to deposit a monolayer of atoms on the existing CdS. For example, a sample containing 2.89×10^{16} CdS QDs with 2.25 nm radius required 3.15 mmol of Zn oleate and S for each monolayer growth. Each monolayer of ZnS is theoretically 0.31 nm in thickness (i.e. $\frac{\sqrt[3]{a}}{3}$ where a = 5.41 Å, the unit cell length of zinc blende[6]). The procedure was repeated to install 2 monolayers of ZnS plus a Zn terminal layer (i.e. collectively referred to as 2.5 monolayers of ZnS shell). The passivated QDs were washed and redispersed in toluene.

QD Film Preparation

The glass vessels or cut microscope slides were cleaned with piranha solution (3:1 H_2SO_4/H_2O_2) for 20 minutes, rinsed with copious amounts of water, followed by silanization with 1 vol% mercaptopropyltrimethoxysilane (MPTMS) in anhydrous ethanol for 2 h. The substrates were rinsed and annealed for one hour under nitrogen at 80 °C. ***Caution!*** *Piranha solution must be prepared and handled with extreme care. It is a strong oxidizing agent that reacts aggressively with organic matter.*

For in situ spectrophotometric experiments (i.e. photoreduction of MV), the QD film was deposited on a MPTMS-treated glass slide (0.5 x 1 cm) via the evaporation-induced self-assembly process. The glass slide was suspended vertically in 4-mL vial containing 2 mL of ~300 µM QD in toluene and placed in the oven at 60 °C for 24 h. Upon evaporating the solvent, the QDs uniformly deposited on the glass surface and one side was wiped clean. The sample was then transferred to a glove box to crosslink the QDs with HDA, as previously established.[4] The films were immersed in 0.5 vol% HDA in ethanol at 80 °C for 2 min, rinsed with ethanol and annealed under nitrogen for 1 hour.[4] A similar procedure was carried out for glass vials for DDE and nitrobenzene reactions.

The amount of deposited QD was determined from the extinction coefficient and absorbance of a toluene solution containing redissolved QDs from a non-crosslinked film. Similar procedure was used for determining moles of QDs in the coated vials.

Photoreduction of Methyl Viologen

A volume of 3 mL 500 µM methyl viologen in water was transferred to a cuvette with a QD-functionalized glass strip (0.5 x 1 cm) inside. The system was thoroughly degassed and sealed. The cuvette was irradiated with blue light (440 nm, Lumencor SpectraX light engine) and in-situ UV-visible absorption spectra (Perkin Elmer Lambda 950) were acquired at 3-min interval using a custom setup. The reduction of methyl viologen was confirmed by monitoring the development of peaks at 396 nm and 605 nm, and the emergence of blue color in the solution. Experiments with 10% v/v methanol as a hole scavenger were conducted similarly. Control experiments in the absence of light and in the absence of QDs were also performed with the same setup.

Photoluminescence Experiments

Photoluminescence (PL) of QD deposited on the glass strips was measured for both doped and undoped samples using a custom-made setup comprising a light source (Lumencor SpectraX) and a spectrometer (Ocean Optics 2000+). PL lifetime measurements were obtained with a Cary Eclipse fluorescence spectrometer with a pulsed Xe lamp.

Dehalogenation Reaction

To a 4-mL vial coated with QDs, an aqueous solution of 2 mL heptyl viologen (500 µM) containing 10 vol% methanol was added. Then 1 mL of 4 mM 1,2-dibromo-1,2-diphenylethane (DDE) in ethyl acetate was added as the organic phase. The vial was sealed and placed under 395-nm LED (SZ-05-U6, Luxeonstar) irradiation for 24 h. The stirring was kept at 250 rpm to form a small vortex between the two layers. After 24 h, the organic layer was separated. Subsequently, the aqueous layer was extracted three times with 0.5 mL portions of ethyl acetate. The ethyl acetate solution was then air dried. Control experiments were carried out in the absence of QDs (i.e., uncoated vials), and in the absence of heptyl viologen or methanol.

The single-phase reaction, in the absence of heptyl viologen, was also performed. A QD-coated vial containing 3 mL of 4 mM DDE in ethyl acetate and methanol (10 vol%) was irradiated at 395 nm for 24h. UV-Vis absorbance of as-is solution was acquired using Perkin Elmer Lambda 950 spectrophotometer, and ^{1}H NMR of isolated sample in d-DMSO was measured using Bruker Avance (300 MHz). Percent conversion of reactants to products was determined by taking the peak area ratios of the doublets of products (7.61-7.59 ppm) to the sum of the products and reactants (7.70-7.68 ppm). All reactions of DDE were run inside the glove box.

Reduction of Nitrobenzene

The reduction of nitrobenzene was carried out in a similar fashion as that of the DDE. In a typical reaction, a QD-coated vial containing 3 mL of nitrobenzene (3.7 mM) and 100 mM ammonium formate in 2-propanol was sealed and placed under 395-nm irradiation for 30 min with stirring. UV absorption spectra of as-is solution were measured at various time intervals, and NMR spectra were collected in d-DMSO after the sample was dried and extracted with dichloromethane.

Physical characterizations

EPR measurement was carried out on a solution of Mn:CdS/ZnS QD dissolved in toluene using a Bruker ECS-EMX X-band EPR spectrometer equipped with an ER4119HS cavity. EPR data was collected at room temperature with the following acquisition settings: 9.367 GHz microwave frequency, 2.15 mW microwave power, 4G modulation amplitude, a 100 kHz modulation frequency, 5000 G sweep width, 0.01 ms time constant, 50 dB receiver gain, and 300s total sweep time. The spectrum was corrected using DPPH (1,1-diphenyl-2-picrylhydrazyl) as a standard.

