

Thermally Activated Delayed Photoluminescence from Pyrenyl Functionalized CdSe Quantum Dots

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The generation and transfer of triplet excitons across semiconductor nanomaterial – molecular interfaces symbolize a key advance poised for significant technological impact. Understanding the rules governing excited state energy flow between nanocrystal sensitizers and molecules is anticipated to have substantial impact in photonics and optoelectronics. Here it is shown that near quantitative triplet energy transfer from CdSe quantum dots to surface anchored 1-pyrenecarboxylic acid (PCA) produces an excited state equilibrium generating thermally activated delayed photoluminescence (TADPL) from the CdSe nanocrystals. Thermal repopulation of the initial semiconductor nanocrystal excited state from the PCA molecular triplet “reservoir” provides the opportunity to visualize sustained photoluminescence (PL) emission characteristic of the quantum dot. We report prototypical examples of this endothermic reverse triplet-triplet energy transfer behavior realized with PCA-functionalized CdSe nanocrystals of varying size/bandgap. The TADPL lifetime deterministically correlates to the energy difference between the CdSe band gap and PCA triplet energy as well as temperature. The resultant TADPL lifetimes range from microseconds (small energy gaps) to the millisecond time regime (large energy gaps) at room temperature under air free conditions with PL quantum yields near 13%. Room temperature data was used to directly correlate the TADPL lifetimes with those measured for the corresponding ³PCA* transient absorption decay kinetics. This strategy enables further exploration of photophysical phenomena in molecularly decorated semiconductor nanomaterials while providing critical design elements necessary for chemically harnessing surface-bound molecular triplets on quantum dot surfaces.

The ability to control the flow of energy between semiconductor nanocrystals and surface-anchored molecular species is of both practical and fundamental significance.¹ In the span of only 3 years, the exothermic transfer of triplet excitons both to and from semiconductor nanocrystals and molecules has become established along with translation of this excited state into bulk solution where further chemistry ensues.^{2, 3, 4, 5, 6, 7} The triplet excited state photochemistry initiated from quantum dot sensitizers becomes enabled as a result of ill-defined spin quantum numbers yielding excited states of strongly mixed singlet and triplet character.^{8, 9} Although many transition metal complexes feature similar electronic structure,¹⁰ the advantage of semiconductor nanocrystals such as CdSe as triplet sensitizers lies in their closely spaced energy conserving singlet-triplet gaps (< 15 meV) and large oscillator strengths.^{8, 11, 12} Akin to molecular sensitizers, triplet excitons can be harvested from CdSe quantum dots via rapid triplet-triplet energy transfer (TTET) to surface-bound acceptor molecules with near unity efficiency.^{5, 13} Since the forward TTET process yields a surface-anchored molecular triplet excited state with lifetimes on the milliseconds time scale, we questioned whether the endothermic reverse TTET (rTTET) process could also be enabled by strategically controlling the CdSe nanocrystal-acceptor energy gap through variation in quantum dot size. The design criteria necessary for enabling this phenomenon is established from purely molecular phenomena, namely triplet excited state equilibrium in metal-organic chromophores^{14, 15, 16, 17} and molecules featuring thermally-activated delayed fluorescence.^{18, 19} In essence, thermal repopulation of the initial quantum dot excited state from a lower energy molecular triplet “reservoir” provides the opportunity to generate markedly enhanced lifetime PL emission characteristic of the quantum dot through TADPL. The lifetime of the equilibrated excited state is readily tuned over several orders of magnitude through variation of quantum dot donor/molecular acceptor triplet energy gap (ΔE_{gap}) and temperature. Herein indisputable PL and transient absorption spectroscopic evidence is provided for thermal equilibrium and rTTET occurring between CdSe nanocrystals of varying size and surface anchored PCA chromophores.

Results and Discussion

The TADPL design strategy is presented schematically in **Fig. 1**; this representation illustrates all relevant photophysical processes and the associated energy levels enabling TADPL. For the TADPL materials, oleic acid (OA) capped CdSe quantum dots (CdSe-OA) were selected as the light-absorbing unit in association with PCA as the triplet acceptor in toluene solutions. This integrated system employed an optimized synthetic procedure to precisely control the number of PCA units ultimately residing on the CdSe surface.⁵ The carboxylic acid moiety enabled adsorption of PCA on the CdSe surface through fast and efficient displacement of the native OA ligands. The final CdSe/PCA donor/acceptor materials were isolated after several precipitation/washing cycles. CdSe core type nanocrystals with sizes ranging from 2.4 nm to 4.6 nm were prepared, corresponding to first exciton bands spanning the visible region between 488 nm to 600 nm, coded as CdSe-488 to CdSe-600 (**Fig. 2**). Photoluminescence spectra display characteristic narrow band CdSe PL emission along with some lower energy trap state emission. The number of PCA molecules per quantum dot – determined using UV-Vis data and the appropriate molar extinction coefficients for CdSe and PCA – increases linearly with CdSe surface area (proportional to πd^2), confirming the reproducibility and repeatability of the ligand exchange process (**Fig. 2**). Moreover, the final isolated CdSe/PCA materials remained stable in toluene solutions for extended time periods showing no signs of PCA desorption. Excitation of the first exciton band in the CdSe/PCA materials promotes triplet exciton migration from the semiconductor to the molecular adsorbate through nearly quantitative TTET.⁵ The kinetics of the forward TTET process in all evaluated materials displays complex kinetics due to the well-established heterogeneous nature of CdSe quantum dots,^{20, 21} requiring the use of a stretched exponential function for adequate modeling.²² Due to favorable thermodynamics ($E(^3\text{PCA}) = 2.00$ eV (620 nm))²³ the prompt CdSe PL in CdSe/PCA constructs is efficiently quenched through Dexter-like triplet energy transfer in all cases. The formation of the resulting $^3\text{PCA}^*$ excited state was confirmed in all of the integrated materials here using nanosecond transient absorption experiments through monitoring the sensitized $T_1 \rightarrow T_n$ transition centered at 430 nm (**Supplementary Fig. 1 and Fig. 3**) following selective excitation of CdSe. The PCA triplet serves as a reservoir for the triplet exciton, akin to molecular species containing two energetically proximate triplet excited states.^{14, 15, 16, 17} The lifetime of the PCA molecular triplet and the TADPL was systematically varied as a function of the CdSe bandgap, which alters the corresponding energy gap between the CdSe excited state and the PCA triplet state, termed here as ΔE_{gap} . When this energy gap was small, rTTET led to repopulation of the initial CdSe excited state, thus enabling delayed PL characteristic of CdSe to be observed. In the case where little to no rTTET was observed, *i.e.* instances with large energy gaps (CdSe-488), the phosphorescence lifetime for the PCA triplet was ~ 50 ms, of similar magnitude with the pyrene triplet lifetime in deaerated solution.²⁴

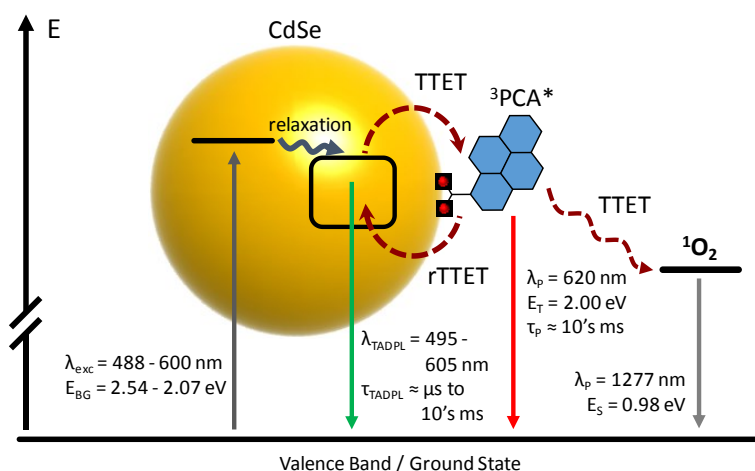


Figure 1| The strategy for generating TADPL CdSe/PCA interfaces. Representation of the TADPL process in CdSe/PCA assemblies, the associated energy levels, and the various PL wavelengths, lifetimes, and decay pathways realized in this study.

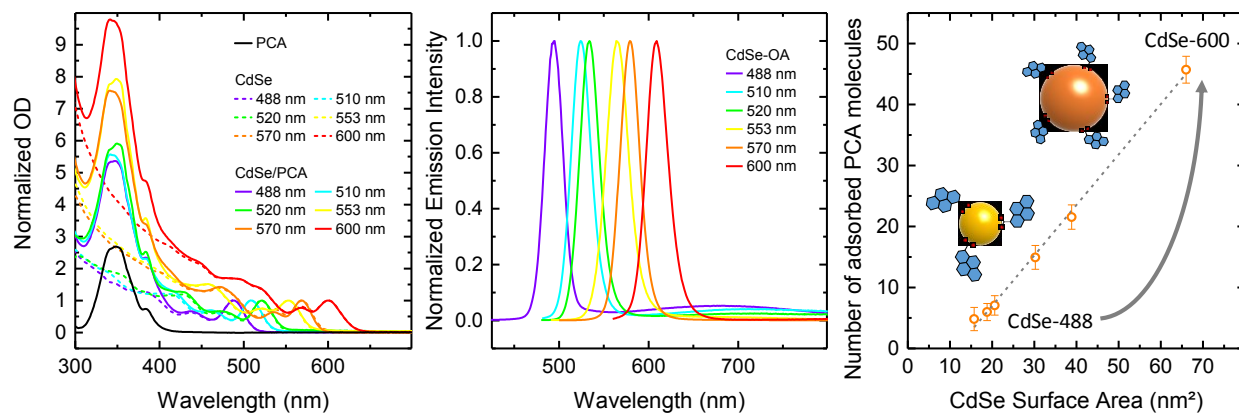


Figure 2 | Static UV-Vis and PL data of the CdSe-OA, CdSe/PdCA, and PCA chromophores and scaling of PCA adsorption with quantum dot surface area. Left: UV-visible spectra of the CdSe-OA, CdSe/PdCA and PCA in toluene at room temperature. **Center:** PL spectra of the as-synthesized CdSe-OA quantum dots in toluene at room temperature under aerated conditions. **Right:** Number of adsorbed PCA molecules measured as a function of quantum dot surface area determined using UV-Vis spectroscopy.

