Supporting Information

Auger-Assisted Electron Transfer from Photoexcited Semiconductor Quantum Dots

Authors: Haiming Zhu,^{1#} Ye Yang,^{1#} Kim Hyeon-Deuk,² Marco Califano,³ Nianhui Song,¹ Youwei Wang,⁴ Wengqing Zhang,⁴ Oleg V. Prezhdo,⁵ Tianquan Lian¹

1 Department of Chemistry, Emory University, Atlanta, Georgia, 30322, USA.

2 Department of Chemistry, Kyoto University, Kyoto, 606-8502, and Japan Science and Technology Agency, PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan 3 Institute of Microwaves and Photonics, School of Electronic and Electrical Engineering, University of Leeds, Leeds LS2 9JT, United Kingdom.

4. State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

5. Department of Chemistry, University of Rochester, Rochester, NY 14642, USA

Content list:

- 1. Experimental details
- 2. Effective mass modeling
- 3. Representative TA spectra of CdSe and CdTe with different acceptors
- 4. Size dependent ET kinetics from CdX QDs to different acceptors
- 5. Determining ET rates for 1:1 QD/acceptor complexes
- 6. Calculation of free energy change (ΔG) and reorganization energy (λ)
- 7. Size dependent ET rate and free energy change in QD/acceptor complexes
- 8. Calculation of hole density of state
- 9. Time-domain ab initio simulation of Auger-assisted ET
- 10. Atomistic semiempirical pseudopotential calculation of Auger-assisted ET

1. Experimental details

Sample preparation Oleic acid (OA) capped CdS, CdSe and CdTe quantum dots were synthesized using hot injection, noncoordinating solvent method following references.^{1,2} By controlling the precursor amount, reaction temperature and time, QDs of different sizes were obtained, as showing in Figure S1. After washing and precipitation, all QDs were dissolved in heptane solution. QD-MB⁺ (MV²⁺, AQ) molecular acceptor complexes were prepared by adding MB⁺ (MV²⁺, AQ) molecules into QDs heptane solution, followed by sonication and filtration to remove undissolved acceptor molecules. The ratio of adsorbed MB⁺ (MV²⁺, AQ) to QD was controlled by the amount of acceptor molecules added and was determined by UV-Vis absorption spectra (Agilent 8453) based on the published QDs extinction coefficients (CdSe,³ CdS and CdTe⁴). The ratios for each QD-molecule complexes with different sizes were controlled to be similar. Since MB⁺, MV²⁺ and AQ molecules are not soluble in heptane, all acceptor molecules are believed to bind to QDs surface.



Figure S1. UV-Vis absorption spectra of synthesized CdS, CdSe and CdTe QDs of different sizes (in heptane) for this study.

Transient absorption spectroscopy The femtosecond and nanosecond transient absorption (TA) spectrometers used for these studies have been described elsewhere.^{5,6} For all TA measurements, the samples were kept in a 1 mm cuvette and constantly stirred by a magnetic stirrer to avoid photodegradation. The excitation wavelength is 400 nm for CdS and CdSe QDs and 495 nm for CdTe QDs. The number of photons per NC is much less than 1 so that the contribution of multiexciton states is negligible (as can be seen from the TA spectrum of free CdS or CdSe QDs which shows negligible decay in 1ns). All data presented are averages of at least two measurements, from which error bars are calculated.

2. Effective mass modeling

To quantify the size dependent driving force and electronic coupling strength, the 1S electron energy levels, wavefunctions and electron-hole Columbic binding energy were calculated by modeling it as a particle confined in spherical well of finite depth.^{5,7} The parameters for effective mass calculations are shown in Table S1.⁸⁻¹¹ Some parameters, especially band edges, vary between literatures.¹² However, such uncertainty does not influence the trend of size dependent driving force and electronic coupling strength. The Schrodinger equation of the QD is solved

numerically to obtain the envelope wavefunction, $\Psi_e(R)$ ($\Psi_h(R)$, and energy, E_{ISe} (E_{ISh}), of the 1S electron (hole). The Columbic binding (E_{e-h}) between the electron and hole is treated as a first-order perturbation,¹³ from which the energy of the first exciton state can be calculated $E_{IS} = E_{ISe} - E_{ISh} + E_{e-h}$. This model has successfully described the 1S exciton energies and wavefunctions in core only QDs and core shell QDs.^{5-7,11,14}

	$m_e */m_0$	$m_{h}*/m_{0}$	ε/ ε ₀	CB/V (vs vacuum)	VB/V (vs vacuum)
CdS	0.19	0.8	9	-3.84	-6.34
CdSe	0.13	0.45	10	-4.04	-5.74
CdTe	0.10	0.35	10	-3.7	-5.17
ligand	1	1	1	-1	-8.4

Table S1. Parameters of bulk CdS, CdSe and CdTe used in the effective mass calculation.

Shown in Figure S2 are the calculated 1S exciton energies (black solid line) as a function of CdS (A), CdSe (B) and CdTe (C) QD radius and comparisons with experimentally determined sizing curves by Peng and coworkers (red circles)⁴. The good agreement between experimental results and our calculations validate this effective mass model. To be self-consistent, we'll rely on the calculated size dependent 1S exciton energy curve to determine our QD radii and associated 1S electron energy levels and 1S electron-hole binding energies in the driving force calculation to be discussed later. In addition, the 1S electron wavefunction $\Psi_{1Se}(R)$ is also obtained from effective mass modeling. The electron density at QDs surface $|\Psi_{1Se}(R)_0|^2$ for different QDs radius is shown in Figure S2D, which reflects the size dependent electronic coupling strength with the adsorbate as discussed in the main text.⁵



Figure S2. Comparisons of calculated QD size dependent 1S exciton energy and Peng's experimental values⁴ for CdS (A), CdSe (B) and CdTe (C). (D) calculated surface electron density $|\Psi_{1Se}(R)_0|^2$ as a function of QD radius.