TEM images were acquired using Hitachi HT7700 with LaB_6 thermionic filament operating at an emission current of 10 mA and accelerating voltage of 100 kV.

X-ray photoelectron spectra of films on indium tin oxide substrates were measured by Thermo Fisher Scientific K-Alpha XPS spectrometer (East Grinstead, UK) with a spot area of 400 μm. A monochromatic Al K_α X-ray source was used to obtain an initial survey spectrum (pass energy (PE) – 200 eV) followed by low resolution spectra of the spectral regions of interest (PE – 150 eV) from which composition was obtained, and higher resolution spectra (PE – 25

eV). Charge compensation was applied using the system's combined e^-/Ar^+ flood gun with the spectra shifted to place the main C-C peak at 285.0 eV. The peak fitting was performed on the high-resolution spectra by the supplied software (Avantage v. 5.9925), using the Smart Background (a modified Shirley background) and a mixed Gaussian-Lorentzian peak shape.

Powder XRD data was obtained with a AXRD Benchtop diffractometer (PROTO) with a Cu K_α source. The spectrum was fitted with wurtzite and zinc blende by utilising the Rietveld refinement[7,8] method and GSAS II software.[9]

The concentration of Mn^{2+} dopant in CdS/ZnS core/shell QDs was determined via ICP-OES with a Thermo Scientific[TM] iCAP PRO Series utilizing the axial detector (Analest, University of Toronto). QDs were digested in concentrated nitric acid at 60 °C over 48 hours. The solution was then diluted with MQ water to 10 mL in a volumetric flask.

CALCULATIONS

I. Internal Quantum Efficiency of Methyl Viologen Reduction

Absorbance of film = 0.2
Film area = 1cm x 0.5 cm = 0.5 cm^2
Irradiation density at 440 nm: 85 mW/cm^2

Photons absorbed by 0.5 cm^2 film:
$$0.085\frac{W}{cm^2} \times (1 - 10^{-0.2}) \times 0.50cm^2 = 0.0157\, W$$

$$\frac{0.0157\,J/s}{4.51E^{-19}\,J/photon_{440nm}} = 3.48E^{16}\,photons/s$$

$$\frac{3.48E^{16}\frac{photons}{s}}{6.022\,E^{23}\frac{photons}{mol}} = 5.79E^{-8}\frac{mol}{s}\,of\,photons$$

Rate of MV$^{\bullet+}$ formation:
Initial MV^{2+} concentration and volume = 500 µM × 3 mL

$$0.00112\,s^{-1} \times 1.5E^{-6}mol = 1.7E^{-9}\frac{mol}{s}\,of\,MV$$

$$IQE = \frac{rate\,of\,product\,formation}{rate\,of\,absrobed\,photons} = \frac{1.7E^{-9}\,mol/s}{5.8E^{-8}\,mol/s} = 0.029\,or\,2.9\%$$

II. Number of photons irradiated, and excitons produced per QD at 85 mW/cm^2:

$$0.085\,W/cm^2 \times 0.50cm^2 = 0.042\,W$$

$$\frac{0.042\,J/s}{4.51E^{-19}\,J/photon_{440nm}} = 9.42E^{16}\,photons/s$$

$$rate\,of\,photons\,irradiated\,per\,QD = \frac{rate\,of\,photons}{number\,of\,QDs} = \frac{9.2E^{16}\frac{mol}{s}}{1.26E^{13}\frac{mol}{s}} = 7400\,photons/s$$

$$rate\,of\,exciton\,produced\,per\,QD = 7400\frac{photons}{s} \times 0.37 = 2700\frac{excitons}{s}$$

III. Internal Quantum Efficiency of Photoreduction of Nitrobenzene to Aniline

Absorbance of film at 395 nm was ca. 0.25 (based on deposition condition and film used in MV reaction). Absorbance by the film on the concave vial wall would be affected by scattering, and thus the IQE is an estimate.

Irradiation density at 395 nm: 150 mW/cm^2

Area of film: 1.87 cm^2

Photons absorbed in 15 min:

$$0.15 \frac{W}{cm^2} \times (1 - 10^{-0.25}) \times 1.87 cm^2 = 0.123 \, W$$

$$\frac{0.123 \, J/s}{5.03E^{-19} \, J/photon_{440nm}} \times 15 \, min \times 60s = 2.21E^{20} \, photons \, absorbed$$
$$= 3.67E^{-4} \, mol \, of \, absorbed \, photons$$

Assuming total conversion of nitrobenzene to aniline (based on ^{1}H NMR):

$$IQE = \frac{product \, formed \, in \, 15 \, min}{photons \, absorbed \, in \, 15 \, min} = \frac{1.11E^{-5} mol \, aniline}{3.67E^{-4} \, mol \, absorbed \, photons} = 3.0 \, \%$$