The TADPL kinetics associated with quantum dot relaxation and the triplet-to-triplet absorption characteristic of $^3\text{PCA}^*$ ⁵ provide definitive spectroscopic handles for confirming the proposed excited state equilibrium and rTTET processes in the CdSe/PdCA materials. Comparison of the room temperature time-resolved PL decays emanating from each of the CdSe quantum dots and the corresponding $^3\text{PCA}^*$ transient absorption kinetics are presented in **Fig. 3** with all relevant fitting parameters collected in **Table 1**. The excited state kinetics in both spectroscopic domains was adequately modeled using the same stretched exponential function (Kohlrausch-Williams-Watts function)²² applied to the forward TTET processes in these materials.⁵ These results seem reasonable since rTTET should reflect similar kinetic complexity with respect to forward TTET indicating a range of CdSe and PCA microenvironments and associated rate constants. The CdSe-488 sample is also displayed to illustrate the situation where little to no rTTET was observed and the phosphorescence and transient absorption decays from the $^3\text{PCA}^*$ species were identical within experimental error. The kinetics measured here were also complex, likely a result of multiple PCA microenvironments on the quantum dots or some small contribution from the rTTET process. Confirmation of the kinetic correlation between each CdSe TADPL intensity decay and the analogous $^3\text{PCA}^*$ triplet absorption decay was achieved across all samples investigated (**Fig. 3 and Table 1**). As discussed further below, the excited state lifetimes of these samples systematically varied between 1.6 μs and 50 ms at room temperature resulting from the modulation in ΔE_{gap} , achieved by simply changing quantum dot size. These experiments universally demonstrate that the quantum dot and PCA excited states are in thermal equilibrium and rTTET from the long-lived $^3\text{PCA}^*$ excited state is solely responsible for the observed delayed emission from the CdSe nanocrystals.

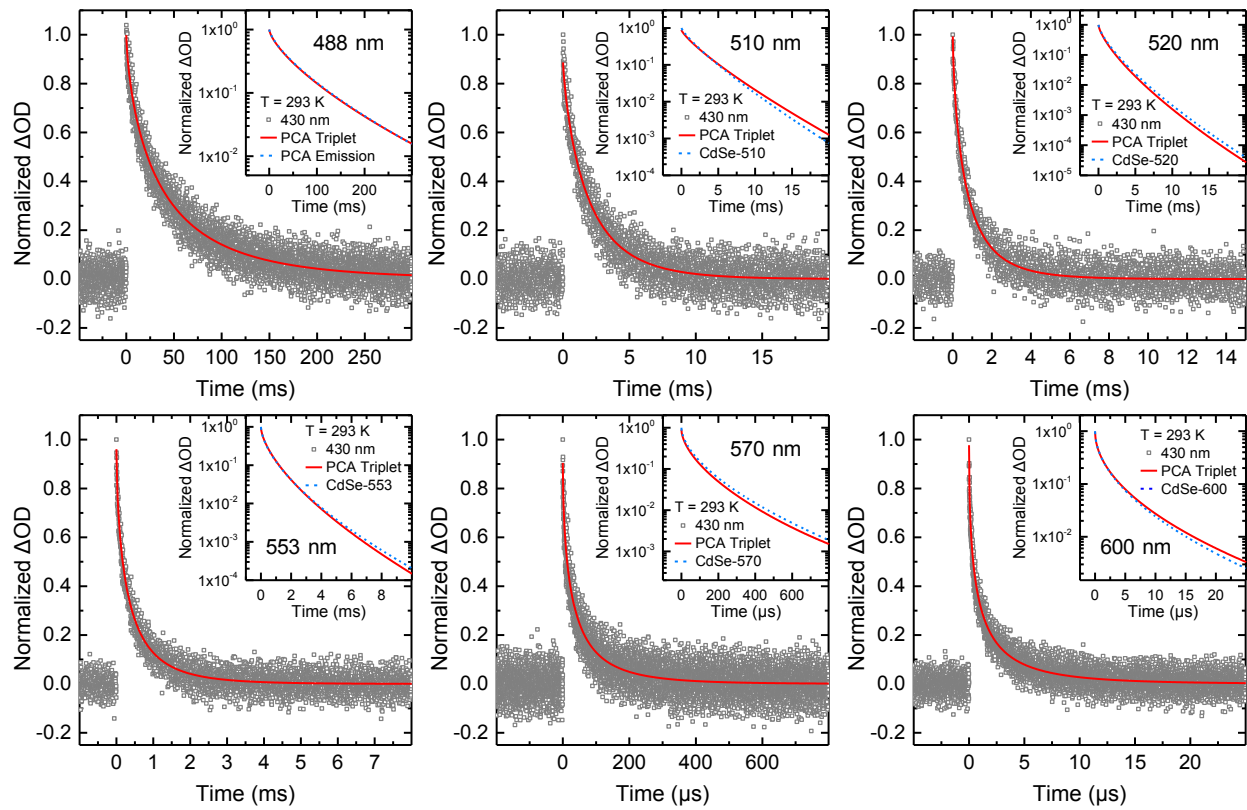


Figure 3| Kinetic evidence of the correlation between transient absorption and TADPL intensity decays in CdSe/PCA materials. PCA triplet excited state transient signal (gray dots) observed at 430 nm in CdSe-488 to CdSe-600 at 293 K in degassed toluene following selective excitation (2 mJ, 5 - 7 ns FWHM) into the CdSe first exciton band (CdSe wavelengths displayed). Red lines show the resulting fits to a stretched exponential function in each case. **Insets** present the direct comparison of the $^3\text{PCA}^*$ decay fit line (red line) and TADPL decay fit line (dashed blue line) on a logarithmic scale for each sample. Results of the combined fits data are collected in **Table 1**.

Table 1| Parameters obtained from fitting the room temperature CdSe TADPL emission intensity decays (λ_{TADPL} as indicated) and their corresponding $^3\text{PCA}^*$ transient absorption decays ($\lambda_{\text{abs}} = 430 \text{ nm}$).^a

	TADPL Signal			$^3\text{PCA}^*$ Transient Absorption Signal		
	β	τ	$\langle\tau\rangle$	β	τ	$\langle\tau\rangle$
CdSe-488	0.701	39.4 ms	51.3 ms	0.691	37.9 ms	49.4 ms
CdSe-510	0.820	1.82 ms	2.03 ms	0.810	1.94 ms	2.14 ms
CdSe-520	0.720	0.80 ms	1.01 ms	0.711	0.72 ms	0.92 ms
CdSe-553	0.610	0.30 ms	0.50 ms	0.638	0.33 ms	0.47 ms
CdSe-570	0.580	33.6 μs	52.9 μs	0.583	32.0 μs	50.0 μs
CdSe-600	0.520	0.80 μs	1.60 μs	0.510	0.82 μs	1.58 μs

^a Data taken from **Supplementary Figs. 2 to 7** and **Fig. 3**. The values were obtained by fitting the corresponding signal with the stretched exponential function $I(t) = I_0 \exp(-t/\tau)^\beta$ using Origin 9.1; $\langle\tau\rangle$ is the average lifetime obtained from these fits: $\langle\tau\rangle = (\tau/\beta)\Gamma(1/\beta)$; β reflects the underlying distribution of time constants.