3. Representative TA spectra of CdSe and CdTe with different acceptors

(i) CdSe QDs

Figure S3. Representative TA spectra of CdSe QDs R=1.3 nm (i) and CdTe QDs R=1.59 nm (ii) with different acceptors.

4. Size dependent ET kinetics from CdX QDs to different acceptors

In principle, ET rate can be determined from either the QD 1S bleach recovery or product (ground state bleach or radical) formation kinetics. For CdS-MB⁺ complexes, the MB⁺ ground state bleach formation kinetics provides a convenient probe for extracting the ET rates, as shown in Figure S4A. Unfortunately, the adsorbate radical features of AQ and MV^{2+} are much smaller than the 1S exciton bleach. Therefore, we use the 1S exciton bleach recovery to follow the ET kinetics of QD-acceptor complexes, as shown in Figure S4B and C. For reason yet to be understood, the ET times from CdSe QDs to MV^{2+} are <100 fs and cannot be reliably extracted to examine its size dependence and are not included in this study. It should be noted that for the largest CdS QDs, where ET is slow, nanosecond TA spectroscopy is employed to help extract the rate constants (ns kinetics are not shown).



(i) CdS QDs



Figure S4. Electron transfer kinetics for (i) CdS, (ii) CdSe and (iii) CdTe QDs of different sizes. MB⁺ ground state bleach formation process was used for CdS-MB⁺ complexes and 1S exciton bleach recovery kinetics for the rest. Also plotted is the extracted ET rate as a function of QD radius.

5. Determining ET rates for 1:1 QD/acceptor complexes

It has been shown that in QD-molecular acceptor systems, there exists a Poisson distribution of the number of adsorbed acceptors on each QD, which gives rise to a distribution of ET rates that depends on the average number of acceptors per QD.¹⁵⁻¹⁷ Despite best efforts, the average adsorbate-to-QD ratio varies in QD-acceptor samples of different QDs, QD sizes and adsorbates. To remove the dependence of ET rates on the adsorbate-to-QD ratio, we first determine the "intrinsic" ET rate in a 1:1 QD: acceptor complexes from the distribution of rates according to the following model.¹⁸ The intrinsic ET rates can then be compared to investigate their dependence on the property of QDs and adsorbates.

The exciton decay kinetics of free QD is given by:

$$N^{*}(t) = N^{*}(0) \cdot g(t) = N^{*}(0) \cdot \sum_{i} A_{i} e^{-k_{i0}t}$$
(S1)

where N*(t) is the excited QD population at time t after the excitation and A_i and k_{i0} are the amplitude and time constant of the ith component of the multi-exponential decay function, g(t). g(t) can be measured directly by studying the free QDs under the same conditions.

For QD-acceptor complexes, the fraction of QDs with *n* acceptors is assumed to obey the Poisson distribution 16,17 :

$$f(n) = \frac{m^n e^{-m}}{n!}$$
(S2)

Here *m* is the average number of adsorbates per QD in the sample, which can be determined from UV-Vis spectra. We further assume that ET rates from QDs to acceptors increase linearly with the number of acceptors per QD. In a QD-acceptor complex with n acceptors, the ET rate is $k_n = n \cdot k_1$, where k_l is the ("intrinsic") ET rate in a QD-acceptor complex with only one acceptor (i.e the 1:1 complex). It is also reasonable to assume that the ET rate is independent of the heterogeneous distribution of intrinsic decay rates in free QDs. With these assumptions, the exciton decay kinetics in an ensemble of QD-acceptor complexes is give by:

$$N^{*}(t) = N^{*}(0) \cdot \sum_{i} A_{i} \sum_{n=0}^{\infty} f(n) e^{-(k_{i0}+k_{n})t}$$
$$= N^{*}(0) \cdot \sum_{i} A_{i} e^{-k_{i0}t} \sum_{n=0}^{\infty} \frac{m^{n}e^{-m}}{n!} e^{-n \cdot k_{1}t}$$
$$= N^{*}(0) \cdot g(t) e^{-m} \sum_{n=0}^{\infty} \frac{m^{n}}{n!} e^{-n \cdot k_{1}t}$$
$$N^{*}(0) \cdot g(t) e^{-m} EXP(m e^{-k_{1}t})$$
(S3)

At $t_{1/2}$, when the excited QD population $N^*(t)$ in QD-acceptor complex decays to half of the initial amplitude $N^*_{t=0}$, we have

$$1/2 = N^{*}(t)/N^{*}(0) = g(t_{1/2})e^{-m}EXP(me^{-k_{1}t_{1/2}})$$

and

 $k_1 = -\frac{1}{t_{1/2}} ln[1 - \frac{ln(2g(t_{1/2}))}{m}]$ (S4)

=

 $t_{1/2}$ and g(t_{1/2}) can be determined from the transient decay kinetics of 1S exciton in QD-acceptor complexes and free QDs, respectively. Together with m determined from UV-vis spectra, the intrinsic ET rate constant in the 1:1 QD-acceptor can be calculated according to eq. S4 for all samples.