If sequential electron reduction with same efficiency:
$$IQE \, for \, each \, step = 0.030^{\frac{1}{6}} = 0.55 = 55\%$$
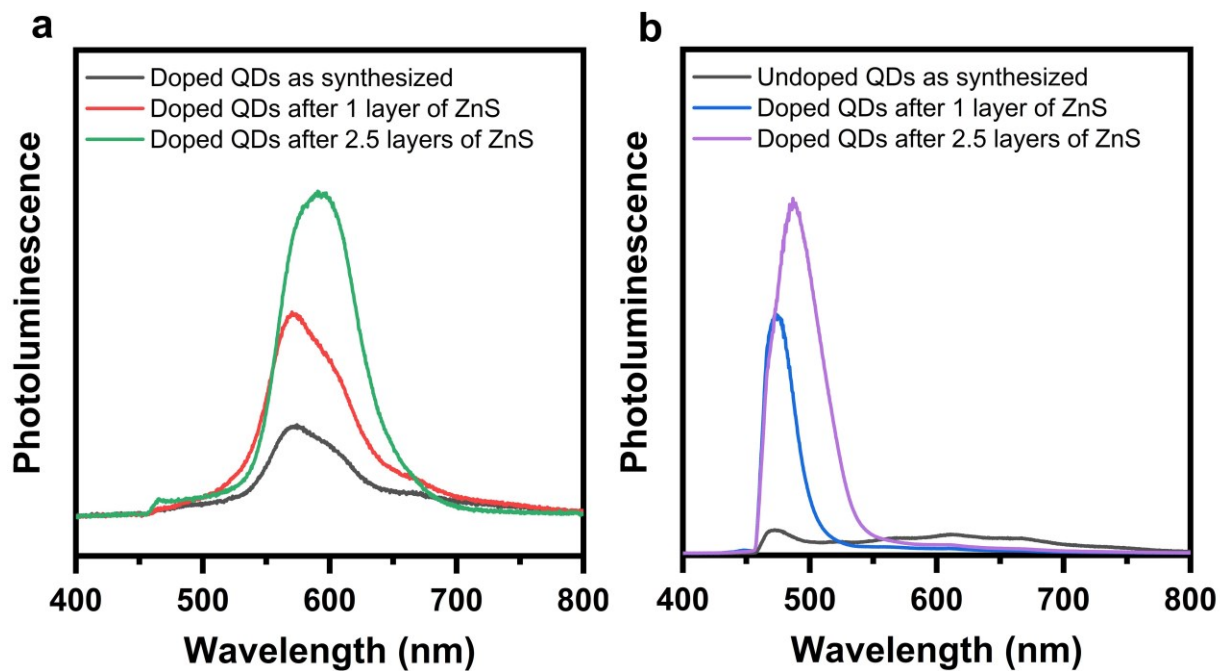
SUPPORTING FIGURES