The effect of rTTET was also observed through time-resolved temperature dependent (193 to 293 K (-80 to 20 °C)) PL spectra following selective excitation of the first exciton band (1S) in the CdSe/PCA materials. The TADPL lifetimes systematically decreased with increasing temperature, except for CdSe-488 where no significant TADPL was observed ($\Delta E_{\text{gap}} = 0.54$ eV) and only PCA phosphorescence could be detected (**Fig. 4**). This 0.54 eV energy separation can be considered the minimum necessary to achieve thermal equilibrium in these constructs at room temperature. Under these circumstances, the equilibrium lies strongly to the right ($K_{\text{eq}} = 10^9$) and the lifetime of the PCA triplet is insufficient to support repopulation of the CdSe excited state. Smaller energy gaps promote more rapid and efficient back transfer, reducing the value for the equilibrium constant, consequently shortening the observed lifetime. Purely molecular based systems featuring triplet equilibrium manifest identical excited state properties as those observed here.^{25, 26} Extremely long-lived CdSe “bright state” PL with lifetimes ranging from microseconds to tens of milliseconds were observed across these samples (**Fig. 4, Table 2, and Supplementary Figs. 2 - 7**) as a result of varying ΔE_{gap} which ultimately impacts K_{eq} .¹⁷ Very efficient TADPL occurred with near constant lifetimes in materials with nearly isoenergetic energy gaps as in CdSe-600 ($\Delta E_{\text{gap}} = 0.07$ eV). The relative TADPL quantum yield increased with increasing temperature for the largest energy gap materials but a threshold was reached for CdSe-553 ($\Delta E_{\text{gap}} = 0.24$ eV), where increasing the temperature above 233 K resulted in lower relative quantum efficiency (**Fig. 4**). Similar behavior was observed for every CdSe/PCA sample with $\Delta E_{\text{gap}} < 0.24$ eV. This was attributed to the thermal activation of surface traps known to affect the singlet exciton quantum efficiencies (and lifetimes) in semiconductor nanocrystals, where the energy threshold for the activation of these surface states in CdSe was previously estimated to be small ($\sim 15\text{-}21$ meV).^{12, 27}

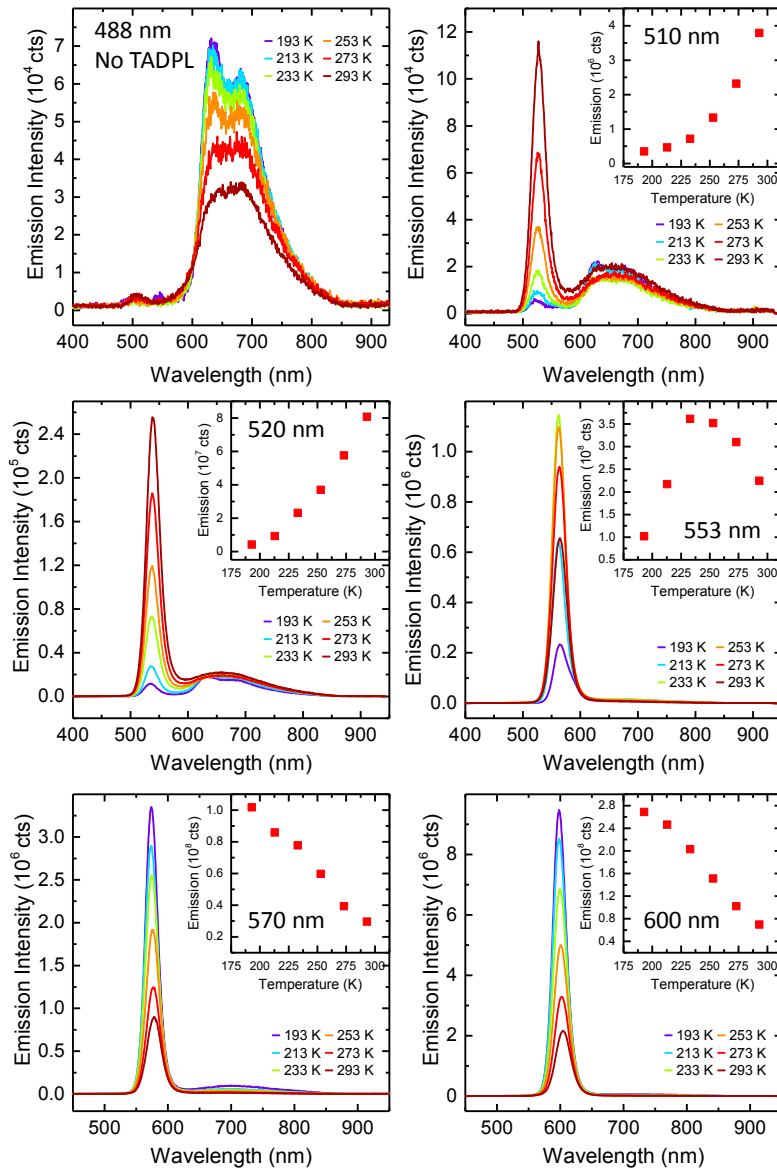


Figure 4 | TADPL behavior measured as a function of temperature in CdSe/PCA materials of varying size. Integrated PL spectra of CdSe/PCA materials from 193 K to 293 K in freeze-pump-thaw degassed toluene following selective excitation (2 mJ, 5 - 7 ns FWHM) into the CdSe first exciton band (wavelengths displayed). Each inset shows the variation of the total integrated TADPL intensity (relative quantum efficiencies) of the CdSe “bright state” as a function of temperature.

Table 2 | CdSe/PCA TADPL average lifetimes measured as a function of temperature.

Temperature (K)	CdSe-488 $\langle\tau\rangle_p$ (ms) ^a	CdSe-510 $\langle\tau\rangle_{TADPL}$ (ms) ^b	CdSe-520 $\langle\tau\rangle_{TADPL}$ (ms) ^b	CdSe-553 $\langle\tau\rangle_{TADPL}$ (ms) ^b	CdSe-570 $\langle\tau\rangle_{TADPL}$ (μ s) ^b	CdSe-600 $\langle\tau\rangle_{TADPL}$ (μ s) ^b
193	71 $\pm$ 2	69 $\pm$ 3	68 $\pm$ 2	36.2 $\pm$ 0.8	2167 $\pm$ 150	6.44 $\pm$ 0.04
213	69 $\pm$ 3	66 $\pm$ 2	58 $\pm$ 1	14.9 $\pm$ 0.4	799 $\pm$ 30	4.43 $\pm$ 0.05
233	71 $\pm$ 1	48 $\pm$ 1	30 $\pm$ 2	5.4 $\pm$ 0.1	338 $\pm$ 8	3.19 $\pm$ 0.02
253	70 $\pm$ 2	21 $\pm$ 0.5	9.7 $\pm$ 0.6	2.1 $\pm$ 0.1	165 $\pm$ 3	2.43 $\pm$ 0.06
273	65 $\pm$ 1	6.5 $\pm$ 0.2	2.9 $\pm$ 0.2	0.94 $\pm$ 0.03	91 $\pm$ 1	1.92 $\pm$ 0.01
293	52 $\pm$ 2	2.0 $\pm$ 0.1	1.0 $\pm$ 0.1	0.46 $\pm$ 0.02	52 $\pm$ 1	1.57 $\pm$ 0.02
ΔE_{gap} (eV) measured ^c	0.509	0.418	0.374	0.251	0.181	0.071
ΔE_{gap} (eV) calculated ^c	0.542	0.433	0.386	0.244	0.177	0.068

^a Phosphorescence decay lifetime of PCA. ^b CdSe TADPL decay lifetime. The values were obtained by fitting the corresponding signal with the stretched exponential function $I(t) = I_0 \exp(-t/\tau)^\beta$ using Origin 9.1. $\langle\tau\rangle$ is the average lifetime obtained from these fits: $\langle\tau\rangle = (\tau/\beta)\Gamma(1/\beta)$. ^c Energy gap values were obtained experimentally from Arrhenius plots (Eq. 1, measured values) and from the energy difference between the absorption maximum of the CdSe first exciton band and the phosphorescence emission of PCA (calculated values).

The variation of the TADPL lifetime across the temperature range (193 to 293 K) measured in each sample was well modeled using an Arrhenius expression successfully applied to molecular systems,²⁸ **Fig. 5**. Given the substantial differences in excited state lifetimes of the two species participating the in equilibrium, excited state decay becomes largely governed by the millisecond lifetime PCA chromophores, as has been observed in triplet equilibrium processes in metal-organic complexes.²⁵ The intersystem crossing related terms in the original equation expression applied to molecular-based thermally activated delayed fluorescence were replaced by the determined TADPL time constants and the phosphorescence lifetime of PCA (τ_p^0) in **Eq. 1** below. This expression illustrates the expected variation in excited state lifetime resulting from changes in CdSe quantum dot-PCA energy gap.

$$\frac{1}{\langle\tau_{TADPL}\rangle} = \frac{1}{\langle\tau_p^0\rangle} + A \times (1 - \Phi_T) \times \exp\left(\frac{-\Delta E_{Gap}}{RT}\right) \quad (1)$$

Here $\langle\tau_{TADPL}\rangle$ is the delayed PL average lifetime derived from stretched exponential fits, $\langle\tau_p^0\rangle$ is the average PCA phosphorescence lifetime measured when TADPL was not operational (50 ms), A is the fastest possible excited state equilibration term, Φ_T is the triplet formation quantum yield, and ΔE_{gap} is the energy difference between CdSe band gap and the ³PCA excited state energy. The activation energy (ΔE_{gap}) in each of these materials was found to be in excellent agreement with the values calculated using the relevant CdSe first exciton energy and the PCA triplet state energy (**Fig. 5**, **Table 2**). This leaves little doubt about the thermally activated nature of excited state decay in the current CdSe/PCA materials and its deterministic behavior poised for further exploration in light-emitting materials.

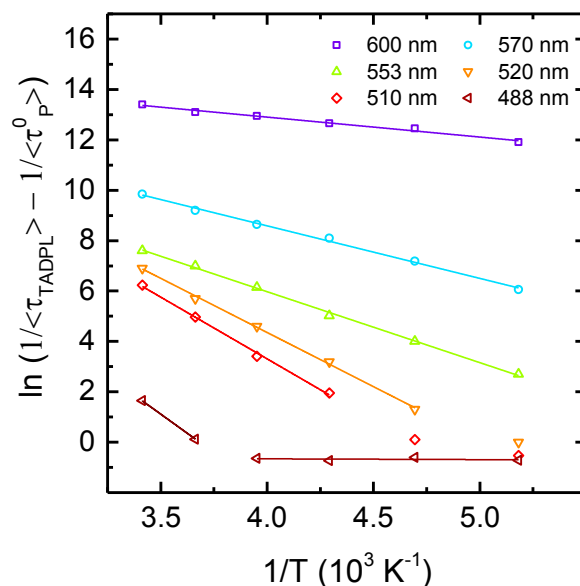


Figure 5| Arrhenius plots of the CdSe/PCA materials. Lifetimes of the CdSe-488 to 600 nm-PCA materials from stretched exponential fits of the TADPL intensity decays measured in deaerated toluene between 193 K to 293 K according to Eq. 1.