6. Calculation of free energy change (ΔG) and reorganization energy (λ)

Free energy change. For QD-molecular acceptor (QD-A) complexes, before electron transfer, the initial state of the whole system is $QD^*(1S_e, 1S_h)$ -A, the corresponding free energy can be written as:

$$E_{i} = E_{1Se} + E_{1Sh} + E_{e-h} + E_{A}$$
(S5)

where E_{ISe} and E_{ISh} are the 1S electron and hole energies, respectively, E_{e-h} the electron-hole binding energy in excited QDs, and E_A the energy of electron acceptor molecule A.

After electron transfer, the final state of the whole system is QD $(1S_h)$ -A⁻ and the system free energy is

$$E_{f} = E_{1Sh} + E_{CS} + E_{c(h)} + E_{A^{-}} + E_{c(e)}$$
(S6)

where E_{CS} is the electron-hole binding energy in charge separated state (with a 1S hole in the QD and an electron in the acceptor molecule), $E_{c(h)}$ the charging energy of putting a hole in the QD, $E_{c(e)}$ the charging energy of putting an electron in acceptor molecule, E_{A} is the energy of reduced acceptor molecule A⁻.

Therefore, the total free energy change of electron transfer is

$$\Delta G = E_{f} - E_{i}$$

$$= (E_{1Sh} + E_{CS} + E_{c(h)} + E_{A^{-}} + E_{c(e)}) - (E_{1Se} + E_{1Sh} + E_{e-h} + E_{A})$$

$$= -E_{1Se} - E_{e-h} + E_{CS} + E_{c(h)} + (E_{A^{-}} + E_{c(e)} - E_{A})$$

$$= -E_{1Se} - E_{e-h} + E_{CS} + E_{c(h)} + E_{A/A^{-}}$$
(S7)

where $E_{A^-} + E_{c(e)} - E_A$ is the free energy change for reducing the acceptor molecule A, which is denoted as E_{A-A} and related to the molecule reduction potential (ϕ_{A/A^-}) by $E_{A/A^-} = e\phi_{A/A^-}$. E_{ISe} and E_{ISh} are calculated from the effective mass modeling.

The QD charging energy $(E_{c(h)})$ has been previously calculated for ET at CdSe QD-metal oxide interface.¹⁹ Similarly, the charging energy $E_{c(h)}$ for QD-molecular acceptor complexes here can be derived as

$$E_{c(h)}(R) = \frac{0.786e^2}{8\pi R\varepsilon_{op}} + \frac{e^2}{8\pi R\varepsilon_{sol}}$$
(S8)

where R is the radius of QDs and ε_{QD} and ε_{sol} are the dielectric constant of QDs and solvent (1.92 for heptane), respectively.

Because the QD is much bigger than the adsorbed electron acceptor molecule, the electron-hole binding energy in charge separated state E_{CS} can be calculated by approximating the molecule as a point charge on the QD surface, as shown in Figure S4A. For simplification, assuming infinite potential from capping ligand, the 1S hole envelop wavefunction of QDs is

$$\psi(r) = \frac{\sin(\pi r / R)}{r\sqrt{2\pi R}} \qquad (S9)$$

Then the distribution of 1S hole is

$$\rho(r) = e |\psi(r)|^2 = e \frac{\sin^2(\pi r / R)}{2\pi R r^2}$$
(S10)

The coulomb attraction between the electron and hole in charge separated state is

$$E_{cs}(R) = \int_{0}^{R} dr \int_{0}^{\pi} d\theta \int_{0}^{2\pi} d\varphi \frac{r^{2} \sin \theta e^{2} \rho(r)}{4\pi \varepsilon_{QD} \sqrt{r^{2} \sin^{2} \theta + (R - r \cos \theta)^{2}}}$$
(S11)

The calculated $E_{c(h)}$, E_{CS} , E_{e-h} for CdSe QDs of different sizes are shown in Figure S5B. Together with E_{ISe} (calculated from effective mass modeling) and molecule acceptor reduction potential energy E_{A-A} , the free energy change (ΔG) for different size QDs can be obtained.



Figure S5. (A) The electron in acceptor molecule is treated as a point charge on QD surface for E_{CS} calculation. (B) Calculated charging energy $(E_{c(h)})$, electron-hole binding energy in charge separated state (E_{CS}) , electron-hole binding energy in excited QDs (E_{e-h}) as a function of QD radius in CdSe.

Reorganization energy. The reorganization energy λ for ET processes contains the inner-sphere contribution from the nuclear displacement of the reactants and products (λ_i) and the outer-sphere contribution (λ_o) from the solvent dielectric response. For QD-molecular acceptor complex, λ_i mostly comes from the electron acceptor molecule and the QD contribution is negligible because of the weak electron-lattice coupling.²⁰ Previous size dependent ET studies of QDs on semiconductor oxides suggest a QD reorganization energy of about 10 meV.^{19,21} Previous quantum mechanical calculations on similar aromatic organic molecules yield λ_i values of 100-300 meV.²²⁻²⁴ The dielectric continuum model predicts a negligible value of solvent reorganization energy λ_o in nonpolar solvents,²⁵ which has been shown to be inconsistent with some experimental results.^{26,27} A molecular solvation model that includes the quadruple contribution yields λ_o in the range 100-200 meV for nonpolar solvents.²⁸ Therefore, the total

reorganization energy (λ) for the QD-molecule acceptor complexes in heptane is estimated to be 200 ~ 500 meV.