Figure S1. Photoluminescence spectra of during the passivation of Mn^{2+} doped CdS QDs (A) and undoped CdS QDs (B) with ZnS. Increasing number of layers of ZnS increases PL. Spectra collected under 440 nm excitation and with a 460-nm long pass filter.
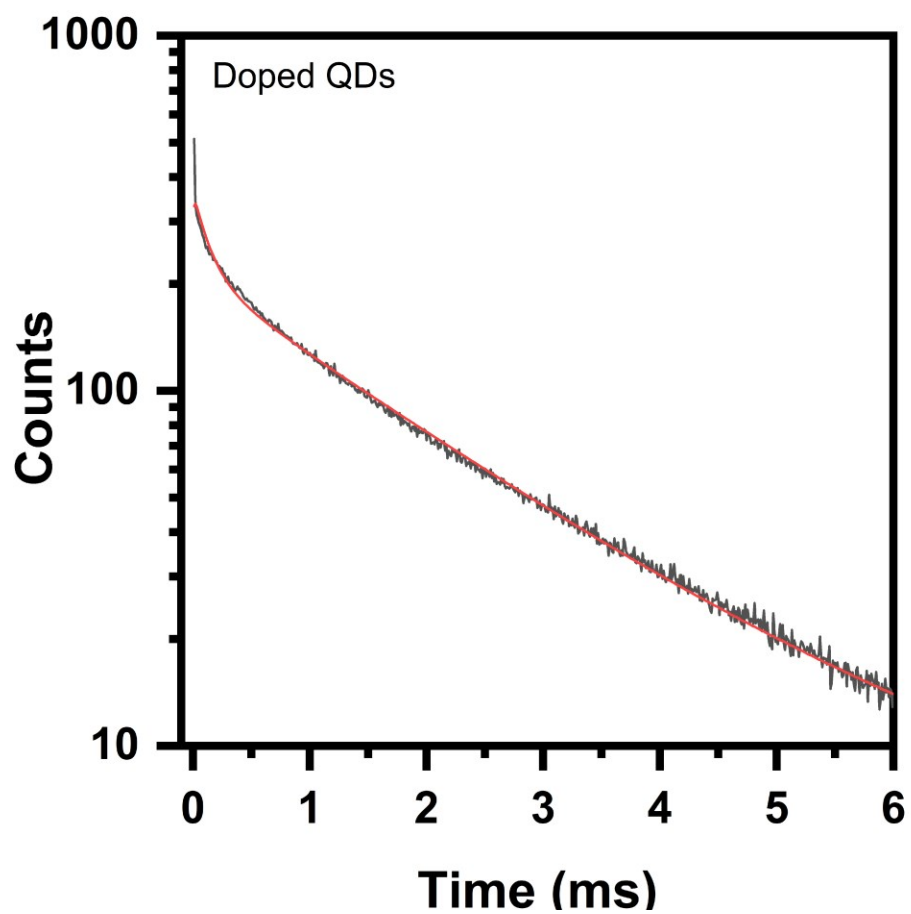
Figure S2. $^4T_1 \rightarrow {}^6A_1$ transition of the Mn^{2+} monitored at 580 nm showing the long-lived PL (black) as a double exponential fit (red) with components $\tau_1 = 0.141$ ms , and $\tau_2 = 1.91$ ms.
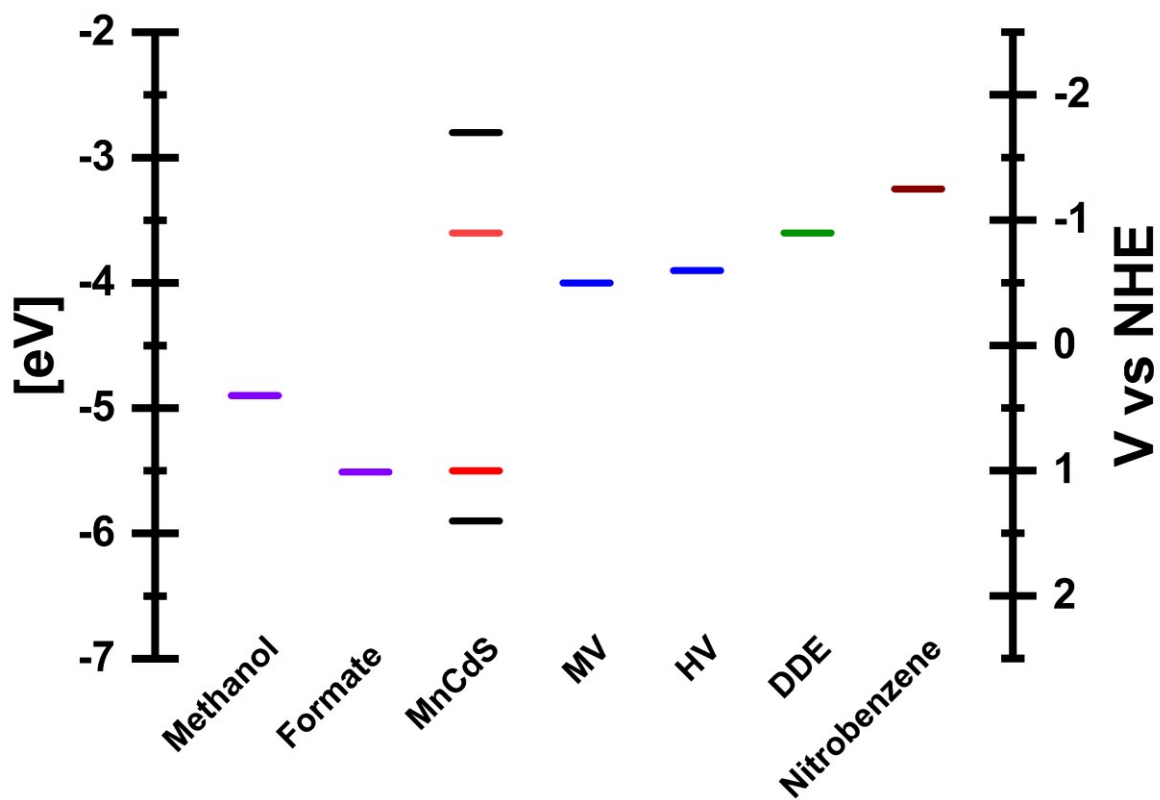
Figure S3. Energy levels of the valence and conduction bands of CdS QD[10] (black), the $^4T_1 \rightarrow {}^6A_1$ transition of the high spin Mn^{2+} in a tetrahedral geometry[11] (red), the oxidation potentials of sacrificial hole scavengers[12,13] (purple) and reduction potentials of viologens[14] (blue), meso-1,1-dibromo-1,2-diphenylethane[15,16] (green) and nitrobenzene[17] (brown).
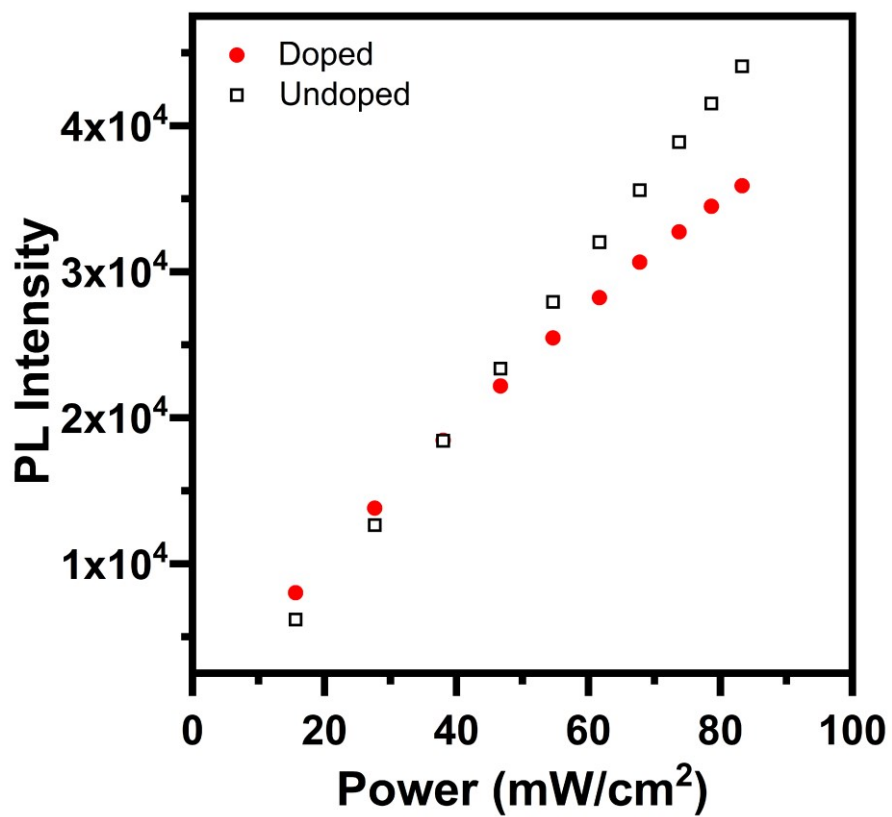
Figure S4. Photoluminescence intensity of doped (red) and undoped (black) QDs versus irradiation power at 440 nm. Deviation of PL intensity of the doped QDs from linear relationship at higher power suggests saturation of Mn^{2+} states and nonradiative Auger processes.
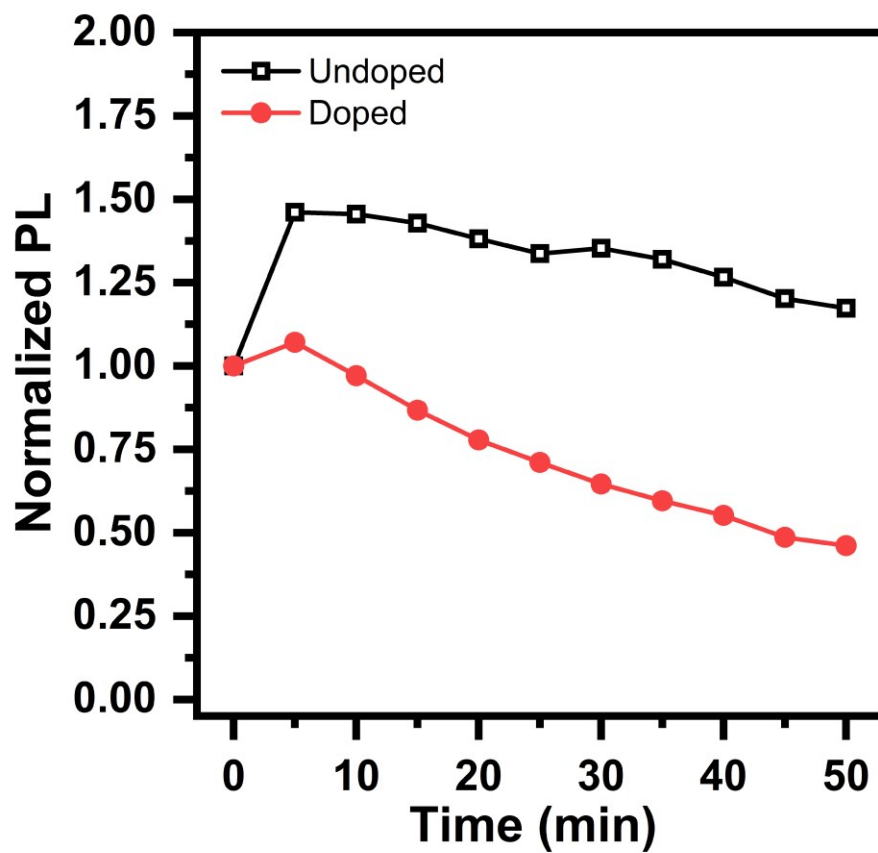
Figure S5. Normalized photoluminescence intensity at 488 nm and 581 nm for the undoped (black) and doped QDs (red), respectively, in water.