Further evidence of the triplet nature of the thermally equilibrated excited state was obtained by monitoring the steady state PL of the CdSe/PCA materials under air-free and air-saturated conditions. Under air-free conditions at room temperature, significant PL was observed from all samples, except for CdSe-488 where no significant rTTET was observed. The PL quantum yield ratio with respect to the initial CdSe-OA native materials is also related to the CdSe-³PCA energy gap. These quantum efficiencies span from < 1% in CdSe-488 – where mostly trap state emission was observed – to 13% for CdSe-600 which is considered nearly defect free (**Supplementary Fig. 8**). The CdSe/PCA TADPL materials clearly display enhanced trap state contributions in comparison to the pristine CdSe-OA nanocrystals. This behavior potentially arises for two reasons: (1) defect generation upon ligand exchange with PCA, which increases the trap state density on the surface; or (2) rTTET from PCA to low-lying CdSe triplet excited states leading to trap state emission. Since the observed PL is blue-shifted compared to the original trap state PL and falls off above 700 nm, which also corresponds to the second vibrational level in PCA phosphorescence, it is more probable that this PL results in undesired rTTET to some low-lying CdSe triplet state rather than surface defects. The contribution of the trap state emission to the global TADPL signal is highly temperature dependent²⁹ and rTTET to these excited states is not considered a dominant process. Despite the favorable thermodynamics, there is no significant impact on the PCA phosphorescence lifetime or quantum yield compared to free PCA in solution at low temperatures. Therefore, the direct population of a trap state is either not occurring or is generated very slowly in comparison to the ³PCA excited state decay. CdSe-570 and CdSe-600 exhibited the highest TADPL quantum yields at room temperature owing to the negligible energy gaps between CdSe and ³PCA (70 meV for CdSe-600, $\Phi_{\text{TADPL}} = 0.13$). Air saturated conditions led to a dramatic decrease of the CdSe emission intensity due to very efficient ground state triplet dioxygen quenching to form excited singlet O₂, ¹O₂ ($E_{^1\text{O}_2} = 0.98$ eV).³⁰ The appearance of a strong sensitized PL signal at 1277 nm corresponding to singlet oxygen phosphorescence confirms this assignment whereas CdSe-OA quantum dots under identical conditions do not photosensitize any ¹O₂ (**Supplementary Fig. 9**). The CdSe/PCA materials appear to be promising candidates for oxygen photosensitization or oxygen sensing as they display no signs of degradation with prolonged photolysis.

Conclusion

The results presented here provide definitive proof of concept that CdSe quantum dots, in conjunction with PCA molecular triplet acceptors, can be employed as hybrid TADPL materials operating through TTET equilibrium. These photochemical processes are similar to ISC and rISC occurring in TADF molecules and directly analogous to TTET and rTTET processes observed in numerous metal-organic chromophores. The current findings illustrate the molecular-like photophysical behavior exhibited by CdSe semiconductor nanocrystals and reveal non-innocent electronic communication with surface-anchored molecules; ΔE_{gap} must be considered for sensitization applications such as photochemical upconversion, photocatalysis, and solar fuels generation. Since the design elements are akin to those in molecular systems, newly conceived semiconductor nanocrystal/molecularly decorated materials with predictable photophysical properties are readily enabled. The prototypes presented here were quantum efficiency limited by the defect-induced PL performance inherent to the CdSe core type quantum dots selected. Core-shell materials therefore appear more suitable for exploration of TADPL processes utilizing this same approach since the overall PL quantum yield would increase substantially.³¹ However, in order to promote efficient TTET from the energized nanocrystal core to the adsorbed triplet acceptor, the thickness of the shell would need to be properly modulated to avoid complete insulation of the triplet exciton. Along these lines, recent evidence supporting sub-monolayer shell approaches towards enhancing triplet exciton transfer at PbS nanocrystal-molecular interfaces appear promising.³² In order to provide the highest quantum efficiency PL achievable from the current materials, a deeper fundamental understanding of the CdSe/PCA interface and how defects are introduced as a result of the surface anchoring chemistry seem necessary. Nevertheless, potential applications in optoelectronics, light emitting devices, photoluminescence sensing, energy transfer phenomena in solid-state devices, as well as fundamental photochemical processes of integrated semiconductor nanocrystal-molecular materials appear imminent.

Methods

Oleic acid capped CdSe (CdSe-OA) synthesis. TOP capped CdSe nanocrystals were synthesized according to a procedure adapted from the literature.³³ Following the CdSe nanocrystal growth, TOP surface ligands were exchanged with oleic acid molecules through L $\rightarrow$ Z type ligand displacement in order to provide oleic acid capped CdSe quantum dots (CdSe-OA).

Sample preparation. The preparation of CdSe/PCA was performed according to the previously reported method.⁵ CdSe/PCA were prepared from as synthesized CdSe-OA quantum dots through ligand exchange of the native OA ligands with PCA molecules in deaerated toluene for 1 hour. The resulting nanoparticle suspensions were subjected to at least three precipitation/centrifugation cycles using acetone. The resulting colored powder was dried and redispersed in spectrophotometric grade toluene and stored under nitrogen in the dark at 2°C prior any experiment.

Temperature dependent experiments. Temperature of the samples was controlled using a Unisoku USP-203 cryostat fitted in the sample compartment of an Edinburgh Instruments LP 920 or FL/FS 920. Temperatures were varied between 193 K and 293 K in 20 K steps. The solution remained liquid over this temperature range ($m_{\text{toluene}} = 178$ K) thus avoiding any issues related to rigidified media.

Time resolved photoluminescence (PL) and transient absorption (TA) experiments. Nanosecond time-resolved PL spectra were collected on a LP 920 spectrometer from Edinburgh Instruments. Samples were prepared by diluting a stock solution of CdSeOA/PCA (following the ligand exchange procedure described above) with spectrophotometric grade toluene to achieve the desired absorbance/concentration. All samples for nanosecond PL and TA experiments were prepared in a specially designed 1 cm² quartz optical cell, with optical densities of 0.4 at the excitation wavelength, *i.e.* the CdSe first exciton band, bearing a side arm round bottomed flask and were subjected to a minimum of three freeze–pump–thaw degas cycles prior to all measurements. Excitation of the samples in these

experiments was accomplished using a Nd:YAG/OPO laser system from Opotek (Vibrant LD 355 II) operating at 1 Hz. The incident laser power was varied using a series of neutral density filters along with appropriate long pass and short pass filters. The spectrometer was equipped with an Andor iStar ICCD detector that permitted the collection of time-resolved absorption and emission spectra. Kinetic traces were analyzed using Origin 9.

Steady state experiments. Static absorption spectra were measured with a Cary 60 UV-vis spectrophotometer (Agilent). Steady-state photoluminescence spectra were recorded with a FL/FS 920 spectrometer (Edinburgh Instruments) equipped with both visible and NIR single photon counting detectors. Excitation was achieved by a 450 W Xe arc lamp equipped with a monochromator and appropriate long pass filters.

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Author Contributions

C.M. contributed to the preparation and characterization of the PCA-containing CdSe materials, all of the photophysical experiments, data analysis, and manuscript composition.

P.M. contributed to the preparation and characterization of the native CdSe-OA materials.

M.Z. contributed to the preparation and characterization of the native CdSe-OA materials and manuscript composition.

F.N.C. contributed to the original research concept, data analysis, manuscript composition, and overall supervision of the project.

Additional Information. Supplementary information is available in the online version of the paper. Correspondence and requests for materials should be addressed to F.N.C.

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Supplementary Information

Methods

General. Nanosecond time-resolved emission spectra were obtained on a LP 920 from Edinburgh Instruments. Steady state UV-visible absorption spectra were recorded on a Cary-60 from Agilent and steady state emission spectra were measured on a FL/FS 920 from Edinburgh Instruments. Temperature dependence studies were performed using a Unisoku USP-203 cryostat fitted in the sample compartment of the corresponding instrument. 1-pyrenecarboxylic acid (PCA, 99%) was purchased from Alfa Aesar. Selenium (99.999%, Acros), 1-octadecene (ODE, tech., 90%, Aldrich), cadmium oxide (CdO, 99.99%, Aldrich), oleic acid (OA, tech., 90%, Aldrich), tri-n-octylphosphine (TOP, 97%, Strem), and n-octadecylphosphonic acid (ODPA, 98%, PCI Synthesis) were used as received from the indicated commercial sources. Spectrophotometric grade toluene was purchased from Alfa Aesar and used without further purification.