7. Size dependent ET rate and free energy change in QD/acceptor complexes

Table S2. Rate constant (k_{ET}) and driving force (- ΔG) for ET from CdX QDs to acceptors (MB⁺, MV²⁺ and AQ) as a function of QD radius.

radius /nm	$CdS-MB^+$		CdS-MV ²⁺		CdS-AQ	
	-∆G/eV	k_{ET}/s^{-1}	-∆G/eV	k_{ET}/s^{-1}	-∆G/eV	k_{ET}/s^{-1}
1.2	1.01	$(2.60 \pm 0.60) \times 10^{10}$	0.57	$(3.50 \pm 0.52) \times 10^{10}$	0.31	$(6.19 \pm 1.55) \times 10^9$
1.27	0.99	$(2.44 \pm 0.34) \times 10^{10}$	0.55	$(2.50 \pm 0.60) \times 10^{10}$	0.29	$(5.34 \pm 0.08) \times 10^9$
1.35	0.97	$(2.11 \pm 0.72) \times 10^{10}$	N/A		0.27	$(4.30 \pm 1.01) \times 10^9$
1.42	0.96	$(1.35 \pm 0.16) \times 10^{10}$	N/A		0.26	$(1.58 \pm 0.47) \times 10^9$
1.53	0.93	$(1.19 \pm 0.07) \times 10^{10}$	0.49	$(9.55 \pm 1.04) \times 10^9$	0.23	$(1.13 \pm 0.13) \times 10^9$
1.6	0.92	$(1.07 \pm 0.14) \times 10^{10}$	N/A		0.22	$(6.51 \pm 0.32) \times 10^8$
1.79	0.9	$(6.26 \pm 0.50) \times 10^9$	0.46	$(3.65 \pm 0.18) \times 10^9$	0.2	$(1.53 \pm 0.34) \times 10^8$
1.96	0.88	$(3.75 \pm 0.45) \times 10^9$	N/A		0.18	$(6.47 \pm 0.77) \times 10^7$
2.15	0.86	$(2.41 \pm 0.60) \times 10^9$	0.42	$(1.46 \pm 0.22) \times 10^9$	0.16	$(1.76 \pm 0.12) \times 10^7$

(i) CdS QDs

(ii) CdSe QDs

radius /nm	C	dSe-MB ⁺	CdSe-AQ		
	-∆G/eV	k_{ET}/s^{-1}	-∆G/eV	k_{ET}/s^{-1}	
0.99	0.9	$(2.70 \pm 0.35) \times 10^{11}$	0.2	$(9.87 \pm 0.77) \times 10^{10}$	
1.05	0.88	$(3.66 \pm 1.37) \times 10^{11}$	0.18	$(1.56 \pm 0.99) \times 10^{10}$	
1.10	0.86	$(5.41 \pm 0.77) \times 10^{11}$	0.16	$(1.43 \pm 0.06) \times 10^{10}$	
1.22	0.83	$(5.25 \pm 1.25) \times 10^{11}$	0.13	$(6.65 \pm 4.23) \times 10^9$	
1.3	0.81	$(4.66 \pm 0.28) \times 10^{11}$	0.11	$(1.35 \pm 0.17) \times 10^9$	
1.36	0.8	$(3.10 \pm 0.40) \times 10^{11}$		N/A	
1.42	0.79	$(3.51 \pm 0.02) \times 10^{11}$	0.09	$(8.50 \pm 1.50) imes 10^8$	
1.5	0.77	$(2.78 \pm 0.45) \times 10^{11}$		N/A	
1.63	0.75	$(2.50 \pm 1.02) \times 10^{11}$	0.05	$(3.10 \pm 2.02) \times 10^8$	
1.74	0.74	$(2.24 \pm 1.88) \times 10^{11}$	0.04	$(1.00 \pm 0.87) imes 10^8$	
1.94	0.72	$(7.13 \pm 0.24) \times 10^{10}$		N/A	

(iii) CdTe QDs

radius /nm	CdTe-MB ⁺		CdTe- MV ²⁺		CdTe-AQ	
	-∆G/eV	k_{ET}/s^{-1}	-∆G/eV	k_{ET}/s^{-1}	-∆G/eV	k_{ET}/s^{-1}
1.11	1.31	$(9.32 \pm 1.80) \times 10^{10}$	0.87	$(2.48 \pm 0.72) \times 10^{12}$	0.61	$(4.22 \pm 0.51) \times 10^{11}$
1.18	1.28	$(8.21 \pm 1.15) \times 10^{10}$	0.84	$(2.36 \pm 0.47) \times 10^{12}$	0.58	$(4.33 \pm 0.97) \times 10^{11}$
1.31	1.24	$(5.88 \pm 0.23) \times 10^{10}$	0.8	$(1.49 \pm 0.47) \times 10^{12}$	0.54	$(1.33 \pm 0.05) \times 10^{10}$
1.4	1.22	$(5.28 \pm 1.37) \times 10^{10}$	0.78	$(1.14 \pm 0.25) \times 10^{12}$	0.52	$(9.42 \pm 0.56) \times 10^{10}$
1.59	1.18	$(6.05 \pm 0.60) \times 10^{10}$	0.74	$(1.25 \pm 1.04) \times 10^{12}$	0.48	$(9.38 \pm 0.18) \times 10^{10}$
1.66	1.16	$(3.49 \pm 0.17) \times 10^{10}$	0.72	$(9.33 \pm 1.86) \times 10^{11}$	0.46	$(3.49 \pm 0.45) \times 10^{10}$
1.84	1.13	$(4.23 \pm 0.64) \times 10^{10}$	0.69	$(6.27 \pm 0.87) \times 10^{11}$	0.43	$(2.72 \pm 4.17) \times 10^{10}$
2.03	1.11	$(3.73 \pm 0.89) \times 10^{10}$	0.67	$(2.69 \pm 0.10) \times 10^{11}$	0.41	$(1.56 \pm 0.23) \times 10^{10}$