a

Absorbance vs Wavelength (nm)

Methyl Viologen
Doped QDs
No Irradiation

b

Absorbance vs Wavelength (nm)
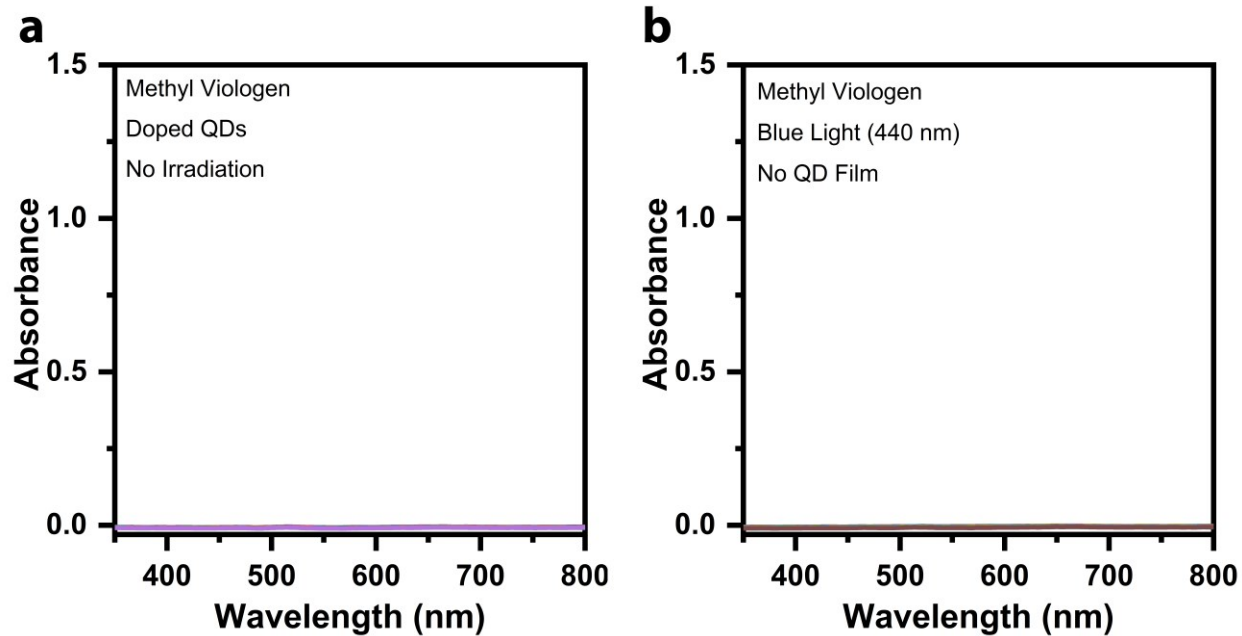
Methyl Viologen
Blue Light (440 nm)
No QD Film