Synthesis of oleic capped CdSe quantum dots. The following procedure adapted from the literature was used³³ to synthesize the oleic acid capped CdSe quantum dots (CdSe-OA). Briefly, TOP (3.0 g), ODPA (0.280 g) and CdO (0.060 g) were mixed in a 50 mL flask, heated to ca. 150°C and exposed to vacuum for 1 hour. Then, under argon, the solution was heated to above 300°C to dissolve CdO until the mixture turned optically clear and colorless. At this point, 1.5 g of TOP was injected into the flask and the temperature was raised to 380 °C. The reaction flask with this Cd precursor was raised up from the heating mantle right before the injection of the Se precursor to obtain small-diameter nanoparticles. The selenium precursor was prepared by dissolving 0.058 g of Se in 0.43 mL of TOP under heating at 200 °C under argon and cooling to room temperature was injected simultaneously into the raised flask (at 360 °C). After the synthesis, the CdSe nanocrystals were precipitated with ethanol, and washed by repeated redissolution in chloroform and precipitation by the addition of ethanol. Finally, the product was stored in toluene. Following CdSe nanocrystal growth, TOP surface ligands were exchanged with oleic acid molecules through L → Z type ligand displacement. In order to preserve a narrow distribution of nanoparticle diameters, the reaction was performed under Cd-saturated conditions by inducing a thermally activated substitution of TOP molecules with carboxylates (Cd(O₂CR)₂). To this end, TOP-capped CdSe NCs were loaded into a flask containing 5 mL of pumped octadecene (ODE) and a Cd(O₂CR)₂ solution prepared by dissolving 0.03 g of CdO in the presence of 0.3 mL oleic acid (OA) at 230 °C. After adding the nanocrystals, the reaction mixture was heated to 230 °C and maintained at this temperature for 30 min. A successful exchange/displacement of ligands was evident through observation of a red-shift of the first exciton absorption band in ligand-exchanged CdS NCs as a result of the increased nanocrystal volume (due to the addition of carboxylate complexes).

Ligand exchange with PCA. Ligand exchange was performed using CdSe-OA in presence of PCA. PCA (2 mg, 8.1 μmol) was added to a concentrated solution of CdSe-OA (OD = 2 at the first exciton band) in toluene (1 mL) and the resulting solution was sonicated for 1 hour at 30°C in the dark under nitrogen. Then, CdSe-OA/PCA nanocrystals were precipitated by adding acetone (3 mL), the mixture was centrifuged at 5800 rpm for 5 minutes, the supernatant was removed and the residue was dispersed in toluene (0.3 mL). The CdSe-OA/PCA nanocrystals were purified using at least 3 repeated dispersion/precipitation/centrifugation cycles. Finally, CdSe-OA/PCA nanocrystals were dispersed in spectrophotometric grade toluene (1 mL) and stored under nitrogen in the dark at 2°C. The average ratio of PCA acceptor to nanocrystal was determined by UV-vis absorption spectroscopy (**Fig. 2**).

Time resolved experiments. Time resolved emission spectra were collected on a LP 920 spectrometer from Edinburgh Instruments where ΔOD remained linear up to 0.8 O.D. in single wavelength acquisition mode detecting at 430 nm. The sample solutions were prepared to possess optical densities of 0.4 at the excitation wavelength, *i.e.* the CdSe first exciton band. Excitation of the samples in these experiments was accomplished using a Nd:YAG/OPO laser system from Opotek (Vibrant LD 355 II) operating at 1 Hz. The incident laser pulse energy was varied using a series of neutral density filters along with appropriate long pass and short pass filters. The same spectrometer was equipped

with an Andor iStar ICCD detector that permitted the collection of time-resolved absorption and emission spectra. Kinetic traces were analyzed using Origin 9.

Steady state spectroscopic measurements. Static absorption spectra were measured with a Cary 60 UV-vis spectrophotometer from Agilent. Steady-state photoluminescence spectra were recorded using a FL/FS920 spectrometer from Edinburgh Instruments equipped with both visible and NIR single photon counting detectors. Excitation was achieved by a 450 W Xe arc lamp equipped with a monochromator and appropriate long pass filters.

Sample preparation. Samples were prepared by diluting a stock solution of CdSe/PCA (following the ligand exchange procedure described above) with spectrophotometric grade toluene to achieve the desired absorbance/concentration. All samples for nanosecond TA experiments were prepared in a specially designed 1 cm² quartz optical cell, with optical densities of 0.4 at the excitation wavelength, bearing a side arm round bottomed flask and were subjected to a minimum of three freeze–pump–thaw degas cycles prior to all measurements. Samples for steady state photoluminescence measurements were prepared in the same 1 cm² sample cell as described above but with optical densities below 0.1 at the excitation wavelength.

Photoluminescence and transient absorption decay analysis. Kinetics were extracted from time resolved emission spectra or single wavelength measurements using either CdSe “bright state” photoluminescence (or PCA phosphorescence when rTTET was not operative) and ³PCA* transient absorption signal. Varied rates of energy transfer were expected depending on the initially populated CdSe excited state and on the environment around the PCA triplet acceptors thus a stretched exponential function was used to capture the rate of TADPL. The data points were fit using the following equation; results from these fitting procedures are shown in **Fig. 5, Supplementary Figs. 2 to 7, Tables 1 and 2 and Supplementary Table 1:**

$$I(t) = A \times \exp\left(-\left(\frac{t}{\tau}\right)^\beta\right)$$

Where A and τ are the amplitude and the stretched lifetime, respectively, corresponding to the CdSe thermally activated delayed photoluminescence (TADPL) lifetime or PCA phosphorescence lifetime and β is the stretching exponent. The average weighted lifetime, $\langle\tau\rangle$, was calculated from the following equation using τ and β values obtained from fitting:

$$\langle\tau\rangle = \frac{\tau}{\beta} \times \Gamma\left(\frac{1}{\beta}\right)$$

Arrhenius plots. The energy gap between the CdSe excited state and PCA triplet state were determined using the previously established mathematical model used in TADF molecular systems. The following equation was used.

$$\frac{1}{\langle\tau_{TADPL}\rangle} = \frac{1}{\langle\tau_P^0\rangle} + A \times (1 - \Phi_T) \times \exp\left(\frac{-\Delta E_{Gap}}{RT}\right)$$

Here $\langle\tau_{TADPL}\rangle$ is the delayed PL average lifetime derived from stretched exponential fits, $\langle\tau_P^0\rangle$ is the average PCA phosphorescence lifetime measured when TADPL was not operational (50 ms), A is the fastest possible excited state equilibration term, Φ_T is the triplet formation quantum yield, and ΔE_{Gap} is the energy difference between CdSe band gap and the ³PCA excited state energy. The previous equation can be rewritten in order to extract ΔE_{Gap} values presented in **Table 1 and Fig. 4:**

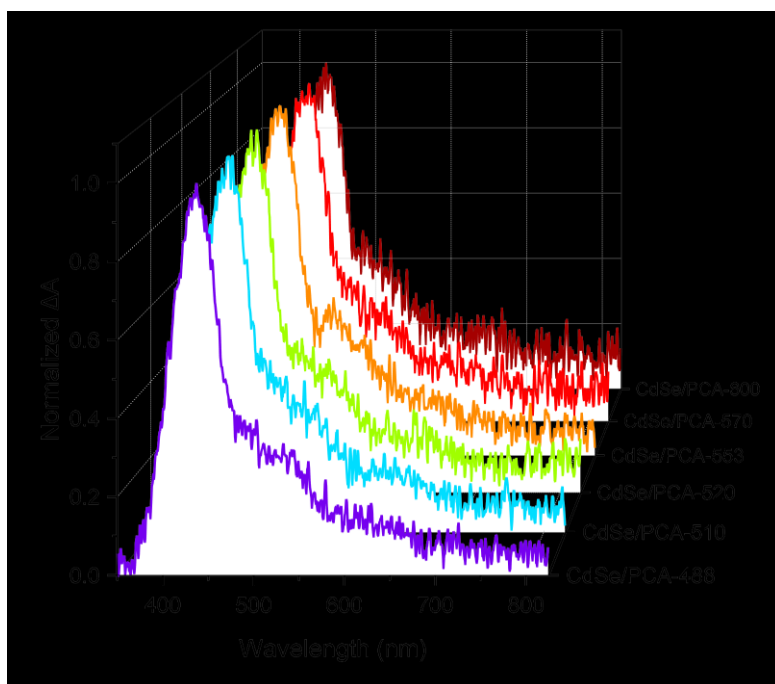
$$\ln\left(\frac{1}{\langle\tau_{TADPL}\rangle} - \frac{1}{\langle\tau_P^0\rangle}\right) = \ln(A \times (1 - \Phi_T)) + \left(\frac{-\Delta E_{Gap}}{RT}\right)$$

Photoluminescence quantum yield measurements. Relative TADPL quantum yields were measured using fluorescein ($\Phi_{std} = 0.95$ in 0.1 M NaOH), Rhodamine B ($\Phi_{std} = 0.31$ in water), Rhodamine 101 ($\Phi_{std} = 1$ in ethanol) or methylene blue ($\Phi_{std} = 0.04$ in water) as references depending on the CdSe material. Optically dilute CdSe-OA and CdSe/PCA solutions were prepared in 1 cm² quartz optical cells under both aerated and deaerated conditions at room temperature. In the solutions, the concentration of CdSe-OA or CdSe/PCA was chosen to give an absorbance of < 0.1 at the excitation wavelength. The TADPL quantum yield (Φ_{uc}) was calculated using the following equation for relative PL efficiencies. The quantum yield values reported in **Supplementary Fig. 8** are the average of three independent measurements.