8. Calculation of hole density of state



Figure S6. (A) Calculated density of state of CdSe QDs with radius between 0.8 nm and 2 nm. (B) Density of state of hole with energy E_h below the valance band edge ($E_h = E-E_v$) for different CdSe QDs radius (solid lines). The dashed lines show the $E_h R^3$ fitting.

The density of state of CdX (X=S, Se, Te) QDs (radius between 0.8 nm and 2 nm) were calculated by using Siesta code with generalized-gradient approximation (GGA). Double- ζ (DZ) is used as a basis set. Only Gama point is used for k-point sample. The supercells contain a vacuum region of at least 10 Å, which is large enough to reduce the periodic interactions. The lattice parameters for CdSe (CdS/CdTe) of our calculation are a=4.419 (4.236/4.716) Å, c=7.212 (6.883/7.725) Å, and the internal parameter for CdSe (CdS/CdTe) is u=0.3757 (0.3779/0.375).

The quantum dots are cut out from the bulk wurtzite lattice by a given sphere radius. The structure is accepted only when the numbers of Cd atoms and X (S, Se, Te) atoms are equal and the dangling bonds is no more than two. And we use the same passivation method as in reference.²⁹ We found that the passivation atoms have negligible effect on states within the valence band. They remove the dangling bond of surface atoms and push the unoccupied surface states into the valence band. The calculated DOS for CdSe QDs are shown in Figure S6A. The hole density of states near the valence band edge for CdSe QDs are shown in Figure S6B. The hole DOS within ~1 eV of the valence band edge can be well reproduced by $DOS = N_{QD}E_hR^3$, where N_{QD} is a material dependent prefactor, E_h is the hole energy below the valence band edge and R is the QD radius.

9. Time-domain ab initio simulation of Auger-assisted ET



Figure S7. Time-domain *ab initio* modeling of Auger-assisted ET from CdSe QD to MB. The QD/MB⁺ complex is drawn with the orbital distributions of the key electronic states: QD HOMO, QD LUMO and MB LUMO.

We have performed real-time atomistic simulation of ET from the CdSe QD electron donor to the MB electron acceptor, accompanied by Auger-type excitation of the hole within the QD. The system under investigation is shown in Figure S8. In order to account for the Auger excitation of the hole, accompanying the ET, we adopted an exciton representation, illustrated in Figure S9. The band gap excitation of the QD is the reactant state. The electron-phonon relaxation in the QD is significantly faster³⁰ than the timescale of the current ET, allowing us to exclude higher energy QD excitons from consideration and to achieve significant computational savings.^{31,32} The remaining states in the exciton basis are product states with the electron transferred to the MB LUMO, indicated in Figure S9 by the red line, and the hole in one of the valence band (VB) orbitals of the QD. There are 43 product states, corresponding to the number of VB states, N_{VB} , considered explicitly. Note that including both conduction and VB states of the QD rapidly increases the size of the exciton basis. For instance, consideration of both single and double excitons extends the basis size to hundreds of thousands for QDs of the size considered here, ^{31,32} and to astronomical numbers for larger QDs.^{33,34} The ET driving force, ΔG , is the difference between the energies of the QD LUMO and the MB LUMO, Figure S9.



Figure S8. Adiabatic exciton basis used in the TDDFT/NAMD simulation. The QD HOMO-LUMO exciton is the reactant state. The product states contain the electron in the MD LUMO and the hole in one of the VB orbitals of the QD.

The time-domain *ab initio* simulations are performed by combining real-time time-dependent density functional theory (TDDFT) with non-adiabatic (NA) molecular dynamics (MD). The original implementation is described in Ref.³⁵ and the extension to Auger-type processes are given in Refs.^{31,32} The atomic vibrational motions are treated using classical mechanics. The evolution of the electronic degrees of freedom is represented by TDDFT, which is formulated in the Kohn-Sham (KS) representation. The adiabatic KS orbitals depend on atomic coordinates, and transitions between adiabatic states occur due to the NA couplings, as explained below. The time-dependent single-electron KS orbitals, $\varphi_p(\mathbf{r}, t)$, are evolved using the standard TDKS equations

$$i\hbar \frac{\partial \varphi_p(\mathbf{r},t)}{\partial t} = H(\varphi(\mathbf{r},t))\varphi_p(\mathbf{r},t), \quad p = 1, \dots, N_e$$
(S12)

where N_e is the number of electrons. The equations are coupled through the non-linear dependence of the Hamiltonian H on the electron density, obtained by summing over all occupied KS orbitals, and other parameters of a chosen DFT functional, e.g. density gradient.