Figure S6. Control experiments with MV^{2+} in water show that both light and QDs are crucial for reaction to take place: (A) Spectra of solution without irradiation; and (B) spectra of solution without QDs upon blue light irradiation.
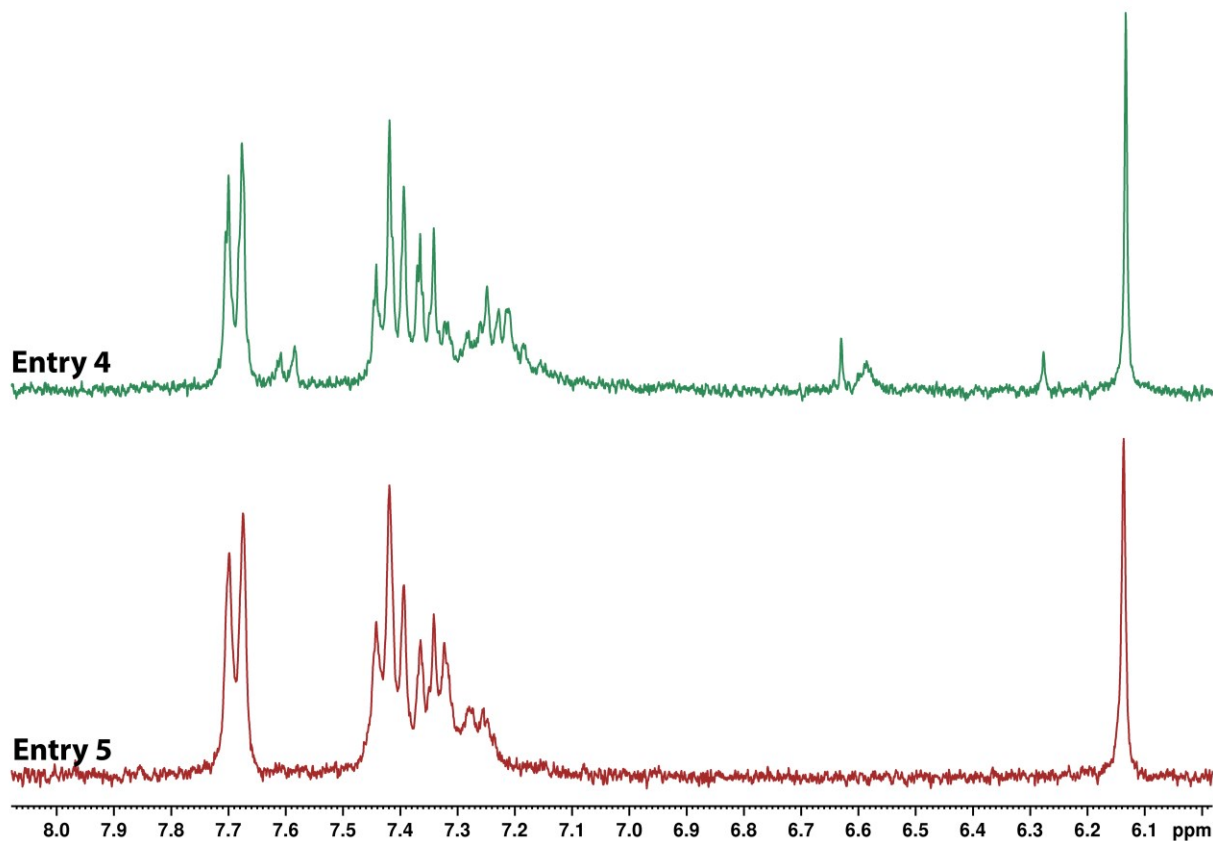
Figure S7. ^{1}H NMR spectra of the organic phase from the biphasic system for the reduction of DDE (in d-DMSO). Control experiment (brown, Entry 5) showed signals of DDE only, conferring the importance of heptyl viologen (HV^{2+}) as the electron shuttle between the two phases. A low concentration of HV^{2+} at 3 mol% (green, Entry 4) yielded 17 % conversion of DDE to stilbene with doped QDs, compared with 100% at 20 mol% of HV^{2+}.
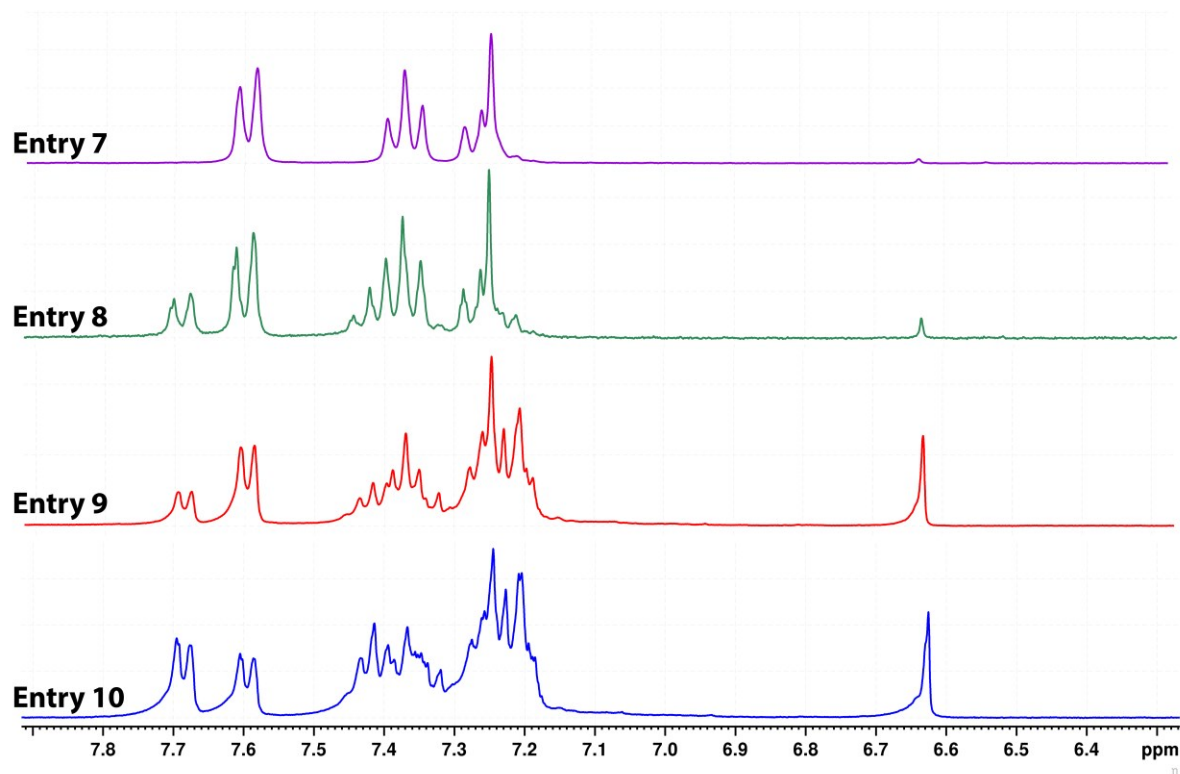