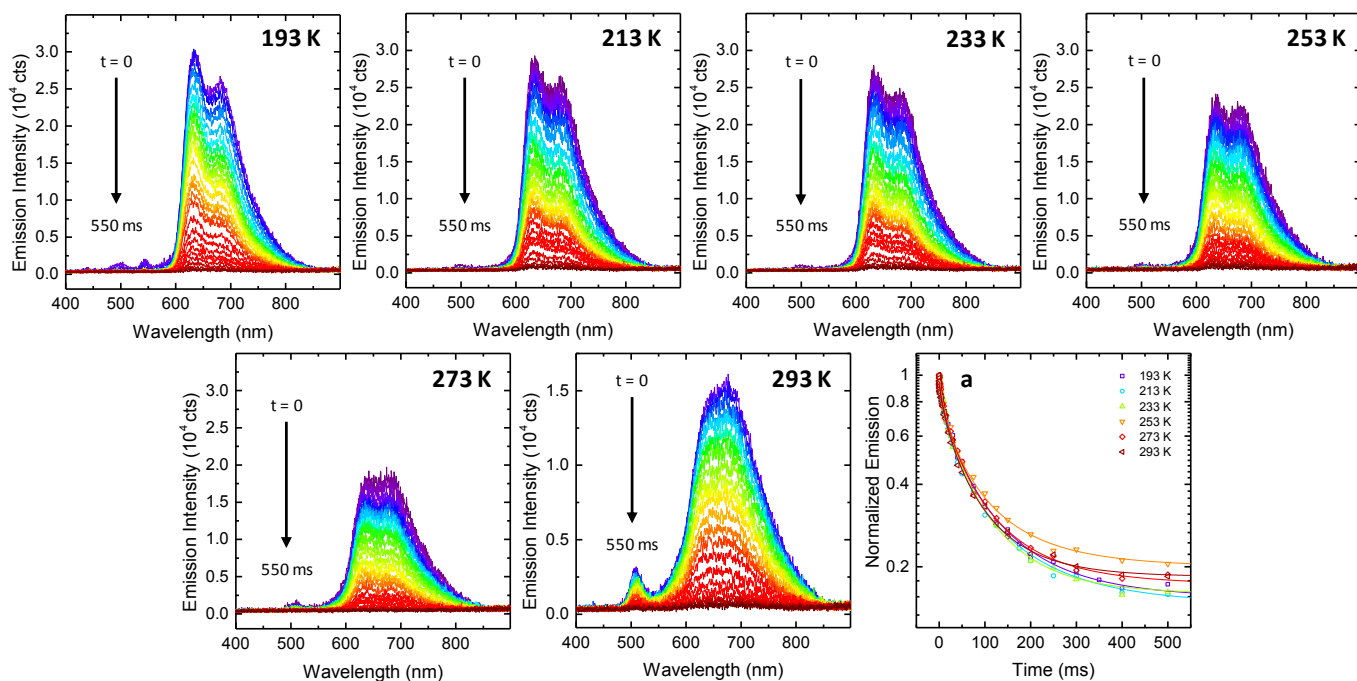
$$\Phi_{TADPL} = \Phi_{std} \times \left(\frac{A_{std}}{A_{CdSe}} \right) \left(\frac{I_{CdSe}}{I_{std}} \right) \left(\frac{\eta_{CdSe}}{\eta_{std}} \right)$$

Here Φ_{std} is the emission quantum yield of the standard, I is the integrated emission intensity of the standard or CdSe materials, A is the absorbance of the standard and CdSe materials at the excitation wavelength, and η is the refractive index of the solvents used.

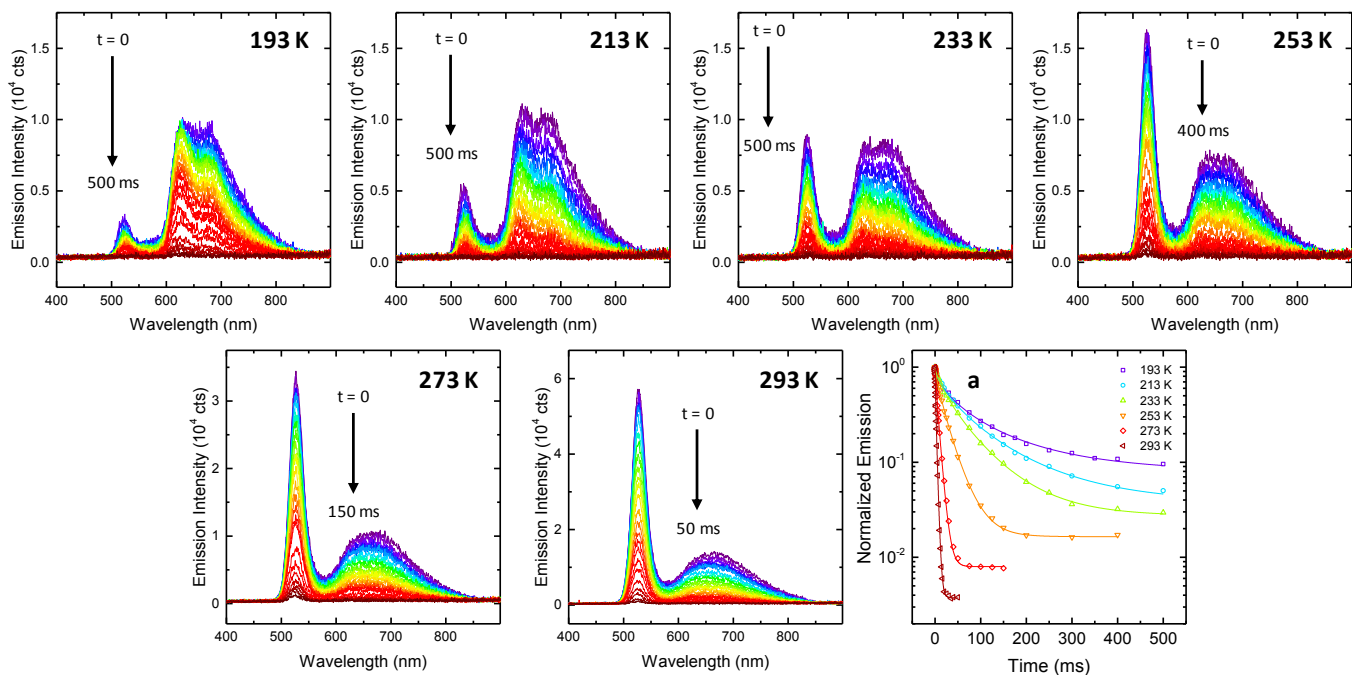
Supplementary Figures



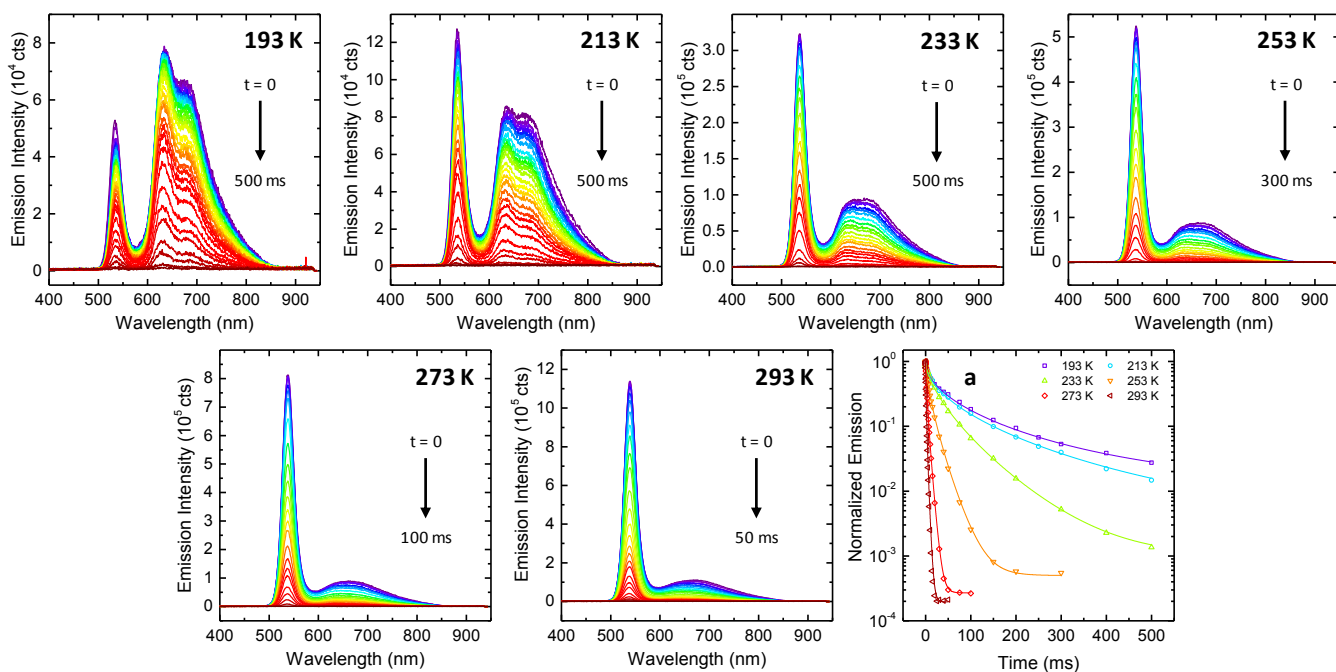
Supplementary Figure 1 | Transient absorption difference spectra of CdSe/PCA (488 to 600 nm) following selective laser excitation (488 to 600 nm, 2 mJ, 5-7 FWHM, time delay = 100 ns after the laser pulse) of the corresponding CdSe first exciton band in degassed toluene between at 293 K. Optical densities in the CdSe samples were maintained below 0.8 through the considered wavelength range. The characteristic ³PCA signal at 430 nm is present in all CdSe materials indicating efficient TTET from CdSe excited state to PCA triplet state.