Expanding the time-dependent KS orbitals $\varphi_p(\mathbf{r}, t)$ in the adiabatic KS orbital basis $\tilde{\varphi}_k(\mathbf{r}; \mathbf{R})$,

$$\varphi_p(\mathbf{r}, t) = \sum_{k=1}^{N_e} c_{pk}(t) | \tilde{\varphi}_k(\mathbf{r}; \mathbf{R}) \rangle,$$
(S13)

transforms eq.(S5) into an equation for the expansion coefficients³⁵

$$i\hbar \frac{\partial c_{pk}(t)}{\partial t} = \sum_{m=1}^{N_{\rm e}} c_{pm}(t) (\varepsilon_m \delta_{km} - i\hbar \boldsymbol{d}_{km} \cdot \dot{\boldsymbol{R}}).$$
(S14)

The adiabatic KS orbitals, $\tilde{\varphi}_k(r; R)$, are obtained by solving the time-independent DFT equation for fixed atomic positions at each moment along the MD trajectory. The NA coupling,

$$\boldsymbol{d}_{km} \cdot \dot{\boldsymbol{R}} = \langle \tilde{\varphi}_k(\boldsymbol{r}; \boldsymbol{R}) | \boldsymbol{\nabla}_{\boldsymbol{R}} | \tilde{\varphi}_m(\boldsymbol{r}; \boldsymbol{R}) \rangle \cdot \dot{\boldsymbol{R}} = \left\langle \tilde{\varphi}_k(\boldsymbol{r}; \boldsymbol{R}) \left| \frac{\partial}{\partial t} \right| \tilde{\varphi}_m(\boldsymbol{r}; \boldsymbol{R}) \right\rangle,$$
(S15)

stems from the dependence of the adiabatic KS orbitals on the phonon dynamics, $\mathbf{R}(t)$, and represents electron-phonon interactions. Since the NA coupling is proportional to the nuclear velocity, $\dot{\mathbf{R}}$, NA transitions would never happen under the Born-Oppenheimer approximation with stationary atoms.

The exciton, two-particle, electron-hole representation of the above equations is obtained using the second quantization formulism. ^{31,32} Starting from the ground state, $|\phi_g(\mathbf{r}; \mathbf{R})\rangle$, single exciton (SE) states, $|\phi_{SE}^{i,j}(\mathbf{r}; \mathbf{R})\rangle$, are defined as

$$\left|\phi_{\rm SE}^{i,j}\right\rangle = \hat{a}_i^{\dagger} \hat{a}_j \left|\phi_{\rm g}\right\rangle \tag{S16}$$

where the electron creation and annihilation operators, \hat{a}_i^{\dagger} and \hat{a}_j , generate and annihilate an electron in the *i*th and *j*th adiabatic KS orbitals, respectively. The total wave function is then expanded as

$$|\Psi(\mathbf{t})\rangle = C_{g}(t) \left|\phi_{g}\right\rangle + \sum_{i,j} C_{SE}^{i,j}(t) \left|\phi_{SE}^{i,j}\right\rangle.$$
(S17)

Similarly to eq.(S7), substitution of eq.(S10) into the TDKS equations leads to the equations of motion for the expansion coefficients appearing in eq.(S10):

$$i\hbar \frac{\partial C_X(t)}{\partial t} = C_X(t)E_X - i\hbar C_g(t)\boldsymbol{d}_{X;g} \cdot \dot{\boldsymbol{R}} - i\hbar \sum_{i',j'} C_{SE}^{i',j'}(t)\boldsymbol{d}_{X;SE,i',j'} \cdot \dot{\boldsymbol{R}}.$$
 (S18)

Now, X corresponds to either the ground state or a SE, E_X is the excitation energy relative to the ground state, and the NA coupling is expressed by

$$\boldsymbol{d}_{X;Y} \cdot \dot{\boldsymbol{R}} = \langle \phi_X | \boldsymbol{\nabla}_{\boldsymbol{R}} | \phi_Y \rangle \cdot \dot{\boldsymbol{R}} = \left\langle \phi_X \left| \frac{\partial}{\partial t} \right| \phi_Y \right\rangle.$$
(S19)

The atomistic simulation of the Auger-assisted ET dynamics is performed by directly solving eq.(S20) with the time-dependent NA couplings and energies obtained from the *ab initio* MD simulation. The initial SE state is created with the electron in the QD LUMO and the hole in the QD HOMO. NA transitions lead to ET and are accompanied by electron-vibrational energy exchange. The adiabatic ET mechanism is also possible within the current simulation; however, it remains less efficient than NA ET, due to a high density of acceptor states and a relatively weak donor-acceptor coupling.³⁶

The electronic structure and adiabatic MD are obtained within the VASP software package, using the PW91 density functional and projector-augmented-wave pseudopotentials.³⁷ The geometry of the QD/MB complex is fully optimized at zero temperature. Then, the complex is heated up to an ambient temperature by repeated velocity rescaling, and a 10 ps microcanonical trajectory is calculated in the ground electronic state using the Verlet algorithm with a 1 fs time-step. 51 initial conditions are sampled from this trajectory to initiate the TDDFT/NAMD simulation. The TDKS equations are solved with a 1 as time-step. The adiabatic KS orbitals and the NA coupling are updated every MD time-step. The obtained results are presented in Figure 4 of the main text.