Figure S8. ^{1}H NMR spectra for monitoring the reduction of DDE in a monophasic system(in d-DMSO). Reactions with doped (purple, Entry 7) and undoped QDs (green, Entry 8) at a catalyst loading of 0.012 mol% where the doped QDs exhibited enhanced activity with only signals of stilbene detected. At a low catalyst loading (0.004 mol%), samples from both doped (red, Entry 9) and undoped (blue, Entry 10) showed incomplete reactions.
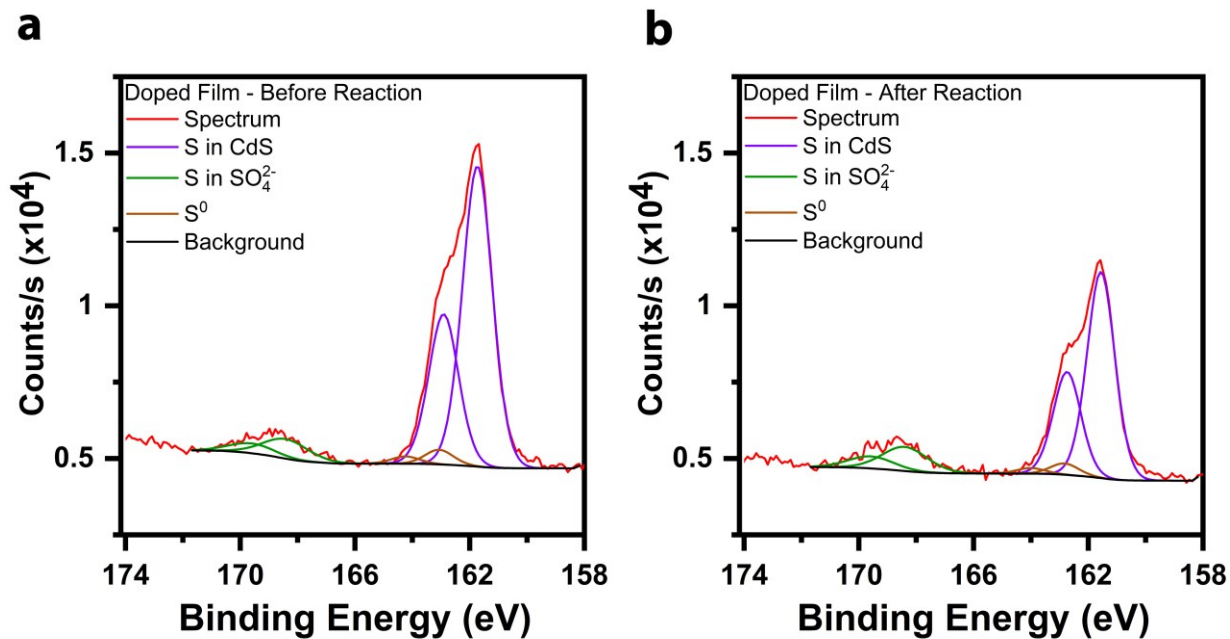
Figure S9. X-ray photoelectron spectra of S 2p of Mn:CdS/ZnS QD films before (A) and after (B) the photoredox reaction of DDE. Experimental spectra shown in red and fitted curves in other colors with each doublet corresponding to the spin-orbit coupling of $2p_{3/2}$ and $2p_{1/2}$.
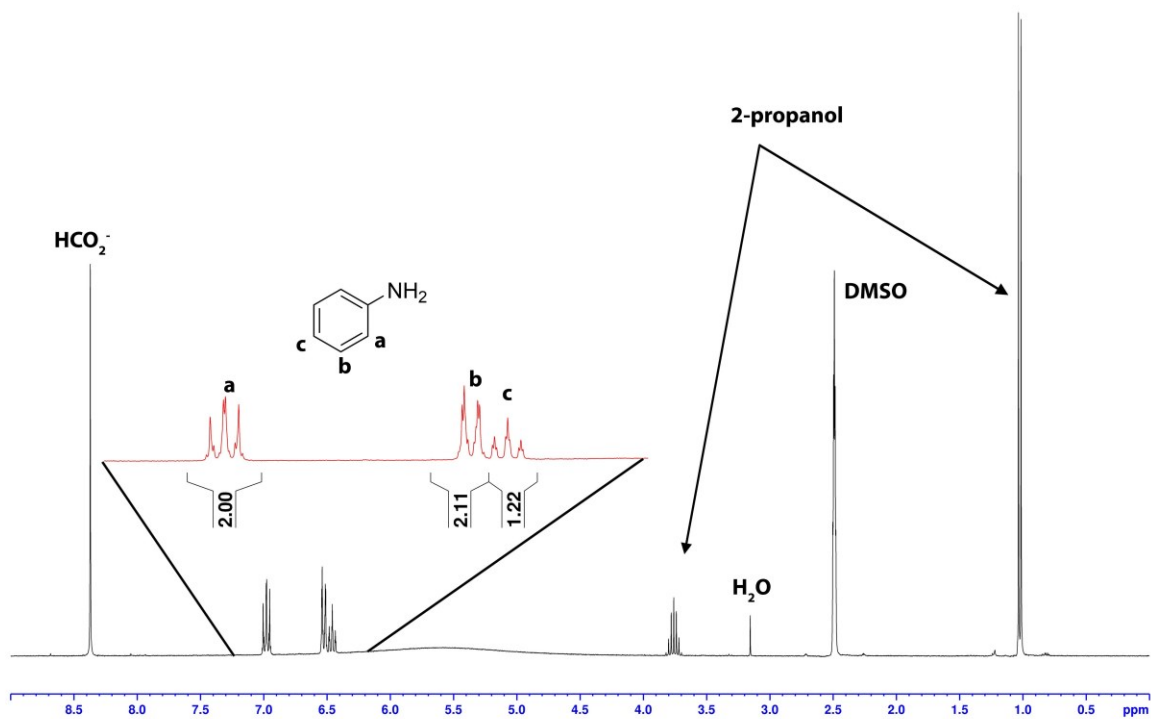
Figure S10. ^{1}H NMR spectrum of post reaction solution depicting successful conversion of nitrobenzene to aniline in d-DMSO. Inset shows the ratio between integrated peaks.