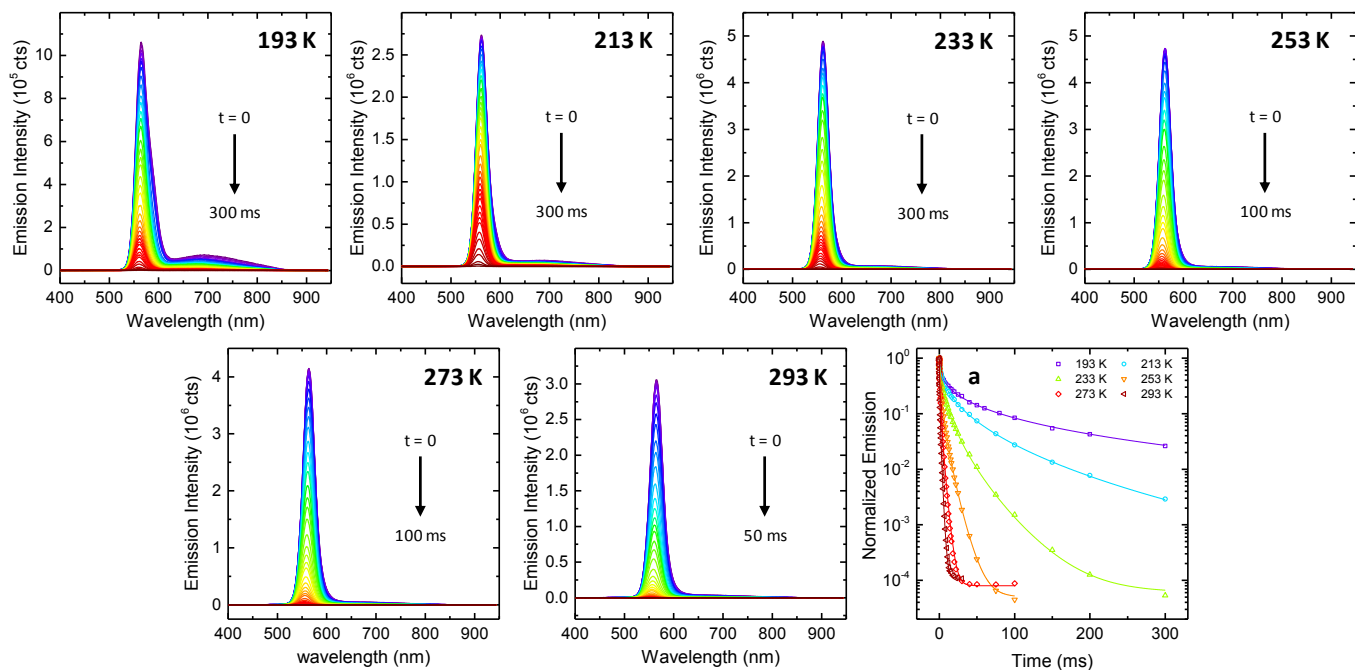
Supplementary Figure 2 | Time resolved emission spectra of CdSe/PCA 488 nm following pulsed laser excitation (488 nm, 2 mJ, 5-7 FWHM) in degassed toluene between 193 and 293 K. **a**, Photoluminescence decay curves (dots) of CdSe/PCA 488 nm and the resulting fit (solid line), according to a stretched exponential function ($I(t) = I_0 \exp(-t/\tau)^\beta$), from 193 to 293 K.



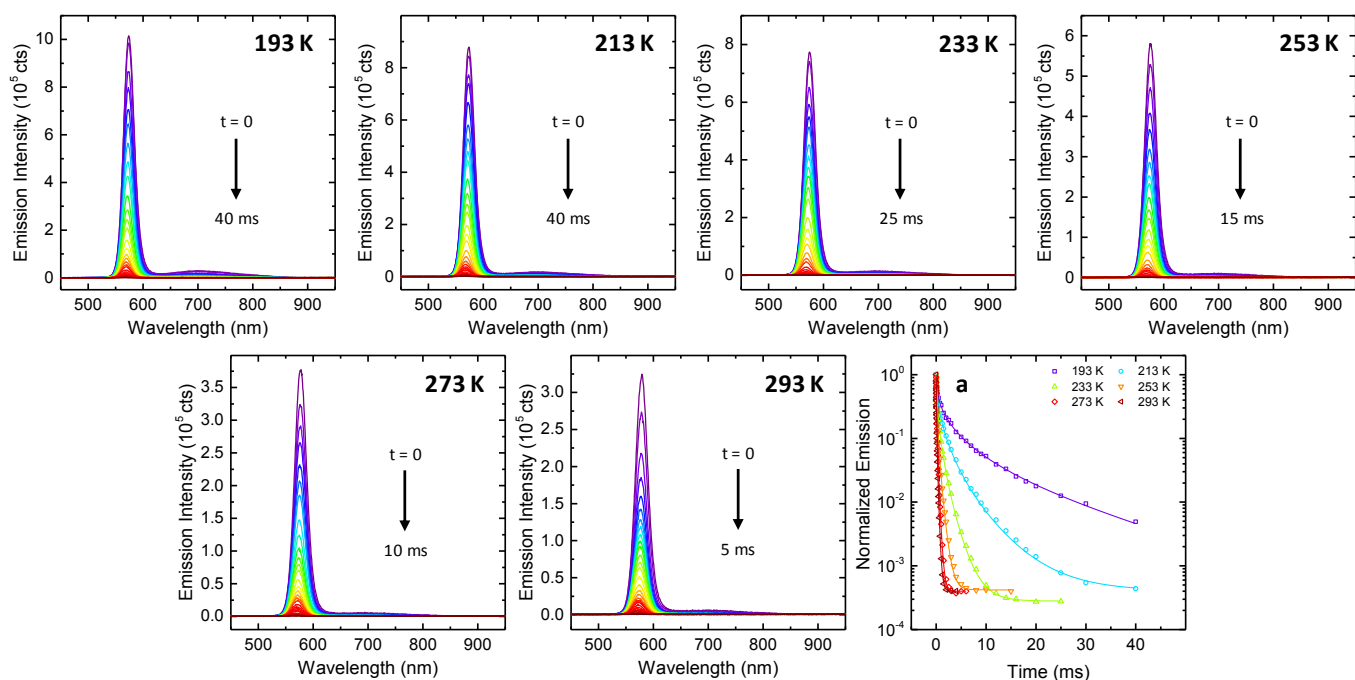
Supplementary Figure 3 | Time resolved emission spectra of CdSe/PCA 510 nm following laser excitation (510 nm, 2 mJ, 5-7 FWHM) in degassed toluene between 193 and 293 K. **a**, Photoluminescence decay curves (dots) of CdSe/PCA 510 nm and the resulting fit (solid line), according to a stretched exponential function ($I(t) = I_0 \exp(-t/\tau)^\beta$), from 193 to 293 K.



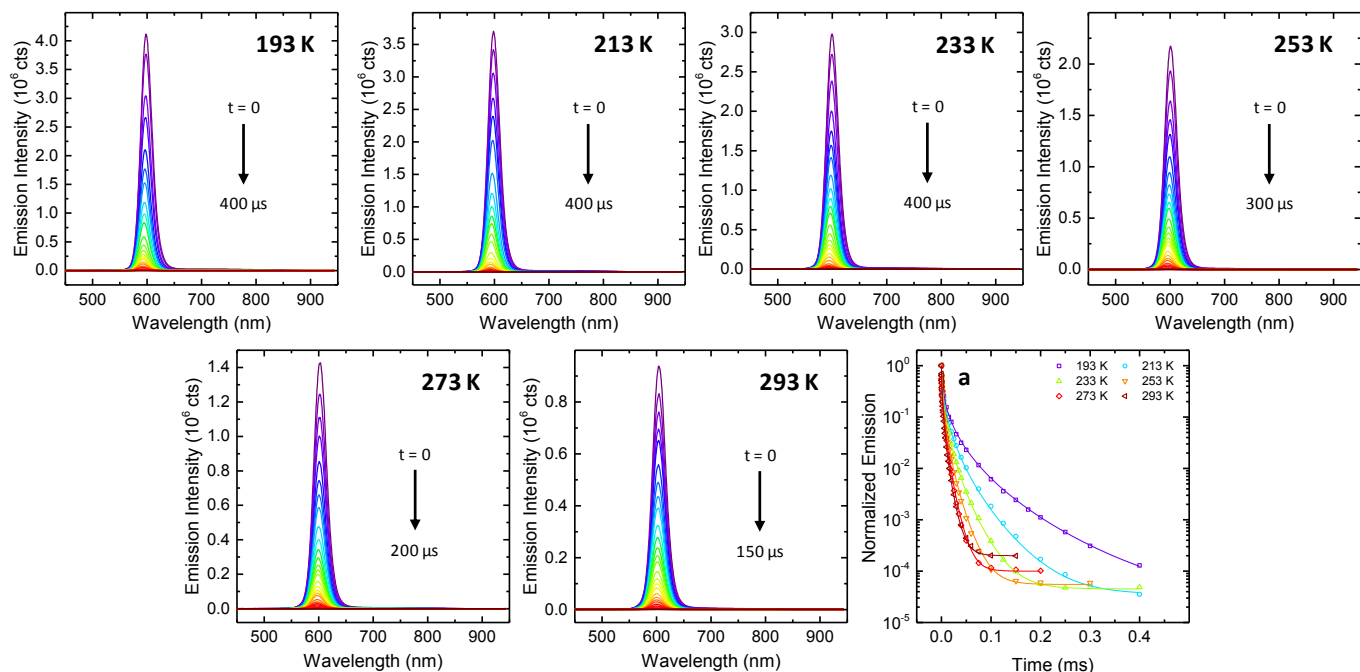
Supplementary Figure 4 | Time resolved emission spectra of CdSe/PCA 520 nm following laser excitation (520 nm, 2 mJ, 5-7 FWHM) in degassed toluene between 193 and 293 K. **a**, Photoluminescence decay curves (dots) of CdSe/PCA 520 nm and the resulting fit (solid line), according to a stretched exponential function ($I(t) = I_0 \exp(-t/\tau)^\beta$), from 193 to 293 K.