11. Atomistic semiempirical pseudopotential calculation of Auger-assisted ET

In order to investigate Auger-assisted ET (AAET) in QDs with sizes in the experimental range, we carried out atomistic semiempirical pseudopotential calculations. As we cannot experimentally determine the exact location of the molecule on the QD surface, for every dot size considered we calculate electron transfer times to traps located at several different positions on the surface (Fig. S10). Consistently with the TDDFT treatment (section S10), the basis used in these calculations is similar to that depicted in Fig. S9: The transition times of an electron from the delocalized QD-LUMO state (in the presence of a QD-HOMO hole - reactant state in Fig. S8) to a localized state on the dot surface with the same energy as the MB-LUMO, accompanied by the excitation of a hole from the delocalized QD-HOMO level to one of a set of $N_{\rm VB}$ =30 delocalized deep levels in the QD VB (product state in Fig. S9), centered around the state with energy $E_{hdeep} = E_{HOMO} - (E_{QD-LUMO} - E_{MB-LUMO})$, were calculated using Fermi's Golden Rule according to³³

$$(\tau_{AAET})_i^{-1} = \frac{\Gamma}{\hbar} \sum_n \frac{|\langle i|\Delta H|f_n \rangle|}{\left(E_{f_n} - E_i\right)^2 + (\Gamma/2)^2}$$
(S20)

where $|i\rangle = |e_{QD-LUMO}; h_{QD-HOMO}\rangle$ and $|f\rangle = |e_{MB-LUMO}; h_{QD-deep}\rangle$ are the initial (reactant) and final (product) states (see Fig. S8), E_i and E_{fn} are their energies (solutions of the single-particle Schroedinger equation, calculated using the plane-wave semiempirical pseudopotential method described in ref.³⁸, including spin-orbit coupling), ΔH is the Coulomb interaction, and \hbar/Γ is the lifetime of the final states. The regional screening developed in ref.³³ was used in the computation of (S22): the microscopic dielectric function of the dot was expressed in terms of a core and a surface term as

$$\epsilon^{-1}(r,r') = \epsilon_{out}^{-1}(r,r') + \left(\epsilon_{in}^{-1}(r,r') - \epsilon_{out}^{-1}(r,r')\right) m(r)m(r')$$
(S21)

where m(r) changes smoothly from 1, when *r* is inside the dot $(r < R_{QD} - d)$, to 0, when *r* is outside $(r > R_{QD} + d)$, yielding $\epsilon(r, r') = \epsilon_{in}$ inside the dot, while $\epsilon(r, r') = \epsilon_{out}$, when *r*, or *r'*, or both are outside the dot (here *d* is chosen = 2 Å, however the Auger rates were found³⁹ to be largely unaffected by the choice d = 1 Å). While ϵ_{in} was assumed to be equal to the CdSe bulk dielectric constant, the choice $\epsilon_{out} = 2$ accounts for the solvent (heptane).



Figure S9. Auger-assisted ET rates calculated in QDs with different sizes (R=1.02 nm, black lines; R=1.46 nm, red lines; R=1.92, green lines) for selected positions of the localized acceptor state on the surface, as a function of the variation of the trap depth $\delta\Delta G$, with respect to the MB LUMO ($\delta\Delta G = 0$, where ΔG is the difference between the energies of the QD LUMO and the MB LUMO, see Fig. S9).



Figure S10. Atomistic mapping of the electron transfer times calculated, for three different QD sizes, with the semiempirical pseudopotential method. The orange and yellow spheres represent Se and Cd atoms, respectively. In every simulation run only a single acceptor (adsorbed to a Cd atom) was present on the surface. The colored spheres represent the different surface Cd atoms to which the acceptor was attached, and the different colors quantify the calculated ET times (at $\delta\Delta G = 0$).

The results are presented in Figures S9 and S10. The overall trend with size is evidenced in Fig. S10, showing Auger-assisted electron trapping rates, calculated for different dot radii as a function of the variation of the trap depth $\delta\Delta G$ with respect to the MB LUMO (which corresponds to $\delta\Delta G = 0$. Here ΔG is the difference between the energies of the QD LUMO and the MB LUMO, as depicted in Fig. S8), for selected positions of the localized acceptor state on the surface. Atomistically accurate maps of the ET transfer times calculated, for each size, for all different surface locations considered, are presented in Fig. S10. We find that the transfer rates for a specific dot size vary slightly depending on the location of the trap on the dot surface, with the smallest dots exhibiting the least sensitivity $[k_{ET} = (4.7 \pm 3) \times 10^{11} \text{ s}^{-1}]$ to the trap position compared to the largest ones $[k_{ET} = (4.6 \pm 3.6) \times 10^{10} \text{ s}^{-1}]$, reflecting different degrees of wave function overlap between delocalized core states and localized surface states (Fig. S11). Despite the simplicity of this approach, where the MB molecule is modeled only through the position of its LUMO, our calculated ET rates reproduce remarkably well our experimental data, both qualitatively (reflecting the observed trend with size) and quantitatively (see Table S2).

Finally, using this approach [Eq.(S22)], we also calculated non-Auger-assisted ET rates between the QD HOMO-LUMO ground (reactant) state ($|i\rangle = |e_{QD-LUMO}; h_{QD-HOMO}\rangle$) and a product state where the electron is in the MB-LUMO but the hole is frozen in the QD-HOMO ($|f\rangle = |e_{MB-LUMO}; h_{QD-HOMO}\rangle$), i.e., there is no energy transfer to the hole. The resulting ET times are at least three orders of magnitude longer (from a few to a few hundreds of nanoseconds) than the calculated AAET times.