SUPPORTING TABLES

Table S1. Binding energies of Cd (3d) and S (2p) in Mn-doped CdS/ZnS core/shell films before and after photoredox reaction compared with literature.

Before Reaction				After Reaction				Literature
Element/ Transition	B. E. (eV)	Conc. (at %) [a]	Peak Assignment	Element /Transition	B. E. (eV)	Conc. (at %) [a]	Peak Assignment	B. E. (eV)
Cd $3d_{5/2}$	405.06	100	Cd in CdS	Cd $3d_{5/2}$	405.09	84.6	Cd in CdS	405.0[18]
Cd $3d_{3/2}$	411.78		Cd in CdS	Cd $3d_{3/2}$	411.81		Cd in CdS	411.8[18]
				Cd $3d_{5/2}$	405.65	15.4	Cd in $CdSO_4$	405.4[19]
				Cd $3d_{3/2}$	412.67		Cd in $CdSO_4$	412.2[19]
S $2p_{3/2}$	161.50	87.8	S^{2-} in CdS	S $2p_{3/2}$	161.56	80.2	S^{2-} in CdS	161.4[18]
S $2p_{1/2}$	162.68		S^{2-} in CdS	S $2p_{1/2}$	162.74		S^{2-} in CdS	162.6[18]
S $2p_{3/2}$	163.10	3.2	S^0	S $2p_{3/2}$	162.83	4.5	S^0	163.3[b19]
S $2p_{1/2}$	164.28		S^0	S $2p_{1/2}$	164.01		S^0	
S $2p_{3/2}$	168.21	8.9	S^{6+} in SO_4^{2-}	S $2p_{3/2}$	168.40	15.3	S^{6+} in SO_4^{2-}	168.6[b19]
S $2p_{1/2}$	169.39		S^{6+} in SO_4^{2-}	S $2p_{1/2}$	169.58		S^{6+} in SO_4^{2-}	

[a] Concentration relative to the total *p (3/2 and 1/2)* or *d* (5/2 and 3/2) signal
[b] Peak energy refers to the average S*p* signal

Table S2: Atomic % composition obtained from XPS of crosslinked Mn:CdS/ZnS QD film before and after reaction. Signals of Indium come from the ITO substrates and that of Si come from MPTMS used to anchor the QDs on the substrate. A significant increase in In 3d signal was observed post reaction, suggesting the loss of QDs. Note that Mn signals overlapped with loss structures of other species and could not be fitted or quantified.

Element/ Transition	B. E. (eV)	Films Before Reaction Atomic %	Films After Reaction Atomic %
Si *2p*	102.21	0.45	0.15
P *2p*	132.47	0.1	0.05
S *2p*	161.98	9.5	7.25
C *2p*	284.96	73.15	73.3
Cd *3d*	405.13	3.6	3.3
O *1s*	532.01	7.95	12.55
Zn *2p3*	1021.96	4.35	2
In *3d*	450.95	0	1.05
N *1s*	399.82	0.85	0.25

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