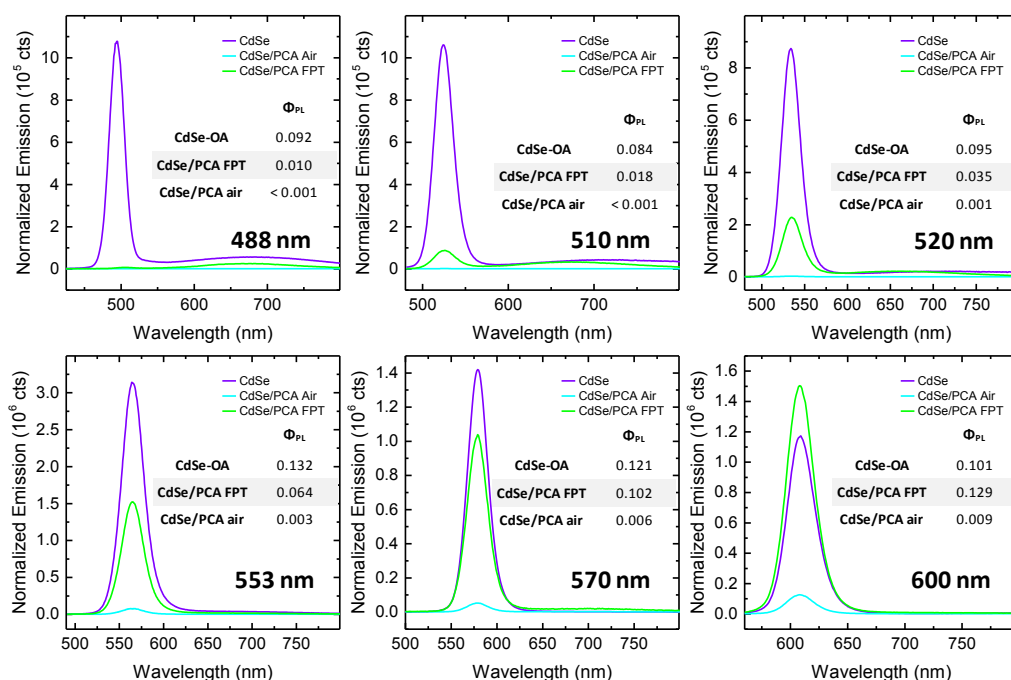
Supplementary Figure 5 Time resolved emission spectra of CdSe/PCA 553 nm following laser excitation (553 nm, 2 mJ, 5-7 FWHM) in degassed toluene between 193 and 293 K. **a**, Photoluminescence decay curves (dots) of CdSe/PCA 553 nm and the resulting fit (solid line), according to a stretched exponential function ($I(t) = I_0 \exp(-t/\tau)^\beta$), from 193 to 293 K.



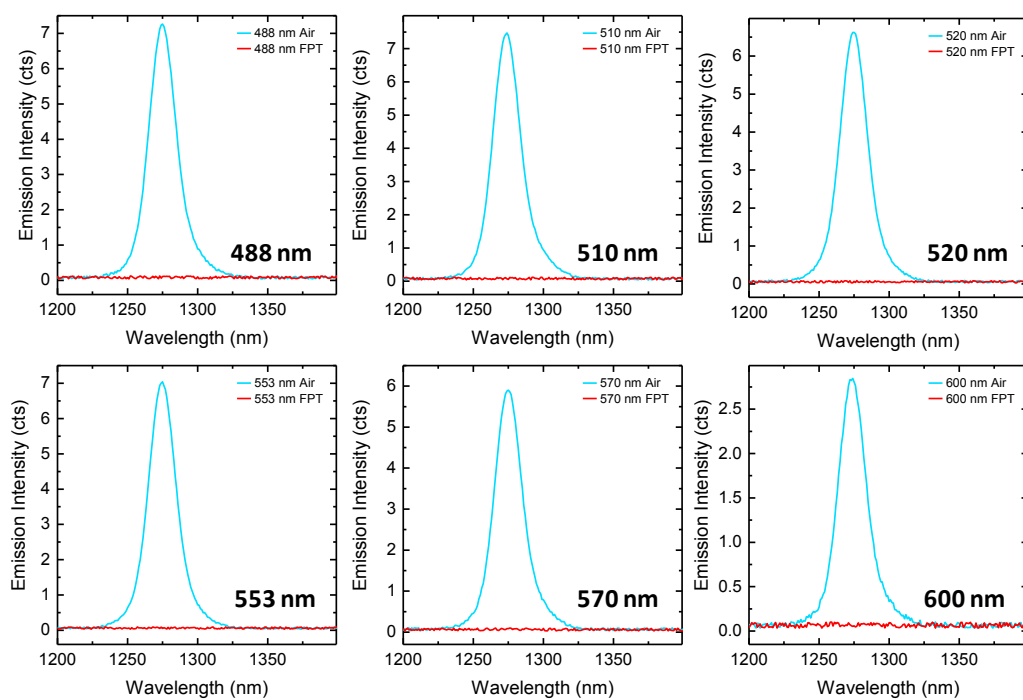
Supplementary Figure 6 Time resolved emission spectra of CdSe/PCA 570 nm following laser excitation (570 nm, 2 mJ, 5-7 FWHM) in degassed toluene between 193 and 293 K. **a**, Photoluminescence decay curves (dots) of CdSe/PCA 570 nm and the resulting fit (solid line), according to a stretched exponential function ($I(t) = I_0 \exp(-t/\tau)^\beta$), from 193 to 293 K.



Supplementary Figure 7 | Time resolved emission spectra of CdSe/PCA 600 nm following laser excitation (600 nm, 2 mJ, 5-7 FWHM) in degassed toluene between 193 and 293 K. **a**, Photoluminescence decay curves (dots) of CdSe/PCA 600 nm and the resulting fit (solid line), according to a stretched exponential function ($I(t) = I_0 \exp(-t/\tau)^\beta$), from 193 to 293 K.



Supplementary Figure 8 | Steady state photoluminescence spectra of CdSe-OA and CdSe/PCA materials from 488 to 600 nm upon continuous excitation of the first CdSe exciton band under air and degassed (FPT) conditions.



Supplementary Figure 9 | Steady state singlet oxygen phosphorescence spectra upon continuous excitation of the CdSe first exciton band in CdSe-OA and CdSe/PCA materials from 488 to 600 nm under air saturated conditions.

Supplementary Table 2 | Parameters obtained from fitting emission intensity decay displayed in **Supplementary Figs. 2 to 7**.

	Temperature (K)	1/T (10 ³ K)	β	τ (ms)	$\langle\tau\rangle$ (ms)
CdSe/PCA - 488	193	5.18	0.676	53.6	70.3
	213	4.69	0.667	55.0	70.3
	233	4.29	0.661	54.0	70.7
	253	3.95	0.671	50.1	69.9
	273	3.66	0.672	48.4	65.1
	293	3.41	0.701	39.4	51.3
CdSe/PCA - 510	193	5.18	0.663	53.1	71.0
	213	4.69	0.686	51.3	66.2
	233	4.29	0.777	42.8	49.6
	253	3.95	0.831	18.6	20.5
	273	3.66	0.872	6.1	6.5
	293	3.41	0.820	1.8	2.0
CdSe/PCA - 520	193	5.18	0.500	33.4	66.9
	213	4.69	0.526	31.7	58.0
	233	4.29	0.646	21.4	29.4
	253	3.95	0.717	7.8	9.6
	273	3.66	0.774	2.5	2.9
	293	3.41	0.720	0.8	1.0
CdSe/PCA - 553	193	5.18	0.357	7.7	36.4
	213	4.69	0.454	6.1	14.9
	233	4.29	0.534	3.0	5.4
	253	3.95	0.600	1.4	2.1
	273	3.66	0.654	0.7	0.9
	293	3.41	0.610	0.3	0.5
	Temperature (K)	1/T (10 ³ K)	β	τ (μ s)	$\langle\tau\rangle$ (μ s)
CdSe/PCA - 570	193	5.18	0.419	737.1	2167.0
	213	4.69	0.481	371.1	799.0
	233	4.29	0.533	189.4	338.8
	253	3.95	0.577	104.5	165.9
	273	3.66	0.613	62.8	91.9
	293	3.41	0.580	33.6	52.9
CdSe/PCA - 600	193	5.18	0.433	2.4	6.4
	213	4.69	0.472	2.0	4.4
	233	4.29	0.506	1.6	3.2
	253	3.95	0.534	1.4	2.4
	273	3.66	0.559	1.2	1.9
	293	3.41	0.520	0.8	1.6