References

- (1) Yu, W. W.; Peng, X. G. Angew. Chem. Int. Ed. 2002, 41, 2368.
- (2) Yu, W. W.; Wang, Y. A.; Peng, X. G. Chem. Mater. 2003, 15, 4300.

(3) Jasieniak, J.; Smith, L.; Embden, J. v.; Mulvaney, P.; Califano, M. J. Phys. Chem. C 2009, 113, 19468.

- (4) Yu, W. W.; Qu, L. H.; Guo, W. Z.; Peng, X. G. Chem. Mater. 2003, 15, 2854.
- (5) Zhu, H.; Song, N.; Lian, T. J. Am. Chem. Soc. 2010, 132, 15038.
- (6) Zhu, H.; Song, N.; Lian, T. J. Am. Chem. Soc. 2011, 133, 8762.
- (7) Zhu, H.; Song, N.; Rodríguez-Córdoba, W.; Lian, T. J. Am. Chem. Soc. 2012, 134,

4250.

- (8) Berger, L. I. Semiconductor materials; CRC Press, 1997.
- (9) Haus, J. W.; Zhou, H. S.; Honma, I.; Komiyama, H. Phys. Rev. B 1993, 47, 1359.
- (10) Wei, S.-H.; Zunger, A. Appl. Phys. Lett. **1998**, 72, 2011.
- (11) Pellegrini, G.; Mattei, G.; Mazzoldi, P. J. Appl. Phys. 2005, 97, 073706.
- (12) Finklea, H. O. Semiconductor electrodes; Elsevier Science Ltd, 1988; Vol. 55.
- (13) Brus, L. E. J. Chem. Phys. 1983, 79, 5566.
- (14) Dabbousi, B. O.; RodriguezViejo, J.; Mikulec, F. V.; Heine, J. R.; Mattoussi, H.; Ober, R.; Jensen, K. F.; Bawendi, M. G. J. Phys. Chem. B 1997, 101, 9463.

(15) Boulesbaa, A.; Issac, A.; Stockwell, D.; Huang, Z.; Huang, J.; Guo, J.; Lian, T. J. Am. Chem. Soc. 2007, 129, 15132.

(16) Morris-Cohen, A. J.; Frederick, M. T.; Cass, L. C.; Weiss, E. A. J. Am. Chem. Soc. **2011**, 133, 10146.

- (17) Song, N.; Zhu, H.; Jin, S.; Zhan, W.; Lian, T. ACS Nano 2011, 5, 613.
- (18) Rodgers, M. A. J.; Da Silva E Wheeler, M. F. Chem. Phys. Lett. 1978, 53, 165.
- (19) Tvrdy, K.; Frantsuzov, P. A.; Kamat, P. V. Proc. Natl. Acad. Sci. 2011, 108, 29.
- (20) Marcus, R. A. J. Chem. Phys. 1965, 43, 679.
- (21) Cánovas, E.; Moll, P.; Jensen, S. A.; Gao, Y.; Houtepen, A. J.; Siebbeles, L. D. A.;
- Kinge, S.; Bonn, M. Nano Lett. 2011, 11, 5234.
 - (22) Klimkāns, A.; Larsson, S. Chem. Phys. 1994, 189, 25.
- (23) Amashukeli, X.; Winkler, J. R.; Gray, H. B.; Gruhn, N. E.; Lichtenberger, D. L. J.
- Phys. Chem. A 2002, 106, 7593.
- (24) Gruhn, N. E.; Macías-Ruvalcaba, N. A.; Evans, D. H. J. Phys. Chem. A 2006, 110, 5650.
 - (25) Marcus, R.; Sutin, N. Biochim. Biophys. Acta 1985, 811, 265.

(26) Reynolds, L.; Gardecki, J. A.; Frankland, S. J. V.; Horng, M. L.; Maroncelli, M. J. Phys. Chem. 1996, 100, 10337.

- (27) Cortes, J.; Heitele, H.; Jortner, J. J. Phys. Chem. 1994, 98, 2527.
- (28) Zimmt, M. B.; Waldeck, D. H. J. Phys. Chem. A 2003, 107, 3580.
- (29) Huang, X.; Lindgren, E.; Chelikowsky, J. R. Phys. Rev. B 2005, 71, 165328.
- (30) Kilina, S. V.; Kilin, D. S.; Prezhdo, O. V. ACS Nano 2009, 3, 93.
- (31) Hyeon-Deuk, K.; Prezhdo, O. V. Nano Lett. 2011, 11, 1845.
- (32) Hyeon-Deuk, K.; Prezhdo, O. V. ACS Nano 2012, 6, 1239.
- (33) Wang, L. W.; Califano, M.; Zunger, A.; Franceschetti, A. Phys. Rev. Lett. 2003,

91, 056404.

- (34) Baer, R.; Rabani, E. *Nano Lett.* **2012**, *12*, 2123.
- (35) Craig, C. F.; Duncan, W. R.; Prezhdo, O. V. Phys. Rev. Lett. 2005, 95, 163001.
- (36) Long, R.; English, N. J.; Prezhdo, O. V. J. Am. Chem. Soc. 2012, 134, 14238.
- (37) Kresse, G.; Furthmüller, J. Phys. Rev. B 1996, 54, 11169.
- (38) Wang, L.-W.; Zunger, A. Phys. Rev. B 1995, 51, 17398.
- (39) Califano, M.; Gómez-Campos, F. M. Nano Lett. 2013, 13, 2047.